Studies in newer methodologies and materials/ material modifications for environmental, pollution control applications specifically for water treatment and desulfurization

by

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20EE17J26065

A thesis submitted to the
Academy of Scientific & Innovative Research
for the award of the degree of
DOCTOR OF PHILOSOPHY
in
ENGINEERING

Under the supervision of
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October-2021

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गुरु म्हणजे परीस आणि शिष्य
म्हणजे लोखंड, लोखंडाचं सोनं
करणाऱ्या गुरुंना, माझे वंदन

Dr. Vinay M. Bhandari

Thesis Dedicated

to

My dear Mother and Father

Mrs. Kewal Balasaheb Mane
Mr. Balasaheb Harishchandra Mane

ACKNOWLEDGEMENT

There are many people whom I would like to thank for their support, both direct and indirect, during my PhD work. It is my pleasure to express my deep sense of thanks and gratitude to my mentor, philosopher and research guide Dr. Vinay M. Bhandari, for all his guidance and wisdom throughout my work, from inception to completion as well as his incredible and unwavering patience in working with me during my research work. Additionally, I thank and acknowledge my DAC committee members Dr. N. P. Argade (Chairperson), Dr. Sanjay P. Kamble (member) and Dr. S. G. Gaikwad (member) for their valuable suggestions, constructive criticism, guidance and encouragement. I also thank Dr. Vivek V. Ranade for all of his support and guidance.

I would also like to thank and acknowledge many current and former lab colleagues and friends for the incredible joy and pleasure of working with them. I thank Dr. Joytsna Jena for her help in microbiological techniques. Special thanks to Dr. Kshama Balapure for her assistance in microbiological studies, help in deep understanding of analysis techniques and paper writing. I would like to thank Dr. Pooja Thanekar for her help in final scrutiny and checking the thesis writeup and support. I would like to thank my friends Pravin Patil and Dr. Kshama Balapure: you were always there for me in the field and when I needed a good friend and research fellow to talk to. I thank my colleagues and other friends: Snehal, Sandeep Patil, Dr. Nalinee Suryawanshi, Nitin Thorat, Priyanka, Prashant Deulgaonkar, Prachi Chavan, Vipul Patil, Divya Dixit, Deepa, Surabhi, and other labmates for their support.

I also thank Dr. Rahul Bhambure and Dr. Dhiman Sarkar for providing lab facilities for microbiological studies. Thanks to Dr. Pandhare, Dr. Rode, Dr. Shelke, Dr. Gaikwad, Dr. T. Raja, Dr. Kulkarni, Dr. Bhat, Gholap sir for access to various analytical facilities such as FTIR, FE-SEM, TEM, BET surface area, TGA, Zeta potential and AAS analysis. I thank National Collection of Industrial Microorganism (NCIM) for providing microbial culture. Also, I would like to thank CEPD office staff Mr. Raheja, Mr. Kedari mama, and Mr. Patne mama.

I would like to thank Department of Science and Technology's Women Scientist Scheme-A and Department of Science and Technology's Water technology Initiative (DST-WTI) project for funding this research. I thank Academy of Scientific & Innovative Research (AcSIR) and CSIR-NCL, Pune for administrative support.

Personally, I thank my, father, sister and brother for their constant support during the entire tenure of PhD and I also thank and acknowledge my mother who has been with me through every step of my life and made me strong. I would also like to thank my in laws for their support. I would like to thank my husband Mr. Utkarsh More for complete support and encouragement. Lastly, I thank to my superboy Shrinath for his genuine smile and cheerfulness.

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Synopsis

AcSIR	**Synopsis of the Thesis to be submitted to the Academy of Scientific and Innovative Research for Award of the Degree of Doctor of Philosophy in Engineering**
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Degree Enrollment No. &Date	**PhD in Engineering Sciences (20EE17J26065); January 2017**
Laboratory	**CSIR-National Chemical Laboratory, Pune-411008**
Title of the Thesis	**Studies in newer methodologies and materials/ material modifications for environmental, pollution control applications specifically for water treatment and desulfurization**
Research Supervisor	**Dr. Vinay M. Bhandari**

1. Introduction

Safe and clean environment is most essential for the ecosystem and Water and Air are two most critical components in this regard. However, with the advanced social structure, human population coupled with increased industrialization in recent years has resulted both water and air sources getting increasingly polluted with wide variety of contaminants, including biological contaminants. The research in providing safe environment, therefore, requires developing sustainable solutions for effective removal of contaminants to protect environment, in general and human life, in particular. The present research addresses two specific studies in this regard; one pertaining to the safe water and other pertaining to clean air: 1 Disinfection of water, 2 Desulfurization of transportation fuels

2. Statement of Problem

2.1 Disinfection of water

World Health Organization (WHO) estimates that more than 3.4 million people die every year from waterborne diseases and thus, disinfection of water is essential for providing safe drinking water by employing suitable methods[1–3]. Broadly, disinfection methods are chemical (Chlorination, ozonation, chemical treatment) and physical/ physico-chemical (UV light, adsorption, membrane and hybrid). The most common chemical method of water disinfection is chlorination. Though chlorination is cheap and effective, the serious disadvantage with most of chemical methods is formation of Disinfection By-products (DBP) that are harmful and some of these are carcinogenic. The common drawbacks of physical and physico-chemical treatments mainly include higher cost and long treatment times. Membrane filtration for water disinfection is not very effective, has many operational problems which ultimately increases cost of treatment. According to WHO guidelines, *E. coli* or thermo-tolerant coliform bacteria, total coliform bacteria must not be present in any 100-ml sample of all water system [3]. In view of stringent regulations and to eliminate the problems associated with common and conventional disinfection methods, developing a new strategy for SAFE drinking water is highly important.

2.2 Desulfurization of transportation fuels

Deep desulfurization is an important operation in petroleum/petrochemical industries to meet stringent norms for sulfur content in fuels such as petrol/diesel to avoid adverse effects of SOx and NOx emission to human health and the environment[4],[5]. In India, the new regulations, in accordance to the recommendations of European Union Environment Protection Agency and USEPA, now mandate drastic reduction in sulfur levels from previous levels of more than 300 ppm to levels below 10 ppm sulfur in transportation fuels (Tier 3)[6]. Sulfur less than 1 ppm is recommended for fuel cell applications to prevent catalyst deactivation[7],[8]. Thus, deep desulfurization is essential for the production of ultra-low-sulfur fuel and to meet the new permissible limits set by the different government regulations.

3. Objectives

- Development of new methodology for water disinfection using mainly cavitation and also adsorption apart from process integration.
- Study on effect of reactor geometry, nature of microorganism, nature of natural additives, kinetics of disinfection, mathematical modeling, and optimization of process.
- Techno-economic feasibility studies.
- Synthesis, design and development of new materials for disinfection of water and desulfurization of liquid fuels and investigate the role of adsorbent modifications.

4. Methodology

The methodology involves in-depth literature review, finding the gaps in the research studies through critical analysis of the literature, developing newer methodologies for disinfection of water using cavitation, adsorption and process integration and for other application such as desulfurization of transportation of fuel using adsorption.

Disinfection studies were carried out on various bacteria e.g. Gram-positive bacteria *S. aureus* (ATCC-6538), Methicillin resistance bacterium, *S. aureus* (MRSA) (ATCC BAA-44, Himedia) and Gram-negative bacteria, *E. coli* (ATCC-8739), *P. aeruginosa* (ATCC 15442). The number of viable bacteria was estimated by plate count method. Hydrodynamic cavitation methodology was employed and experiments were carried out using a pilot plant having capacity of 1 m^3/h. Different types of cavitating devices were employed and compared. A Vortex diode (chamber diameter 66 mm, Throat diameter 11 mm, MoC- SS 316) CSIR-NCL design (US9422952B2, 2016) was used for vortex flow based cavitation and orifice with 3 mm diameter single hole as a linear flow cavitation device. Effect of operating parameters such as pressure drop, concentration etc. were evaluated. For hybrid cavitation methodology, different natural oils such as Clove oil, Nilgiri oil, Castor oil, Dalchini oil, Peppermint oil, Lemongrass oil, Tea tree oil, Ginger oil, Lavender oil, Tulsi oil, Turmeric oil and Neem oil were used and different plant extracts such as Ginger extract, Turmeric extract and Mango ginger extract were used as natural additives (0.1%) to evaluate performance behavior and to enhance efficiencies.

In adsorption methodology, Spherical Activated Carbons (SACs) were prepared from cation exchange resin, T42H (Thermax Ltd. Pune) by carbonizing the polymeric resin in an inert atmosphere of nitrogen in a temperature-programmed horizontally aligned electrical tube furnace at 600 ^{o}C for 3 h. Different types of SACs were prepared using two different methods of material modification for incorporation of different metals. Five different SACs (SAC, M1-SAC-Ni, M1-SAC-Cu, M2-SAC-Ni and M2-SAC-Cu) were tested for disinfection and desulfurization study. Study of antimicrobial property was performed against *E. coli* and *S. aureus* using 0.5% of adsorbent loading and 20 ml of bacterial solution. Adsorption studies in desulfurization were carried out using model fuel, thiophene, benzothiophene and dibenzothiophene in n-octane, having known initial sulfur concentration and adding known amount of adsorbents. The sulfur concentration was analyzed using Total sulfur analyzer TN-TS 3000 and Gas chromatography (GC-FPD).

Different characterization methods were used such as Field Emission Scanning Electron Microscopy

(FE-SEM) and TEM (Transmission Electron Microscopy) for morphological changes of bacterial cell after disinfection and to prove efficacy of cavitation treatment and adsorption and also for morphologies of the carbon samples and elemental analysis. BET surface area, pore size and pore size distribution for adsorbents were determined by Autosorb-1 using nitrogen adsorption. Barrett-Joyner-Halenda (BJH) method was used to determine the cumulative pore volume and average pore diameter. Pyrolysis of resins was investigated by thermo gravimetric analysis (TGA) and differential scanning calorimeters (DSC) analysis. Functional groups identification was done using FTIR analysis.

5. Results/ Summary/ Conclusions

I. A novel hybrid cavitation process for enhancing and altering rate of disinfection by use of natural oils derived from plants

The study is an attempt to improvise the hydrodynamic cavitation methodology for effective disinfection of water and also to suggest prototype development for practical application. The enhancement in the disinfection efficiency was evaluated specifically for the effect of pressure, temperature, pH, microbial inoculum size and also on effect of different additives for the two model microbial strains, gram-negative (*Escherichia coli*) and gram-positive (*Staphylococcus aureus*). The efficacy of the hydrodynamic cavitation was evaluated for the two types of flows/cavitation devices – linear flow in the case of orifice and vortex flow for vortex diode. The vortex diode requires significantly lower pressures, 50% lower as compared to orifice for the similar extent of disinfection. While the bacterial disinfection at high temperature is known, the usefulness of hydrodynamic cavitation is especially evident at ambient conditions and the process is effective even at very high concentrations of bacteria, not reported so far. The reactor geometry also has significant effect on the disinfection. The present study, for the first time, reports possible use of different natural oils such as castor oil, cinnamon oil, eucalyptus oil and clove oil in conjunction with hydrodynamic cavitation. The nature of oil modifies the cavitation behavior and an order of magnitude enhancement in the cavitation rate was observed for the two oils, eucalyptus and clove oil for a very small concentration of 0.1%. The increased rates of disinfection, of the order of 2–4 folds, using oil can drastically reduce the time of operation and consequently reduce cost of disinfection. A possible mechanism is proposed for the effect of oil and hydrodynamic cavitation in cell destruction through the rupture of cell wall, oxidative damage and possible DNA denaturation. A cavitation model using per pass disinfection was used to correlate the data. The increased efficiency using oils and possible benefits of the developed process, where natural oils can be perceived as biocatalysts, can have significant advantages in practical applications

II. Destroying antimicrobial resistant bacteria (AMR) and difficult, opportunistic pathogen using cavitation and natural oils/plant extract

The study reports, for the first time, a new and techno-economic strategy for effective removal of antimicrobial resistant bacteria (AMR) and difficult, opportunistic pathogen using cavitation and natural oils/plant extract. A hybrid methodology using natural oils of known health benefits has been discussed in combination with conventional physico-chemical method of hydrodynamic cavitation that not only provides efficient and effective water disinfection, but also eliminates harmful effects of conventional methods such as formation of disinfection by-products apart from reducing cost of treatment. A proof-of concept is demonstrated by achieving exceptionally high rates for practically complete removal of antimicrobial resistant (AMR) and relatively less researched, gram-negative opportunistic pathogen, *Pseudomonas aeruginosa* and gram-positive methicillin resistant, *Staphylococcus aureus* using a natural oil-Peppermint oil and two different cavitating reactors employing vortex flow (vortex diode) and linear flow (orifice) for hydrodynamic cavitation. > 99% disinfection could be obtained, typically in less than 10 min, using vortex diode with operating pressure drop of 1 bar and low dose of 0.1% peppermint oil as an additive, depicting very high rates of disinfection. The rate of disinfection can be further increased by using simple aeration which can result in significant lowering of oil dose. The conventional device, orifice requires relatively higher pressure drop of 2 bar and comparatively more time (~20 min) for disinfection. The cost of the disinfection was also found to be significantly lower compared to most conventional processes indicating techno-economic feasibility in employing the developed hybrid method of disinfection for effectively eliminating bacteria including AMR bacteria from water. The developed approach not only highlights importance of going back to nature for not just conventional water disinfection, but also for eliminating hazardous AMR bacteria and may also find utility in many other applications for the removal of antimicrobial bacteria.

III. Safe water and technology initiative for water disinfection: Application of natural plant derived materials

The study reveals use of natural resources such as plant extracts and natural oils for water disinfection.

Differences between oil and water soluble additives were highlighted for plant extracts and insoluble natural oils. A hybrid hydrodynamic cavitation process was quite effective in both the cases and high rates of disinfection were achieved. Studies were reported using oils (ginger, turmeric, lavender, tulsi) and rhizome derived plant extracts such as ginger, turmeric and mango ginger, as additives in process intensification (0.1% v/V). A vortex based cavitation device (vortex diode, nominal capacity 1 m3 /h) was used with pressure drop of 1 bar. A high disinfection of 96% and 88% was obtained in 15 min for ginger oil and mango ginger extract respectively as compared to 44% using cavitation alone. Acoustic cavitation gave 94% and 30% disinfection with and without additive-mango ginger extract. The FTIR analyses before and after cavitation, with ginger additive, showed no by-products formation and indicated gingerol as active component in disinfection. The per-pass disinfection values were also higher, up to 5 times than cavitation alone. Hybrid hydrodynamic cavitation using natural plant derived materials can offer a promising technology alternative in disinfection.

IV. Developing Spherical Activated Carbons from Polymeric Resins for Removal of Contaminants from Aqueous and Organic Streams

Spherical activated carbons from polymer resin were developed with metal modifications, before/after carbonization using copper and nickel, for gradation of zeta potential (-5.01 to 8.64mV) and high metal loading (up to 12.3%). The materials provide improved removal of various contaminants from aqueous and organic streams- removal of bacteria from water and sulfur removal from fuel. The metal modified spherical activated carbons were highly effective for removal of both gram-negative, *E. coli* and gram-positive *S. aureus* bacteria. The copper modified spherical activated carbon could eliminate 99.9-100%, both bacterial content proving efficacy in water disinfection with a very high rate ~1.33×105 (CFU/ml.s). The zeta potential has significant impact with higher disinfection for high values; ~10-15% disinfection can be improved up to 100% for zeta potential changes from -5 to 8.6mV. Kinetics of disinfection was studied by accounting for zeta potential in the conventional rate model and efficacy of both the models was compared. The fit of revised model was excellent. The spherical activated carbons can be useful for removal of slightly polar contaminants from organic streams and a high capacity of 12.8, 20 and 28 mgS/g for thiophene, benzothiophene and dibenzothiophene respectively. The developed materials can provide useful applications in the area of environmental pollution control.

Overall, the present research has resulted in development of a new technology for disinfection of water, *Safe Water and Sustainable Technology Initiative from Indian Knowledgebase*, SWASTIIK, believed to be at Technology Readiness Level (TRL) of 4-6.

6. Future directions

- SWASTIIK for water disinfection is a new concept and needs to be strengthened by studying different process integration approaches using different Ayurvedic plant extracts and natural oils for increased effectiveness and possible health benefits.
- SWASTIIK technology has capacity to replace/integrate existing conventional chlorination process in water treatment plants. In future, more study will be required.
- Hybrid cavitation process of disinfection also has potential for household application. A compact unit can be developed for household use for providing safe disinfected water.
- In the current COVID-19 scenario, increased immunity can be acquired by combinations of different natural oils. The home appliance can come with different "Natural Oil Cartridges" for the specific needs of people in this regard. Newer materials as adsorbents can be excellent technology for final polishing, be it water treatment or pollution control.

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8. Publications

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2. Maya B. Mane, Vinay M. Bhandari, Kshama Balapure, Vivek V. Ranade. *Destroying antimicrobial resistant bacteria (AMR) and difficult, opportunistic pathogen using cavitation and natural oils/plant extract*. Ultrasonics - Sonochemistry 69 (2020) 105272. https://doi.org/10.1016/j.ultsonch.2020.105272
3. Maya B. Mane, Vinay M. Bhandari, Vivek V. Ranade. *Safe Water and Technology Initiative for Water Disinfection: Application of Natural Plant Derived Materials*. Journal of Water Process Engineering 43 (2021) 102280. https://doi.org/10.1016/j.jwpe.2021.102280
4. Maya B. Mane, Vinay M. Bhandari. Developing Spherical Activated Carbons from Polymeric Resins for Removal of Contaminants from Aqueous and Organic Streams. . Int. J. Environ. Sci. Technol. (2021). https://doi.org/10.1007/s13762-021-03684-6

List of Abbreviations

AAS	Atomic absorption spectrophotometer
AC	Acoustic cavitation /activated carbon
ADS	Adsorptive desulfurization
AMR	Antimicrobial resistant
AOP	Advanced oxidation process
BDS	Biodesulfurization
BOD	Biological oxygen demand
BT	Bezothiophene
COD	Chemical oxygen demand
CNF	Carbon nanofiber
CT	Concentration time
DBP	Disinfection by-products
DBT	Dibenzothiophene
DMDBT	Dimethyl dibenzothiophene
DWTPs	Drinking Water Treatment Plants
ECO	Electrochemical oxidation
EDS	Extractive desulfurization
EDX	Energy Dispersive X-ray Spectroscopy
FCC	Fluid catalytic cracking
FE-SEM	Field Emission Scanning Electron Microscope
FTIR	Fourier Transform Infrared Spectroscopy
GAC	Granular activated carbon
GC-FPD	Gas Chromatography - Flame Photometric Detector
GWD	Guinea-worm disease
HA	Humic acid
HAA	Haloacetic acid
HCR	Hydrodynamic cavitation reactor
HDS	Hydrodesulfurization
IR	Infrared
LED	Light-emitting diode

MBT	Methyl benzothiophene
MD	Membrane Distillation
MF	Microfiltration
MOF	Metal organic framework
MWNT	Multi wall carbon nanotube
NC	Nanocomposite
NF	Nanofiltration
NP	Nanoparticle
ODS	Oxidative desulfurization
PAA	Peracetic acid
RADS	Reactive adsorptive desulfurization
RO	Reverse Osmosis
SAC	Spherical activated carbon
SARS	Selective adsorption for removing sulfur
SODIS	Solar disinfection
SWNT	Single wall carbon nanotube
T	Thiophene
TEM	Transmission Electron Microscopy
THM	Trihalomethane
TGA	Thermo gravimetric analysis
TN-TS	Total nitrogen-total sulfur analyzer
TReND	Transport reactor for naphtha desulfurization
UF	Ultrafiltration
US-EPA	U.S Environmental Protection Agency
UV	Ultraviolet
UVGI	Ultraviolet germicidal irradiation
UV/PS	UV-activated persulfate
VD	Vortex diode
WHO	World Health Organization
WWTPs	Waste Water Treatment Plants
XRD	X-ray Diffraction

Nomenclatures

A	Initial bacterial count, CFU/mL
B	Bacterial count after 2h of incubation, CFU/mL
C	Concentration, CFU/mL
C_0	Initial concentration, CFU/mL for disinfection and mg/L for desulfurization study
C_e	Equilibrium concentration of sulfur, mg/L
k	Disinfection rate constant
k_G	Growth rate constant
n	Number of passes
P	Pressure, bar
ΔP	Pressure drop, bar
P_E	Cost of electricity, Rs/kWh
Q, q	Flow rate, m^3/s
m	Weight of adsorbent, g
t	Time, s
V	Volume, L
Φ, φ	Per-pass disinfection factor
t	Residence time, s
ζ	Zeta potential, mV

Chapter 1

Introduction

Chapter 1
Introduction

Safe and clean environment is most essential for the ecosystem/living cycle and, Water and Air are two most critical aspects in this regard. In the early ages of no industrialization and low population, the air and water, both were relatively pure for the consumption. However, with the advanced social structure, human population coupled with increased industrialization in the last couple of centuries has resulted both water and air sources getting increasingly polluted with wide variety of contaminants, including biological contaminants. Consequently, it has become imperative to devise appropriate methodologies using newer materials, techniques for solving the current problems of unsafe water and air to make these safe for the living. The research in Environmental Technologies, therefore, requires developing sustainable solutions for reduction, removal or prevention of contaminants to protect environment, in general and human life, in particular. The present research work addresses two specific studies in this regard; one pertaining to the safe water and other pertaining to clean air:

- Disinfection of water
- Desulfurization of transportation fuels

Indeed, knowing the importance of both the above-mentioned specific problems for decades, a large number of methodologies are already developed and are also being continuously developed/ evolved in search of sustainable solutions. The existing methodologies involve typically physical treatments, chemical treatments and/ or hybrid methodologies of the type, physico-chemical. The existing treatment methods have several drawbacks such as by-product formation, difficulty in removal of refractory contaminants, limited scalability and cost intensive processes. As a result, the research in the development and application of new/ novel treatment methods/ technologies is essential to eliminate the major disadvantages associated with existing methodologies and arrive at cost-effective and sustainable solutions for both water disinfection and removal of sulfur from fuels consequently reaching goals of safe water and safer air respectively.

This research is an attempt to evolve newer methodologies that are effective with higher efficiencies as compared to conventional methodologies and also are cost-effective thereby leading to techno-economical alternatives.

1.1 Disinfection of water

Disinfection of water is essential for removing pathogenic microorganisms that are responsible for causing a number of water borne diseases- ~88 % of diseases in the developing world due to unsafe drinking water. World Health Organization (WHO) estimates that more than 3.4 million people die every year from waterborne diseases and hence, disinfection is essential for providing safe drinking water by employing suitable methods [1–3]. Broadly, the disinfection methods are chemical (Chlorination, ozonation, chemical treatment) and physical/ physico-chemical (UV light, cavitation, membrane). The common drawbacks of the disinfection methods include high cost and long treatment times. Membrane filtration for water disinfection is not very effective, has many operational problems which ultimately increases the cost of treatment. The most common chemical method of water disinfection is chlorination. The problems associated with the chemical methods are many and vary according to the nature of the chemical used for disinfection. However, a serious disadvantage with most of the chemical methods is the formation of Disinfection by-products (DBP) that are extremely harmful and can be carcinogenic in nature. According to world health organization (WHO) guidelines, *E. coli* or thermo-tolerant coliform bacteria, total coliform bacteria must not be present/detectable in any 100-ml sample of all water intended for drinking, treated water entering and in the distribution system [3]. In view of these stringent regulations and also inadequacies associated with the common and conventional disinfection methods, developing new strategy for SAFE drinking water is highly important.

1.1.1 Current scenario

Earth is covered by 71% water of which only 2.5% is available as fresh water, remaining as ocean based and saline. Of the total fresh water, only 1% of water is available for daily needs including drinking water while the remaining part is occupied in glaciers, snowfields. The net availability of drinking water is far less for the entire human population [4]. Thus, the limited available water for drinking is required to be safe for consumption which naturally demands satisfactory treatment to avoid serious diseases caused by water-borne pathogens. In India, near about 80% diseases are caused by unsafe drinking water, improper sanitization and water-borne pathogens which are commonly found in water sources such as river, wells, and lakes apart from regular water distribution sector. Untreated or partially treated surface and ground water contaminated with pathogenic bacteria are the main cause of water-borne diseases such as diarrhoea, cholera, typhoid, dysentery, amoebiasis, hepatitis and many more [5,6]. In recent years, another new emerging concern is the emergence or presence of antimicrobial resistant bacteria (AMR) in drinking water; especially even after conventional water treatment [7]. Effective treatment methods are necessary for such new and more difficult emerging problems apart from the usual difficultly in removal of pathogens. Overall population of India is expected to reach exceptionally high number of 1.6 billion by year 2050 [8]. For such large population, water starved regions are likely to complicate water availability for agriculture, industry, household and drinking water. The limitations on availability of water further emphasizes the need for the disinfection of water. The disinfection methods are required to kill wide variety of bacteria, viruses subsequently prevent diseases caused by water-borne pathogens and protect environment. The disinfectant used must have a residual effect after treatment to avoid recontamination of pathogens from distribution pipes. Many disinfection techniques inactivate the pathogens but have adverse effect or are toxic to aquatic organisms. These aspects also highlight the need for the apt selection of disinfection technique.

The most commonly used conventional technique for water disinfection is chlorination/chlorine. It is easily available, low in cost, reliable and effective treatment method against wide range of microorganisms. It can be directly applied as a chlorine gas or in liquid form as a chlorinating chemical. The other chemical disinfectants such as chloramines, chlorine dioxide, ozone etc. can also be used. Disinfection by-products (DBP) formation is the main disadvantages of chlorine-based disinfection techniques as many disinfection by-products are carcinogenic in nature. As an alternative to chlorination, many other physical disinfection methods such as UV/plasma/IR irradiation, filtration, RO etc. and other physico-chemical methods such as cavitation also can be used in varying degree. Each disinfection method has its own merits and demerits and can be used based on the end requirements, water quality and available resources.

1.1.2 Health risk and government norms

Unsafe drinking water may carry bacteria, viruses or parasite. In general, bacteria and viruses are found in surface water as well as in ground water, while parasite or protozoa are also found in surface water. Table 1.1 lists the categories of different microbes, their sources and possible health risks [6].

The harmful bacteria, coliform such as *E. coli* and *Enterococci* are known as fecal contaminants, commonly found in water, and causes serious diseases such as diarrhea. Approximately 11% of death of children reportedly occur due to coliform. Other commonly found bacteria such as *vibrio cholerae*, *Salmonella typhii* and *Shigella* species cause cholera, typhoid and dysentery diseases respectively. The campylobacteriosis disease is because of *Campylobacter jejuni* bacterial infection showing symptoms of fever, acute pain like abdominal cramps and diarrhea. The Mycobacterium species such as *M. avium*, *M. chelonae*, *M. fortuitum*, *M. gordonae*, *M. kansasii*, and *M. xenopi* present in water distribution systems of hospitals and potable water causes nosocomial infection [6].

The viruses are typically small in size compared to bacteria and can pass through filter media which retains the bacteria. Hence, it is difficult to remove viruses using common filtration techniques. The enteric viruses for example; *hepatitis A*, *polioviruses*, *Norwalk virus*, *rotavirus*, *echoviruses*, *coxsackie viruses* are fecal contaminants causing various diseases like diarrhea, fever, hepatitis, paralysis and meningitis. The importance of providing safe water can be realized by the numbers; globally, over half a million in year 2000 to significantly reduced number of only 215000 in 2013 of *rotavirus* deaths of children of less than 5 years suffering from diarrhea [6],[9].

Unlike bacteria or viruses, protozoa are adapting microbes in the environment. Dracunculiasis, also known as Guinea-worm disease (GWD), is caused by *Dracunculus medinensis*. *Cryptosporidium parvum* oocysts are found in water due to fecal contamination and pose environmental threat due to its resistance to chlorine, as well as difficulty in removal by simple filtration due to its small size. *Giardia* cysts are found on vegetables such as potatoes, radishes, coriander, carrot and mint. Another parasite such as *Balamuthia*, *Naegleria*, *Sappinia*, and *Acanthamoeba* genus are free living amoebae found in humans causing diseases like encephalitis, keratitis, pneumonitis, and dermatitis. In view of the possible health risks, the world health organization (WHO) has prescribed norms or permissible limits for microorganisms [6]. Table 1.2 lists guidelines for microbial quality[a] (for *E. coli* or thermotolerant coliform bacteria).

Table 1. 1: Categories of microorganisms

Category of Microbes	Name of microorganism	Health hazard/Disease	Source	Ref.
Bacteria	*Escherichia coli, Vibrio cholera, Salmonella typhi, Shigella, Campylobacter jejuni, Mycobacterium species, cyanobacteria*	Cramps, nausea, diarrhea, headaches, cholera, typhoid fever and bacillary dysentery	Unsanitary sewage disposal, poor personal and domestic hygiene, unsafe drinking water	[6]
Viruses	*Enteric viruses: hepatitis A, polioviruses, Norwalk virus, rotavirus, echoviruses, coxsackie viruses, Polyoma viruses, Cytomegalovirus*	Infection to gastrointestinal or respiratory tracts resulting in diarrhea, fever, hepatitis, paralysis and meningitis		[6]
Parasite	*Dracunculus medinensis, Cryptosporidium parvum, Giardia lamblia, Free-living amoebae (FLA)*	Dracunculiasis, Cryptosporidiosis, Giardiasis, encephalitis, keratitis, pneumonitis, and dermatitis		[6]

Table 1. 2: Guidelines for microbial quality

Sr. No.	Source of Microorganisms	Guideline value
1	All water directly intended for drinking[b,c]	Must not be detectable in any 100 ml sample
2	Treated water entering the distribution system[b]	Must not be detectable in any 100 ml sample
3	Treated water in the distribution system[b]	Must not be detectable in any 100 ml sample

[a] Immediate investigative action must be taken if *E. coli* are detected.

[b] Although *E coli* is the more precise indicator of faecal pollution, the count of thermotolerant coliform bacteria is an acceptable alternative. If necessary, proper confirmatory tests must be carried out. Total coliform bacteria are not acceptable as an indicator of the sanitary quality of water supplies, particularly in tropical areas, where many bacteria of no sanitary significance occur in almost all untreated supplies.

[c] It is recognized that in majority of rural water supplies, especially in developing countries, faecal contamination is widespread. Especially under these conditions, medium-term targets for the progressive improvement of water supplies should be set.

1.1.3 History of disinfection technique and general outline

Disinfection of water has been carried out over centuries. In old days, clear water without any mud content or sediment was typically considered as clean water. In early 2000 B.C., ancient civilizations used different simple disinfection techniques to improve odor and taste of water such as-

1. Exposure of the drinking water to sunlight, followed by filtration with charcoal or cloth
2. Boiling of water before filtration
3. Water storage in copper or silver jugs/pots
4. Use of Alum for removal of turbidity followed by filtration; sand filtration (late in the year of 1800 in different parts of Europe).

Year 1854 saw many deaths in London city because of cholera epidemic. The English Doctor John Snow discovered that the cause of cholera was drinking water from public well and their origin of contamination was sewage waste. Initially the prevention of spread of cholera was done by closing water pumps and the reason behind cholera outbreak remained unknown. Later studies revealed the bacteriological existence and identification of microbes. Disinfection of drinking water was then suggested by different scientists. In 19th century, the effect of chemical disinfectant such as chlorine was discovered and since then chlorination has been largely applied for water disinfection to improve quality and for prevention of spread of diseases.

Several bacteriological guidelines were set in 1914 by U.S public services and were updated and revised from time to time. In 1974, research showed that the continuous use of chemical disinfectant such as chlorine for making safe drinking water results in the formation of disinfection by-products (DBPs) e.g. trihalomethane (THM) by reaction of chlorine with naturally occurring organic matter and some of these DBP produced have carcinogenic harmful effect. The presence of naturally occurring organic nanoparticulate matter gives colour to the water because of presence of humic substances (humic, fulvic and hymatomelanic acids). The reaction of humic substances with chlorine produces chloroform ($CHCl_3$) and THMs. Further, the use of chlorine was restricted to some extent, without compromising health by U.S Environmental Protection Agency (US-EPA) in 1979 [10][11]. It was also suggested that the other, safer, disinfection techniques should be used.

1.1.4 Chemical treatment methods

The chemical treatment methods include chlorination (by chlorine gas, sodium hypochlorite solution, solid calcium hypochlorite, chloramines), ozonation, Ozone (O_3), use of halogens[12]: bromine (Br_2), iodine (I), bromine chloride (BrCl), metals: copper (Cu^{2+}), silver (Ag^+), potassium permanganate ($KMnO_4$), etc. [1],[13], [14],[15]

1.1.4.1 Halogen compounds

Several halogens and their compounds such as chlorine gas, sodium hypochlorite solution, solid calcium hypochlorite, chloramines, bromine (Br_2), iodine (I), Bromine chloride (BrCl) are widely used as chemical disinfectants [12],[14].

Halogens are very strong oxidizing agents which extensively destroy the cell wall or membrane of microorganisms, protein and nucleic acid of cell. Also, it damages the most important process for cell survival i.e. oxidative phosphorylation. All halogens used in disinfection operation are required to be used in appropriate quantity to avoid disinfection by-product formation. Each chemical disinfectant has its own advantages and disadvantages which are listed in Table 1.3 below.

Table 1. 3: Different halogens compounds used in disinfection operation[12],[14]

Halogen compounds	Characteristics	Advantages	Disadvantages
Chlorine gas	toxic, yellow-green gas, liquid in high pressure cylinders	Very effective in removing almost all gram positive and negative pathogenic microbes and used as primary & secondary disinfectant.	Dangerous gas (lethal at concentrations as low as 0.1 percent air by volume).
Sodium hypochlorite (NaOCl) solution	Readily available in the range of 5 to 15 % chlorine, more expensive than chlorine gas	Easy to handle than chlorine gas	Should be stored with care in specific condition such as a cool, dark, dry area because hypochlorite decompose easily and cannot be stored more than a month; corrosive in nature.
Solid calcium hypochlorite $Ca(OCl)_2$	White granular, powdered and tablet form contains 65% chlorine and easily dissolves in water	It is very stable and long duration storage can be possible.	Like NaOCl solution, $Ca(OCl)_2$ is also corrosive material having a strong odor and requires proper handling and care. It can produce enough heat to cause fire or explosion after reaction when it comes in contact organic material like wood, cloth, and petroleum products. Also, it absorbs moisture, forming chlorine gas readily. Therefore, containers which are used for shipping must be emptied completely or carefully resealed remaining $Ca(OCl)_2$.
Chloramines	Formed by either addition of ammonia in water containing chlorine or when water containing ammonia is chlorinated (hypochlorous acid or hypochlorite).	It is produced onsite and 99% disinfection can be achieved within a few minutes, effective bactericidal effect and produce fewer disinfection by-product. Also, can be used as secondary disinfectant to avoid bacterial regrowth.	It is a weak disinfectant and compared to free chlorine. It is less effective for viruses or protozoa. Detrimental reaction can occur for nitrogen trichloride and has also harmful side effects to human; gives bad taste and odor to water.

1.1.4.2 Other chemical methods

Other chemical methods involve use of metals [16], potassium permanganate, hydrogen peroxide, ferrate, zero-valent Iron nanomaterials, ozone etc. There are several heavy metals that are reported for disinfection of water, including mercury, copper, silver, gold and zinc. Some metals like mercury have high toxicity and environmental risks associated with them and are banned for their usage as disinfectant.

From ancient times, pots or vessels of metals such as copper or silver are used as a primary disinfectant because of their biocidal property. Some of the commercial applications are described below.

1.1.4.2.1 Copper-silver ionization

The electrolysis of copper-silver ionization was developed in the 1950's and because of its effectiveness was widely applied for water disinfection. This process of disinfection became popular when used by NASA's Apollo spaceship in 1960 for production of SAFE drinking water without use of chlorine. Further this electrolysis technique of copper-silver ionization was successfully applied in many areas for example, in England, about 120 hospitals for *Legionella* bacteria deactivation, swimming pool water disinfection in U.S., cooling towers, fishpond disinfection, recycle of water by water bottling companies in U.S [17].

Advantages

1. *Legionella* bacteria and biofilm effectively get deactivated by ions such as Cu^{2+} and Ag^{+} after electrolysis which binds with negatively charged microorganisms for deactivating.
2. The metal ions remain in the water for longer duration compared to UV
3. Non-corrosive nature, low maintenance, no storage and transport difficulty.

Disadvantages

1. The performance of copper-silver ionization technique gets affected by pH of water as

well as high dissolved solid concentration. The presence of chlorine, nitrates in water adversely affect effectiveness of silver ions.

2. Some microorganisms are resistant to silver ion.
3. Ineffective in dead end region where very little water flow.
4. According to US-EPA National Secondary Drinking Water regulations, 2002, maximum allowable limit for copper and silver is 1 mg/L and 0.1 mg/L respectively.

1.1.4.2.2 Potassium permanganate

It is a strong oxidizing agent extensively used for disinfection of drinking water before the use of hypochlorites and also applied for washing of fruits and vegetables in 1-5% of concentrations [18].

Advantages

It has good oxidation properties, ease of storage, transportation and application. It is effective against bacteria, viruses and parasites.

Disadvantages

Longer treatment time, imparts pink color to water, causes irritation to the skin, mucous membrane, can affect respiratory, skin and if swallowed it can be fatal. In some cases, jaundice and drop in blood pressure can occur in overdose.

1.1.4.2.3 Hydrogen peroxide

It is a strong oxidizing agent and can be used as liquid, gel or in gas formulations in many applications which includes, medical, veterinary, industrial, and other antimicrobial applications. It is used for pollutant removal and inhibiting the microbial growth in water disinfection without forming any residue or gas. It is safe in use and has capacity to remove any residue left behind by chlorination technique. While handling and transportation of hydrogen peroxide care should be taken, otherwise may cause irritation to eye, skin, mucous membrane and lungs after contact. It is reported by American International Agency on Cancer

Research studies that high level/concentration and longtime exposure of hydrogen peroxide can have carcinogenic effect [19].

1.1.4.2.4 Acids (e.g. Acetic acid and Citric acid)

Acidic disinfectants such as acetic acid, citric acid and peracetic acid, etc. can be used for water disinfection. It kills microorganisms by changing pH of water, as acidic pH is harmful to many microbes, destroys the bonds of proteins, nucleic acids and precipitating proteins. Because of pH dependency for its antimicrobial activity, corrosiveness and toxicity at high concentration, the use of acid as disinfectant is limited or acetic acid can be used in diluted forms.

1.1.4.2.5 Ozone

In late 1800s, ozone was first used in water treatment. Ozone is colorless, unstable gas with three oxygen atoms and has strong oxidizing ability and for deactivation of bacteria/viruses. It has good disinfection ability/capacity against bacteria and viruses as compared to conventional chlorination. After oxidation, insoluble particles can be removed by filtration. Ozone is produced in situ from ozone generator with the help of oxygen, the energy required either by an electric discharge field or by ultraviolet radiation (simulation of the ultraviolet rays from the sun) or made through electrolytic and chemical reactions [15].

Advantages

1. It is a strong oxidizing agent, effective under wide range of pH condition, even with short residence time and have strong antimicrobial property compared to chlorination for bacteria, viruses or protozoa.
2. This process does not require harmful chemicals
3. It also has ability to remove different pollutants such as organic, inorganic, microorganisms, bad taste and odor problem.

Disadvantages

1. It requires high operation cost and maintenance is difficult.

2. Incomplete disinfection and regrowth of microorganisms may occur.
3. Disinfection by-products includes aldehyde, ketone, carboxylic acid and brominated by-products produced have carcinogenic effects.
4. Post-filtration, such as activated carbon filter, is necessary
5. It may require pretreatment to remove hardness.
6. Solubility issue- less soluble in water.
7. Potential fire hazard and toxicity issues associated with ozone generation.

1.1.5 Physical /Physico-chemical treatment methods

There are several physical treatment methodologies available for removal of pathogenic bacteria such as ultraviolet light (UV) radiation, gamma rays, sound, heat and filtration. Most of these treatment methods can have scale up problem, are time consuming and can be cost intensive processes [20,21]. Therefore, new approaches are required to produce clean water. Membrane technology, RO, metal modified adsorbent /Nanocomposite in adsorption, advanced oxidation process for instance hydrodynamic cavitation, acoustic cavitation are some other alternatives. In the following sections various physical/ physico-chemical treatment methods are described as disinfection methods.

1.1.5.1 Ultraviolet (UV) radiation

UV is an electromagnetic radiation of wavelength ranging from 100 nm to 400 nm, longer than X-rays but shorter than visible light. The natural source of UV irradiation is sun whose rays contain 10% of total electromagnetic radiation. Commonly, UV can be categorized in three groups, ultraviolet A (UVA), ultraviolet B (UVB), ultraviolet C (UVC). UVA is long wave with wavelength range from 315 to 400 nm, black light also known as soft light not absorbed by ozone layer. UVB is medium wave or intermediate UV with wavelength range from 280 to 315 nm, Dorno radiation, mostly absorbed by ozone layer. UVC is short wave with wavelength range from 100 to 280nm, completely absorbed by ozone layer and atmosphere, also known as hard UV, used as germicidal to kill or inactivate microorganism by damaging nucleic acid and protein. There are different types of UV lamps utilized for inactivation of microbes [22,23].

- Mercury-based lamps emit UV light at wavelength 253.7nm operating at low vapor pressure

- Ultraviolet light-emitting diode (UV-C LED) lamps emit UV light at wavelengths between 255 and 280 nm.
- Pulsed-xenon lamps emit UV light at wavelength 230 nm
- Ultraviolet germicidal irradiation (UVGI) system uses short wave, UVC with ow-pressure mercury-vapor discharge tube.

Advantages

1. It is effective and inactivates all types of harmful bacteria, viruses, pathogens.
2. No use of harmful chemicals and no disinfection by-product formation
3. Short contact time.

Disadvantages

1. Regular maintenance and lamp replacement are essential.
2. Point disinfection-It only kills microorganisms at one point in water system and do not provide any residual germicidal effect in downstream
3. Specific requirement of Flow rate-At high flow rate, water will pass without sufficient UV exposure and at very low flow, heat may build up and damage the UV lamp.
4. Suspended particles must be removed- UV light cannot pass through the water in presence of suspended particles or in cloudy or turbid water. Water must be clear otherwise microorganisms get shielded from the UV light.
5. Pre-filter is necessary in order to remove any suspended particles present in water
6. Reinfection- UVGI system not resistant to reinfection, if any bio-residue present.
7. Cost intensive operation.

1.1.5.2 Solar disinfection (SODIS)

The SODIS method was developed in 1980s and Swiss Federal Institute for Environmental Science and Technology, in 1991, implemented it for household water purification to prevent diarrhea in developing countries. In the SODIS method, PET or glass bottles made up of heat conducting material (e.g. black colour bottles) containing contaminated water is exposed to sunlight for UV radiation for greater than 6 hr of time duration. Due to direct exposure to UV radiation with wavelength 320-400 nm, temperature of water raises, thereby effecting inactivation of bacteria. A large number of factors affect efficacy of the process which include geographic latitude and altitude of the place, season, exposure period or time of the day, presence of clouds, temperature, volume of the bottle, material of the bottle, turbidity and so on [24].

Advantages

1. This process is simple, safe and effective method of disinfection
2. Suitable for household application
3. Due to low investment cost, this process is economical (easily available resources like plastic or glass bottle and sunlight)

Disadvantages

1. This method is not suitable for treating large volumes
2. This process depends on various environmental factors specially during rainy or cloudy season
3. It does not remove chemical residue
4. Pretreatment of higher turbidity water is required using flocculation and/or filtration
5. Time consuming
6. Requirement of large number of intact, clean, suitable plastic bottles

1.1.5.3 Heat treatment

From ancient times, heat treatment is used for water disinfection. Rather than disinfection, it is a sterilization technique and can be done by two ways: steam sterilization and dry heat sterilization. In steam sterilization, denaturation of microbes is accomplished by application of saturated steam at temperature from 125°C to 130°C and pressure 0.2-0.3 MPa for around 10-30 min. In case of dry heat sterilization, hot air is used at 160°C for 2hr. Under these conditions, microorganism get killed due to heat effects and oxidation effects. The technique is effective, fast, simple, and without any toxic residues.

1.1.5.4 Filtration methods

Filtration is a well-known and important process for every water treatment plant and is used for separation or removal of particulate matter from water by forcing water through porous media. This porous media can be natural or synthetic; sand, gravel and clay are natural whereas membrane filtration and reverse osmosis are synthetic media. The slow sand filtration (SSF) is used to remove chemical contaminants as well as pathogens. SSF is a simple, easy to operate and low-cost process that employs different layers of sand. Below the water source, fine sand with smaller particle size of 0.15–0.3 mm is present which provides large surface area for filtration as well as for the formation of biofilm. Most of the disinfection occurs in this biofilm. So, this process is called as biofiltration [25]. It effectively removes turbidity and achieves more than 4 log reduction of bacteria, cysts. There is no requirement of chemical pre-treatment, backwashing and automation. The major drawbacks of SSF is that the raw water should have low turbidity and low algae counts. The colour removal is not satisfactory and the process is a time consuming process [26].

Membrane filtration is a simple methodology. Based on pore size, membranes are of different types such as microfiltration (MF), ultrafiltration (UF) and nanofiltration (NF) can be used by allowing water to pass and retain contaminants of size larger than 0.5–5, 0.005–0.5 and 0.0007–0.005 μm respectively. The reverse osmosis (RO) can remove all types of contaminants of size larger than water molecule. The materials of membrane include woven fibers, ceramics, metallic or polymeric. In order to reduce the fouling or scaling problem and enhance the performance, the membranes are often modified which ultimately increases the cost of treatment. All membrane filtrations effectively remove bacteria and viruses except microfiltration which does not remove viruses. The major drawback of membrane techniques is the cost and biofilm formation. RO also has another disadvantage that it removes essential ions from water [27].

1.1.5.5 Distillation

Distillation is a process to obtain pure water through evaporation of raw water in the form of steam; upon condensation, the condensate is collected as a distilled water. The non-volatile organic compounds and inorganic compounds are not evaporated and left behind as residue.

The performance and life of distillation unit can be increased by combining initially with an ion exchange unit where hardness of water get removed. The main advantage of distillation technique is that even if raw water contains harmful chemicals or pesticide, the distilled water is safe for drinking purpose. The major disadvantage is that it does not contain essential minerals.

Membrane Distillation (MD) is an emerging technology that employs micro-porous hydrophobic membrane having pore size of 10 nm-1μm for separation of volatile components, water molecule from non-volatile ions, macromolecules, colloids, and microorganisms, in aqueous solution and produces almost pure water. In this technique, temperature difference on membrane creates gas-liquid interface separated by membrane. Water is evaporated on hot side, and due to hydrophobicity of membrane, it allows only steam/ water vapors to migrate the other side of membrane where condensation of steam/water vapor takes place on cold side giving clean water. As compared to RO and distillation, in MD clean water is obtained at temperatures below the boiling temperature. It is also possible to use MD for water with suspended solids. The major disadvantage of MD is poor performance in real life application, due to problems such as leakage and recycling of residual effluent is not possible due to presence of *Fusarium sp.* in effluent. The integrated with photo-Fenton process or as ‘‘Solar Membrane Distillation’’ for complete removal of microorganisms [28].

1.1.6 Hybrid Disinfection Techniques: Advanced Oxidation Process (AOP)

The advanced oxidation process was first proposed for drinking water application in 1980s. AOP is a pysico-chemical treatment method to remove organic contents from water and wastewater by oxidation using strong oxidizing agents such as $^{\bullet}OH$ radicals. The hydroxyl radicals are generated by oxidants such as ozone (O_3), hydrogen peroxide (H_2O_2), oxygen (O_2) and energy sources such as UV light or catalyst like TiO_2. Several combinations of oxidants and sources are reported for water and wastewater treatment,

1. Ozone based AOPs: Ozonation at elevated pH, Peroxone process (O_3/H_2O_2), O_3/catalyst (catalyst: e.g. Co(II), TiO_2, Al_2O_3, MnO_2)
2. UV based AOPs: UV/H_2O_2, UV/O_3, UV/Cl_2, UV/$SO_4^{\bullet -}$

3. Electrochemical AOP: Electrodes doped with SnO_2, PbO_2, RuO_2, boron-doped diamond (BDD), and TiO_2
4. Catalytic AOPs: Fenton process, photocatalytic catalyst (e.g. TiO_2, WO_3 or ZnO)
5. Physical AOPs: Application of electron beam, ultrasound, plasma or microwave

AOPs are highly effective and have wide range of applicability. The main drawback of AOPs is the cost intensive nature (chemicals used for oxidation are expensive) apart from requirement of pre-treatment to remove chemical residue like bicarbonate ions (HCO_3^-) which may react with hydroxyl radicals and limited applicability for large scale operation [29],[30].

1.1.6.1 Electrochemical oxidation (ECO)

This process is relatively inexpensive, easy to operate and can inactivate a wide range of microorganisms and has applications in different water and wastewater treatment such as in drinking water, sewage water and industrial processed water. The main drawback is toxic by-product formation. The most common method of ECO is electro-chlorination where free chlorine (HOCl, OCl^-) is generated through electrolysis of saline water. Along with this active chlorine species, other reactive oxygen species such as $^{\bullet}OH$, O_3, H_2O_2, and $^{\bullet}O_2^-$, get produced by electrolysis. These strong oxidizing agents further react with microorganisms and disinfection is achieved [31,32].

1.1.6.2 Cavitation based disinfection techniques

Cavitation is a physico-chemical process involving formation, growth and collapse of microbubbles within a liquid which is typically facilitated by sound waves or pressure variation. After the collapse of cavities, extreme temperature (~5000 K or more) and pressure (~1000atm or more) conditions get generated at the point of implosion, splitting water and consequently in situ generation of hydroxyl radicals by homolytic cleavage of water molecule that subsequently oxidizes microorganisms. The combined effect of mechanical, shock wave and thermal shock coupled with chemical oxidation causes rapid cell death. Acoustic cavitation, hydrodynamic cavitation, optic cavitation and particle cavitation are the four types of cavitation. However, for disinfection of water, only acoustic cavitation and hydrodynamic cavitation are mainly reported. The cavitation process is a complex process and different mechanisms have been hypothesized in different literature with details of generation of different oxidizing species ($HO^\bullet$, $H^\bullet$, $HOO^\bullet$, $HO_2^\bullet$, and H_2O_2). Further, many of the reaction pathways are less understood. If this cavitation phenomenon occurs due to the passage of high frequency sound waves, then it is called acoustic cavitation (ultrasonication) and if it occurs due to the pressure variations in the flowing liquid due to the change in the geometry of the flowing system, it is called hydrodynamic cavitation [33,34],[35].

1.1.6.2.1. Acoustic cavitation

It is generated by ultrasound irradiation with a high intensity with wave frequency of 10 kHz to 10 MHZ. When these high frequencies of ultrasound waves are applied, mechanical vibrations are produced with expansion and compression in alternate cyclic succession. During compression and rarefaction or expansion cycle, due to positive and negative pressure forces, the molecules gets together and apart respectively. Initially, cavitation nuclei gets accumulate, then its size of bubble or cavities increases as cyclic succession and then unstable size of cavities are collapse and as cavities collapse, large amount of energy is generated. This energy further damages DNA of microorganisms. Cell disruption by ultrasound is dependent on the mechanical effects of gaseous cavitation in the liquid. It occurs due to the mechanical stresses arising from the shock waves of cavity collapse and from flows and turbulence generated by pulsating cavities. To enhance the performance of AC, the process can be integrated with different chemical and physical disinfection processes such as AC with H_2O_2 or ozone. The major drawback of AC is difficulty in scale-up for large scale water treatment plant[36].

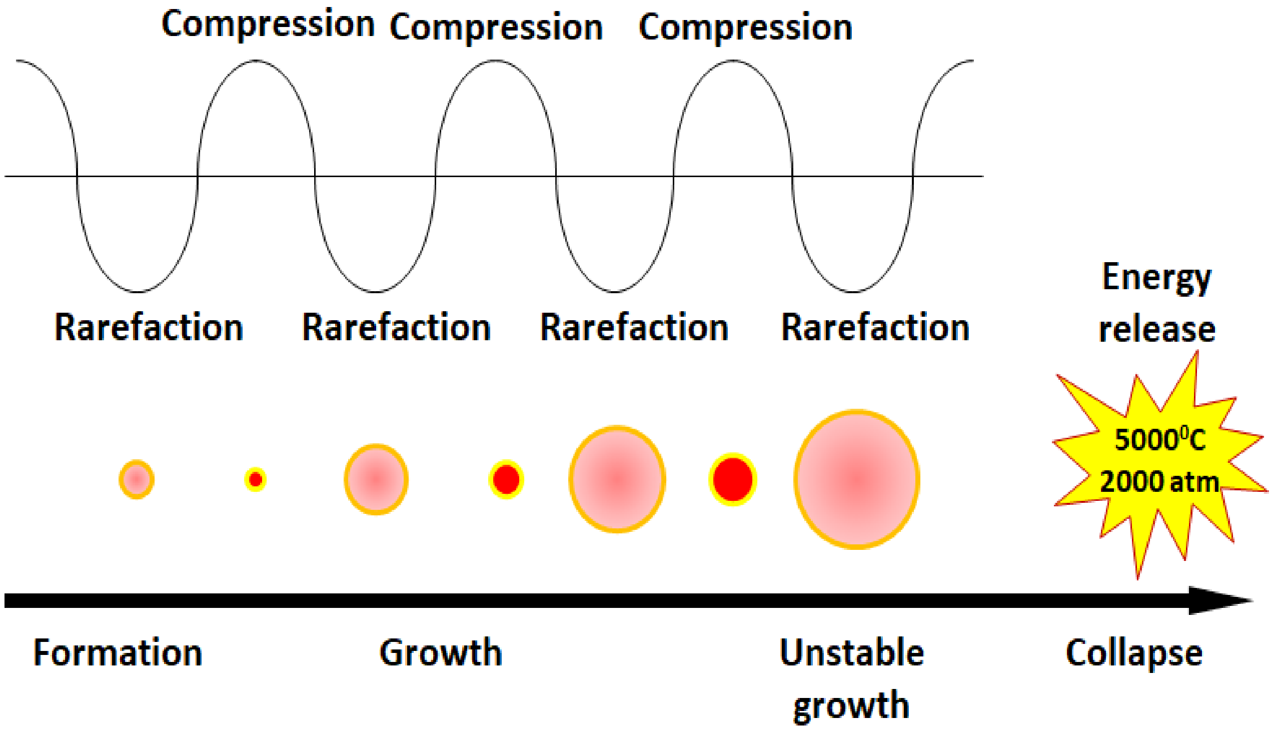

Figure 1.1 Phenomena of acoustic cavitation

1.1.6.2.2. Hydrodynamic Cavitation

In hydrodynamic cavitation, cavities or bubbles are generated when flow of water passes through a constriction, provided in a mechanical device, for effecting sudden drop in local pressure; below vapor pressure that causes part liquid to vaporize and form cavities. As, cavities or bubbles come out of cavitation zone, growth and implosion of cavities take place. After the collapse of cavities, similar to acoustic cavitation, a very high amount of energy gets released in the form of high temperature, pressure condition. At the point of implosion, water splits homolytically resulting in generation of strong oxidizing agent such as hydroxyl radicals. This destroys the cellular structure of bacteria in a mechanism similar to that in acoustic cavitation. A large number of different types of cavitating devices are reported with different designs and are classified in two groups. 1. Rotational type of devices (With moving elements) 2. Non-rotational type of device (without moving elements). In rotational type of device such as rotor and stator type of devices, complete removal of microbes is achieved but with high energy input. The non-rotational type of devices can be divided into two types: laminar flow based devices such as commonly used orifice, and venturi, and swirl/vortex flow based device such as vortex diode. The non-rotational type of device requires lower energy, in general. The time of operation can vary depending upon the type of cavitating device or process intensification. To minimize the time of operation required for hydrodynamic cavitation, different hybrid approaches were reported such as HC with ozone, HC with hydrogen peroxide, HC with ultrasound, HC with different chlorine-based disinfectant, HC with ultraviolet etc. The conventional hybrid approaches have difficulty in scale up. Our research reports hybrid technology using combination of HC + natural oil/natural extract having antimicrobial properties. The use of natural oil or natural extract having antimicrobial property intensifies the process drastically, order of magnitude increase in the rates of disinfection, and can provide health benefits due to natural oils. The benefits of this technology are no disinfection by-product formation, no use of harmful chemicals as a oxidant, lower energy consumption, substantially reduced time of operation, ease of scale up and consequently, cost effectiveness [33,34],[35],[37].

1.2. Desulfurization of transportation fuels

1.2.1 Problem statement

Deep desulfurization is an important operation in petroleum/petrochemical industries to meet stringent norms for sulfur content in fuels such as petrol/diesel to avoid adverse health effects of SOx emission to the human health and the environment [38]. Deep desulfurization is also critical in the case of Fuel Cell to avoid poisoning of catalyst. In most of the petroleum refineries, the gasoline and diesel are obtained by straight run distillation and diesel from several cracking processes such as thermal cracking, hydro cracking and fluid catalytic cracking (FCC). A common, generalized strategy for desulfurization of the fuels is difficult due to differences in the nature of sulfur compounds in various fractions of fuel [39]. Further, removal of sulfur gets increasingly difficult as the sulfur contents gets reduced as the refractory compounds are difficult to get removed using conventional methods. Governments worldwide mandate the removal of sulfur from fuels, though the norms may vary from place to place. In India, the emission norms/limits for sulfur in gasoline and diesel were 500 and 350 ppm respectively in early years of 2000, the new regulations are in accordance to the recommendations of European Union Environment Protection Agency and USEPA, now mandate levels below 10 ppm sulfur in transportation fuels (Tier 3) [40]. For fuel cell, small traces of sulfur in gasoline can deactivate the catalyst and less than 1 ppm sulfur concentration is recommended [41].

The sulfur containing compounds in crude oil are listed in Figure 1.2. The common sulfur compounds include mercaptans, thiols, sulphides, disulfides, thiophene, 2-methyl thiophene, 3-methyl thiophene, 2,4-dimethyl thiophene, benzothiophene, 2-methyl benzothiophene, dibenzothiophene, 2,4-dimethyl dibenzothiophene and many more. Compounds such as thiophenes, alkylated thiophenes and alkylated benzothiophenes are most difficult to remove and are typically referred as refractory sulfur compounds. After combustion of fuel, the sulfur compounds produce SOx, have major contribution in air pollution and which causes acid rain. The sulfur contaminants deactivate the catalyst in fuel cell also adversely affecting many desulfurization operations such as HDS where, desulfurization is based on the catalyst[42]. Rapid catalyst deactivation is also reported due the presence of sulfur compounds in bitmun derived crude oils[43]. Thus, the removal of sulfur compounds to the extent of deep desulfurization is essential for production of ultra-low-sulfur fuel and to meet the new permissible limits set by the different government regulations.

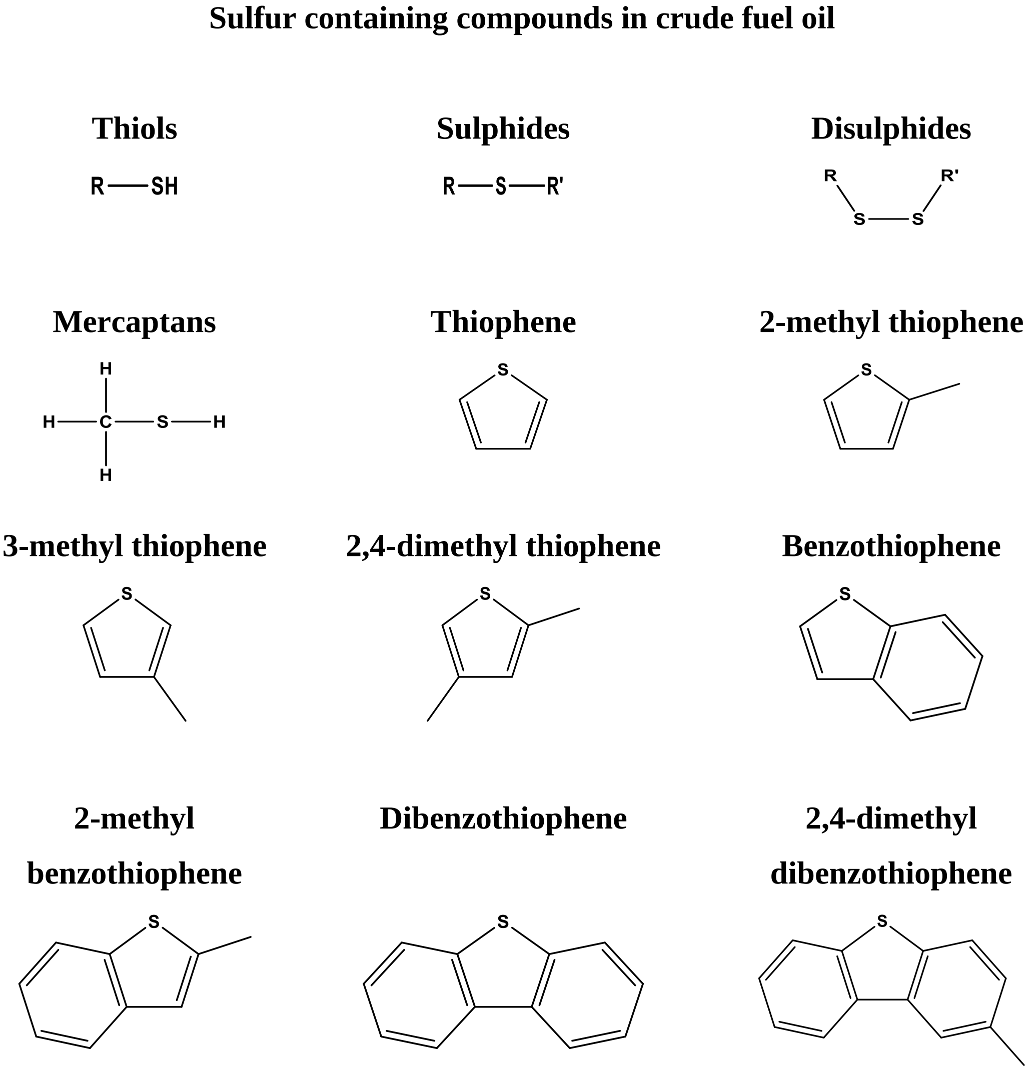

Figure 1.2: Sulfur compounds in crude fuel oil

1.2.2 Techniques used for desulfurization of transportation fuels

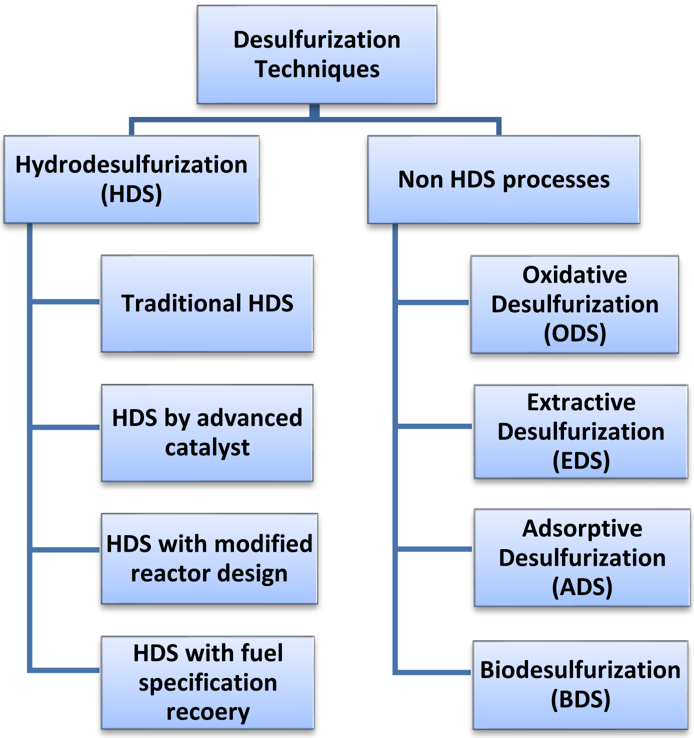

Figure 1.3: Classification of different desulfurization techniques for removal of sulfur compounds from liquid fuels.

1.2.2.1 Hydrodesulfurization (HDS)

HDS is a catalytic process used commercially in petroleum refineries for removal of sulfur compounds such as sulphides, disulfides, mercaptans, thiophene and their derivatives from products of petroleum refinery namely petrol (or gasoline), diesel fuel, jet fuel and fuel oils. HDS is typically operated at a high pressure (upto 10 MPa) and high temperatures (300-400ºC). The HDS catalysts are usually Ni/Co/Mo on Al_2O_3 traditional supporting material used as it provides a high surface area and high thermal and mechanical stabilities [44]. Hammadi et al. indicated possible reaction pathways for desulfurization model fuel DBT by hydrodesulfurization. The first route is for direct desulfurization where, biphenyl formed after direct elimination of sulfur atom whereas, in second route, the DBT is partially hydrogenated first and then hydrogenolysis of the C-S bond for elimination of sulfur takes place. In both pathways, cyclohexylbenzene as a primary product is formed [45]. Thus, sulfur containing compounds are hydrogenated to produce H2S, which is then separated.

HDS is widely used in refineries around the world and the process can effectively remove aliphatic sulfur compounds such as thiols and sulfides but has limitations in removing highly refractory aromatic sulfur compounds such as Thiophene (T) and their alkylated derivatives. The refractory sulfur compounds such as Benzothiophene (BT), Dibenzothiophene (DBT), and 4,6 dimethyl dibenzothiophene (4,6DMDBT), require intensive operating conditions, large amount of expensive hydrogen, as well as expensive durable catalyst for removal and also, quality of spent liquid fuels is hampered owing to reduction of octane number because of side reactions [46].

Moreover, HDS considered to be a highly cost intensive process if ultra-low sulfur norms are to be achieved by HDS alone. Also, severe operating conditions (high temperature, pressure and high consumption of costly hydrogen) increases the operating cost. The drawback of this process also include fouling of catalyst and release of hydrogen sulfide which causes air pollution. Considering these shortfalls, refineries are looking for more efficient and less energy intensive complementary or alternative methods.

A large number of alternative techniques to HDS are reported/ being reported for deep desulfurization- biodesulfurization (BDS), catalytic oxidative desulfurization (ODS) [47], adsorptive desulfurization (ADS) [48] and Extractive desulfurization (EDS) [49].

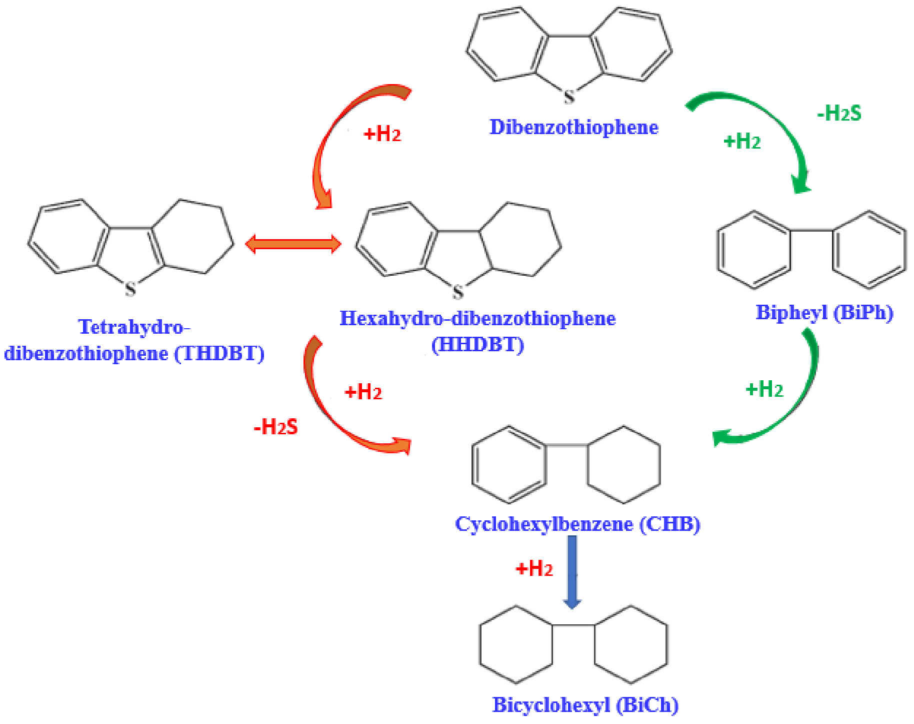

Figure 1.4: Pathways for hydrodesulfurization of DBT [45]

1.2.2.2 Oxidative desulfurization (ODS)

In ODS, the refractory sulfur compounds (thiophene, benzothiophene, dibenzothiohene or more) are oxidized by different oxidants such as H_2O_2, O_3, H_2SO_4, NO_2 and tBuOOH and converted to less harmful products. The less harmful products may be sulfoxides or sulfones and these can be subsequently removed by different methods like adsorption or extraction at ambient conditions.

The main disadvantage of this process is in finding a suitable oxidants because inappropriate oxidant may lead to the unwanted side reactions. Another disadvantage is secondary treatment; solvent selection in extraction is critical due to extraction impacting the quality of the fuel [39],[50],[51],[52].

The other advanced oxidation processes such as photo-assisted oxidation [53], ultrasound-assisted oxidations, and cavitation [47] have been widely reported for desulfurization. Recently, suryawanshi and co-workers have reported a non-catalytic hydrodynamic cavitation-advanced oxidation process for desulfurization of fuels which is highly effective- 100% thiophene sulfur removal was obtained and the new process is considered to have potential to be used as alternative technique for deep desulfurization in industry [54–56].

1.2.2.2.1 Petrostar process

In this ODS process, chemical oxidation removes sulfur from diesel fuel. This is a three-step process- first, water emulsion with diesel fuel, oxidation as a second step using catalyst such as peroxyacetic acid to form less harmful sulphone and finally third step in the form of separation of sulphone by extraction [57],[58].

1.2.2.2.2 SulphCo's systems

This process operates at relatively mild conditions such as low temperature, pressure and there is no phase change catalyst. Also, it requires half of capital cost compared with new high pressure hydrotreater. The estimated capital cost of SulphCo's system is \$1000bbl^{-1}[59].

1.2.2.3 Extractive desulfurization (EDS)

In EDS, solvents having a higher affinity for sulfur containing compounds are selected for selective removal of sulfur compounds. The mixture of suitable solvent with fuels is transferred to the separation unit wherein sulfur compound rich solvent phase gets separated which is then transferred to a distillation unit for solvent recovery. Multiple extraction units may be required until required level of output is obtained. This method has relatively low energy consumption. Despite of this cost advantage, EDS method has not gained popularity due to difficulty in finding appropriate solvents and tedious recovery procedure.

The solvent used for EDS is required to be chemically and thermally stable, non-volatile, non-flammable and easily regenerated due to lower vapour pressure. The use of ionic liquids as a solvent for extractive desulfurization and oxidative-extractive desulfurization has been reported in 2001 and it has been popular area of research since then. The ionic liquids reported are $[PF6]^-$, alkyl sulphates, pyridinium, dialkyl pyridinium, pyrrolidinium, alkyl sulfate, thiocynate, imidazolium, bis (trifluoromethyl sulfonyl) imide, acetate etc. or organic salt combined with cations and anions.

The disadvantages of this process are difficulty in the selection of solvent as selective extraction is necessary to maintain the quality of fuel, cost intensive process, study of thermodynamic data quite cumbersome, regeneration of the ionic liquids are difficult, may reacts with other constituents of the fuel and corrosion problem due to inappropriate solvent [60–63].

1.2.2.4 Biodesulfurization (BDS)

It is one of the alternative techniques to HDS due to its selective sulfur compound removal, specificity and mild operating conditions. In BDS, the microbial strains like *Rhodocuccus desulfovibriodesulfuricans*, *Arthrobacter*, *Brevibacterium*, *Pseudomonas stutzeri*, *Rhodococcus rhodochrous* MTCC 3552, *Rhodococcus erythropolis* are used to enhance the activity of desulfurization. These strains consume sulfur compounds as a main energy source from fuels by oxidation or reduction and convert to sulfate or hydrogen sulfide respectively. The oxidation of sulfur compound is a desirable pathway than the reduction of sulfur compounds from fuels because in oxidation pathway there is no further secondary treatment but in the reduction pathway clauss process can be used to convert hydrogen sulfide to elemental sulfur.

The main disadvantages of BDS are- slow process, requires high cost and difficult to recover or recycle of the biocatalyst or microbial strain after use, emulsion formation and major problem with commercialization due to complex reactor design [64–66].

1.2.2.5 Adsorptive Desulfurization (ADS)

Desulfurization by adsorption is based on the nature of sorbent and its capability to adsorb the refractory sulfur compounds from liquid fuels. Adsorptive desulfurization is considered to be the most demanding area of research due to various reasons such as simple, easy to operate, mild operating conditions, economical, ease of regeneration of adsorbent such as alumina, metal oxide, zeolite, metal sulfuide, silica and activated carbon [67–72]. Adsorptive deep desulfurization of transportation fuels has been a subject of discussion from decades, encompassing numerous adsorbents and modifications for improving the adsorption capacity, selectivity and ease of regeneration. Adsorption can be an excellent supplementary process in the existing HDS commercialized process and has the potential to meet ultra-low sulfur mandates at lowered costs. Thus, newer insight is essential in this regard on the various aspects ranging from adsorbent types to different modifications for materials or processes [54]. A wide variety of adsorbents have been used for deep desulfurization starting from activated carbon [73],[48], alumina, silica based sorbents [74], zeolites [75], metal oxides [76], metal–organic frameworks [77–79], graphene-like boron nitride [80], and metal-exchanged and -impregnated activated carbon, zeolite, and mesoporous materials have been reported. Adsorptive desulfurization can be categorized into two groups such as conventional adsorptive desulfurization and reactive adsorptive desulfurization. In conventional adsorptive desulfurization, sulfur compounds get adsorbed through physical adsorption and can be easily regenerated by simply thermal treatment and in reactive adsorption, the sulfur compounds get chemically bounded to the adsorbent as a sulfide after interaction/reaction of sulfur compounds with active sites of the adsorbent. Extensive research on ADS is carried out and is discussed in detail in Chapter 2.

The commercial application based on adsorptive desulfurization of liquid fuels are explained in following discussion.

1.2.2.5.1 Transport reactor for naphtha desulfurization (TReND) process

This process was developed by Research Triangle Institute. TReND is reactive adsorption process which uses regenerable metal oxide as sorbent. The operating temperature ranging from 426-535^0C with or without the presence of hydrogen gas [57],[58].

1.2.2.5.2 Selective adsorption for removing sulfur (SARS) compounds (PSU-SARS Process)

The SARS process employs adsorbent at low temperature and pressure with minimum or without consumption of hydrogen for ultra-deep desulfurization. Due to mild operating conditions, it avoids olefin hydrogenation and no change in properties of the fuels such as octane and cetane number thereby reducing operating cost of desulfurization process compared to HDS which requires more expensive H_2. SARS is believed to be cost effective approach to achieve zero sulfur fuel by removing less reactive sulfur compounds that remain after industrial HDS process. The main objective of SARS is finding a suitable adsorbent which selectively adsorbs sulfur compounds without compromising fuel quality with high capacity, high selectivity in presence of competing aromatic and olefin compounds, high reactivity towards sulfur compounds, fast kinetics and easily regenerated [66,68].

To obtain a vivid understanding of the interaction phenomena between sulfur compounds and adsorbents, the mechanisms of desulfurization are also thoroughly discussed and is classified into two groups: 1) Conventional adsorption desulfurization and 2) Reactive adsorption desulfurization.

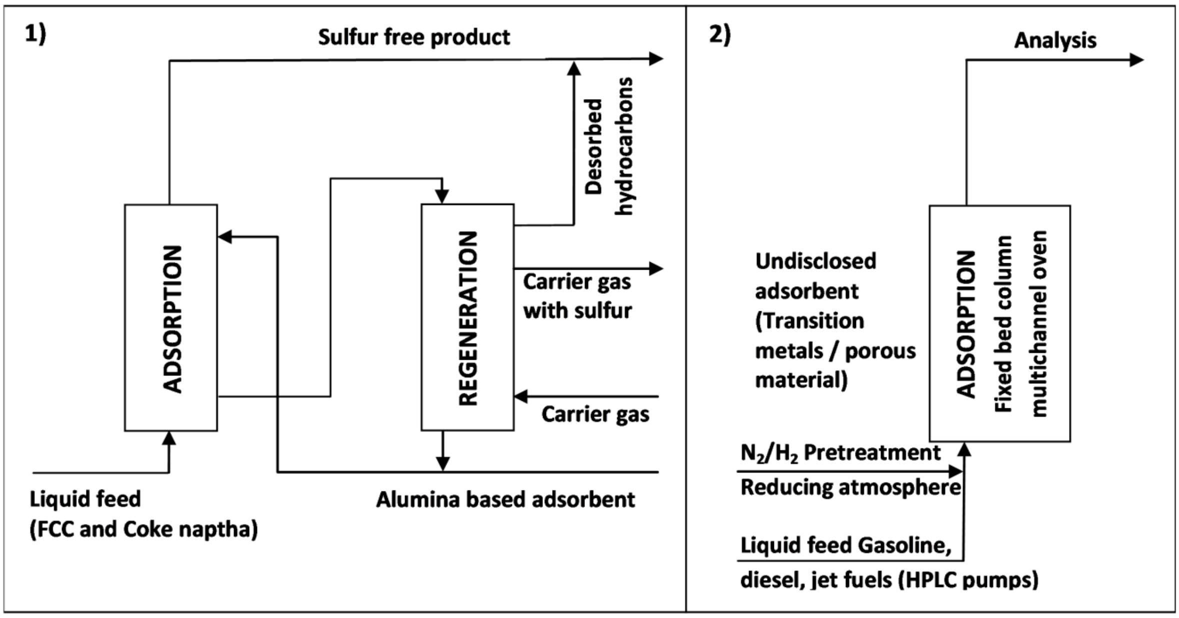

Figure 1.5: Schematic representation of 1) IRVAD process (from Irvine 1998), 2) PSU-SARS process [41,84]

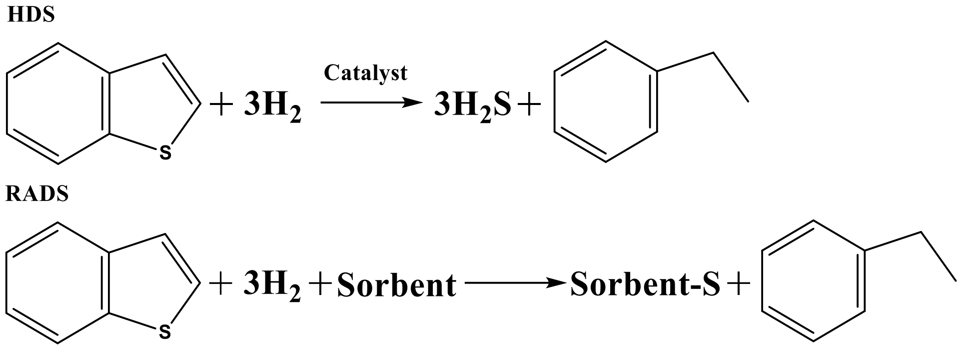

Figure 1.6: Schematic representation of reactions with sulfur compound in HDS and RADS processes [86]

1.2.2.5.2.1 Conventional adsorption desulfurization

In this physical adsorption, the organosulfur compounds interact with adsorbent to form π bonding at low temperature (below 300 ºC), low pressure (~atmospheric pressure), without H_2 consumption and low heat of adsorption. So, the sulfur compounds can get easily desorbed by changing process conditions for instance thermal/heat treatment (increasing temperature) or by lowering pressure. Further adsorbent can be easily regenerated from waste stream. The adsorbent used in adsorptive desulfurization are pure and modified activated carbon [54,81]·[82], silica [72], alumina [67], zeolite [71,83], metal oxide [70] and different catalyst like CoMo etc. Two types of processes have been developed for example, PSU-SARS[41,84] and IRVAD[85] as shown in Figure 1.5.

The IRVAD process Figure 1.5 (1) consists of counter current operation of a moving alumina based adsorbent and FCC naphtha (Irvine 1998) under 240 ºC temperature and gives 90% sulfur reduction. The regeneration of spent/used adsorbent was done by thermal treatment by slightly increasing temperature and then regenerated adsorbent recycled back for reuse. The PSU-SARS as shown in Figure 1.5 (2) process operates at a temperature under 250 ºC with transition metal based zeolite adsorbent and after adsorption less than 20 ppm sulfur remain in gasoline, diesel and jet fuel.

1.2.2.5.2.2 Reactive adsorption desulfurization (RADS)

The reactive adsorptive desulfurization (RADS), S-Zorb process of Phillips Petroleum, USA (2001, 2003), utilizes a propriety solid sorbent. This process is operated in the temperature range of 377 to 502^{0}C and pressure of 7-21 kg/cm^2 in presence of hydrogen. During RADS the sulfur is adsorbed on the adsorbent surface and remaining hydrocarbon portion is released into the process stream [57,58].

The Reactive adsorption desulfurization (RADS) technology has been commercially developed by Tao, Y SINOPEC Engineering Inc[86] and its sorbent may consists of SiO_2 (20 wt%–60 wt%), alumina (5 wt%–15 wt%), ZiO (15 wt%–60 wt%) and Ni and/or Co (a few wt%). ZiO and Ni are active components and mixture of alumina and silica are matrix (Sinopec's S-Zorb process). The principle of operation of RADS is different from HDS and the reaction schemes of both are represented in Figure 1.6. The different studies on RADS[87,88] report metal based adsorbents such as nickel/zinc oxide (Ni/ZnO), aluminium oxide (Al_2O_3), silicon dioxide (SiO_2), titanium dioxide (TiO_2), zirconium dioxide (ZrO_2) or Y zeolite to capture sulfur species then convert to metal sulfide. High selectivity and capacity are advantages of RADS performance. This technology is designed to desulfurize naphtha containing 2000 ppm sulfur in feed to less than 10 ppm of the sulfur in one step, in presence of H_2.

1.2.3 Challenges for deep desulfurization of transportation fuels to reach emission norms

1. Considering the drawbacks of HDS process in the existing refineries, it is required that a new process be developed as a supplementary/ alternative process. The modifications in the existing HDS process includes modifying in process variables, replace or modify catalyst and also, modification of reactor configuration.
2. The cost of desulfurization technology is a major problem. For example, about Rs. 28.8k crore will be required for upgradation of Indian PSUs for producing auto fuels with enhanced specifications [89].

From the above discussion, it is evident that industrially hydrodesulfurization is mainly used for removal of sulfur compounds. However, HDS is effective for removal of aliphatic sulfur compounds such as thiols, sulfides and disulfides, and has difficulty for removal of heterocyclic sulfur compounds which is important for achieving ultra-low sulfur levels.

Thus, the challenge is to develop new adsorbents/modified adsorbents, low cost materials, adsorbents from waste materials with high capacity, newer modification strategies and good selectivity for selective adsorption.

1.3 Scope and organization of the thesis

From the detailed literature review, it is evident that hydrodynamic cavitation holds great potential for disinfection of water, without forming disinfection by-products. Process integration can provide higher rate of disinfection thus minimizing the time of operation and cost of operation. Also, in the adsorption studies, materials and material modification has excellent disinfection efficiency and desulfurization capacity. Metal modification having antimicrobial property can provide higher rate of disinfection and also, in the case of desulfurization, the transition metal modification can provide strong bonding with refractory sulfur compounds. These hybrid approaches for water disinfection and desulfurization of transportation fuels appear to be more promising and have been sparsely reported.

In view of the above critical analysis, the present research precisely focuses on newer developments in the area of disinfection of water, including study of different approaches using hydrodynamic cavitation and study of different modified materials synthesized from ion exchange resins or waste material to enhance the rate of disinfection. The objectives of the study include:

Development of Water Treatment Methodology

- Disinfection of water using new materials and methods-adsorbents and cavitation
- Investigate effect of different process parameters for effective bacterial removal
- Mathematical modelling and kinetics of disinfection
- Process Integration/Intensification
- Techno-economic feasibility evaluation

Newer materials and methods for Desulfurization of Fuels

- Synthesis, design and development of new material/ nanocomposite for desulfurization of liquid fuels
- Obtain insight into sulfur removal behavior on adsorbent

The thesis is organized into 9 Chapters, including introduction, literature survey, analytical techniques and measurements, A novel hybrid cavitation process for enhancing and altering rate of disinfection by use of natural oils derived from plants, Destroying antimicrobial resistant bacteria (AMR) and difficult, opportunistic pathogen using cavitation and natural oils/plant extract, Safe water and technology initiative for water disinfection: Application of natural plant derived materials, Developing Spherical Activated Carbons from Polymeric Resins for Removal of Contaminants from Aqueous and Organic Streams and Overall conclusions and Summary, scope for future work.

Chapter-1: This chapter provides background, current scenario, history, and importance of the research topic disinfection of water and desulfurization of liquid fuels. It provides brief overview of the different processes of disinfection of water, desulfurization of liquid fuels

Chapter-2: This chapter elaborates the state of art of review of the literature in the area of disinfection of water and desulfurization of transportation fuels, identifies research gaps in both areas. This chapter also forms basis for the new findings and for identification of the research gap.

Chapter-3: Chapter 3 provides the information on analytical and characterization techniques used in research work. Details of Instrument and operating practice, specifically relating to Field Emission Scanning Electron Microscope (FE-SEM), Energy Dispersive X-ray Spectroscopy (EDX), Transmission Electron Microscopy (TEM), Fourier Transform Infrared Spectroscopy (FTIR), X-ray Diffraction(XRD), Surface Area Analyzer, Thermo gravimetric analysis (TGA), Atomic Absorption spectrophotometer (AAS), Bacteria analysis for disinfection of water, Gas Chromatography - Flame Photometric Detector (GC-FPD) and Total Sulfur analyzer (TN-TS) are provided.

Chapter-4: A novel hybrid cavitation process for enhancing and altering rate of disinfection by use of natural oils derived from plants

The study is an attempt to improvise the hydrodynamic cavitation methodology for effective disinfection of water and also to suggest prototype development for practical application. The enhancement in the disinfection efficiency was evaluated specifically for the effect of pressure, temperature, pH, microbial inoculum size and also on effect of different additives for the two model microbial strains, gram-negative (*Escherichia coli*) and gram-positive (*Staphylococcus aureus*). The efficacy of the hydrodynamic cavitation is evaluated for the two types of flows/cavitation devices – linear flow in the case of orifice and vortex flow for vortex diode. The vortex diode requires significantly lower pressures, 50% lower as compared to orifice for the similar extent of disinfection. While the bacterial disinfection at high temperature is known, the usefulness of hydrodynamic cavitation is especially evident at ambient conditions and the process is effective even at very high concentrations of bacteria, not reported so far. The reactor geometry also has significant effect on the disinfection. The present study, for the first time, reports possible use of different natural oils such as castor oil, cinnamon oil, eucalyptus oil and clove oil in conjunction with hydrodynamic cavitation. The nature of oil modifies the cavitation behavior and an order of magnitude enhancement in the cavitation rate was observed for the two oils, eucalyptus and clove oil for a very small concentration of 0.1%. The increased rates of disinfection, of the order of 2–4 folds, using oil can drastically reduce the time of operation and consequently reduce cost of disinfection. A possible mechanism is proposed for the effect of oil and hydrodynamic cavitation in cell destruction through the rupture of cell wall, oxidative damage and possible DNA denaturation. A cavitation model using per pass disinfection was used to correlate the data. The increased efficiency using oils and possible benefits of the developed process, where natural oils can be perceived as biocatalysts, can have significant advantages in practical applications

Chapter-5: Destroying antimicrobial resistant bacteria (AMR) and difficult, opportunistic pathogen using cavitation and natural oils/plant extract

The study reports, for the first time, a new and techno-economic strategy for effective removal of antimicrobial resistant bacteria (AMR) and difficult, opportunistic pathogen using cavitation and natural oils/plant extract. A hybrid methodology using natural oils of known health benefits has been discussed in combination with conventional physico-chemical method of hydrodynamic cavitation that not only provides efficient and effective water disinfection, but also eliminates harmful effects of conventional methods such as formation of disinfection by-products apart from reducing cost of treatment. A proof-of concept is demonstrated by achieving exceptionally high rates for practically complete removal of antimicrobial resistant (AMR) and relatively less researched, gram-negative opportunistic pathogen, Pseudomonas aeruginosa and gram-positive methicillin resistant, Staphylococcus aureus using a natural oil-Peppermint oil and two different cavitating reactors employing vortex flow (vortex diode) and linear flow (orifice) for hydrodynamic cavitation. > 99% disinfection could be obtained, typically in less than 10 min, using vortex diode with operating pressure drop of 1 bar and low dose of 0.1% peppermint oil as an additive, depicting very high rates of disinfection. The rate of disinfection can be further increased by using simple aeration which can result in significant lowering of oil dose. The conventional device, orifice requires relatively higher pressure drop of 2 bar and comparatively more time (~20 min) for disinfection. The cost of the disinfection was also found to be significantly lower compared to most conventional processes indicating techno-economic feasibility in employing the developed hybrid method of disinfection for effectively eliminating bacteria including AMR bacteria from water. The developed approach not only highlights importance of going back to nature for not just conventional water disinfection, but also for eliminating hazardous AMR bacteria and may also find utility in many other applications for the removal of antimicrobial bacteria.

Chapter-6: Safe water and technology initiative for water disinfection: Application of natural plant derived materials

The study reveals use of natural resources such as plant extracts and natural oils for water disinfection. Differences between oil and water soluble additives were highlighted for plant extracts and insoluble natural oils. A hybrid hydrodynamic cavitation process was quite effective in both the cases and high rates of disinfection were achieved. Studies were reported using oils (ginger, turmeric, lavender, tulsi) and rhizome derived plant extracts such as ginger, turmeric and mango ginger, as additives in process intensification (0.1% v/V). A vortex based cavitation device (vortex diode, nominal capacity 1 m3 /h) was used with pressure drop of 1 bar. A high disinfection of 96% and 88% was obtained in 15 min for ginger oil and mango ginger extract respectively as compared to 44% using cavitation alone. Acoustic cavitation gave 94% and 30% disinfection with and without additive-mango ginger extract. The FTIR analyses before and after cavitation, with ginger additive, showed no by-products formation and indicated gingerol as active component in disinfection. The per-pass disinfection values were also higher, up to 5 times than cavitation alone. Hybrid hydrodynamic cavitation using natural plant derived materials can offer a promising technology alternative in water disinfection.

Chapter-7: Developing Spherical Activated Carbons from Polymeric Resins for Removal of Contaminants from Aqueous and Organic Streams

Spherical activated carbons from polymer resin were developed with metal modifications, before/after carbonization using copper and nickel, for gradation of zeta potential (-5.01 to 8.64mV) and high metal loading (up to 12.3%). The materials provide improved removal of various contaminants from aqueous and organic streams- removal of bacteria from water and sulfur removal from fuel. The metal modified spherical activated carbons were highly effective for removal of both gram-negative, E. coli and gram-positive S. aureus bacteria. The copper modified spherical activated carbon could eliminate 99.9-100%, both bacterial content proving efficacy in water disinfection with a very high rate ~1.33×105 (CFU/ml.s). The zeta potential has significant impact with higher disinfection for high values; ~10-15% disinfection can be improved up to 100% for zeta potential changes from -5 to 8.6mV. Kinetics of disinfection was studied by accounting for zeta potential in the conventional rate model and efficacy of both the models was compared. The fit of revised model was excellent. The spherical activated carbons can be useful for removal of slightly polar contaminants from organic streams and a high capacity of 12.8, 20 and 28 mgS/g for thiophene, benzothiophene and dibenzothiophene respectively. The developed materials can provide useful applications in the area of environmental pollution control.

Chapter-8: This chapter provides the overall conclusions, and summary.

Chapter-9: This chapter provides scope for future work in the area of water treatment and deep desulfurization of liquid fuels has been highlighted.

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Chapter 2
Literature Review

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Clean environment is one of the most essential requirements for the living species in this world and water and air form two important components in this regard. It is necessary for people to have access to safe water and also, safe air, both essentially non-polluted. The quality of water and air for human consumption can be improved by pollution control measures for effective removal of contaminants; chemical as well as biocontaminants. Disinfection of water for drinking and deep desulfurization of fuels are some major processes concerned with life. Disinfection of water and desulfurization of liquid fuels are being extensively discussed and researched for a long time; disinfection being practiced over ages since ancient times! However, efforts are still required for more effective, easy to operate, techno-economical methodologies, especially to eliminate the drawbacks of the existing technologies. This chapter reviews the literature based on disinfection of water and desulfurization of transportation fuels. A specific attention is provided for commercially viable disinfection options and to critically analyse the literature for identifying research gaps. The advantages and disadvantages, especially from the point of view of techno-economic feasibility, have been highlighted.

2.1 Disinfection of water

Typically, approximately 81.6% of drinking water is provided from surface water (i.e. rivers and lakes), 10.3% from groundwater and 8% from springs. Access to safe drinking water is a serious problem mainly because of growing populations, water stress, disease causing microorganisms/ biocontaminants, toxins released by algal blooms and so on [1]. The harmful biocontaminants are bacteria, viruses and protozoan parasites (e.g. Cryptosporidium). Though some of the bacteria are harmless and beneficial for health, many of the harmful bacteria may cause serious health problem if present in water. The infections caused by pathogenic bacteria can be such harmful to the human body that may even cause death for aged people or people having low immunity. For example, pontiac fever of pneumonia is caused by *Legionella pneumophila* bacteria [2]. Another common bacteria *E. coli*, representing fecal contaminant, causes serious problems such as food poisoning and diarrhea, which might lead to death. The removal of microbes can be done by a series of unit operations such as coagulation, followed by sedimentation and filtration (e.g. membrane filtration) [3]. The physical forms of water treatment processes only remove microbes without inactivating the microbes or without destroying cellular structure or content. To stop the multiplication of pathogenic bacteria in water reservoirs, there are many conventional and proven methods at present. Such treatments help in reducing the adverse impact of biocontaminants. In US, introduction of disinfection step in water treatment reduced cholera by 90%, typhoid by 80% and amoebic dysentery by 50% [4]. The selection of suitable disinfection method depends upon several factors such as the water characteristics including type and concentration of microorganisms, quality after treatment, toxicity of disinfecting agent, formation of disinfection by-products, plants characteristics whether Waste Water Treatment Plants (WWTPs) or Drinking Water Treatment Plants (DWTPs), costs/economy [5]. Also, the disinfection efficiency is affected by many common interferences that reduce the microbial inactivation, e.g. ferrous, manganese ions, nitrites, sulphides and organic substances that reduce the concentration of oxidizing disinfectants and also participate in generating disinfection by-products with adverse health effects.

2.1.1 Disinfection methods

The disinfection technologies can be divided into three groups.

1. Natural processes (Slow sand filtration, infiltration/percolation in the soil, wastewater stabilization ponds and constricted wetlands)
2. Conventional physical and chemical methods (chlorine, chlorine dioxide, ozone, peracetic acid and ultraviolet (UV) radiation)
3. Advanced methods and/or hybrid/combinations (Electrochemical, Photocatalytic, Copper-silver ionization, UV-LEDs, Ozone + H_2O_2, Ozone + UV radiation, H_2O_2 + UV radiation, UV radiation + TiO_2, Membranes technology, Cavitation)

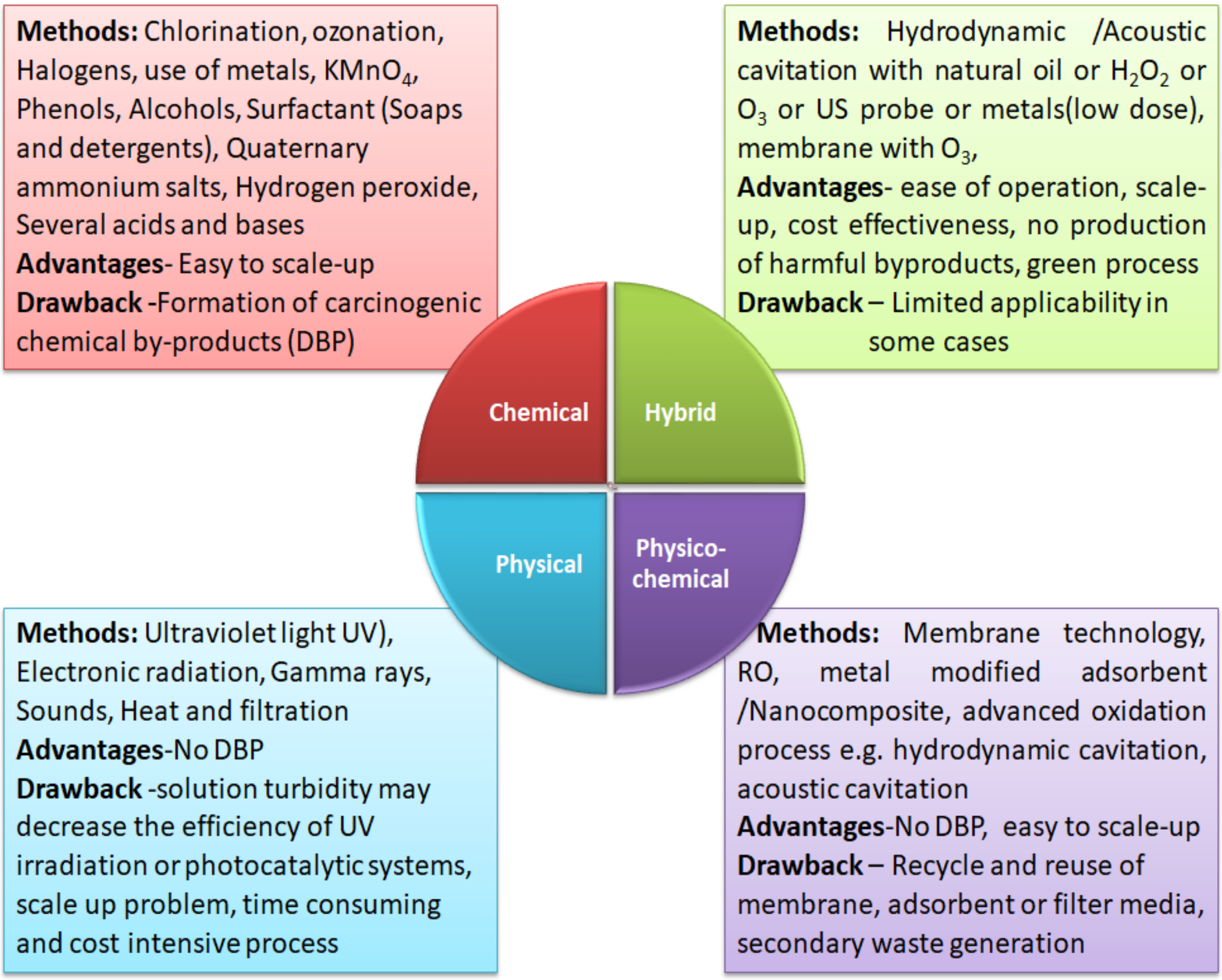
2.1.1.1 Natural disinfection processes

Sand filtration is one of the oldest methods in which the purification of water takes place on superficial biofilm present on the filter medium. Nearly 2-log reduction or ~99% disinfection can be obtained for common bacteria and viruses [6]. The other common methods include porous filter media such as clay, ceramic filter; ceramic filter having 0.2µm pore size produces disinfection, in log reduction, for *E. coli* >7.9, *Shigella dysenteriae* >6.9, *Vibrio cholera* >4, *Giardia lamblia* >6.5, *Cryptosporidium parvum* >3 and for *Entamoeba histolytica* >5.9. Infiltration/Percolation in the Soil consists of layer of sand with 1.5-2 m thickness gives nearly 5-log reduction of *fecal coliform* and complete removal of Helminth eggs [7]. Several large-scale natural disinfection methods like wastewater stabilization ponds consist of an oxidation basin of size 1.5-2m depth with retention time of 10–50 days in series with final basin of height 0.5-1m for aeration. Verbyla et al. reviewed 71 different wastewater treatment pond systems that exhibited weak to moderate virus removal and usually, 1-log reduction for every 14.5–20.9 days was achieved [8].

In natural disinfection processes, the main disinfection by physical means was achieved by sedimentation, adsorption or mechanical filtration and by chemical means includes releasing of oxygen from plants, antibiotic substances by macrophytes or acidic substances like tannic acid and Gallic acid secreted from rhizomes of aquatic plants caused disinfection of several microbes *Pseudomonas*, *Escherichia coli*. The macrophytes *Scirpus* and *Phragmites* causes 3-log reduction of *Total* and *Fecal coliform* [9].

The simple method of solar disinfection utilizes solar/ultraviolet range of light for direct or exogenous inactivation of microorganisms; direct disinfection is mediated through chromophores such as nucleic acid, protein after absorption of light. Indirect disinfection is achieved through production of reactive oxygen from transfer of energy or electron to dissolved oxygen or other solution constituents after excitation of chromophores. Solar disinfection in solar pond is reported where the water is covered with glazing (sheets of plastic or glass). Due to the greenhouse effect of glazing cover, the temperature of pond increases up to 63^0C which is close to pasteurization temperature (~65^0C). In 1 min of exposure time, 90% deactivation takes place for protozoa (*Giardia, Cryptosporidium, Entamoeba*), bacteria (*V. cholerae, E. coli, Shigella, Salmonella Typhi*) and in 5 min of time of exposure 99.99% deactivation can be achieved [10,11],[12].

Figure 2.1 lists different classes of disinfection methods other than natural process, with advantages and disadvantages.



Methods: Chlorination, ozonation, Halogens, use of metals, $KMnO_4$, Phenols, Alcohols, Surfactant (Soaps and detergents), Quaternary ammonium salts, Hydrogen peroxide, Several acids and bases

Advantages- Easy to scale-up

Drawback -Formation of carcinogenic chemical by-products (DBP)

Methods: Hydrodynamic /Acoustic cavitation with natural oil or H_2O_2 or O_3 or US probe or metals(low dose), membrane with O_3,

Advantages- ease of operation, scale-up, cost effectiveness, no production of harmful byproducts, green process

Drawback – Limited applicability in some cases

Methods: Ultraviolet light UV), Electronic radiation, Gamma rays, Sounds, Heat and filtration

Advantages-No DBP

Drawback -solution turbidity may decrease the efficiency of UV irradiation or photocatalytic systems, scale up problem, time consuming and cost intensive process

Methods: Membrane technology, RO, metal modified adsorbent /Nanocomposite, advanced oxidation process e.g. hydrodynamic cavitation, acoustic cavitation

Advantages-No DBP, easy to scale-up

Drawback – Recycle and reuse of membrane, adsorbent or filter media, secondary waste generation

Figure 2.1: Different classes of disinfection processes other than natural process with their advantages and disadvantages

2.1.1.2 Conventional disinfection methods

The conventional disinfection methods such as chlorination (by chlorine gas, sodium hypochlorite or calcium hypochlorite), use of ozone, chlorine dioxide, and chloramines are effective and inexpensive chemical disinfectants. However, these can react with naturally occurring organic compounds and inorganic matter bromide or iodide, anthropogenic compounds and produce disinfection by-products for example, trihalomethanes, N-Nitrosodimethylamine, and haloacetic acids having mutagenic, carcinogenic effects. The DBPs can cause premature birth, low birth weights, miscarriage, stillbirth and congenital disorder [13],[14]. Furthermore, the chemical disinfectant are also ineffective for microorganism that get hidden in biofilm or in loose deposits. The other conventional physical disinfection methods are heating, UV or ionization radiation, microwave, plasma, and membrane separation which are relatively effective and also does not produce any DBPs. However, these methods require high equipment cost, long treatment times and have treatment capabilities mainly on small scale [15]. The most commonly used disinfection methods are discussed in detail in next section. Chlorination has been the subject of investigation for many years due to formation of harmful DBPs and has been reviewed by many researchers. Reviews of chlorination chemistry and possible disinfection by-products formation also highlight the importance of this disinfection study.

In this critical review, after initial overview of chlorination process, acute toxicity of chemical disinfection and other commonly used disinfection methods are discussed, followed by discussion on different advanced disinfection processes. Finally, novel approaches for disinfection of water are evaluated.

2.1.1.2.1 Chlorination

Chlorination is the most common technology used today worldwide, in general and Asian countries, in particular. It is easy to use/handle, has less labour requirement and is cost-effective and therefore is being widely used as a primary disinfectant from many decades for disinfection of water. In addition, residue of chlorine prevents recontamination in distribution system. The major sources of chlorination for water disinfection are chlorine gas, sodium hypochlorite and calcium hypochlorite [16],[14].

Chemistry of chlorination

When the chlorine gas or sodium hypochlorite or calcium hypochlorite mixed with water it results in production of hypochlorous acid, HOCl and, in its disassociated form of OCl^- negatively charged hypochlorite ion collectively known as "free available chlorine". The HOCl is more effective strong disinfectant than OCl^-.

$$Cl_2(g) + H_2O \rightarrow HOCl + H^+(aq) + Cl^-(aq)$$

$$NaOCl + H_2O \rightarrow HOCl(aq) + Na^+(aq) + OH^-(aq)$$

$$Ca(OCl)_2 + 2H_2O \rightarrow 2HOCl(aq) + Ca^{2+}(aq) + 2OH^-(aq)$$

After any chlorination, dechlorination is to be done for removal of any chlorine residue [16],[14].

2.1.1.2.2 Chlorine gas

The chlorine gas is liquefied under pressure and is typically stored as liquid in cylinders or in tank for large scale application. Chlorine is highly toxic and requires stringent safety measures. The mixing of chlorine gas in water in chlorinator produces hypochlorous acid (HOCl) for disinfection [14],[17].

2.1.1.2.3 Sodium hypochlorite

It is produced by reaction between chlorine and sodium hydroxide with a maximum concentration of 15% w/w Cl_2. It is safe, easy to use and expensive compared to chlorine gas but it is unstable in nature and can get converted into sodium chlorate. To improve its stability caustic soda (0.5%) is added which is corrosive in nature. The factors affecting the degradation of sodium hypochlorite solutions includes:

- The presence of certain metals such as Iron, Copper, Cobalt or Nickel;
- Contact of bulk hypochlorite solution to UV Light/sunlight;
- At high temperature more rapid loss of sodium hypochlorite solution with time.

To reduce the decomposition and increase its stability, the pH of sodium hypochlorite is maintained alkaline. The alkaline pH leads to scaling at dosing area which reduces pipe diameter, pump capacity and flow rates [16],[18].

2.1.1.2.4 Calcium hypochlorite ($Ca(OCl)_2$)

It is in the form of white powder, as tablets or as granules for use in chlorination. The granular calcium hypochlorite is either in the chlorinated lime form or in the high-test hypochlorite. The chlorinated lime is the mixture of $Ca(OH)_2$, $CaCl_2$, $Ca(OCl)_2$ and also contains 65-80% w/w inert material in the powdered calcium hypochlorite. The high-test hypochlorite (HTH) tablet contains 30-35% w/w inert material. The calcium hypochlorite feeders are manufactured for both large and small scale. For larger flows, volumetric or gravimetric feeders are used whereas for smaller flows (typical in medium-sized and small schemes), high test hypochlorite in solid tablet form is used (65% w/w Cl_2). Application in tablet or granular form prevents clogging and blockage of pumps and equipment [16],[17],[18].

2.1.1.2.5 Electrochlorination

Electrochlorination is based on production of sodium hypochlorite (0.5-1% w/w Cl_2) through electrolysis of dilute brine (aqueous sodium chloride / high purity salt). At low concentration, NaOCl is stable but cannot be stored for more than 24 to 36 hours. The soft water is used to avoid scaling to electrode. During electrochlorination, hydrogen gas is produced as a by-product which is an explosive hazard and proper venting should be maintained to the storage tank. The selection of electrode is an important step in the electrochlorination, the plate type of electrode with chemical resistant is preferred for this operation. Sodium hypochlorite is produced by continuous electrochlorination of brine [19].

The representation of electrochemical reaction is:

$$NaCl + H_2O \rightarrow NaOCl + H_2$$

Sodium chloride + Water=Sodium hypochlorite + Hydrogen gas

At Anode,

$$2Cl^- + 2e^- \rightarrow Cl_2$$

At Cathode,

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2$$

Overall reaction is

$$Cl^- + H_2O \rightarrow OCl^- + H_2$$

The efficiency of the process depends upon feed rates of brine, dilution of brine, the temperature of the dilute brine entering the cell, the electrode (particularly anode) condition, hypochlorite storage conditions to avoid degradation of product and the water used for the process (required to be free of hardness -calcium and magnesium ions). The total hardness of the feed water required is typically less than 15 mg $CaCO_3$/l. As per EPA 2011 manual, the material for anode is made up of a titanium base with a precious metal oxide coating and the cathode typically of either Hastelloy C (a nickel-based alloy) or titanium.

The degradation of hypochlorite product is principally due to:

- Vitalisation of chlorine (accelerated during forced air venting)
- If tank is contaminated, decomposition of hypochlorite to O_2 and NaCl
- At high temperature electrolysis lead to formation of chlorate by-product
- Maximum storage time should ideally be limited to between 36 and 48 hours, even if up to 72 hours (if storage tanks are clean) [20].

2.1.1.2.6 Chlorine dioxide (ClO_2)

Chlorine dioxide is a yellow-green gas and is unstable strong oxidising agent, more or equally powerful bactericidal agent than chlorine. The representation of the reaction for production of chlorine dioxide from sodium hypochlorite and hydrochloric acid:

$$5NaClO_2 + 4HCl \rightarrow 4ClO_2 + 5NaCl + 2H_2O$$

It is reported that the strong oxidising activity of chlorine dioxide can disinfect microorganisms through inactivation/interruption in enzymatic and protein synthesis [20],[7].

2.1.1.2.7 Ozone

It is an unstable gas, extremely reactive oxidizing agent produced by electrolysis, photocatalytic, radiochemical reaction or electric shocks. After formation of ozone, it rapidly gets dissociated into an oxygen molecule and nascent/atomic oxygen. The disinfection efficiency of ozone is higher than chlorine.

The representation of dissociation of ozone:

$$O_3 \rightarrow O_2 + O^{\cdot}$$

Due to its bactericidal power, it can be used in combination with UV or can be used alone for reduction of colour, UV absorbance and organic pollutant along with microbial inactivation. The capital costs for ozonation are comparatively high. For small system, the cost of electricity is of 26 to 43% of the total operating and maintenance costs [7].

2.1.1.2.8 Peracetic acid (PAA)

It is one of alternative chemical disinfection method for chlorination and is produced by reaction between hydrogen peroxide and acetic acid. When used, PAA decomposes into strong oxidising agent hydrogen peroxide, reactive oxygen radicals or hydroxyl radicals which react on cell wall or cell membrane of microorganisms apart from disturbing enzymatic activity and DNA system. It also further increases the BOD, COD due to the formation of acetic acid in final effluent [21]. The representation of dissociation of peracetic acid is:

$$CH_3CO_3H + H_2O \rightarrow CH_3COOH + H_2O_2$$

Lubello et al. [22] reported hybrid disinfection of PAA with UV radiation and excellent disinfection behaviour than H_2O_2 with UV radiation and which is 4.5-5.5 log reduction than 3-3.5 log reduction respectively.

2.1.1.2.9 Ultraviolet (UV) irradiation

UV is electromagnetic radiation (1-400 nm) and lies between X-rays and visible light. In disinfection of water, it can be applied as a secondary or tertiary treatment process rather than primary treatment process. Effectiveness of the process largely depends upon suspended particles, particle sizes, or concentrations of dispersed microorganisms. It is highly effective against pathogenic microorganisms for example (oo)cyst of Cryptosporidium and Giardia. Its performance can be enhanced by combining with other disinfection methods [23],[24].

2.1.1.2.10 Disinfection by-products (DBPs)

In the chlorination process, a part of disinfectant reacts with natural organic matter, inorganics and metals. The total chlorine is combination of combined chlorine and free chlorine. The combined chlorine reacts with ammonia and nitrogen present in water and unavailable for disinfection. The free chlorine is the residual chlorine available for disinfection.

The chlorine combines with organic matter and produces organochlorine by-products. The major four chlorinated compounds are collectively called as the trihalomethanes (THMs). According to EU drinking water Regulations SI 278 of 2007, maximum allowable limit for total THMs is of 100 µg/l [25]. Another 9 organochlorine by-products are haloacetic acids (HAAs). WHO recommends a provisional guideline value of 0.7 mg/l for both chlorate and chlorite and for bromate of 0.01 mg/l based on health considerations [26]. Table 2.1 lists disinfection by-product formation by different disinfection processes.

Table 2.1: Disinfection by-product formation by different disinfection processes

Processes	By-product issues
Chlorination	Organochlorine by-products, THMs- bromoform (tribromomethane); dibromochloromethane; bromodichloromethane; chloroform
Chlorination	Organochlorine by-products, HAAs- Monochloroacetic acid (MCAA), Dichloroacetic acid (DCAA), Trichloroacetic acid (TCAA), Monobromoacetic acid (MBAA), Dibromoacetic acid (DBAA), Tribromoacetic acid (TBAA), Bromochloroacetic acid (BCAA), Dibromochloroacetic acid (DBCAA), Dichlorobromoacetic acid (DCBAA)
Hypochlorite	Inorganic by-products, bromate and chlorate
Chloramination	No significant by-product issues. Only nitrate formation in distribution system (indirect issue)
Ozone	If the concentration of bromide is high in water then bromate formation, N-nitrosodimethylamine (NDMA)
Chlorine dioxide	Inorganic by-products e.g. chlorate, chlorite
UV	No significant by-product issues

The production of THM and HAAs compounds is a function of pH, temperature, contact time, free chlorine concentration, type and concentration of oxidizable organic content in water. HAA production decreases with increasing pH. The control measures to limits the formation of

THMs include:

- Avoid chlorinating raw untreated surface water/groundwater and treat surface/ground water before chlorination to remove any other organic matter.
- Limit the use of free chlorine concentration, use low pH and minimum contact time
- Dechlorination
- Use chloramination to provide a residual in disinfection or use other alternative oxidant or UV as primary disinfectant.
- THMs can be removed by air stripping, GAC or nanofiltration, this method is costly compared with minimising formation, and is little used.
- The DBPs are dependent on pH and alkalinity.
- In case of hypochlorite and chlorine dioxide; chlorate and chlorite DBPs are formed due to inorganic content in water and it can be minimized by controlling the dosage of chlorine dioxide or minimizing storage time of hypochlorite solution.

The organic content is more in surface water sources compared to ground water. The organic matter can be minimized by proper coagulation, filtration methods. The oxidation and/or GAC filtration may be essential to reduce elevated levels of dissolved organic matter such as humic substances (either in dissolved form or in the colloid form) before disinfection. The concentration of organic content varies from season to seasons- for examples in rainy season, organic content is more indicating increased production of disinfection by-products. Thus, there is a need for alternative technology or modification in existing technology or follows key controlling measures to avoid formation of DBPs [27].

2.1.1.2.11 Acute toxicity

Acute toxicity is another problem of chemical disinfectant and is produced due to residuals of chemical disinfectants present in treated water. The disinfection step is the last process of every water treatment plant (Waste Water Treatment Plant (WWTP) or Drinking Water Treatment Plant(DWTP)). The purpose of residual present in water is to avoid recontamination of microorganism during transportation, storage and supply. The chemical residuals such as chlorine and PAA are toxic to aquatic life. The free chlorine residue of concentration <0.18 mg/L and 2 mg/L for PAA has shown acute toxicity for *Daphnia magna, Vibrio fischeri* and *Pseudokirchneriella subcapitataa* [28].

2.1.1.3 Advanced disinfection methods

Considering the disadvantages of conventional disinfection methods, several new methods have been proposed such as membrane filtration, electrochemical, photocatalytic, UV-LEDs, copper-silver ionization, solar disinfection, advanced oxidation processes and hydrodynamic cavitation. Table 2.2 lists some of the advanced disinfection methods and a detailed literature review of cavitation-advanced disinfection methods is provided in tables 2.3 and table 2.4.

2.1.1.3.1 Membrane filtration

Membranes are semi-permeable physical barrier for removal of microorganisms, particulate, natural organic matter, when driving force is applied. The types of membrane filtration are microfiltration, ultrafiltration, nanofiltration and reverse osmosis. It has ability to provide quality water, no chemical disinfectant demand, is compact, has ease of operation, less maintenance and less or no sludge generation. Microfiltration has pore size range of 0.1–10µm and is able to remove suspended solids, macromolecules and also bacteria but not suitable for virus removal application. Ultrafiltration has pore size of 0.01–0.1µm and is typically used for removal of macromolecules, viruses, humic acids and DBP precursors. In addition to this other two types of filtration, nanofiltration and reverse osmosis have pore size of 0.001-0.1µm and <0.001µm respectively. Nanofiltartion is useful for removal of microcystins (produced by many cyanobacteria species), color, Volatile Organic Compounds (VOCs), pesticides, MTBE (Methyl tert-butyl ether), sulphates, phosphates etc. Reverse osmosis is useful for removal of viruses, protozoan (oo)cysts, other Metal ions, metals such as arsenic, lead from water/waste water [29],[30]. Table 2.2 describes the effectiveness of membrane filtration in disinfection of water. Efficiency of membrane filtration depends upon the quality of water; water should be free from solids specially in case of RO pre-treatment is essential for removal of suspended, colloidal solids. Fouling is a major problem of membranes and it can be minimized by the combined operation of low-pressure membrane filtration followed by high pressure membrane filtration.

2.1.1.3.2 Advanced Oxidation Processes (AOPs)

There are different AOPs reported for oxidation of organic and inorganic micropollutants and also can be used for microbial disinfection. Some of the combinations are reported for disinfection such as ozone with hydrogen peroxide [31], ozone with UV radiation[32], hydrogen peroxide with UV radiation [33] and titanium oxide with UV radiation [34]. The chemical oxidants such as hydrogen peroxide, ozone, titanium oxide produce different strong oxidising agent such as hydroxyl radicals, HO_2^{-}, H_2O_2 which oxidise cell wall of microorganisms causing cell death. These AOPs are advantageous over chemical disinfection processes as no disinfection by-product is formed. The disadvantages are the high operating cost and limited large-scale application. However, with some modifications many of these processes can have potential for real life applications e.g. high efficiency UV lamp, solar based photocatalysis or visible light catalysts, or enhanced reactor designs.

The oxidation process of hydrogen peroxide and ozone is known as peroxone and is most effective disinfectant compared to ozone alone. The concentration time (CT) value required for ozone is greater than peroxone for *Giardia muris* inactivation for 1 log reduction, ozone and peroxone CT value is 1.6-2.8 and 1.2-2.6 (mg.min.L^{-1}) respectively and similarly for 2 log reduction ozone and peroxone CT value is 3.4-5.4 and 2.6-5.2 (mg.min.L^{-1}) respectively [31].

The other oxidation processes include those induced by application of UV with ozone, photochemical reaction generating redox radicals; $^{\bullet}OH$, H_2O_2 more effective than ozone alone. Fang et al. reported synergistic effect of UV/ozone simultaneous with ozone, concentration as low as 0.05 mg/L more effective (~ 4 log reduction) than ozone-UV, UV-ozone sequential manner than UV alone and then Ozone alone (~1.5 log reduction) for *E. coli* reduction [32]. Use of H_2O_2/UV combination improved the inactivation of bacteria, and viruses marginally as compared to UV alone and H_2O_2 was not effective[35,36]. On the other hand, solar irradiation with H_2O_2 with Fe^{2+} showed high inactivation for *e. coli* 250% than 200% for Fe^{2+}/hv, 150% H_2O_2/hv and 100% for *hv* only [33]. The photocatalytic disinfection of *E. coli* using 0.1 g of TiO_2 with UV irradiation was effective and 100% disinfection was reported in 2-3 min [34].

The UV/PS; UV-activated persulfate technology is most effective for removal of *M. aeruginosa* compared with UV-C treatment. In the UV/PS process, approximately 98.2% of algal cells were removed over a period of 120 min with 1500 mg/L of dosage. Synergistic study is carried out, PS alone showed very little to no significant removal at 1500 mg/L (about 6 mM) dosage in 120 min, upon application UV irradiation could degrade algal cells to obtain 21.8% disinfection within 120 min and UV/PS hybrid process displayed the 98.2% removal efficiency [37].

Table 2.2: Advanced disinfection methods

Disinfection methods	**Features**	**Microorganism & Disinfection efficiency**	**Ref.**
Microfiltration	Porosity 0.1-10 µm, P 1-5 bar	*E. coli & Fecal coliform* **5.4–6 LR** *Giardia Muris* >**4–6 LR** *MS2 Coliphages* **0.3–2 LR**	[29],[38]
Ultrafiltration	Porosity 0.01-0.1 µm, P 1-7 bar	*E. coli & Fecal coliform* **5.5–>6 LR** *Giardia Muris* **>4–6 LR** *MS2 Coliphages* **0.4–2 LR**	[29],[38]
Nanofiltration	Porosity 0.001–0.1 µm, P 5–10 bar	*MS2 Coliphages* **2-3 LR**	[29],[38]
Reverse Osmosis	Porosity <0.001 µm, P 15–70 bar	*MS2 Coliphages* **3.5-4.5 LR**	[29],[38]
UV+PAA	*E. coli*	PAA=2-8 mg/L, UV= 100-300 mJ/cm^2, **100%** *E. coli* (10-30 min)	[39]
Sono-Electro disinfection	*E. coli* ~10^3 CFU/mL	Sono disinfection **1 LR** (60 min) US: 200W Electro-disinfection **3 LR** Current density:11.46 A/m^2 Sono-electro disinfection **3 LR** US: 200W, Current density: 8.91 A/m^2	[40]
Solar photocatalytic	*E. coli* ~10^6 CFU/mL	Solar photolysis **1 LR** (40 min) Solar photocatalytic (absence of HA) **6 LR** (60 min) Se-doped TiO$_2$, N-doped TiO$_2$ & Se-N-co-doped TiO$_2$ Solar photocatalytic (presence of HA) **6 LR** (60 min) (Se-doped TiO2 & Se-N-co-doped TiO$_2$) Solar photocatalytic (presence of HA) **6 LR** (90 min) (N-doped TiO$_2$)	[41]
Ultrasound (US) + UV radiation	*E. coli*, *Total coliform* ~10^3 CFU/mL	US: 350W, *E. coli* **1.6 LR**, *T. coliform* **1.7 LR** (15 min) UV: 1656 mJ/cm^2 US: 1400W, *E. coli*: **>4 LR**, T. coliform: **3.9 LR** (15 min) UV: 1656 mJ/cm^2	[42]
UV-activated persulfate (UV/PS) technology	*M. aeruginosa*, PS of 1500mg/L	PS **0** (120 min) UV **21.8** (120 min) UV/PS **98.2** (120 min)	[37]

2.1.1.3.3 Cavitation Technology

Among all the advanced processes, cavitation technology can be considered to be the most promising technology for effective removal of wide range of microorganisms, simple, easy to operate, can be applied for large scale operations. Cavitation is a process of rapid change in phase of water to gaseous vapor/bubbles/vapor, followed by growth and implosion of cavities in an extremely small duration. Depending upon the mechanisms of cavities generation, the cavitation is classified into 4 classes.

1. Acoustic Cavitation
2. Hydrodynamic Cavitation
3. Optic Cavitation
4. Particle Cavitation

Out of these above classes, acoustic and hydrodynamic cavitation are practical methodologies and vast research for disinfection of water using acoustic and hydrodynamic cavitation reactors has been reported in the literature. In the acoustic cavitation reactors, cavitation is induced as an effect of acoustic wave propagation with ultrasound waves of frequency of tens of kHz to tens of MHz by a transducer in water. Because of its structure and working mechanism make acoustic cavitation difficult to scale up to practical/ large scale applications as the cavitation intensity is not uniform and decreases with the distance from the horns in the acoustic cavitation reactor. Hydrodynamic cavitation reactors (HCRs) on the other hand have potential in large scale applications/ industrial level/ corporation level [43],[44].

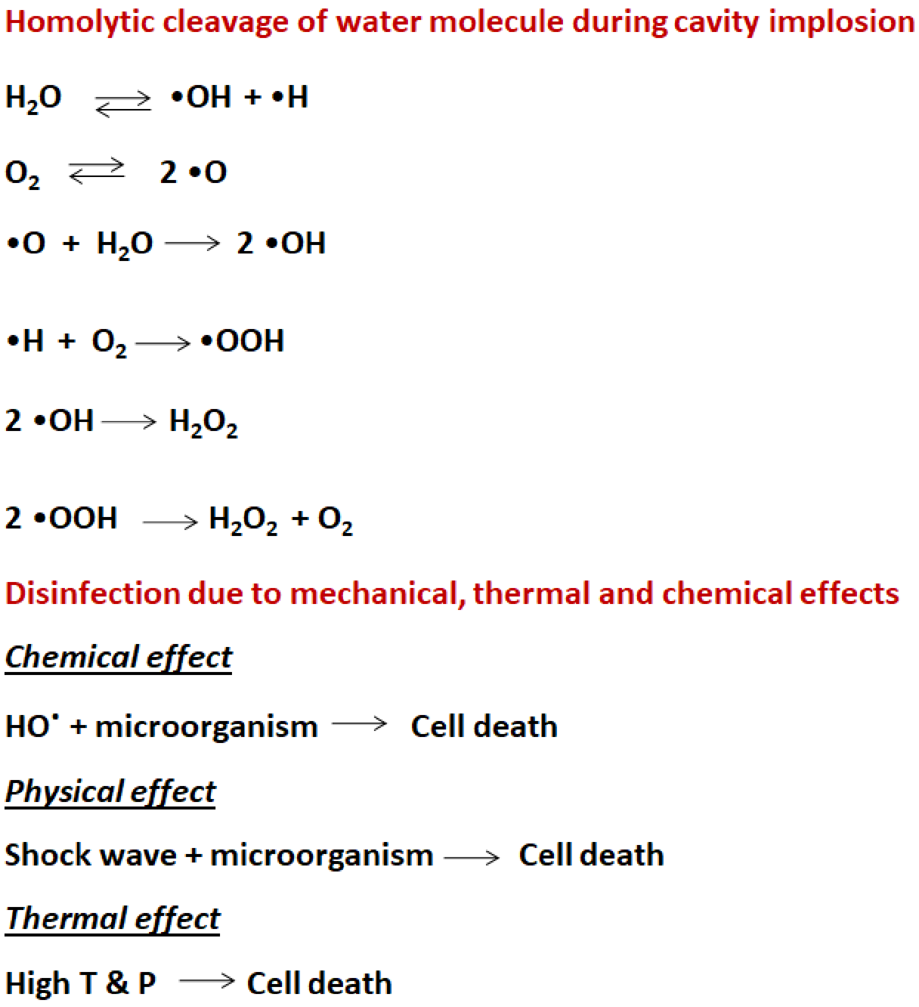
2.1.1.3.4 Energy release in hydrodynamic cavitation

The energy release from cavity implosion and mechanical, thermal and chemical effects [45],[46,47].

Mechanical effect: The mechanical effect is principally by high shear stress, shockwave and microjet with high velocity. The shear stress releases pressure upto 35 kPa, shock wave released by compression of bubbles adiabatically with a pressure of 5500 bar and an average velocity of 2000 m/s, microjets produce maximum water hammer pressure of 450 MPa with a velocity of 100 m/s.

Thermal effects: As the cavities collapse, local hot spots get generated with extremely high temperatures of 2000-6000K depending on the distance. The rates of heating and cooling at this spot within microseconds is above 1010 K/s.

Chemical effect: Homolytic cleavage of water molecule results into generation of $^{\bullet}H$ and $^{\bullet}OH$ active free radicals. These are strong oxidizing agents and can induce series of oxidation reactions and different oxidising agents for destruction of microorganisms. Figure 2.2 illustrates the generation of active radicals, oxidising species and the effect of Mechanical, Thermal and Chemical effects on microorganisms.



Homolytic cleavage of water molecule during cavity implosion

$H_2O \rightleftharpoons \bullet OH + \bullet H$

$O_2 \rightleftharpoons 2\,\bullet O$

$\bullet O + H_2O \longrightarrow 2\,\bullet OH$

$\bullet H + O_2 \longrightarrow \bullet OOH$

$2\,\bullet OH \longrightarrow H_2O_2$

$2\,\bullet OOH \longrightarrow H_2O_2 + O_2$

Disinfection due to mechanical, thermal and chemical effects

Chemical effect

$HO^{\bullet}$ + microorganism $\longrightarrow$ Cell death

Physical effect

Shock wave + microorganism $\longrightarrow$ Cell death

Thermal effect

High T & P $\longrightarrow$ Cell death

Figure 2.2: Generation of active radicals, oxidising species and the effect of Mechanical, Thermal and Chemical effects

2.1.1.3.5 Hydrodynamic Cavitation Reactors (HCRs)

The hydrodynamic cavitation reactors (HCRs) are classified into two groups - 1) Rotational HCRs driven by electric motor and 2) Non-rotational HCRs requiring use of pumps. In rotational HCRs, after acceleration, static pressure drops and generates cavitation. In non-rotational HCRs, cavitation is generated using sudden constriction in the flow path which decreases the static pressure and increases velocity of the fluid. The rotational HCRs such as Rotor-stator type of reactor [48], rotating disc or simple milling cutter [49] are used for water disinfection. Both the rotational and non-rotational HCRs are claimed to be cost effective and capable of being scaled up for large scale application. The non-rotational HCRs such as orifice [50], venturi [51], vortex diode [52,53] are typically used to investigate the capability of hydrodynamic cavitation in inactivation of microorganisms. Figure 2.3 shows some of different types of HCRs reported in the literature during the past years. The performance of different types of HCRs is compared in Table 2.3 and Table 2.4.

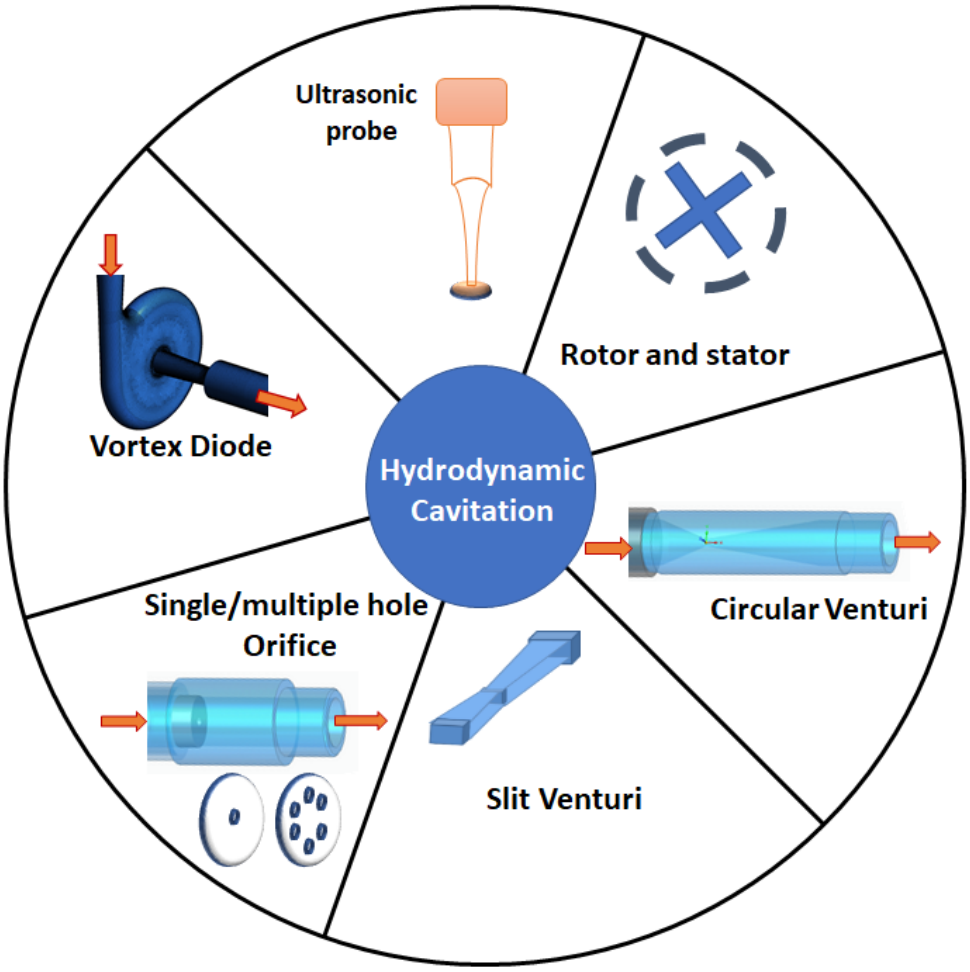


Figure 2.3: Different cavitating devices of HCRs

2.1.1.3.6 Performance evaluation of rotational HCRs

The disinfection efficiency of rotational HCRs is based on mechanical impact and shear force. Mezule et al. used milling cutter to create bubbles and heat energy and found 75% disinfection in short treatment time of only 3 min for *E. coli* disinfection [49]. The energy efficiency and disinfection effectiveness are not satisfactory and far lower than other rotational and non-rotational HCRs. Sun et al. [54] studied the inactivation of *E. coli* by heat generated by rotor and stator type of device operated at rotational speed of 3600 rpm and obtained disinfection of 35.43% and 100% for *E. coli* inactivation at flow rates of 8 and 11 L/min, respectively for 14min duration. It also showed that thermal performance of rotational devices are based on flow rate, increased flow rate enhanced the heat generation rate. Kwong et al. reported disinfection using thermal effect/ heat generation employed by cone shaped dimples located on front cover, rotating disk and rear cover. As the rotor is rotated, the dimples in front cover generate three separation regions, in which the static pressure drops below the critical value thereby activating cavitation [55]. The thermal effect is most predominant mechanism for water disinfection in rotational HCRs. Šarc et al. [56] investigated the effect of supercavitation flow pattern by rotation generator and venturi for Gram negative (*L. pneumophila, E. coli*) and Gram positive (*B. subtilis*) bacteria. It was found that the supercavitation with high shear forces of rotation generator disrupted bacterial cells and disinfection to the extent of 3 log reduction of all bacteria was reported which is higher than conventional venturi. Similarly, Cerecedo et al. obtained 100% *E. coli* inactivation in 7-8 min [48]. The thermal efficiency for rotational HCRs such as rotor and stator type of device [54] is 91%, heat generator [55] 86%, shockwave power reactor [57] 84%, reportedly higher than non-rotational HCR such as triple-frequency flow cell [43] 75.4%, dual-frequency flow cell [43] 55%, high speed homogenizer [46] 43%, high pressure homogenizer [46] 54%, orifice plate [46] 60%. This is due to higher conversion of electricity to heat and resulting higher temperature is responsible for inactivation of microorganisms. The main disadvantages of the rotational HCRs are they required higher energy input and the process become cost intensive operation. Table 2.3 represents the studies of disinfection using rotational hydrodynamic cavitation reactors.

Table 2.3: Studies of disinfection using rotational hydrodynamic cavitation reactors

Cavitation System	**Condition**	**Disinfection Efficiency (%)**		**Ref.**
Rotational type of cavitating device				
Motor driven by simple milling cutter (shear induced HC)	Energy input of 490 W/L *E. coli*		**75** (3 min)	[49]
Rotor-Stator type (For 3000 rpm, R_{rotor} = 55 mm, R_{stator} = 75.5 mm For 2400 rpm, R_{rotor} = 77.5 mm, R_{stator} = 96.5 mm)	*E. coli,* 10^5 CFU/mL	3000 rpm 2400 rpm	**99.9** (10 min) **100** (7.8 min)	[48]
Rotor-Stator type (Conical dimples of D=10mm and 4.5mm depth on the rotor, front cover=30 dimples and back cover=24	*E. coli,* 10^8 CFU/mL	3600 rpm, 8 L/min 3600 rpm, 11 L/min	**35.43** (14min) **100** (14min)	[54]
Rotation Generator 9025 rpm	*E. coli, L. pneumophila and B. subtilis* 10^8 CFU/mL	*E. coli,* *L. pneumophila,* *B. subtilis,*	**99.95** (150 min) **99.98** (60 min) **99.98** (120 min)	[56]
Rotor-Stator type (Conical dimples of D=10mm and 4.5mm depth on the rotor, front cover=30 dimples and back cover=24	*E. coli,* 10^6 CFU/mL	4200 rpm, 1.4 m^3/h	**100** (4 min)	[58]

2.1.1.3.7 Performance evaluation of non-rotational HCRs

Due to simplicity in design, no moving parts, easy to construct, easy to control temperature and use, the non-rotational type of hydrodynamic cavitation reactors find wide acceptance in various applications such as water disinfection, food processing, and wastewater treatment. However, their overall cost effectiveness for disinfection are unsatisfactory. In early studies [59,60],[61],[62] of disinfection, the microorganism degradation is measured in terms of protein or enzyme release and the effectiveness of process or cell disruption is measured in terms of protein and enzyme released in mg/mL. The recombinant DNA technology is used for production of valuable biochemicals from microorganisms in economic ways.

High speed homogenizer, orifice, ultrasonic horn/acoustic cavitation are reported for extraction of protein and enzyme from yeast *Saccharomyces cerevisiae*, *Alcaligenes eutropus* and bacteria *E. coli* [61],[62]. The use of Ultrasonication has limitations on large scale operations for cell disruption and extraction of protein and enzyme. Multiple studies on hydrodynamic cavitation were performed and their performances were compared with different cavitation reactors and sonicators. Save and co-workers reported the comparison of the performance of cavitation reactors for the cell destruction. The cell destruction increases with increase in soluble protein content because of shear stresses, impact and turbulence effect.

Hydrodynamic cavitation was found more energy efficient than blade mixer and ultrasonic horn/acoustic cavitation [59,60]. In the study of Balasundaram et al. the release of enzyme which is present in periplasmic space of yeast was effected by hydrodynamic cavitation by use of multiple hole orifice, sonication and high-pressure homogenizer. However, the hydrodynamic cavitation resulted in very low release rate of cytoplasmic content compared to sonication and high pressure homogenizer [61]. The performance of hydrodynamic cavitation depends on the type of cavitation device and process integration. In the study of Anand et al., the performance of high-pressure homogenizer was enhanced by pre-treatment with chemicals for examples, guanidium hydrochloride (G-HCl), Triton X-100, pH or EDTA. The pretreatment with EDTA for maximum intracellular protein recovery for *E. coli* inactivation was also reported [62]. Table 2.4 lists studies of disinfection using non-rotational hydrodynamic cavitation reactors.

2.1.1.3.8 Effect of different process parameters

The performance of cavitation depends upon different treatment conditions such as temperature, pressure, oxidising agents, inlet velocity and rotational speed (for rotational HCRs), additives, and treatment duration. The study of effect of different process parameters for non-rotational HCRs are listed below and research gap is evaluated for further research.

2.1.1.3.8.1 Effect of pressure

The effect of operating pressure is the basic parameter that can determine the physical effects in cavitation such as number of cavities in cavity generation. The optimum inlet pressure and/or pressure drop can vary with reactor geometry and configuration. Therefore, optimization of pressure drop is utmost important to achieve complete disinfection of microorganism. Point of inception in cavitation can be found out by plotting pressure drop/operating pressure vs. flow rate and finding deviation from square law. Square law is $Q^2 = a \times \Delta P$ where Q is the flow rate, ΔP is pressure difference between upstream and downstream pressure and “a” is the point of inception. Point of inception is the point from which cavities starts to form. For satisfactory cavitation operation, operating pressure is selected higher than that at the point of inception [52],[63].

According to Pradhan and Gogate [64], the optimum pressure is always required to enhance the degradation rate. At higher pressures, number of cavities generation is also very high, thus larger bubbles are formed, subsequently it may escape from water without/incomplete collapse. Incomplete collapse of cavities reduces the production of hydroxyl radicals leading to decrease the disinfection efficiency. Badve et al. [17] observed increase in the disinfection with increase in inlet pressure of cavitating devices (i.e. orifice, venture) up to certain level of pressure and then it starts to decreasing. Jain et al. [65] reported 97% of disinfection for *E. coli* using orifice at 2 bar pressure drop and 0.0158 kWh energy consumption. Increase in pressure drop up to 10 bar resulted in only 1% of increase in disinfection though it required 11 times more energy consumption for the same treatment duration of 60 min. This higher energy requirement of conventional cavitation device can be minimized by employing other cavitation devices such as multiple hole orifice or vortex diode. The use of multiple hole orifice exhibited contradictory results. Jyoti and pandit [66] reported that, for the hydrodynamic cavitation with multiple hole orifice as cavitating device higher disinfection of 92% was achieved whereas, in the study of Arrojo et al. [1], only 32.7% disinfection was reported for multiple hole orifice which was lower than disinfection using venturi of 91.1%. Jain et al. [65] found that the lower-pressure drop of just 1 bar can give better results for the disinfection using vortex diode as a cavitating device as compared to other cavitating devices reported in the literature.

2.1.1.3.8.2 Effect of temperature

Liquid temperature has impact on cavitation performance through various parameters such as viscosity, surface tension, vapor pressure, and dissolved gas content of the fluid. The effect is translated in terms of formation of bubbles, bubble radius and cavities life [67]. During hydrodynamic cavitation treatment, the bulk temperature increases continuously as a consequence of implosion of cavities. As temperature increases, the cavitation intensity increases first and after reaching peak point of temperature 50 to 70 ^{0}C, cavitation intensity decreases. This is because of excessive generation of bubbles, vapor cloud formation and lower release of energy after incomplete collapse. This type of effect is predominant in rotational HCRs where disinfection occurs mainly due to thermal effect [56],[54],[58].

The high temperature operation may therefore adversely affect the effectiveness of water disinfection by cavitation, though contribution due to high temperature in disinfection increases. Compared to rotational HCRs, effect of temperature in non-rotational HCRs has not been systematically studied so far.

2.1.1.3.8.3 Effect of Initial concentration

Initial concentration of microorganism is an important parameter. Loraine et al. [50] found more than 99% disinfection for bacteria removal over wide range of concentration. Jyoti and Pandit [68],[69], however, reported significantly lower disinfection efficiency for lower concentration of microbes has as compared to higher concentration.

2.1.1.3.8.4 Effect of pH

The pH of water also has significant impact on the disinfection process. It was reported that under acidic conditions disinfection is significantly enhanced. Farkade et al. reported that the heat stress and the pH pre-treatment prior to ultrasonication can increase disinfection by 3 fold and 19 fold respectively for enzyme β- Galactosidase extraction from *Kluveromyces lactis* [70],[71].

2.1.1.3.8.5 Effect of addition of additives: Hybrid approach for disinfection of water

Hybrid methods are also explored for the water treatment and also for the degradation of various pollutants in wastewater treatment. It typically combines different processes or makes use of additives (addition of chemicals, integrating with physical methods) with hydrodynamic cavitation for improved disinfection performance. The addition of several oxidants leads to increased oxidative damage of microorganisms and also intensifies the rate of generation of highly reactive hydroxyl radicals. Hybrid approaches of disinfection in HC for obtaining synergies include utilizing various strong oxidising agents such as H_2O_2 [66], O_3 [69],[72],[73],[74], ClO_2 [75], NaClO [76] and Fenton agents [77]. Also, HC combined with physical methods was reported such as plasma discharge [78], ultrasonic flow cell [79], and utilization of copper coil as a cooling coil [80]. Recently new green hybrid method using 0.1% of natural oils having antimicrobial properties was reported [52,53]. The synergistic effect is the ratio of disinfection rate of the hybrid method to the sum of the disinfection rates of each individual method. The value, if greater than one, confirms synergism. The utilization of additives not only improves the disinfection efficiency, but also significantly reduces the time and additive usage required in disinfection operation.

Jyoti and Pandit [66], [69] reported use of oxidants such as hydrogen peroxide and ozone with hydrodynamic cavitation for increased disinfection efficiency from 92% for HC alone to 96% for HC with H_2O_2 and from 76% for HC to 100% for HC with O_3. HC generates extreme conditions of pressure, temperature and •OH radicals after implosion of bubbles. The additional H_2O_2 and O_3 creates higher concentrations of •OH radicals and intense disinfection effects.

Chand et al. [72] confirmed the synergistic effect of HC and O_3 using conditions of O_3 flow rate of 5 L/min for 15 min followed by second dose after 90 min for 15 min. A high enhancement was reported in the destruction of *E. coli* from 24.6 to 73.1% compared with HC alone at the same inlet pressure.

Wu et al. [73] compared HC, ozone (O_3), and HC with O_3 methods for disinfection of *M. aeruginosa* with operating pressure of 118–284kPa. The elimination rates after 60 min using HC and O_3 alone were 13% and 35% respectively. The hybrid HC+O_3 significantly improved the disinfection efficiency and in only 10 min of treatment, 99% disinfection obtained under the same conditions with reduced O_3 usage by 95%.

The performance of hydrodynamic cavitation is enhanced by integrating HC with several chemical disinfectants. The synergistic effect for the destruction of *E. coli* using HC and chlorine dioxide was reported by Maslak and Weuster-botz [75]. 99% *E. coli* inactivation was obtained with reduced time (6 min) and with low dosage 0.25 ppm of ClO_2 with HC compared with HC alone and ClO_2 alone.

Process integration using chlorine dioxide and sodium hypochlorite as an oxidant along with hydrodynamic cavitation was also reported and combination of hydrodynamic cavitation with chlorine dioxide gave 100% disinfection whereas ClO_2 alone and HC alone exhibited only 80% and 67.3% of disinfection respectively in 60 min. It not only reduced the quantity of ClO_2 required for complete disinfection but also helps in minimizing the production of DBPs [76].

Karamah et al. [74] discussed hybrid approach of hydrodynamic cavitation with ozonation using orifice as a cavitating device. It was found that the ozonation is better than cavitation alone and the dose of ozonation gets reduced when combined with hydrodynamic cavitation, thereby lowering the cost of operation. The hybrid approach gave 100% disinfection which is higher than cavitation alone 24% in 60 min of time of operation. The reason behind higher disinfection efficiency was increased mass transfer of ozone, increased surface area leading to more small bubbles formation in water consequently more generation of hydroxyl radicals.

The use of chemicals along with HC in drinking water disinfection is under scrutiny primarily because of the disinfection byproducts generated in the process. Therefore, an alternative method without use of chemicals is necessary. Abramov et al. [78] reported hydrodynamic cavitation + Plasma discharge to produce intense cavitation, UV light, shock waves and charged particles effecting *E. coli* deactivation and organic pollutant (Methanol) degradation. The disinfection performance was discerned using cavitation noise spectra and plasma emission spectra. The mechanism of hydrodynamic cavitation along with plasma discharge involved homogenization, cavitation, radicals and ozone, UV light and prolonged oxidation after treatment. It was also observed that plasma discharge-glow intensity for silver electrode is higher, then graphite and then for brass. The intense effect of *E. coli* inactivation for silver electrode was higher, 98% compared to graphite electrode, 56% and brass, 44% for single pass requiring further treatment to obtain 99.99% lethality for silver and graphite electrode and 96% for brass. After treatment, the treated water contained 0.8 mg/L of silver ions. According to various Environment Protection Agencies the permissible silver ion content in water should be far less than reported above; e.g. US - 0.1 mg/L, Russia- 0.05 mg/L and in some of European countries, less than 0.01 mg/L. The use of silver electrodes along with HC is therefore not practical in commercial application. Dalfre Filho et al. [80] reported cavitating jet apparatus operated at various pressures and with cooling systems made with various materials. More than 99% inactivation of *Escherichia coli* was achieved with HC with copper cooling coil using 10 MPa pressure and in 30 min.

In the process integration approach, hydrodynamic cavitation when coupled with chemical additives or oxidant, process may produce harmful disinfection by-products. Also, process integration with physical methods requires maintenance and conventional cavitation devices are energy intensive. The high energy requirement, cost and formation of harmful disinfection by-products necessitates need for green, novel hybrid approach of hydrodynamic cavitation for disinfection of water.

2.1.1.3.8.6 Effect of treatment time

Long-duration treatment required in chemical methods or chemical coupled hybrid methods produce harmful poisonous and stable organic by-products apart from increasing the energy requirement and cost of operation. In general, the conventional hydrodynamic cavitation operation for obtaining complete disinfection requires long treatment times. Many a times, longer treatment does not always improve disinfection efficiency and it is important to determine the optimal duration for a particular HCR. Rotational hydrodynamic cavitation study by Šarc et al. [56] indicated decrease in the cavitation intensity after 60 passes. Similar results were obtained by Chand et al. [72] and Jain et al. [65] where increased duration decreased the performance of disinfection.

Table 2. 4: Studies of disinfection using non-rotational hydrodynamic cavitation reactors

Cavitation System	Condition	Disinfection Efficiency (%)	Ref.
Mixer Blender	*S. cerevisiae*	9000 rpm **0.17**[b] (15 min) 14,000 rpm **0.14**[b] (40 min)	[60]
High Speed Homogenizer	*S. cerevisiae*	5000 rpm **0.11**[b] (15 min) 10,000 rpm **0.21**[b] (15 min)	[81]
High Pressure Homogenization	P_d=5000 psig, *S. cerevisiae*	**0.0757**[a] (10 min) **0.541**[b] (10 min)	[61]
Multiple hole orifice 33 holes of 1mm diameter	P_d=75 psig *S. cerevisiae*	**0.00462**[a] (10 min) **0.009**[b] (10 min) **0.00669**[a] (50 min) **0.155** [b] (50 min)	[61]
Sonication frequency of 20 kHz with a power rating of 600W	20 min	**0.0053**[a] (20 min) **0.580**[b] (20 min)	[61]
Multiple hole orifice 33 holes with D=1 mm	P=5.17 bar ~100 Faecal *coliforms*/100 mL	5 mg/l H_2O_2 **9** (15 min), **21** (60 min) HC **38** (15 min), **92** (60 min) HC + 5 mg/l H_2O_2 **60** (15 min), **96** (60 min) HC/1.72 bar+US **60** (15 min), **80** (60 min) HC/1.72 bar+US +5 mg/l H_2O_2 **75** (15 min), **90** (60 min)	[66]
Ball type valve	P=5.17 bar ~100 Faecal *coliforms*/100 mL	2 mg/l O_3 **78** (15 min), **100** (60 min) HC **57** (15 min), **76** (60 min) HC + 2 mg/l O_3 **88** (15 min), **100** (60 min)	[69]
Liquid whistle Reactor	P=500 psi *E. coli* 10^8-10^9 CFU/mL	HC **22** (180 min) HC+O_3 **75** (180 min)	[72]
Orifice and Venturi (Single hole orifice: D=5 mm, Multiple holes orifice: 6 holes with D of 2 mm, 25 holes with D of 1 mm Venturi: minimum cross section Minimum cross sections of 4 × 10^{-5} m^2, 2 × 10^{-5} m^2, and 1 × 10^{-5} m^2)	P=2.5 bar *E. coli* 10^7 CFU/mL	Orifice **32.7** (120 min) Venturi **91.1** (120 min)	[1]
Multiple hole orifice (12 holes of D=1.0mm)	ΔP=1-12 bar *E. coli* 10^7 CFU/mL	0.25-0.3 mg/l ClO_2 >**99** (3-6 min) HC + ClO_2 **99.99** (6 min)	[75]

Orifice Commercial orifice (DYNAJETS)	*E. coli, K. pneumoniae, P. syringae, P. aeruginosa, B. subtilis*, 10^6 CFU/mL	*E. coli* /Orifice 2.1 bar, **~99.999** (60 min) *K. pneumoniae* /Orifice 2.1 bar, **99.999** (60 min) *P. syringae* / O 16.5 bar, **~99.9999** (20 min) *P. aeruginosa* /O 16.5 bar, **~99.9** (90 min) *B. subtilis* /O 2.1 bar, **~99.99** (120 min)	[50]
Suction- or extrusion-orifice orifice plate (20 mm ID; 1 mm thickness) with various single-holes (5, 10 or 12mm)	*M. aeruginosa* 118–284kPa	12 mm orifice HC **15** (10 min) O_3 **35** (10 min) HC+O_3 **99** (10 min)	[73]
Venturi (Converging-diverging nozzle with D of 53mm and minimum D of 30mm)	P_{dis}=350kPa *M. aeruginosa* 10^6 CFU/mL	**99** (18 min)	[51]
Multiple hole orifice (33 holes with D=1 mm, 33 holes with D=2 mm, 20 holes with D=2 mm, 17 holes with D=3 mm)	0.45 MPa 2500–3000 CFU/mL	HC (33 holes, D=2 mm) **67.3** (60 min) 0.5 mg/L ClO_2 **78.2** (60 min) 1.0 mg/L ClO_2 **~80** (60 min) 2 mg/L NaClO **~50** (60 min) HC+0.5 mg/L ClO_2 **~99** (60 min) HC+1.0 mg/L ClO_2 **100** (60 min) HC+2 mg/L NaClO **~79** (60 min)	[76]
Orifice Pipe D=12.70 mm with orifice (D) of 2.00 mm.	*E. coli* (~10^8 CFU/mL)	P=8 MPa **34** (15 min) P=10 MPa **57** (15 min) P=12 MPa **82** (15 min) Copper coil as a cooling system P=5 MPa **97.31** (15 min) P=10 MPa **99.89** (15 min) P=5 MPa **99.77** (30 min) P=10 MPa **99.97** (30 min)	[80]
Orifice (17 holes with D of 1mm)	*E. coli*, 10^5 CFU/mL	HC **24** (60 min) HC+O_3 **100** (60 min)	[74]
Venturi (Total L=60mm with throat D of 1mm)	P_L=0.2 bar, *E. coli, L. Pneumophila* 10^8 CFU/mL	*E. coli,* **75.4** (120 min) *L. pneumophila* **99.3** (60 min)	[56]
Ultrasonic Treatment+Fenton	Sono-Fenton *Microcystis aeruginosa*, 10^6 CFU/mL	20 kHz **20.29** (5 min) 800 kHz **14.80** (5 min) 20 kHz Sono-Fenton **89.26** (5 min) 800 kHz Sono-Fenton **44.39** (5 min)	[77]

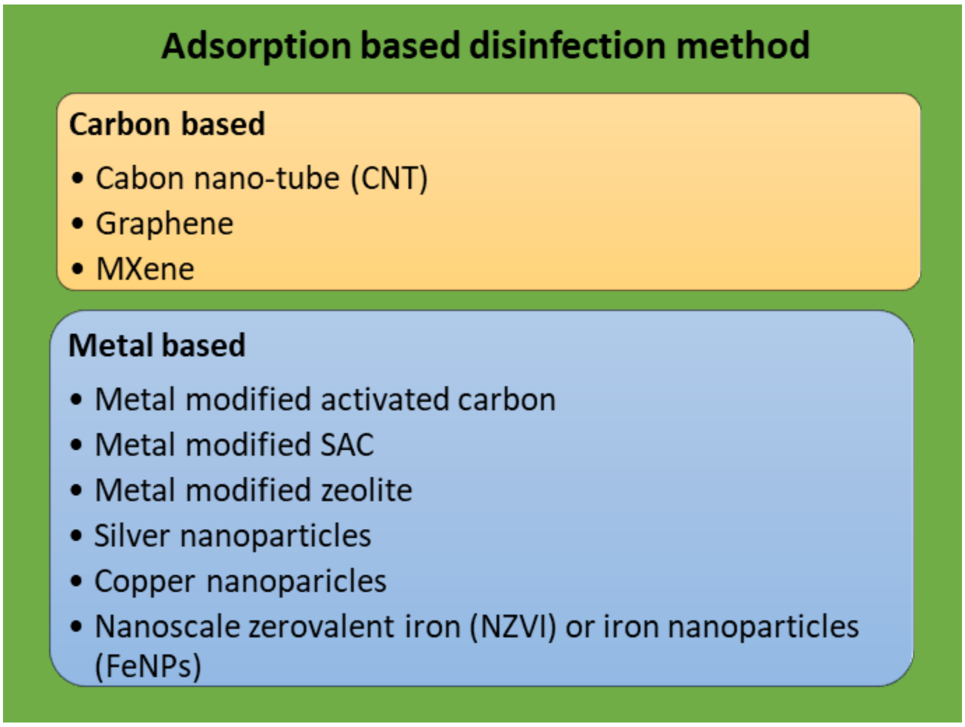
Orifice	*E. coli* ~10^3 CFU/mL	**99.4** (360 min)	[82]
Ultrasonic emitter+ Plasma discharge	P=6MPa *E. coli* 10^7 CFU/mL	Silver wire **46** (1 treatment) HC + Silver electrode **98** (1 treatment)	[78]
Vortex diode 66 mm chamber diameter of 1 m^3/h	ΔP=0.5,1, 2 bar *E. coli, S. aureus* 10^4 CFU/mL	*E. coli,* ΔP=0.5 bar **99** (60 min) ΔP=1 bar **99** (60 min) ΔP=2 bar **98** (60 min) *S. aureus* ΔP=0.5 **63** (60 min) ΔP=1 bar **98** (60 min) ΔP=2 bar **98** (60 min)	[65]
Orifice Single hole with 3 mm diameter	ΔP=2, 5,10 bar *E. coli, S. aureus* 10^4 CFU/mL	*E. coli* ΔP=2 bar **97** (60 min) ΔP=5 bar **99** (60 min) ΔP=10 bar **98** (60 min) *S. aureus* ΔP=2 bar **68** (60 min) ΔP=5 bar **88** (60 min) ΔP=10 bar **98** (60 min)	[65]

[a] Amount of Invertase released in mg/mL

[b] Amount of protein released in mg/mL

2.1.1.3.9 Adsorption for disinfection

In addition to cavitation, development of materials and material modification for adsorption having unique antimicrobial properties can be considered economical, viable and effective option for disinfection of water. Extensive studies have been reported on various materials/adsorbents, natural to synthetic, particularly on the use of nanoparticle and metal modified adsorbents, nanocomposite in general for disinfection of water. Effective disinfection and good selectivity towards pathogens make carbon-based adsorbents suitable as a filter or for "point of use" application. Adsorption process takes place by physical contact of adsorbent surface with contaminated water. In this process the antimicrobial property of the surface/nanomaterials/ active metal deactivate the pathogens and microbial inactivation typically occurs by electron transfer, direct oxidation of constituents of microorganisms such as proteins and DNA/RNA. Secondary by-products also get produced in processes such as dissolved heavy metal ions or nanomaterials, reactive oxygen species that cause additional microbial deactivation. Due to simple form of adsorption processes and also its low energy requirement, the process is considered to be very attractive as a physical disinfection process. The commonly used process involves carbon based disinfection process or metal-material based disinfection process [83–85]. Figure 2.4 illustrated different classes of adsorption-based disinfection method.



Adsorption based disinfection method

Carbon based

- Cabon nano-tube (CNT)
- Graphene
- MXene

Metal based

- Metal modified activated carbon
- Metal modified SAC
- Metal modified zeolite
- Silver nanoparticles
- Copper nanoparicles
- Nanoscale zerovalent iron (NZVI) or iron nanoparticles (FeNPs)

Figure 2.4: Different classes of adsorption-based disinfection method

Table 2.5 listed different studies of disinfection using Adsorption. The carbon based adsorbents such as single wall carbon nanotubes (SWNTs) [86], multi wall carbon nanotubes (MWNTs), SWNT-MWNT [85], graphene, graphene oxide [87], MXene [88] without modification exhibited 87.6% (120 min), 68.2 (120 min), 93.8 (120 min), 2.6 log reduction (60 min), 3.6 log reduction (60 min), 70% (24 h) respectively. The physicochemical properties of carbon nanotubes (for both SWNTs and MWNTs) such as surface area, electrophilic nature, oxidative stress and antimicrobial property cause microbial death. Higher percentage of metals in the SWNTs yields higher toxicity [89]. The antimicrobial effect in other carbon-based adsorbents such as fullerenes (C60) and g-C_3N_4 can be attributed to photochemical property [90,91].

The metal based adsorbents is an important class of adsorption based disinfection processes. The disinfection of water by modified activated carbon spheres (ACS) was studied by Yamamoto et al. [92], [93] and the MgO modified ACS from Mg modified resins gave 25% disinfection for *S. aureus* and 70% for *E. coli* in 6 h and in another study it was 100% disinfection in 24 h for same bacteria using ZnO modified ACS. The antimicrobial activity was due to generation of super oxide and hydrogen peroxide on the surface of ZnO or MgO modified ACS.

Matsumura et al. [94] reported generation of reactive oxygen species in the bacteria cell by use of silver ions and its action on cell results in bactericidal effect. Effect of silver modified zeolite was compared with silver nitrate and ~ 100 % disinfection for *E. coli* was reported and bactericidal activity was affected by presence of inorganic salts and ion chelators. Metal modification was thus effective for enhancing the disinfection efficiency.

The importance of zeta potential in metal modification for water disinfection was studied by pal et al. [95]. Changes in the zeta potential from negative to positive by modifying surface of activated carbon by aluminium hydroxychloride (AHC), and diatomaceous earth by zinc hydroxide, showed greater disinfection performance compared to negatively charged zeta potential of unmodified activated carbon. Both AHC modified activated carbon and nano AgBr supported AC provided greater than 6 log reduction for *E. coli*.

The filtration by activated carbon is economical and widely used for removal of organic matter, unpleasant taste and odor. During water purification microbes tend to adhere to the surface of activated carbon. The modification of activated carbon with antimicrobial agent is necessary. Surface modification by various metal like Fe, Ag and silica-Ag nanoparticles was reported by many researchers and is still being explored in different forms [96],[97],[98],[99],[100]. The antimicrobial properties of metals, reactive oxygen species generation combined destroy the cell membrane and cellular functionalities of microorganisms, leading to cell death.

Hussain et al. [101] reported adsorption followed by electrochemical disinfection and achieved >8.5 log reduction of *E. coli;* adsorption alone gave 6.5 log reduction in 10 mins. The authors studied effect of different parameters like direct electrochemical disinfection, electro-chlorination and pH effects. The electrochemical disinfection was achieved by high current density, the electro-chlorination was achieved by chloride present in the catholyte electrochlorination and pH effect in disinfection was due to formation of acid in the anode compartment.

Similarly, Yin et al. [102] developed chloride-form anion-exchange resin adsorption followed by electrolysis to control halogenated DBP and to achieve 3.36 log reduction for *E. coli, P. aeruginosa and S. aureus*. This approach effectively removed not only common *E. coli*, but also chlorine resistant *P. aeruginosa and S. aureus* bacteria. For electrolysis Ti/RuO_2-IrO_2 anode and graphite cathode with current intensity of 0.4 Å was used.

The surface modification can change the zeta potential. However, this aspect has not been studied in detail. Also, relationship between metal % and zeta potential to enhance the disinfection efficiency needs to be elucidated.

Table 2.5: Studies of disinfection using Adsorption

Adsorbent	Condition	Disinfection Efficiency (%)	Ref.
Mg/SAC at 1000ºC	*E. coli* and *S. aureus* 10^6-10^7 CFU/mL	*E. coli* **~70** (6 h) *S. aureus* **~25**	[92]
Spherical activated carbon coated with zinc oxide	*E. coli* and *S. aureus* 100CFU/mL	**100** (24 h)	[93]
Ag/zeolite	*E. coli* 2 × 10^7CFU/mL	**~99-100** (40 min)	[94]
AC: Modification using aluminium hydroxyl chloride; nano AgBr- AC	*E. coli*; 10^7 CFU/mL.	**99.99** > 6 LR	[95]
SWNT	*E. coli*	SWNT **87.6** (2 h)	[86]
MWNT and SWNT-MWNT	*S. epidermidis* *E. coli* 10^4 CFU/mL	*S. epidermidis* MWNT **48.1** (2 h) SWNT-MWNT **61.1** (2 h) *E. coli* MWNT **68.1** (2 h) SWNT-MWNT **93.8** (2 h)	[85]
SWNT with metallic	*E. coli* 10^7 CFU/mL SWNT-S (<5% metallic), SWNT-X (~30% metallic), SWNT-M (>95% metallic)	Aggregate Assay experiment **40**, <5% M; **52**, ~30% M; **70**, >95% M Deposition assay experiment **25**, <5% M; **50**, ~30% M; **78**, >95% M	[89]
Plasma treated AC impregnated with silver Nanoparticles	*E. coli* 10^3 CFU/mL	Plasma treated Ag/AC **~100** (10 min) Ag/AC **~100** (60 min)	[96]
Adsorbent with electrochemical treatment	E. coli 10^7−10^9 CFU/mL Graphite flake 100 g/L	Graphite flake **99.98** (5 min) Graphite flake with electrochemical **>8.5LR**	[101]
nano-silica silver nanocomposite (NSAgNC)	*E. coli* and *P. aeruginosa*	NSAgNC 1.5 mg/mL **~99.9** (5h)	[97]
Ag/AC by wet impregnation	*E. coli* 10^4 CFU/ml	**~100 (**25 min)	[98]
2D $Ti_3C_2T_x$ (MXene) Nanosheets	*E. coli* and *B. subtilis* 10^4 CFU/ml	*E. coli* and *B. subtilis* MXene Nanosheet **~70** (24 h)	[88]

MoS_2/rGO & MoS_2/MXene 100 µg/mL MoS_2	*B. subtilis* 10^3 CFU/ml	MoS2/rGO **60** (3 h) MoS2/MXene **75** (3 h)	[103]
Fe nanoparticles (NP) Nanocomposite NC-450; (SPION + CF) NCm1; NCm_1(SPION + CF + Clarified butter)	*E. coli* 10^7 CFU/mL	NC-450 **59** (60 min) NCm_1 **82** (60 min) NP **91** (60 min)	[99]
Fe nanoparticles (NP), Nanocomposite NC-ALV-450 and NC-OCT-450 10 mg/mL	*E. coli* 10^7 CFU/mL	NP **91** (60 min) NC-ALV-450 **90** (60 min) NC-OCT-450 **96** (60 min)	[100]
Anion-exchange resin adsorption followed by electrolysis	*E. coli, P. aeruginosa and S. aureus*	Adsorption followed by electrolysis **3.36 LR** (19 s)	[102]

2.2 Desulfurization of transportation fuels

Desulfurization of transportation fuel is increasingly important due to environmental concern of SOx emission from liquid fuels and also because of increasingly stringent conditions on sulfur contents in different fuels apart from the requirement of near zero sulfur fuels for fuel cell applications [104]. The removal of refractory sulfur compounds from gasoline, diesel, jet fuels etc., becomes increasingly difficult as the sulfur content is reduced. The nature of sulfur compounds is different for different fuel fractions such as mercaptanes, sulfides, disulfides, thiophene, benzothiophene, dibenzothiophene and many more, in the form of alkylated thiophene derivatives. These sulfur compounds after combustion produce SO_x which acts as precursors for the acid rain, causes ozone layer depletion, reduces soil fertility and also, leads to several health problems [105]. According to World Health Organisation (WHO), around 3 million people die prematurely every year due to air pollution [106]. Moreover, in the refinery downstream processes, sulfur presence deactivates catalysts and causes corrosion problems to refinery equipment, pumps and pipelines [107]. Depending upon the type of source, the crude oil contains total sulfur of 0.05-6 wt% [108] and according to various environmental regulations the total sulfur concentration present in transportation fuels such as gasoline and diesel should be lower than 10 ppm. The following Table, Table-2.5, represents different permissible limits imposed by different countries [109].

It is very difficult or too expensive to use the conventional hydrodesulfurization (HDS) technology to bring down the sulfur content to below 10 ppm. New approaches that are more economical and convenient will be required for producing ultra-clean gasoline and diesel fuels meeting the current and future EPA regulations as well as for producing fuel cell-grade transportation fuels for fuel cell applications.

Table 2.6: Permissible limits for liquid fuels (gasoline and diesel) in different countries[109]

Liquid fuel	Country / Year	USA	European Countries	India	Japan	China
Gasoline	2016	30	10	150 (nationwide) 50 (selected cities)	10	50
	2017	30	10	50	10	50
	2018	30	10	50	10	10
	2019	15	10	50	10	10
Diesel	2016	15	10	350 (nationwide) 50 (selected cities)	10	50
	2017	15	10	50	10	50
	2018	15	10	50	10	10
	2019	15	10	50	10	10

2.2.1 Desulfurization methods

Transportation fuels contain organo sulfur compounds, mainly thiophene and its derivatives together with 5-50 wt% of aromatics and olefins. The major challenge for separating the sulfur compounds from the transportation fuels is to find a suitable method that selectively removes the sulfur compounds under mild conditions leaving the coexisting aromatics and olefins intact. In this section, mainly adsorption is discussed for removal of sulfur from fuels [110].

Hydrodesulfurization (HDS) is primarily used in industry to remove sulfur from crude oil. HDS efficiently eliminates aliphatic sulfur compounds such as mercaptanes, sulfides and disulfides from fuels but is challenged by more sterically hindered aromatic refractory sulfur compounds such as thiophene, benzothiophene, dibenzothiophene and other alkylated thiophene derivatives. For removal of these refractory sulfur compounds, HDS requires high energy in terms of higher temperature, pressure conditions and high dosage of catalyst (operating conditions) rendering the entire process uneconomical [111],[112]. In recent years, several alternative desulfurization methods have been studied such as oxidative desulfurization, bio-desulfurization, adsorptive desulfurization, pervaporation desulfurization and extractive desulfurization. Recent trends indicate preference to nanocomposites and doping of nanometal or polyoxometalate as a promotor/ as a support. Various reactor designs such fixed bed, slurry bed, fluidized bed, trickle bed are reported for operation. Adsorptive desulfurization is one of the most promising, competitive method due to the advantages such as ease of operation, environmentally friendly, economical method and for its ability to decrease sulfur content to <1 ppm.

Adsorption mainly depends upon the nature of adsorbents and hence selection of adsorbent is very important. Focus is on the development of new and suitable adsorbents which are easy to prepare, require mild operating conditions, have high adsorption capacity, high porosity, high selectivity and most importantly, can be easily regenerated, have low cost and are environmental friendly. Different types of adsorbents include carbon-based adsorbents, zeolites, silica-based adsorbents, metal adsorbents (reduced metals, metal oxides and metal sulfides) and metal-organic frameworks (MOFs).

To enhance the performance of desulfurization, modification of surface may be useful in the form of acid treatment, alkaline treatment, thermal treatment, modification with various metals etc. Metal ions such as Al, Co, Ni, Ag, Cu, Pd, Zn, Ga, Ce, etc and support materials including zeolite, alumina, carbon, metal organic framework and other mesoporous materials have been reported for sulfur adsorption [113],[114,115]. However, the lack of appropriate acid or active sites limit its selectivity and capacity for thiophenic sulfur compound.

2.2.2 Evaluation of Adsorptive Desulfurization performance

The performance of deep desulfurization by adsorption is evaluated by different parameters and different studies

1. Batch and column studies
2. Adsorption capacity of adsorbent
3. Regeneration study
4. Economic analysis

In many literature reports, the adsorption equilibrium capacity for sulfur is low. The adsorption capacity is calculated as ratio of amount of adsorbate adsorbed (mg) per unit weight of adsorbent (g). For industrial column operation, good adsorption capacity is required else, huge adsorbent quantity will be needed. Satisfactory column operation is reflected in the form of breakthrough curve and breakthrough capacity, exhaustion capacity and degree of column utilization can be evaluated.

2.2.3 Activated Carbon

The activated carbon is the most commonly used adsorbent for various applications such as removal of colour, removal of contaminants/ pollutants from various streams. High surface area, different modifications, wide variety of source materials, low production cost are the attractive features its consideration. The activated carbons can be modified by several treatment methods to improve its performance. Carbon-based adsorbents such as spherical activated carbon (SAC), ordered mesoporous carbons are quite chemically stable under nonoxidizing conditions, exhibits mechanical stability, hydrophobic, factors that favour adsorptive desulfurization in transportation fuels. Metal modifications also assist in removal of refractory sulfur compounds through coordination bond formation and π-complexation mechanisms. The selection of metals and cost of modification is a major consideration apart from difficulty in regeneration. For example, metal organic framework (MOF) is not suitable option for industrial application because of its expensive organic precursor [116].

Activated carbons, in general, have large surface area, typically in the range of 500-1000 m^2/g. Due to the porous nature of material, it can easily allow dispersion of chemicals for internal and external surface modification of carbon in chemical modification. The surface modification can be done by many ways such as physical, chemical or biological modifications. In Chemical modification, the surface can be modified by acidic, basic treatment or treatment with foreign particles such as transition metals. In the physical modification, the surface of activated carbon can be modified by thermal treatment (heating at higher temperature in furnace) and the biological treatment provides biological modification on the surface. The adsorption capacity of the activated carbon is influenced by surface area, pore size, pore size distribution, inherent functional groups and modifying surface functionalities. The surface characteristics play an important role in the improving adsorption capacity. The surface area varies depending upon pore size, for example, the micopore surface have <20Å pore diameter with surface area of

100-1000 m^2/g, mesopore or transitional pores surface have 20-500 Å pore diameter with surface area of 10-100 m^2/g and macropores have >500 Å pore diameter with surface area of 0.5-2 m^2/g [117],[118]. It is necessary to understand the nature of surface modification, a key parameter, in improving the adsorption performance.

Activated carbons are made from different starting materials such as biomaterials- wood, bamboo, rice husk, coconut, dates stones, cassia fistula, sucrose, organic waste and other starting materials such as coal, resins, polymer and rubber tires. In literature, other carbon materials are also reported such as carbon aerogels, carbon cloth, carbon nanotubes, carbon nanofibers and graphite for desulfurization of liquid fuels.

Several studies have explored the adsorptive desulfurization, for T, BT, DBT and 4,6-DMDBT, from both model and commercial fuels using many types of adsorbents. Yang and co-worker studied removal of different sulfur compounds from liquid fuels using different metal modified adsorbents such as Cu_2O/SBA-15, Cu_2O/MCM-41, Pd/AC (where AC denotes for Activated Carbon), CuCl/AC, $PdCl_2$/AC, $PdCl_2/Al_2O_3$, Cu(I)Y zeolite, CuCl/MCM-41, CuCl/SBA-15, and Ag-Y etc and proposed that sulfur compounds get adsorbed on adsorbent via π-complexation and that metal modified activated carbons give higher selectivity for refractory sulfur compounds than other adsorbents for e.g. T < BT < 2-MBT < DBT for $PdCl_2$/AC, and T < DBT < 2-MBT < BT for Cu(I)-Y zeolite. Also, it was found that the adsorption rate is higher for modified activated carbon than other adsorbents [119],[120],[121],[122],[123].

Herna´ndez-Maldonado et al. reported studies on Cu(I)-, Ni(II)-, and Zn(II)-modified zeolites where copper modified zeolites have higher affinity and selectivity for sulfur compounds than Ni and then other metals; Cu(I)-Y(VPIE) > Ni(II)-Y(SSIE) > Ni(II)-X(LPIE) > Zn(II)-X(LPIE) > Zn(II)-Y(LPIE) [124].

Yang and co-workers have investigated different modification approaches on activated carbon such as the use of steam and concentrated H_2SO_4 to enhance the adsorption capacity for DBT removal (sulfur content of 220 mg/dm^3 in heptane). Adsorption experiments were carried out on fixed-bed flow reactor under ambient temperature and pressure with five different modified commercial activated carbons such as AC, AC_{W900} (AC treated by steam at 900^0C for 25 min), AC_{S250} (AC treated by concentrated H_2SO_4 (96%) at 250^0C for 4 h), AC_{WS} (combined treatment of steam and H_2SO_4) and AC_{WSN} (AC_{WS} heated under the nitrogen flow at a rate of 10^0C/min from room temperature to 900^0C and kept at 900^0C for 12 h). Results showed that AC_{WS} and AC_{S250} have an enhanced adsorption performance with capacity of 47.1 mgS/g, 33.3 mgS/g compared with other modified AC and the unmodified AC with capacity of 23.6 mgS/g, 2.06 mgS/g, 10.9 mgS/g for AC_{WSN}, AC_{W900}, AC respectively [125].

Song and co-workers [126–128] have performed adsorptive desulfurization of various types of fuels using different transition metals supported on different porous materials such as activated carbon, zeolites and metal oxides. Their studies suggested direct sulfur-adsorbent (S-M) interaction rather than via π-complexation and proposed a new process for desulfurization that consisting of three main stages - selective adsorption removing sulfur (SARS) compounds step, recovery of the concentrated sulfur compounds and third stage as hydro-desulfurization of the concentrated sulfur compounds.

Shi et al. [129] reported activated carbons derived from sucrose via hydrothermal carbonization and following KOH activation. The adsorption capacity of 41.5 mg/g was reported for removal of refractory thiophenic compounds (BT, DBT and DMDBT) from model oil with good selectivity, in the order of DMDBT>DBT>BT and high adsorption rates- within 5 mins 97% saturation was obtained. This was attributed to abundant small micropores, appropriate mesopore fraction and presence of various oxygen functionalities in the carbon and therefore cellulose derived activated carbon was suggested as a promising material.

Alhamed and Bamufleh [130] developed granular activated carbon from dates' stones where chemical activation was done using $ZnCl_2$. A model diesel oil composed of n-$C_{10}H_{34}$ and dibenzothiophene (DBT) was used. The results exhibited ~86% of the DBT adsorption during the first three hours and adsorption increased to a maximum value of around 92.6% in 48 hours.

Saleh and Danmaliki [131] prepared activated carbons from rubber through pyrolysis, activation and chemical treatment (acid treatment with 4M HNO_3 for 3h at 90^0C). Adsorption capacity for DBT removal was found as 8.6 mgS/g, 493 m^2/g of surface area, a pore volume of 0.77 cm^3/g, and pore size of about 6 nm.

Saleh et al. [132] prepared activated carbon-manganese oxide nanocomposite from waste material-tyres as a starting materials to improve the surface properties for sulfur removal. 10% optimum metal loading in nanocomposite showed significant adsorption efficiency. The adsorption capacity for T, BT and DBT was 4.5 mg/g, 5.7 mg/g and 11.4 mg/g respectively. The sulfur compounds were believed to be adsorbed on modified activated carbon through π complexation and direct sulfur-metal (S-M) interaction.

Transition metals have capability to enhance adsorptive desulfurization through π complexation and S-M interaction. Prajapati et al. [133] developed nickel (Ni)-doped activated carbon beads (ACBs) and further modified with carbon nanofibers (CNFs). The comparison of the two with other nickel modified reported adsorbents indicated adsorption capacity of Ni doped ACBs without CNF was ~3.5 times higher than that of in-situ Ni-CNF/ACBs (with CNF) specially for the refractory sulfur compound dibenzothiophene, which was attributed to the higher surface area and pore volume of the adsorbent. In-situ Ni-CNF/ ACBs showed higher capacity for thiophene than that of Ni/ACBs, in spite less surface area and pore volume, indicating that the π- complexion interactions were the main mechanism than physisorption.

Jha et al. [134] examined the performance of Mongolian Anthracite-based Activated Carbon PMAC 1/3 and PMAC 1/4 in the adsorption of DBT in n-heptane. The activated carbon was made by preheating mixture of anthracite and KOH for removal of volatile compounds up to 400^0C, followed by increasing the temperature to 750^0C for activation. A high surface area for PMAC 1/3: 2038 m^2/g and PMAC 1/4: 2784 m^2/g) was obtained and DBT adsorption capacity of 84.67 mgS/g, 74.97 mgS/g for PMAC1/3 and PMAC 1/4 respectively was reported.

Selvavathi et al. [135] reported desulfurization using diesel oil with total sulfur concentration of 290 ppm, mainly containing dibenzothiophene (DBT), 4 methylbenzothiophene (4MDBT) and 4,6-dimethyl-dibenzothiophene (4,6-DMDBT). Two commercial activated carbons A and B, were modified - nickel impregnated on modified activated carbons. Alumina, silica and Y-zeolite samples were also used for the adsorptive desulfurization. Results showed that acid modified activated carbon gave higher adsorption capcity than other nickel modified adsorbent and unmodified commercial adsorbents.

Zhang et al. [136] studied removal of aromatic organosulfur compounds using modified Na-Y zeolite (by ion exchange with the various single Cu^{2+}, Zn^{2+}, Ag^{+} and the combined Cu^{2+}–Zn^{2+},

Zn^{2+}–Nd^{3+}, Ni^{2+}–Nd^{3+} metals). It was observed that the desulfurization efficiency for direct adsorption is higher than oxidation-adsorption and direct-oxidation. The adsorption capacity for CuZn-Y(I) and Ag-Y was ~17.3 mgS/g. Similarly, Shan et al. [137] reported adsorption capacity of 13.44 mgS/g on bimetallic ion exchanged zeolites Cu-CeY, higher than single metal modified adsorbents.

Suryawanshi et al. [138] extensively investigated effects of single and double metal modifications apart from nature of metal modification and similarly found higher capacity for bimetallic modification over single metal modification and unmodified adsorbents. Double metal modification on commercial activated carbon, TAC-Ni-Cu, showed higher adsorption capacity 23 mgS/g than double metal modification on biomass derived activated carbon 13mgS/g for DBT removal. The modification method was further improved using acoustic assisted impregnation and capacity of TAC-Ni-Cu was enhanced to 38 mgS/g. This indicated that the combined effect of metal modification and process intensification can significantly improve the desulfurization efficiency.

Zaidi et al. [139] investigated adsorption and adsorption coupled with ultrasonication for desulfurization of dibenzothiophene in cyclohexane. The activated carbon was prepared from *Pongamia pinnata*, nickel modification by wet impregnation method and adsorption performance was compared with commercial adsorbent DARCO. The adsorption coupled with ultrasonication enhanced the initial desulfurization efficiency from 42.84 to 63.53% in the first 30 min but for biomass derived activated carbon and nickel modified activated carbon showed enhancement in efficiency; desulfurization capacity of DARCO 13.18 mg/g, PP 30.9 mg/g, Ni/PP 66.18 mg/g for 200 ppm initial concentration.

Sorokhaibam et al. [140] developed biomass- *Cassia fistula* derived activated carbons and further modified by phosphoric acid. The adsorptive desulfurization showed higher capacity for DBT than BT and T which were 7.5, 3 and 4.5 respectively.

Lan et al. [141] studied the performance of activated carbon spheres derived from polystyrene based ion exchange resins for adsorption of dibenzothiophene (DBT). The activated carbon was made by carbonization of polystyrene ion exchange resin, further using KOH activation and resulted in a surface area of 2696 m^2/g and total pore volume of 1.46 cm^3/g. The model fuel used was prepared by dissolving DBT in n-octane with initial concentration of DBT solution varying from 250 mg/L to 2000 mg/L. Results indicated a maximum DBT adsorption capacity of 39 mg/g.

Li et al. [142] reported silver modified aspherical activated carbon, prepared by first ion-exchange of phenolic weak acid cation exchange resin (PR) with 0.2M $AgNO_3$ 24h and then carbonization followed by CO_2 activation. The surface area was 283 m^2/g for unmodified SACand 210 m^2/g for silver modified SAC and saturation capacities of Ag/SAC for fixed bed adsorption found to be 0.733, 0.925 and 1.143 mgS/g for T, 3-MT and 2,5-DMT respectively. The selectivity of the Ag/SAC adsorbent for different sulfur compounds followed the order: 2,5-DMT > 3-MT > T. The effects of aromatics such as toluene and cyclohexene on the desulfurization performance were also studied. The results showed that the presence of aromatics led to a reduction of total saturation capacity by toluene and cyclohexene by 57 and 33 %, respectively.

Anand et al. [143] reported hybrid route for desulfurization by adsorption followed by bio-desulfurization. Sulfur (T and DBT) removal by adsorption was investigated using Ni nanoparticles-dispersed porous carbon beads of ~ 0.8 mm size followed by biodegradation using *Bacillus zhangzhouensis* bacterial strain. This sequential approach achieved ~99% desulfurization of DBT and T where higher concentration of thiol compounds used in adsorption and relatively lower concentration of thiol compounds used in bacterial treatment.

The literature scrutiny (Table 2.7) indicates that the metal modified adsorbents show higher capacity for refractory sulfur compounds mainly due to S-M interaction, especially for DBT removal and higher sulfur compounds.

Table 2.7: Comparison of sulfur adsorption capacity of various adsorbents from liquid fuels

Adsorbent	**Sulfur compound**	**Capacity, mgS/g**		**Ref.**
Y zeolites (with Cu, Ni, Zn, Pd, and Ce ions)	JP-8 jet fuel (750 ppmw S)		**BT, 2-MBT, 5-MBT**	[126]
		HY	**3.6, 4, 4.3**	
		HCuY	**3.1, 3.8, 3.9**	
		HNiY	**3.1, 4.4, 3.6**	
		HZnY	**2.8, 3.9, 3.4**	
		HPdY	**4.2, 4.7, 4.7**	
		HCeY	**3.5, 4.7, 4.4**	
Cu(I)-, Ni(II)-, and Zn(II)-zeolites	Jet fuel (364.1 ppmw S), diesel (297.2 ppmw S) and gasoline (335 ppmw)		**Gasoline**	[124]
			Breakthrough capacity	
		Cu(I)-Y(LPIE-RT)	**4.6**	
			Saturation capacity	
		Cu(I)-Y(LPIE-RT)	**12.6**	
			Diesel	
			Breakthrough capacity	
		Cu(I)-Y(LPIE-RT)	**5.3**	
		Cu(I)-Y(VPIE)	**8.9**	
		Ni(II)-X(LPIE-RT)	**4.6**	
		Ni(II)-Y(SSIE)	**5.1**	
			Saturation capacity	
		Cu(I)-Y(LPIE-RT)	**12**	
		Cu(I)-Y(VPIE)	**13**	
		Ni(II)-X(LPIE-RT)	**8**	
		Ni(II)-Y(SSIE)	**9.3**	
			Jet fuel	
			Breakthrough capacity	
		Cu(I)-Y(VPIE)	**12.6**	
		Zn(II)-X(LPIE-RT)	**2.8**	
		Zn(II)-Y(LPIE-RT)	**1.4**	
			Saturation capacity	
		Cu(I)-Y(VPIE)	**23**	
		Zn(II)-X(LPIE-RT)	**6.3**	
		Zn(II)-Y(LPIE-RT)	**3.7**	
Cu(I)Y-zeolite and Ni/SiO_2-Al_2O_3	Gasoline		**Breakthrough capacity**	[128]
		Cu(I)Y-zeolite	**0.22**	
		Ni/SiO_2-Al_2O_3	**0.37**	

CuCl/AC, PdCl$_2$/AC, PdCl$_2$/Al$_2$O$_3$, and Cu(I)-Y zeolite	JP-5 jet fuel	**Breakthrough capacity** CuCl/AC **1.02** PdCl$_2$/AC **2.08** PdCl$_2$/Al$_2$O$_3$ **3.2** Cu(I)-Y **2.08** **Saturation capacity** CuCl/AC **4.8** PdCl$_2$/AC **9.09** PdCl$_2$/Al$_2$O$_3$ **19.7** Cu(I)-Y **14**	[119]
CuCl/AC, PdCl$_2$/AC, Pd/AC, PdCl$_2$/Al$_2$O$_3$	BT, MBT	**BT, MBT** **Breakthrough capacity** AC **1.31, 2.2** CuCl/AC **1.54, 2.75** PdCl$_2$/AC **2.2, 4.03** Pd/AC **1.22, 2.02** PdCl$_2$/Al$_2$O$_3$ **1.09, 2.02** **Saturation capacity** AC **3.52, 1.8** CuCl/AC **2.24, 4.58** PdCl$_2$/AC **2.91, 5.98** Pd/AC **1.57, 2.94** PdCl$_2$/Al$_2$O$_3$ **1.66, 3.23**	[122]
AC$_{WS}$ and AC$_{S250}$ AC$_{WSN}$, AC$_{W900}$, AC	DBT	AC$_{WS}$ **47.1** AC$_{S250}$ **33.3** AC$_{WSN}$ **23.6** AC$_{W900}$ **20.6** AC **10.9**	[125]
Metal modified MCM-41, SBA-15 CuCl/MCM-41, PdCl$_2$/MCM-41, CuCl/SBA-15, PdCl$_2$/SBA-15	JP-5 jet fuel	MCM-41 **0** CuCl/MCM-41 **18.2** PdCl2/MCM-41 **47** SBA-15 **0.32** CuCl/SBA-15 **16** PdCl2/SBA-15 **34**	[144]
Ion-exchanged Na-Y zeolites (Single ion-exchanged Cu^{2+}, Zn^{2+}, Ag^{+} and Combined Cu^{2+}–Zn^{2+}, Zn^{2+}–Nd^{3+}, Ni^{2+}–	DBT 500 ppm	Uncalcinated NaY **9.1** NaY **12.6** Ag-Y (I) **17.3** Zn-Y **14.9** Cu-Y **13.6**	[136]

Nd^{3+}) Na-Y, Ag-Y(I), Zn-Y, Cu-Y, CuZn-Y (I), ZnNd-Y and NiNd-Y		CuZn-Y (I) **17.2** ZnNd-Y **15.6** NiNd-Y **12.6**	
Cu-Ce bimetal ion-exchanged Y zeolites	T, BT, and 4,6-DMDBT in isooctane ~500 ppm	Ce(IV)-Y **11.84** Cu(I)-Y **12.8** Cu-CeY **13.44** With 20 wt% of toluene Ce(IV)-Y **10.6** Cu(I)-Y **2.9** Cu-CeY **11.2**	[137]
Activated carbon	BT, DBT	~0.5-1	[145]
AC, Acid modified AC, Ni/AC	DBT, MDBT, DMDBT	Carbon A **0.45** Modified carbon A (350, 600, 800^{0}C) **1.2, 1.6, 1.5** Carbon B **0.31** Modified carbon B (350, 600, 800^{0}C) **0.9, 1.1, 0.99** Ni/carbon A **0.81** Ni/carbon B **0.58** Silica **0.27** Alumina **0.18** HY-zeolite **0.14** Ni/silica **0.23** Ni/Alumina **0.11** Ni/HY-zeolite **0.07**	[135]
Zeolite NaY, NiY, CeY and NiCeY	DBT in toluene, 500 ppm	NaY **2.3** NiY **5.4** CeY **6.6** NiCeY **7.8**	[113]
AC	T, BT, DBT	T, BT, DBT **4.16, 11.52, 16.32**	[146]
Nickel-based micro-meso porous silica (Ni/MMS), (50 g/L)	T, BT, DBT in octane, ~100-500 ppm	20% Ni/MMS T, BT, DBT **15, 11, 3** Commercial gasoline **1.8** 20% Ni/MMS+Effect of aromatics; 0.5% Toluene T, BT, DBT **12.6, 9.8, 2.3**	[147]
AC	T	**0.96**	[148]
Resin derived AC and KOH activation	DBT	**~39**	[141]
Ag/SAC	T, 3-MT and 2,5-DMT	**Saturation capacity** T, 3-MT, 2,5-DMT **0.733, 0.925, 1.143**	[142]

Sucrose derived AC	BT, DBT and DMDBT	Model oil (BT+DBT+DMDBT) **41.5**	[129]
Biomass derived AC	T, BT, DBT	T BT, DBT **4.5, 3, 7.5**	[140]
Zn/GAC	DBT	**14**	[149]
Ni/Clinoptilolite zeolite (70 g/L)	Iso-propyl mercaptan (IPM), T, BT, DBT in Isooctane, ~100 ppm	Zeolite **2.36, 2.1, 1.65, 1.26** Ni/zeolite **10.1, 6.3, 3.6, 2.7**	[150]
MnO-10%/AC	T, BT, DBT	T, BT, DBT **4.5, 5.7, 11.4**	[132]
Carbon nonofiber Ni-CNF/ACB	T, DBT	T, DBT **88.2, 8.2**	[133]
Ni/ACB	T, DBT	T, DBT **85, 27.3**	[133]
Ni$_2$P/SBA-15 adsorbents	DBT in Decahydro naphthalene	DBT **18**	[151]
Double metal modifications TAC-Ni-Cu CFP-Ni-Cu	T, DBT	**T, DBT** TAC-Ni-Cu **~2, ~38** CFP-Ni-Cu **~4, ~13**	[138]
Mongolian Anthracite-Based Activated Carbon	DBT in n-heptane (500 ppm)	PMAC 1/3 **84.7** PMAC 1/4 **74.7**	[134]
ADS followed by BDS, (5 g/L) **Precursor:** Phenolic beads, Polymerization Ni nanoparticles-dispersed porous carbon beads **Bacteria**: *Bacillus zhangzhouensis*	DBT and T in n-octane (300–1200 mg/L)	ADS (DBT or T) **~50 mg/g, >80%** ADS+BDS (DBT or T) **~99%**	[143]
Biomass derived AC, (8 g/L), Precursor: *Pongamia pinnata* **Nickel modification and adsorption with ultrasonication**	DBT in cyclohexane 200 ppm Adsorption only (3h)	DARCO, PP, Ni/PP **13.2, 30.9, 66.2**	[139]
Metal Organic Frameworks by hydrothermal method MIL-101(Cr), MIL-100(Fe), Cu-BTC	DBT, DMDBT in octane	**DBT, DMDBT** MIL-101 (Cr) **6.6, 5.5** MIL-100 (Fe) **6.5, 7.9** Cu-BTC **18.4, 9.15**	[114]
Rubber tyres-derived activated carbons	DBT in 85% hexane and 15% toluene (150 ppm)	Rubber tyres-derived AC **8.6**	[131]

Summary of literature review and gaps in research

Disinfection of Water

The conventional, extensively researched and widely applied world over, chemical process for disinfection is chlorination due to its lowest cost, effectiveness, in general and ease of application. The major disadvantages include carcinogenic disinfection by-product formation and acute toxicity of various chemical disinfection method. Other alternative physical methods such as UV irradiation, filtration and electrochemical disinfection methods have difficulty in large scale water treatment applications and limitations due to turbidity, treatment time and cost. Membrane technology is one promising disinfection method, can effectively remove all kinds of microorganisms, however has limitations of bio-fouling, secondary waste, recycle and reuse of membranes apart from higher cost. Disinfection using hydrodynamic cavitation (HC) is known from more than two decades. Various types of hydrodynamic cavitation reactors (HCRs) were reported with varying success in an attempt to develop clean technology and an alternative to chlorination. HCRs have capacity to completely inactivate different types of microorganisms due to harsh conditions of mechanical, thermal and chemical effects resulting from collapse of cavitation bubbles with less harmful or no disinfection by-product formation. Rotational HCRs are shown to be more effective with less time of operation, but energy requirements for rotational HCRs are high, rendering them as cost intensive operation apart from safety constraints because of uncontrollable energy produced at high speed of operation. In comparison, non-rotational HCRs appears to be safe, easy to operate and also effective in disinfection, though with the cost much higher than conventional chlorination. Different forms of process intensification, newer designs of cavitating device can make the operation much more effective and economical than HC alone or other methods.

Literature review indicates several challenges and research directions that should be considered are outlined below.

(1) Newer forms of cavitating devices such as vortex diode that employ vortex flow can be more effective in disinfection.
(2) Detailed investigations are essential on effect of concentration, pH, nature of microorganism, temperature, pressure, and other operating parameters apart from process

intensification.

(3) Cavitation based model should be established in terms of the more realistic parameters such as per-pass disinfection, cavitation yield, energy input and effectiveness. However, systematic research on above parameter is lacking which requires further investigations.

(5) To improve the effectiveness of disinfection operation, research on the synergistic effects between HC and natural additives on disinfection is needed.

(6) Process integration in terms of other methods of disinfection such as adsorption and development of newer adsorbents, metal modifications and characterization of disinfection behaviour on the basis of surface tension/ zeta potential.

(7) To develop newer green technology for disinfection of water.

Desulfurization of Fuels

In petroleum/refineries HDS is extensively used method for desulfurization which requires specialized catalyst and very high temperature and pressure conditions. There has been extensive research in terms of development of newer catalysts, catalyst modifications and so on to reduce the cost and also to increase the desulfurization efficiency, especially for the removal of refractory sulfur compounds. There are many other critical problems due to complex chemistry of sulfur compounds, effect of aromatics, nitrogen compounds, poisoning of catalyst and so on. No other method, except adsorptive desulfurization, has shown significant potential for deep desulfurization and for removal of refractory sulfur compounds. Thus, it is necessary for development of alternative desulfurization process, newer adsorbents and for studies on deep desulfurization. The sulfur removal using adsorption is one of the best possible alternative or supplementary process for HDS. Activated carbon, zeolite, metal organic frameworks, metal oxides, SBA-15, Al_2O_3 are frequently used adsorbents for sulfur removal and different modification are being researched to enhance the desulfurization performance. Activated carbon and their modified forms are viable options. Recent development includes graphene, nanofibers, nanotubes, nanocarbon, aerogels, carbon cloth etc. Different surface modifications are extensively studied such as metal modification, acid and base modification for carbon-based adsorbents. Lot of research has been reported for single/double metal modifications because S-M interactions provide stronger chemical bonding force than π complexation. Development of adsorbent from waste material and their modifications in this regard can be highly useful in this regard.

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Chapter 3
Characterization Methods

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This chapter deals with different characterization methods and analytical techniques used in this research. The analytical instruments include Field-Emission Scanning Electron Microscope (FE-SEM), Transmission Electron Microscopy (TEM), Fourier Transform Infrared Spectroscopy (FTIR), X-ray Diffraction (XRD), Surface Area Analyzer, Thermo gravimetric analysis (TGA), Atomic Absorption spectrophotometer (AAS), Bacteria analysis for disinfection of water, Analysis of sulfur in fuel.

3.1 Field-Emission Scanning Electron Microscope (FE-SEM)

FE-SEM characterization is an useful characterization tool in different fields such as biology, chemistry or physics to capture microstructure image of the surface of materials or cells. FE-SEM is operated at a high vacuum (10^{-7} to 10^{-10}mbar) to avoid disruption of the electron beam due to gas molecules and produces secondary and backscattered electrons used for imaging. In order to characterize the material and microorganisms in this study, Field Emission Scanning Electron Microscopy (FESEM, FEI Nova NanoSEM-450, Make: EDAX Inc, USA) was used to capture the microstructure image. Due to the advanced design of the electron optics, this analytical instrument can generate ultra-high imaging resolution without the specimen size restrictions of conventional in-lens SEM/E-SEM. Schottky field-emission source can provide high imaging resolution in range of kV, at both low (high-resolution) and high (microanalytical) imaging. Samples of microorganisms and adsorbents were analysed for both, cavitation study and adsorption study. Samples containing microorganisms were fixed with 4% (v/v) glutaraldehyde in 0.1M phosphate buffer at pH 7.0 for 1 h, further washed with 0.1M phosphate buffer for 10 min. Subsequently, the dehydration of fixed samples was carried out before the analysis using series of graded ethanol solutions (30, 50, 70, 90 and 100% ethanol) for 30 min each. Adsorbents without microorganisms were dispersed in Isopropanol, subsequently drop cast over silicon wafers and then after drying, the samples were analysed. Every sample was coated using aurum prior to the morphological observation. In addition to morphological analysis by FE-SEM, elemental content of same sample was analysed using energy-dispersive X-ray (EDX). EDX is an X-ray technique attached to FE-SEM instruments where the imaging capability of the microscope identifies the specimens of interest [1,2].

3.2 Transmission Electron Microscopy (TEM)

Detailed examination of microorganism was carried out using TEM (Transmission Electron Microscopy; Tecnai G2 20 STwin; LaB6 filament as the electron source, Make: USA) and High resolution-TEM, HR-TEM (JEM F200, imaging at high resolution) working at 200 kV.

The complex set-up of transmission electron microscope consists of three main components- illumination system, lens, and the imaging system. Illumination system consists of a source where electrons are extracted from a filament. As per the requirements, the user can adjust the strength of the condenser lenses. High-energy electron source in TEM called as the ‘‘Gun’’ produces a stream of electrons which is then focused using “condenser lenses” into monochromatic thin beam. This beam interacts with a very thin specimen in order to be subsequently analysed. A portion of transmitted electron beam is again focused with the help of set of lenses named as “objective lenses” into image. This image is then magnified, through the ‘‘intermediate and projector lenses’’ and produced using phosphor image screen. Thicker or denser region of the sample represented darker areas in the image where fewer electrons get transmitted and thinner or less dense region of the sample represented the lighter areas in the image in which more electrons get transmitted [3,4].

In the present study, samples from disinfection were examined for studying cell destruction and cell death. Samples were prepared in the same manner as FE-SEM analysis, then drop cast over copper grid and after drying were analysed.

3.3 Fourier transform infrared spectroscopy (FT-IR)

FTIR analysis provides spectra of functional groups present in sample and based on this information the structure of molecule can be identified. The atoms of molecule vibrate with respect to its mean position and Infrared (IR) spectroscopy is based on this vibrational motion of atoms. Near IR region wavelength is between 10,000 and 4000 cm^{-1} while mid-IR region of high spectral resolution data is in the range of 5000 and 400 cm^{-1}. When monochromatic light beam passes through a sample, the vibrating molecules are either absorbed or transmitted or produce photoconductive energy and get displayed in the form of absorbance or transmittance or photoconductivity spectra. Each functional group has its specific vibrational frequencies and there are different modes of vibrations which includes stretching and bending. These vibrational frequencies are very sensitive and can change according to environment, adjacent species and molecular dipoles. Along with these, other factors that can cause changes in the IR spectra include coupling and vibration-rotation bands, combination and overtone bands and fermi resonance.

FTIR analysis is useful technique, has ease of operation and can use sample of all physical states (solid or liquid or gas) for characterization. Infrared spectroscopy include various types such as Fourier Transform Infrared (FTIR) Spectroscopy, Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) Spectroscopy (Micro-ATR-FTIR / Macro-ATR-FTIR) Spectroscopy, Two-Dimensional Infrared Correlation Spectroscopy (Linear / Non-Linear Two-Dimensional IR Spectroscopy), Atomic Force Microscopy Based Infrared (AFM-IR) Spectroscopy, IR Photodissociation Spectroscopy, IR Correlation Table Spectroscopy, Near-IR Spectroscopy (NIRS), Mid-IR Spectroscopy (MIRS), Nuclear Resonance Vibration Spectroscopy, Thermal IR Spectroscopy and Photothermal IR Spectroscopy. Thus, depending upon the application of FTIR, various sources and detectors are used. For example, In NIRS, tungsten-halogen lamps and sulfide photoconductors as sources and a detector are used respectively. In MIRS, Globar or Nernst and deuterium tryglycine sulfate incorporated in pyroelectric device as sources and a detector are used respectively [5,6],[7].

In this work, for analysing functional groups of adsorbent, FTIR-2000 (Perkin Elmer, USA) was used. For analysing functional groups of natural oils and plant extracts, Perkin Elmer’s Spectrum One FTIR Spectrometer were used with mid-IR spectra ranging from 400 to 4000 cm^{-1} was selected.

3.4 X-ray diffraction (XRD)

XRD is an important non-destructive diffraction technique in material science to determine the crystallographic structure of the materials. In this analysis, material is irradiated by incident X-rays and then measurement of material's intensities with respective scattering angles is obtained. Based on the diffraction pattern, crystalline phases and orientation can be identified and information can be obtained on deviations in the material from original and after modification or treatment. In addition to this, different aspects that can be studied include determination of crystals orientation, unknown ingredients, size, thickness of thin films or multi-layers, atomic arrangement and structural properties such as lattice parameters, strain, grain size, epitaxy, phase composition, preferred orientation. XRD can be classified as micro (μXRD), parallel Beam XRD, parallel Beam XRD for Powder, parallel Beam XRD for Stress, parallel Beam XRD for Crystal, parallel Beam XRD for Texture, protein Crystallography and neutron Diffraction.

In the present study, powder XRD was used with wide angle mode for characterization of the material in a PAN analytical X'pert Pro dual goniometer diffractometer (40kV and 30mA). The samples were scanned between 2θ range of $10-90^0$ with scanning rate of 6.67°/min and scan step size of 0.0084. Cu Kα (λ = 1.5418 Å) radiation was used with a Ni filter. After scanning, the result were recorded in the form of Intensity Vs angle of diffraction (2θ).

Braggs law, $2dsin\theta = n\lambda$, was applied where d is spacing between diffracting planes, θ is incident angle, n is an integer, and λ is the beam wavelength. The d spacing was compared with International center for diffraction data (ICDD) [8,9].

3.5 Surface area analyser

Surface area analyser is used for evaluating the properties, which largely affect the performance of solids, such as surface area, pore size and pore shape, chemically active sites, and many others. The structure of surface and reactivity of adsorbent determine the way in which the adsorbent interacts with gas. Inert gas such as nitrogen is used for gas sorption in surface area analyser. The pore size, pore size distribution and surface area are determined by different computational methods such as Barrett, Joyner and Halenda (BJH), single point or multi point Brunauer - Emmett - Teller (BET) method, and Dubinin-Radushkevich (DR) method etc. In this work, The BET surface area, pore size and volume are determined by Autosorb-1 (Thermo Scientific) using nitrogen adsorption. BJH method is used to determine the cumulative pore volume and average pore diameter[10].

3.6 Thermo gravimetric analysis (TGA)

TGA is a thermoanalytical technique in which a change in mass of sample is measured by thermobalance. This analysis monitors changes in adsorbent weight loss through decomposition, oxidation, loss of volatiles and moisture in a given temperature range. The results are represented in terms of a plot of temperature (or time) versus mass (or mass percentage). TGA is a useful tool to find stability of material in terms of thermal and oxidative stability, shelf life of material, decomposition pattern and volatiles or moisture content at a constant heating rate. In the present study, carbonizations of resins at constant heating rate in inert atmosphere were characterised with the help of thermo gravimetric analysis (TGA) and differential scanning calorimeters (DSC) analysis (Mettler Toledo TGA/SDTA851e model)[11,12].

3.7 Atomic Absorption spectrophotometer (AAS)

This analysis technique can provide complete elemental analysis or metal content. It consists of high precision, double beam optics to provide good performance, exceptional optical stability and detection limits. AAS is based on the principle of absorption of light of specific wavelength by metal element in order to measure their concentration in the sample. AAS quantifies the absorption of energy by atoms or ions of the sample at ground state. The atoms absorb ultraviolet or visible light and make excited/transition to higher energy levels. The concentration of the analyte/element /metal can be calculated with respect to measured amount of light absorbed. The metal content of adsorbent in present study was measured with the help of atomic absorption spectrophotometer (Thermo Fisher Scientific iCE 3300) [13,14].

3.8 Bacteria analysis for disinfection of water

Bacterial cultures were grown on 50 mL Nutrient Broth (Himedia Nutrient HiVeg broth); incubated at 37 °C, 200 rpm in an incubator-shaker for overnight. The incubation was given to the mid-point of bacterial log phase, which was determined by UV-VIS spectrophotometer at 600 nm, to ensure bacterial population is in robust stage of growth and not in saturation or death phase. The known concentration of bacterial culture was added to the 20 L of water to obtain final concentration of ~10^4 CFU/mL.

The number of viable bacteria present in the system was estimated by plate count method. A sample of 10 mL was withdrawn from the cavitation tank at regular intervals of 15 to 60 min for spreading to sterile petri dish containing N. agar medium. The plates were incubated at 37°C for 24 h, and the colonies were counted as colony forming unit per milliliter (CFU/ml).

$$CFU/ml = \frac{Number\ of\ colonies\ on\ \mathrm{N.\,agar\ plate}}{\mathrm{volume\ plated\ (mL)}} \times dilution\ factor$$

The Field Emission Scanning Electron Microscopy (FESEM, FEI-Nova NanoSEM-450) was carried out to observe the morphological changes of bacterial cell after disinfection and to prove efficacy of cavitation treatment. Samples were withdrawn at different time intervals (0 min: before cavitation, with oil treatment and after 60 min of treatment) and were fixed with 4% (v/v) glutaraldehyde in 0.1 M phosphate buffer (pH 7.0) for 1 h, subsequently washed with phosphate buffer (0.1 M) for 10 min. Further, the fixed samples were dehydrated by using graded series of ethanol solutions (30, 50, 70, 90 and 100% ethanol) for 30 min each before the analysis.

TEM (Transmission Electron Microscopy; Tecnai G2 20 STwin; LaB6 filament as the electron source) analysis was carried out for detailed examination of disinfection process and to study effects of combined cavitation with oil treatment with respect to cell destruction and cell death [15,16].

3.9 Analysis of sulfur in fuel

The sulfur concentration of initial and treated samples were analyzed using two instruments in present study. TN-TS 3000, total sulfur analyzer (Thermoelectron Corporation, Netherlands) and Gas Chromatograph (Agilent GC 7980A).

GC-FPD

Initial and treated samples were analyzed using Gas chromatography (Agilent GC, 7890A). For sulfur analysis, CPSil 5CB column (30m× 320µm×4 µm) was used with flame photometric detector (FPD). Helium gas with flow rate of 2 mL/min was used as a carrier gas and a split ratio was maintained as 10:1. The injector section 250^0C temperature was maintained with injection volume of 0.2µL and set 25min analysis time. The oven temperature was ramped in first at 20^0C /min from 40 to 100^0C and then 60°C/min from 100^0Cto 230^0C. In GC-FPD, two calibrations were used for measuring sulfur concentration-0-100 ppm and 100-500 ppm. Reproducibility and uncertainty were checked. Reproducibility was found satisfactory and error found typically less than 2% [15,16].

TN-TS total sulfur analyser

The sulfur content was analysed using total sulphur analyser, TN-TS 3000 (Thermoelectron Corporation, Netherlands). Samples introduced into furnace, oxidation of sulfur into SO_2 takes place with a mixture of helium and oxygen gas. Helium was used as a carrier gas which transmits gas/sample. The gas travels through perma pure membrane dryer, where water removes from gas stream and glass-fiber filter, where soot and other particles was removed. Next, the conditioned gas flow enters the UV-fluorescence sulfur detector. For measurement of total sulfur content in initial and treated samples two separate calibrations were used. First calibration was in the range of 0 to 50 ppm and second calibration in the range 50 to 500ppm. Reproducibility and uncertainty were checked, the total uncertainty was found up to 2 ppm and 5 ppm for 0-50 ppm range and for 50-500 ppm range respectively. Repeatability was found satisfactory and error found within 1% indicating complete reproducibility [17],[18].

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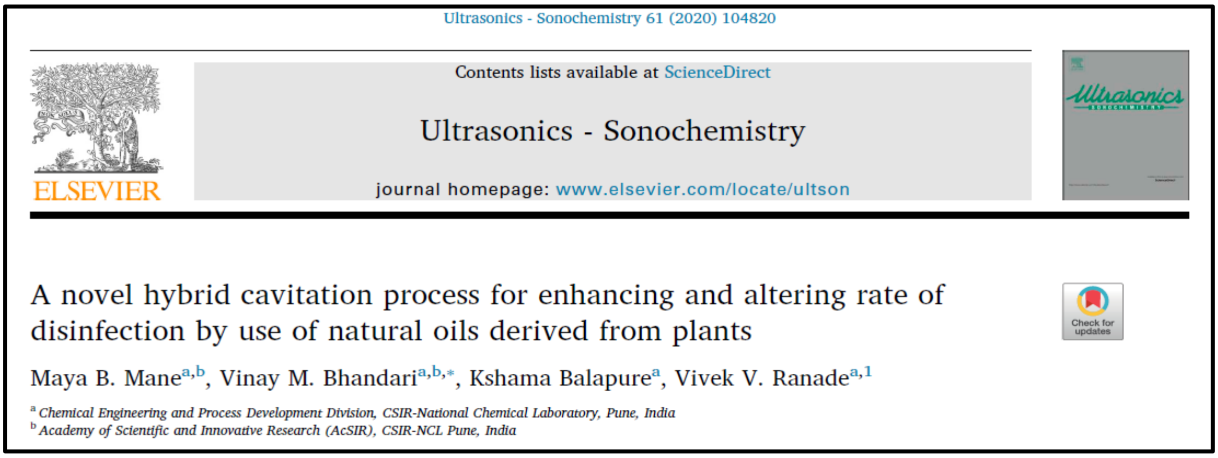

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A novel hybrid cavitation process for enhancing and altering rate of disinfection by use of natural oils derived from plants

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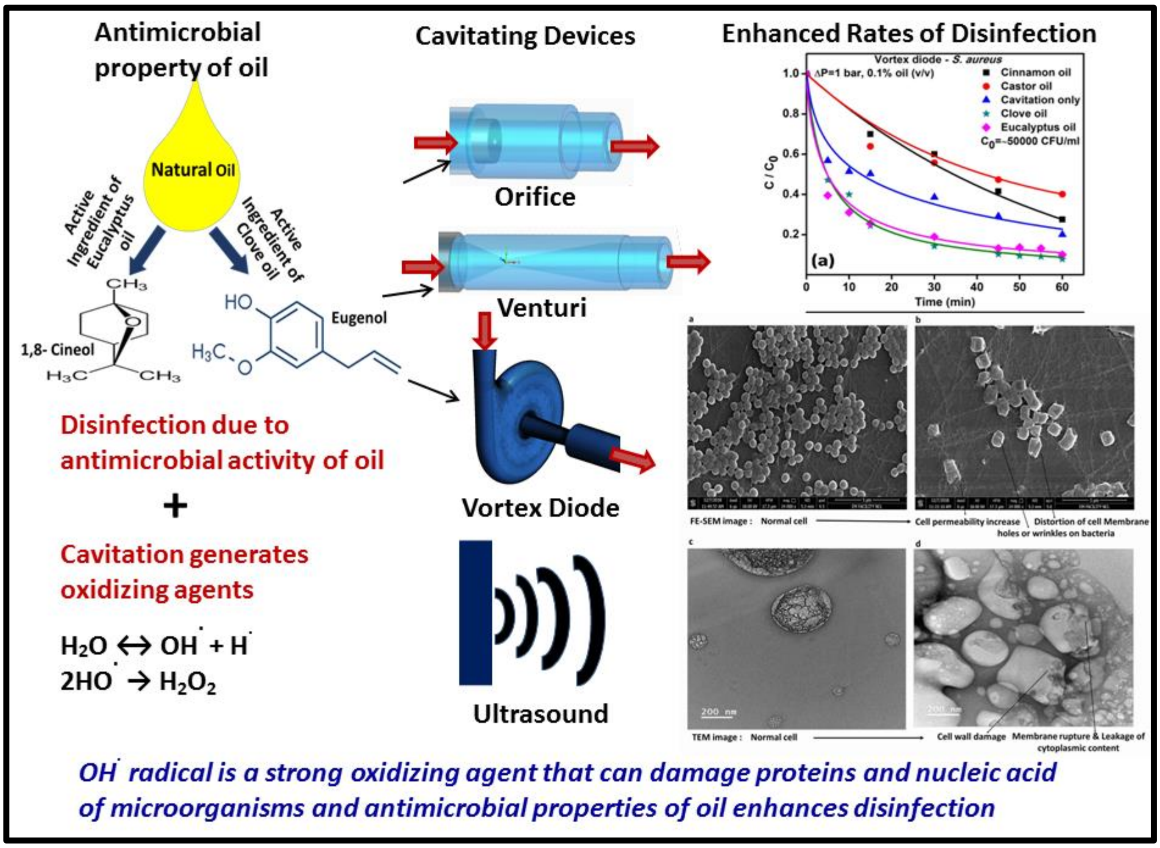
Chapter 4



Maya B. Mane, Vinay M. Bhandari, Kshama Balapure, Vivek V. Ranade. A novel hybrid cavitation process for entering and altering rate of disinfection by use of natural oils derived from plants. *Ultrasonics – Sonochemistry* 61 (2020) 104820. https://doi.org/10.1016/j.ultsonch.2019.104820

Chapter 4

A novel hybrid cavitation process for enhancing and altering rate of disinfection by use of natural oils derived from plants

Abstract

The present study is an attempt to improvise the hydrodynamic cavitation methodology for effective disinfection of water and also to suggest prototype development for practical application. The enhancement in the disinfection efficiency was evaluated specifically for the effect of pressure, temperature, pH, microbial inoculum size and also on effect of different additives for the two model microbial strains, gram-negative (*Escherichia coli*) and gram-positive (*Staphylococcus aureus*). The efficacy of the hydrodynamic cavitation is evaluated for the two types of flows/ cavitation devices – linear flow in the case of orifice and vortex flow for vortex diode. The vortex diode requires significantly lower pressures, 50% lower as compared to orifice for the similar extent of disinfection. While the bacterial disinfection at high temperature is known, the usefulness of hydrodynamic cavitation is especially evident at ambient conditions and the process is effective even at very high concentrations of bacteria, not reported so far. The reactor geometry also has significant effect on the disinfection. The present study, for the first time, reports possible use of different natural oils such as castor oil, cinnamon oil, eucalyptus oil and clove oil in conjunction with hydrodynamic cavitation. The nature of oil modifies the cavitation behavior and an order of magnitude enhancement in the cavitation rate was observed for the two oils, eucalyptus and clove oil for a very small concentration of 0.1%. The increased rates of disinfection, of the order of 2-4 folds, using oil can drastically reduce the time of operation and consequently reduce cost of disinfection. A possible mechanism is proposed for the effect of oil and hydrodynamic cavitation in cell destruction through the rupture of cell wall, oxidative damage and possible DNA denaturation. A cavitation model using per pass disinfection was used to correlate the data. The increased efficiency using oils and possible benefits of the developed process, where natural oils can be perceived as biocatalysts, can have significant advantages in practical applications.

4.1 Introduction

The quality of water has been a major concern worldwide and Asia is one of the worst affected region facing the problem of water contamination with pathogenic bacteria [1]. In addition, scarcity of drinking water also has become a major issue worldwide due to increased human population and industrialization. The scarcity of water can be alleviated to a certain extent by recycling and reusing the water. However, environmental pollution due to industrial effluents/ sewage water /biological pollutants impacts the quality of water. The biological pollutants are known to cause various water-borne diseases such as amoebiasis, shigellosis, cholera, typhoid fever, Hepatitis A or E and so on [2], consequently reflected in increasingly more number of deaths because of consumption of unsafe drinking water. Thus, there is an urgent need to formulate newer methodologies that are easy to implement and can generate safe drinking water. According to various norms, the desired total coliforms organism in drinking water should be zero. To comply with this stringent regulation, it is necessary to develop an efficient, green and viable technology for water treatment [3].

Though a number of conventional treatments such as chemical and physical water disinfection methods have been used for microbial decontamination, most of these have limitations/ drawbacks resulting into inadequate efficacy translating into limited applicability [4,5]. The conventional physical methods include heating, radiation, microwave, filtration, UV irradiation and plasma. Many of these, though effective, have scale-up problems, high cost and long treatment time. UV irradiation typically has insufficient light scattering ability and is ineffective towards bacterial photoreactivation repair mechanism [6]. Membrane technology for water disinfection also have operational difficulties along with fouling problem, many times requiring frequent replacement of membrane thereby increasing the cost of treatment. Chemical treatment methodologies such as chlorination and ozonation, though have been widely used with ease of scale-up, have been considered environmentally not friendly in recent years due to unpleasant smell and by-products of the disinfection process can be mutagenic and carcinogenic in nature [7]. Some of the disadvantages of chlorination methods can be eliminated using adsorption technologies employing newer adsorbents/ nanocomposites that are capable of eliminating bacteria [8,9,10]. Chemical methods are also unable to decontaminate bacteria from water because of mass transfer limitations and are unable to remove biocides resistant bacteria, bacteria residing in biofilm or any sediment [7].

Hydrodynamic cavitation is believed to be one of the most suitable physico-chemical process for disinfection and is gaining attention in recent years. It has several advantages such as ease of operation, easy scale-up, cost effectiveness, no production of harmful byproducts, representing greener approach and one that can work without use of harmful chemicals [11]. The principle of cavitation involves formation, growth and collapse of cavities of bubbles which is facilitated by specific cavitating device. The collapse of cavities is such that it generates extreme conditions of pressures (~1000 atm or more) and temperatures (~5000 K or more) at the point of implosion and as a consequence homolytic cleavage of water resulting into generation of hydroxyl radicals takes place and these oxidizing hydroxyl radicals participate into chemical oxidation of organic species [12,13]. There can be *insitu* generation of hydrogen peroxide, another oxidizing agent. The overall process is complex and intimate details of generation of different species (HO·, H·, HOO·, HO_2·, and H_2O_2) and subsequent reaction pathways are less understood. Though, in principle, cavitation is classified into four types on the basis of mode of generation of cavities: acoustic, hydrodynamic, optic and particle; from water treatment point of view, only acoustic and hydrodynamic cavitations are considered to be most promising. In the case of acoustic cavitation, cavities get generated by inducing ultrasound waves in the liquid medium (> 16 kHz), while in hydrodynamic cavitation, it is achieved by realising low pressure regions (using small constrictions, rotational flows or their combinations) in the flowing fluid. Although significant work has been reported in the area of sonochemical reactors, its application in water disinfection for real life is practically invisible due to the reasons of high cost of treatment (capital investment as well as power consumption) and difficulties related to scale – up. The cavitating device can be simple linear flow based venturi or orifice or rotational flow based device such as vortex diode [7,11,13,14,15,16]. Most of the studies were carried out using single and multiple hole orifice plate or venturi for water disinfection [17,18]. However, the study of effect of various parameters such as temperature, pH and inoculum size on hydrodynamic cavitation has been reported largely for organic pollutant degradation using conventional devices. Sun et al. [19] reported rotational hydrodynamic cavitation reactor and disinfection efficiency of reactor towards *E.coli* removal. Cerecedo et al.[20] explored various geometries of the cavitation channels between rotor and stator for disinfection of large numbers of *E.coli* and *E. faecalis* bacteria. Madge and Jenson, [21]used 20-kHz ultrasound unit for disinfection of domestic wastewater and found that the disinfection of fecal bacterial efficiency increased with ultrasound power. A number of hybrid techniques have also been reported for disinfection mainly for hydrodynamic cavitation, acoustic cavitation, hydrogen peroxide, ozone, UV etc. and for different reactor geometries [14,15,22, 23]. However, there are several limitations of conventional devices and efficiencies were not very high. Further rotor based devices and methodologies are expensive and impose higher operating/ maintenance costs [5,24]. The philosophy of enhancing performance of conventional hydrodynamic cavitation for disinfection relies on either intensification using ozone, hydrogen peroxide etc or by process integration with method such as UV; both approaches depict only incremental benefits at rather increased cost. Naturals oils can have antibacterial, antifungal and antiviral and antioxidant properties [25] and find use in various applications such as food preservations, aromatherapy and fragrance industries. The antibacterial properties are largely due to the high contents of oxygenates (Phenolics/alcohols). The antibacterial properties of a large number of essential natural oils such as Eucalyptus, clove oil have been well reported [2,26,27, 28]. However, there are no reports showing systematic study on disinfection of pathogenic bacterial from water through addition of natural oil, for real life application or in cavitation. The addition of natural oil in cavitation is expected to enhance and/or alter disinfection process and hence can be suitably used. Further, application of natural additives such as oils can also reduce the cost of operation. Thus, it is instructive to evaluate effect of additives such as oils having disinfection properties in conjunction with cavitation for increased rates of disinfection and for improved efficiency.

In the present study, we explore a newer form of process, for the first time, to provide proof of concept for hydrodynamic cavitation using different natural oils and for different reactor geometries for two model microbial strains- gram negative (*Escherichia coli*) and gram positive (*Staphylococcus aureus*). A newer form of cavitating device, vortex diode and gram-positive *S. aureus* bacteria were investigated in detail and the generality of results was also confirmed using conventional type of cavitation device-orifice and more commonly reported gram-negative bacteria, *E. coli*. Different oils such as clove oil, eucalyptus, cinnamon and castor oil have been studied for their impact on cavitation. A plausible disinfection mechanism was evaluated to confirm the role of cavitation and oil in cell destruction. A cavitation based model using per pass disinfection was successfully applied. The developed newer method is expected to provide practical, low cost and improved operation for complete destruction of bacterial cellular structure/ death of cell. The results of this work would also lead to newer designs of cavitation reactor and easy scale-up.

4.2 Materials and Methods

4.2.1 Materials

Staphylococcus aureus (ATCC-6538) and *E. coli* (ATCC-8739) were obtained from NCIM-National Collection of Industrial Microorganism at CSIR, National Chemical Laboratory, Pune, India. The different natural oils such as clove oil (Scientific Name: *Syzygium aromaticum* MW 205.642, Boiling point 250 °C, Solubility 2460 mg/L at 25°C, density 1.0652 g/cc at 20 °C), Nilgiri oil (Scientific Name: *Eucalyptus globulus*, MW 154.23, Boiling point 176.4, solubility 3500 mg/L at 21°C, density 0.9267 g/cc), Castor oil (Scientific name: *Ricinus communis*, MW 933.45, Boiling point 313 °C, Solubility less < 1 mg/mL at 68 °F), Dalchini oil (Scientific Name: *Cinnamon verum*, MW 282.383, solubility 1 volume in 3 volumes of 70% ethanol at 20 °C, density, 1.052-1.070 g/cc) were procured locally and used as it is without any prior treatment.

4.2.2 Cavitation reactors

A vortex diode (66 mm chamber diameter) of 1 m^3/h nominal capacity of CSIR-NCL design (US9422952B2, 2016) was used as a cavitating device for vortex flow based cavitation. Another cavitating device of conventional type, orifice was also locally made using 3 mm diameter single hole for linear flow based cavitating device. Details of experimental set-up and operation are provided in the experimental section and Figure 4.1.

4.2.3 Bacterial cultures growth

Bacterial cultures were grown on 50 mL Nutrient Broth (Himedia Nutrient HiVeg broth); incubated at 37 °C, 200 rpm in an incubator-shaker for overnight. The incubation was given to the mid-point of bacterial log phase, which was determined by UV-VIS spectrophotometer at 600 nm, to ensure bacterial population is in robust stage of growth and not in saturation or death phase. The known concentration of bacterial culture was added to the 20 L of water to obtain final concentration of ~10^4 CFU/mL.

The number of viable bacteria present in the system was estimated by plate count method. A sample of 10 mL was withdrawn from the cavitation tank at regular intervals of 15 to 60 min for spreading to sterile petri dish containing N. agar medium. The plates were incubated at 37 °C for 24 h, and the colonies were counted as colony forming unit per milliliter (CFU/ml).

$$CFU/ml = \frac{Number\ of\ colonies\ on\ N.agar\ plate}{volume\ plated\ (mL)} \times dilution\ factor$$

4.2.4 FE-SEM and TEM analysis

The Field Emission Scanning Electron Microscopy (FESEM, FEI-Nova NanoSEM-450) was carried out to observe the morphological changes of bacterial cell after disinfection and to prove efficacy of cavitation treatment. Samples were withdrawn at different time intervals (0 min: before cavitation, with oil treatment and after 60 min of treatment) and were fixed with 4% (v/v) glutaraldehyde in 0.1 M phosphate buffer (pH 7.0) for 1 h, subsequently washed with phosphate buffer (0.1 M) for 10 min. Further, the fixed samples were dehydrated by using graded series of ethanol solutions (30, 50, 70, 90 and 100% ethanol) for 30 min each before the analysis.

TEM (Transmission Electron Microscopy; Tecnai G2 20 STwin; LaB6 filament as the electron source) analysis was carried out for detailed examination of disinfection process and to study effects of combined cavitation with oil treatment with respect to cell destruction and cell death.

4.2.5 Disinfection using hydrodynamic cavitation

A schematic of the hydrodynamic cavitation using different cavitating devices is shown in the Figure 4.1 along with the photograph of experimental set-up housing the different cavitating devices and the present work focuses on two devices namely orifice and vortex diode. The essential components of the experimental set-up include a high pressure multistage centrifugal pump, a 50 L volume water storage tank, cavitating devices, temperature control (JULABO Chilling system, Model FL 1701, 20 L); pressure and flow controls/indicators etc. The details of experimental set-up are described in our earlier publications [12,13,16] therefore have not been repeated here. Typically, 20 L volume of contaminated water was used for each experiment. The water was pumped through desired cavitating device under controlled conditions. The flow rate was controlled using bypass. The inception of cavitation was confirmed in the pressure drop range of ~ 30 to 50 kPa and 125 to 180 kPa (0.3 to 0.5 bar and 1.25 to 1.8 bar) for vortex diode and orifice respectively from the data of pressure drop vs. flow rate and analyzing the deviation of pressure drop from the usual square law (ΔP proportional to square of flow rate or mean velocity) specific to cavitating device. In view of the obtained cavitation inception, the disinfection experiments were carried out at pressure drop conditions of 0.5, 1.0 and 2.0 for vortex diode and for 2, 5 bar for orifice. For the study of oil effect, a known quantity of natural oil was added in the water tank (0.1% or 20 mL for 20 L volume) at the start of the experiment. Samples (10 mL) were withdrawn at regular intervals and colony forming units (CFU) were determined. The reproducibility of the experiments was checked and was found satisfactory.

4.2.6 Disinfection using acoustic cavitation

Acoustic cavitation was carried out using ultrasound- 40 kHz frequency and 500 W of power (UCP-20 Sonication Unit). A 200 ml of water containing known amount of bacteria was exposed to acoustic cavitation for a period of 15 min. Samples were withdrawn every 5 min and percentage of disinfection estimated. The experiments were performed using both with and without oil addition (Oil addition of 0.1% similar to that in hydrodynamic cavitation).

4.2.7 Disinfection without cavitation

The contaminated water sample of the same mix of that used for cavitation was separately studied by keeping in incubator shaker at 120 rpm and at 37 ^{0}C; with and without oil addition. Samples were withdrawn at regular time intervals and percentage of disinfection estimated.

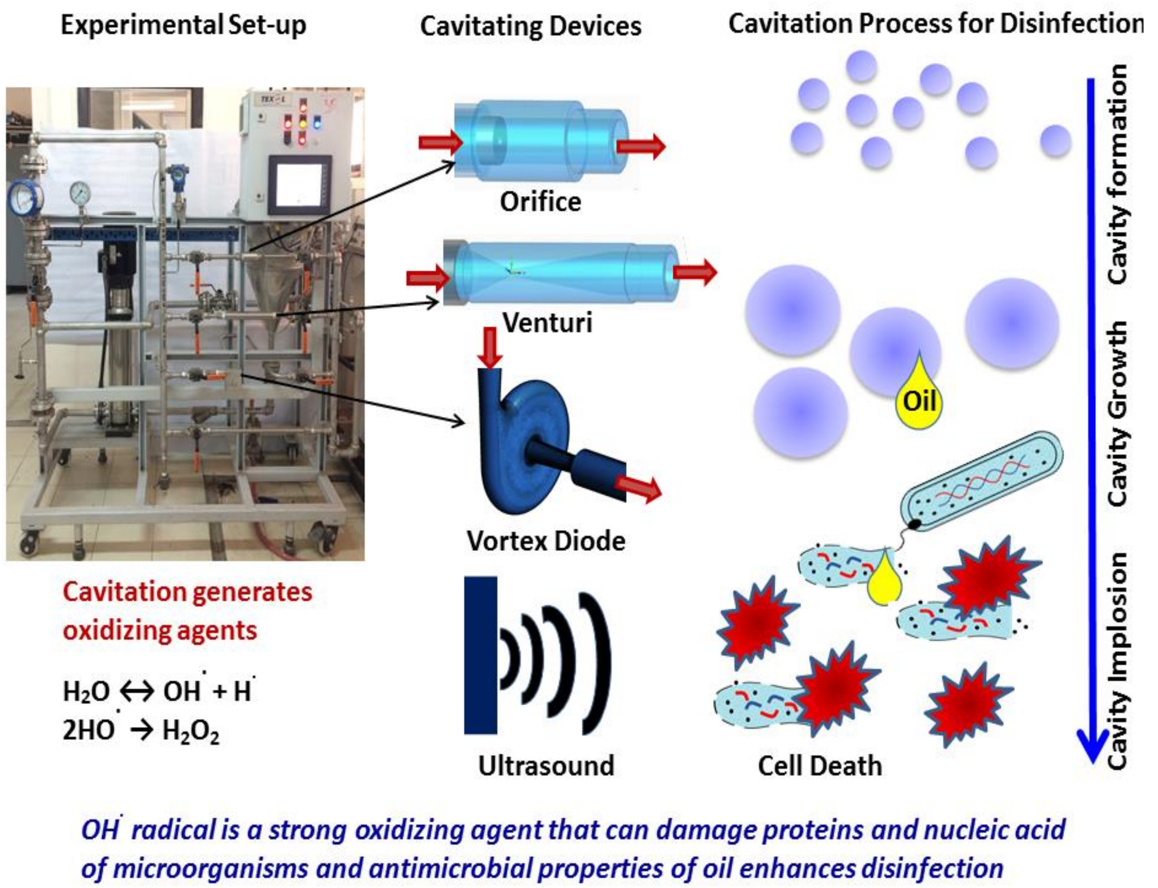


Figure 4.1: Experimental set-up and schematic of disinfection using cavitation

4.3 Results and Discussion

S.aureus and *E. coli* were selected as model organisms in the present study to provide proof of concept for application of hydrodynamic cavitation using natural oils for disinfection. *Staphylococcus aureus* is a facultative anaerobic or aerobic gram-positive bacteria having cocci shape, formed in singly, pairs, and irregular clusters and causes variety of skin disease, pustules, septicemia and pneumonitis. *E. coli* is a Gram-negative, facultative anaerobic, rod-shaped, coliform bacterium mostly occurred in water and known to cause various diseases, including pneumonia, urinary tract infections, and diarrhea. Effect of different process parameters were studied, in isolation as well as in conjunction with natural oil to bring out differences in the cavitation behavior. Effect of different reactor geometry was also evaluated in this regard. The detailed characteristics of natural oils are shown in Table 4.1.

4.3.1 Effect of pressure drop

Pressure drop (ΔP) is one of the most critical parameters in cavitation reactors as it dictates the number density and quality of the cavities based on the cavitation device type. Apart from quantity and quality of the cavities, the implosion of cavities is most critical to the real oxidation mechanism. Further, high shear generated during the cavity collapse may also physically break open the outer shell of microbes and therefore cause disinfection [29].

In our earlier studies, the effect of pressure drop for disinfection was discussed in detail and hence, only the essential and new findings in this regard are discussed below [4]. The optimization of pressure drop is utmost important to achieve complete disinfection of microorganism. The results for vortex diode showed that extent of *S. aureus* removal was enhanced from 75 to 89% with increasing pressure drop from 0.5 to 1 bar respectively. Increasing the pressure drop to 2 bar, the *S. aureus* removal efficiency could be further increased to 97 % within one hour, which indicates the consistency and efficacy of vortex diode for disinfection of pathogenic bacteria.

The optimum pressure is typically in between lowest and highest operating pressure corresponding to the low cavity density and cavity cloud respectively [30]. High pressures can also lead to escaping cavities from water without collapse, reducing the production of hydroxyl radicals and therefore reduced disinfection efficiency. Badve et al. [31] also observed increased inlet pressures (i.e. orifice, venturi) leading to increased disinfection up to certain pressure followed by decrease. The present study, however, found consistently increasing disinfection in the case of vortex diode up to 2 bar pressure drop.

4.3.2 Effect of pH on disinfection of *S. aureus*

The effect of pH for disinfection using cavitation has not been investigated so far which could be important from the point of view of wastewater treatment, recycle and reuse. The effect of pH was studied at three different conditions of pH: 4, 7 and 10. All the experiments were conducted at optimized inlet pressure of 1 bar. Figure 4.2 shows the results on disinfection of *S. aureus* at different pH with and without cavitation. While acidic conditions favor disinfection, the cavitation is equally effective at neutral pH which is important from its practical application point of view. The acidic pH tends to make microorganisms sensitive to hydrogen ion and enzymatic proteins are affected leading to loss of enzyme catalytic activity and simultaneous denaturation [32]. At pH 4, little disinfection was observed without cavitation, compared to that with cavitation. It is also possible to exploit increased rate of disinfection due to acidity by reducing the treatment time, as 72.0 % disinfection was observed within 15 min, while in the same time 37 and 20 % of disinfection observed at pH 7.0 and pH 10 respectively. Thus, cavitation, in conjunction with lower pH can have improved disinfection behavior. The enhancement of disinfection at lower pH can be attributed to the lower rate of recombination of hydroxyl radical, thereby making more hydroxyl radicals available for oxidation. It can be presumed that at acidic pH, bacterial enzymes will denature and higher concentration of hydroxyl radicals is possible at interface compared to bulk liquid when the bacteria is in ionic form leading higher percentage of disinfection. The positive effect of acidic pH in cavitation is however largely studied for organic pollutant degradation [17,30,33].

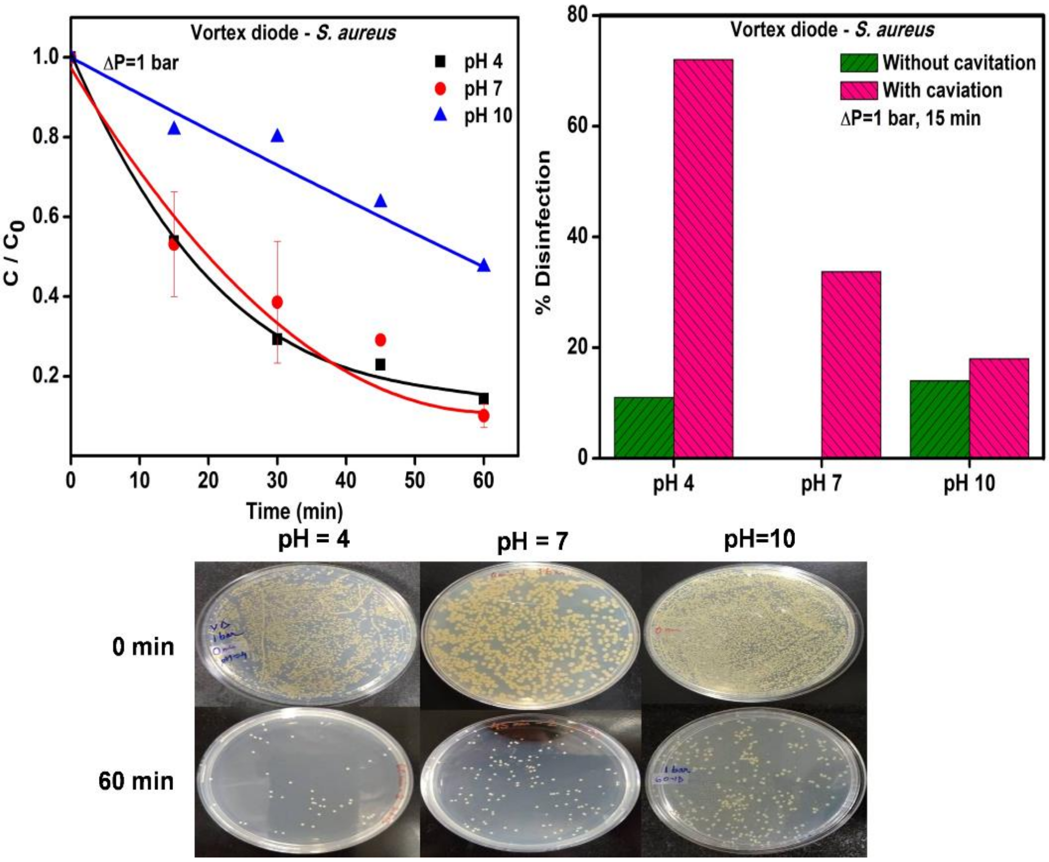


Figure 4.2: Effect of pH on water disinfection by hydrodynamic cavitation by vortex diode

4.3.3 Effect of temperature on disinfection of *S. aureus*

Temperature plays an important role, for both disinfection and cavitation. Heating to a certain temperature is also one form of disinfection method, though not practical for treating large volumes or isolated small volume treatments. Again, the effect of temperature has been reported in the case of hydrodynamic cavitation for the degradation of organic pollutants, but not many systematic studies for disinfection. In the present study, disinfection of *S. aureus* was investigated using three different temperature viz. 28 (ambient), 40 and 50 °C, with and without cavitation. It can be seen from Figure 4.3 that in case of without cavitation, disinfection follows the known trend of increasing efficiency with increased temperature and at 50 °C, about 53 % disinfection could be seen within 15 min and 80.7 % within 60 min as probability of cell death increases [34]. In the case of cavitation, the effect of temperature is marginal, but importantly, the efficacy of cavitation technique is evident at ambient conditions.

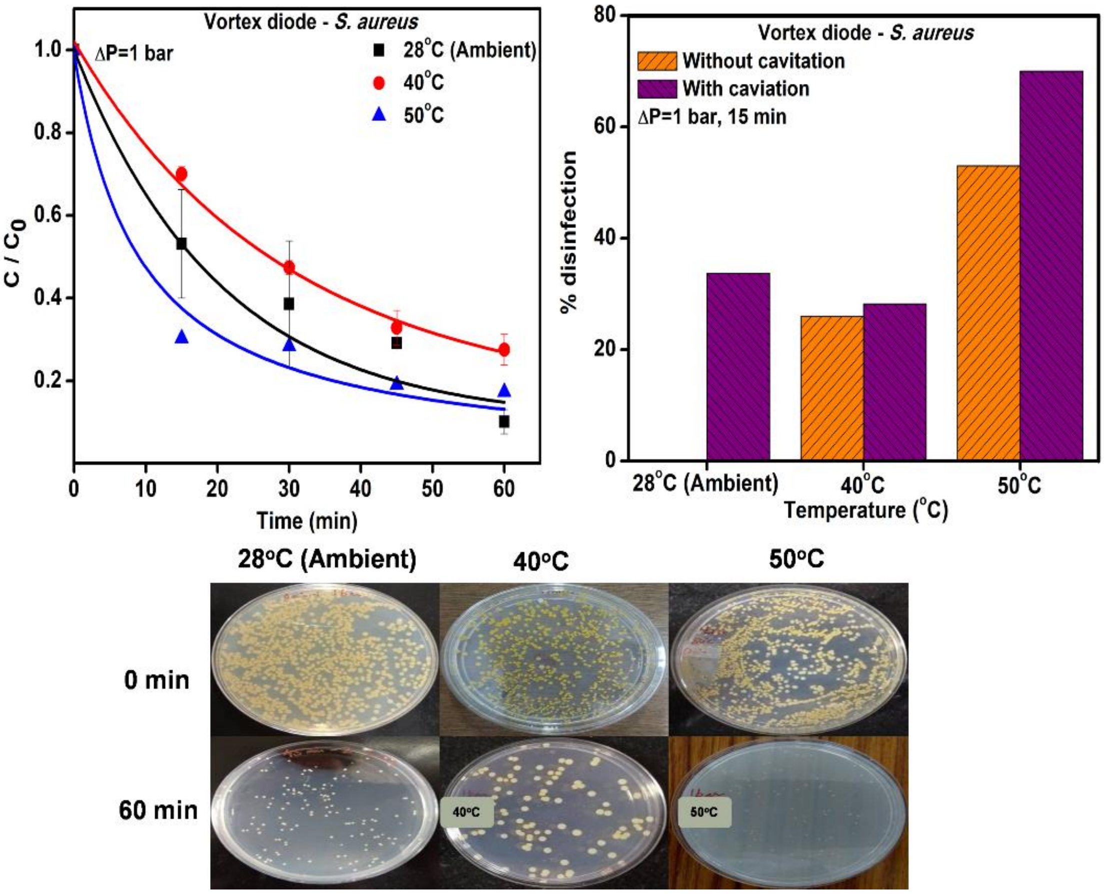


Figure 4.3: Effect of temperature on water disinfection

It may be noted that with increase in the temperature, viscosity, surface tension and gas solubility reduce, thus cavitation intensity and the number of cavity nuclei also can reduce [33]. There are conflicting reports on degradation of pollutants (dyes) with cavitation at increased temperatures indicating both increase and decrease in the rates beyond certain temperature suggesting uncertainties in the cavitation phenomenon at higher temperatures [35, 36].

4.3.4 Effect of increasing inoculum size

Bacteria concentration in wastewaters can be from insignificant to a very high- >10^5 CFU/mL. The higher concentration of bacteria poses a significant risk to human health and fatal to aquatic life. In the present study, effect of initial bacterial concentration was investigated in the range 20,000 to 2,00,000 CFU/mL. The results of the effect of concentration are shown in Figure 4.4. It is evident that the disinfection percentage remains almost constant, largely in the range 70 - 90 % for increasing inoculum size, which shows reliability and efficacy of cavitation reactor, vortex diode in this particular case, for different concentrations of bacteria. Interestingly, for the effectiveness of the cavitation process, microorganisms should be present in cavitation region so that they get killed by collapsing of cavities in their vicinity [37]. However, for the effect of bacterial concentration, a number of situations may arise such as large number of cavities and less number of microorganism; comparable number of cavities and microorganisms or in another extreme, less number of cavities and largely outnumbered microorganisms. The other uncertain elements of process such as number of cavities collapse or fruitful implosion with deactivation of bacteria, that are not measurable, add to unpredictable behavior of the process. Geometry of the cavitating device is also an important aspect in this regard and vortex diode is found to be much more effective as compared to conventional devices [4,11,18].

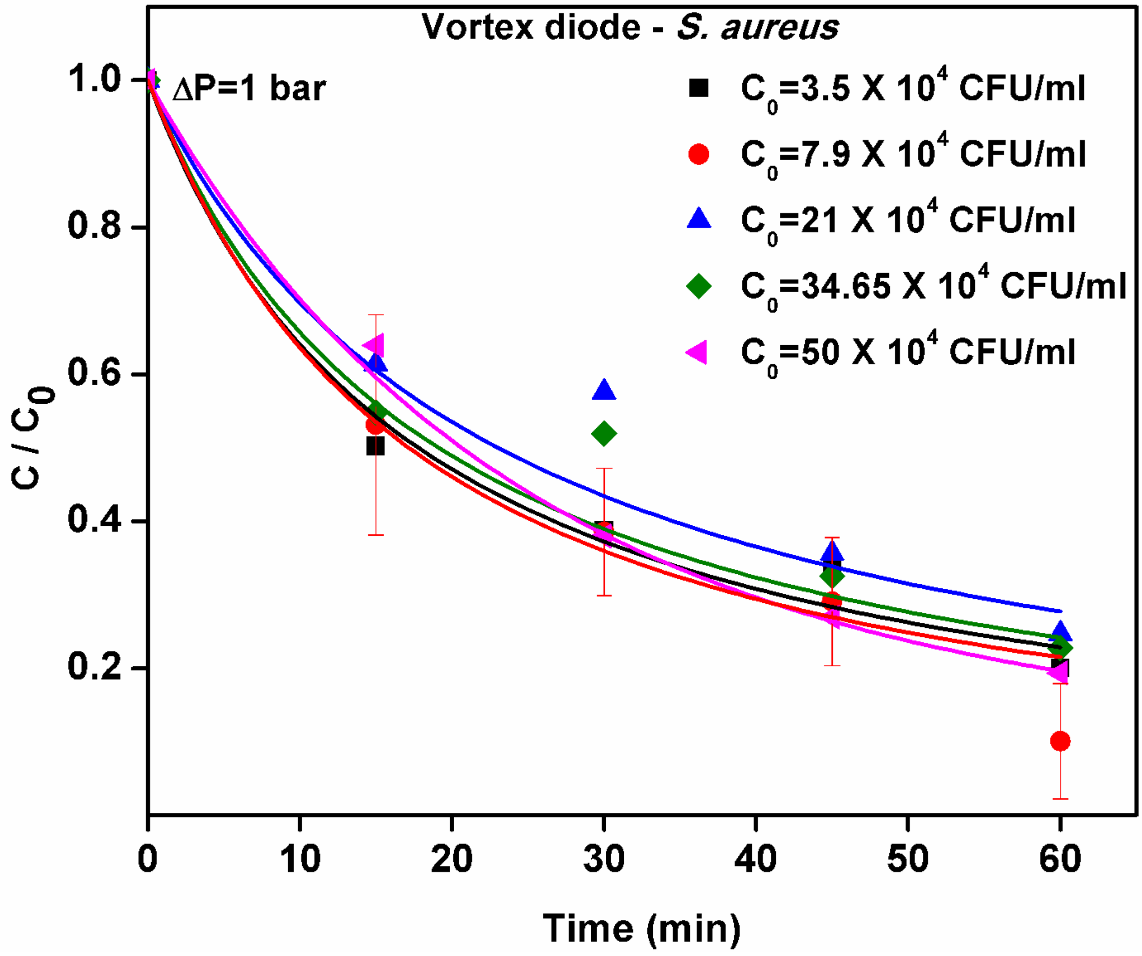


Figure 4.4: Effect of inoculum size on water disinfection

4.3.5 Exploring use of natural oils in cavitation for disinfection

Medicinal plants are rich source of antimicrobial active compound. It would be prudent to exploit the presence of active compounds of natural oils for disinfection of water, without adversely affecting the quality of water. For the first time, the effect of such oils/extracts is being reported for large scale disinfection application and with cavitation. While, such oils can be easily separated after the treatment, it may also be possible to use positive ingredients from such natural extracts/oils for improving quality of treated water. The properties of some initial selected oils; clove, eucalyptus, cinnamon and castor oil are given in Table 4.1. The primary basis of selection of these oils for studies in cavitation is that these oils are not harmful in nature. The effect has been evaluated using different cavitating devices i.e. vortex diode, orifice and also for acoustic cavitation.

The results of disinfection are given in Figure 4.5 for the four oils and for vortex diode as a cavitating device; for clove oil and orifice as a cavitating device. The proof of concept is also provided for acoustic cavitation and clove oil in Figure 4.5c. Only a fraction of oil, 0.1% of total volume of water was added in all the experiments. There are a number of observations from these results (Figure 4.5 and Table 4.2). First, the oil can have both positive and negative impact in terms of extent of disinfection:

1. Clove oil and eucalyptus oil have best effect in terms of increased efficiency while castor and cinnamon oils have lower disinfection efficiency compared to hydrodynamic cavitation alone for vortex diode as a cavitating device.
2. A very important aspect of the results of Figure 4.5a, is that there is an order of magnitude increase in the rates of disinfection, implying significantly reduced time of operation. For example, in the case of clove oil and eucalyptus oil, the increase in the rates in initial period is as high as 2-4 folds in 15-20 minutes compared to cavitation alone.
3. The results clearly indicate positive impact of clove and eucalyptus oil, both in terms of rate of disinfection as well as for increased disinfection.
4. Similar results are observed in case of orifice using a pressure drop of 2 bar (Figure 4.5b). It is to be seen that orifice requires significantly higher pressures, almost double or more, as compared to vortex diode for similar extent of disinfection. In 15 minutes, ~ 32 % disinfection of *S. aureus* was observed by orifice, which was enhanced to 55 % by addition of clove oil.
5. The concept of cavitation using oil for disinfection was validated using acoustic cavitation as well and from the results of Figure 4.5c it is evident that acoustic cavitation using oil (0.1%) has hugely increased the disinfection; without oil and with acoustic cavitation alone, there was negligible disinfection. Use of clove oil with acoustic cavitation here gave ~51 % disinfection in 15 minutes.
6. For the case of cinnamon oil and castor oil, the disinfection rates were adversely affected.

7. It is evident that selection of natural oils is crucial for improving the rates and extent of disinfection that could also positively impact in reducing the cost of operation.

Table 4.1: Properties of natural oils used in present study

Sr. No.	Name of oil	Viscosity (poise)	Surface tension (dyne/cm)	Active ingredient (%)	Reference
1	Clove	0.066 ± 0.006	5.8 ± 0.72	Eugenol (83.13%)	[38]
2	Eucalyptus	0.337 ± 0.033	7.33 ± 1.49	1,8-eucalyptol (72.71)	[38]
3	Cinnamon	0.041 ± 0.001	23.04 ± 0.07	Cinnamaldehyde (82.5%), eugenol (0.5%)	[38]
4	Castor	6-8	39	Ricinoleic acid (85-95%)	https://www.drugfuture.com/chemdata/castor-oil.html

It is quite instructive to evaluate the differences in the disinfection behaviour of different oils, especially from the view point of cavitation where bubbles/cavities get formed, grow and finally collapse to yield desired impact. Three factors can directly affect the collapse or implosion of cavities- the surface tension of the bubble, the inertia of the fluid and the pressure of the gas inside the cavities [39]. The pressure difference between the inside and outside of a cavity depends upon the surface tension and the size of the cavity. Thus, the properties of oil can modify the cavitation behaviour according to their physical properties. Apart from the physics of the bubbles and their altered collapse, antibacterial activity of the natural oil is another important aspect. A high antibacterial activity of *eucalyptous* oil reported by Lu et al. [40] and Bachir and Benali, [26]. The high disinfection ability of *eucalyptous* oil is due to the presence of 1,8-cineole active compound. The active compound of eucalyptus oil can destroy the permeability of bacterial membranes, leading to loss of electrolytes such as K^+, Na^+ and Ca^{+2} [40]. Similarly, clove oil has high bactericidal activity due to high level of eugenol [27]. The eugenol can react with the phospholipids of the cell membrane altering its permeability and as a consequence denature cell protein. The denaturation of cell protein causes death to cell [41]. The lower disinfection using *cinnamon* (62%) and castor oil (60%) may be attributed to adverse effect on number and quality of the cavities, as both the formation and energy release rate depends on surface tension and viscosity of oil. Increasing surface tension reduces size of the cavities and promotes less violent collapse [42]. Thus, in the present case, lower disinfection is observed for oils having high surface tension properties (castor oil 39 dyne/cm, cinnamon 23.04 dyne/cm) compared to oils having low surface tension (eucalyptus oil 7.3 dyne/cm, clove oil 5.8 dyne/cm). Further, microbial inactivation is process in which viability of organisms exposed to oil additive varies with time [40]. The inactivation depends on the type of microorganism, type and concentration of oil additive, and environmental conditions such as temperature and pH. Thus, the effect of oil can be significantly different for different microorganisms. However, these aspects are complex in nature due to interacting physical, chemical and microbial attributes and hence require more detailed investigations. The methodology was extended for the removal of gram-negative bacteria (*E. coli*) and only the proof of concept is provided by using clove oil and vortex diode as a cavitating device using the optimum pressure drop of 1 bar. The results are shown in Figure 4.5d which clearly confirm order of magnitude increase in the initial rates of disinfection compared to cavitation alone and practically complete removal can be obtained in 90-100 min.

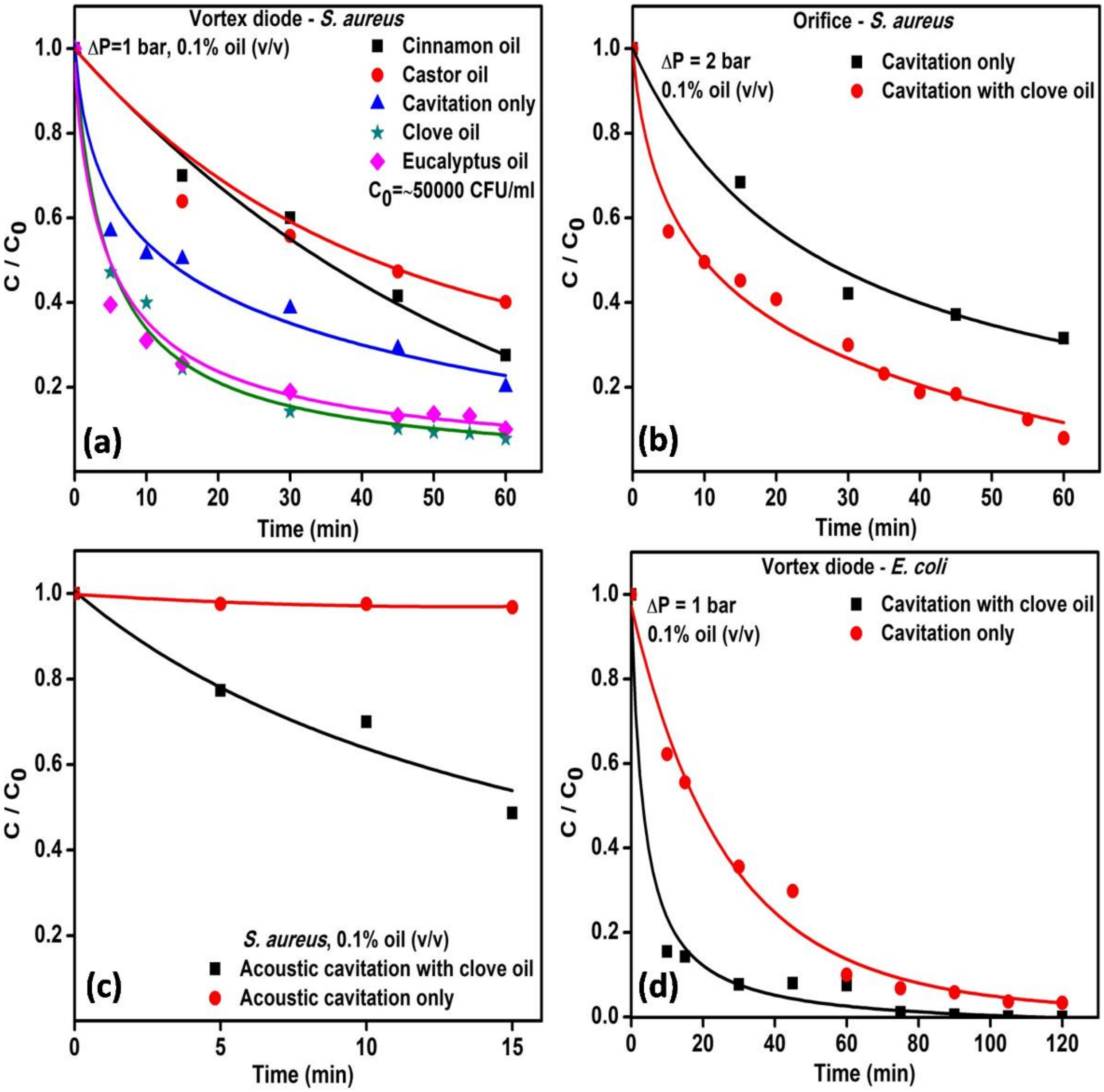


Figure 4.5: Effect of oil in cavitation for disinfection. (a) Vortex diode – *S. aureus* (b) Orifice- *S. aureus* (c) Acoustic cavitation- *S. aureus* (d) Vortex diode- *E. coli*

4.3.6 Kinetics of disinfection

A development of model based on per-pass conversion for hydrodynamic cavitation was presented in our earlier work [4] and the same is extended to evaluate kinetic data of the present study under different conditions. The cavitation process can be schematically shown as per Figure 4.6.

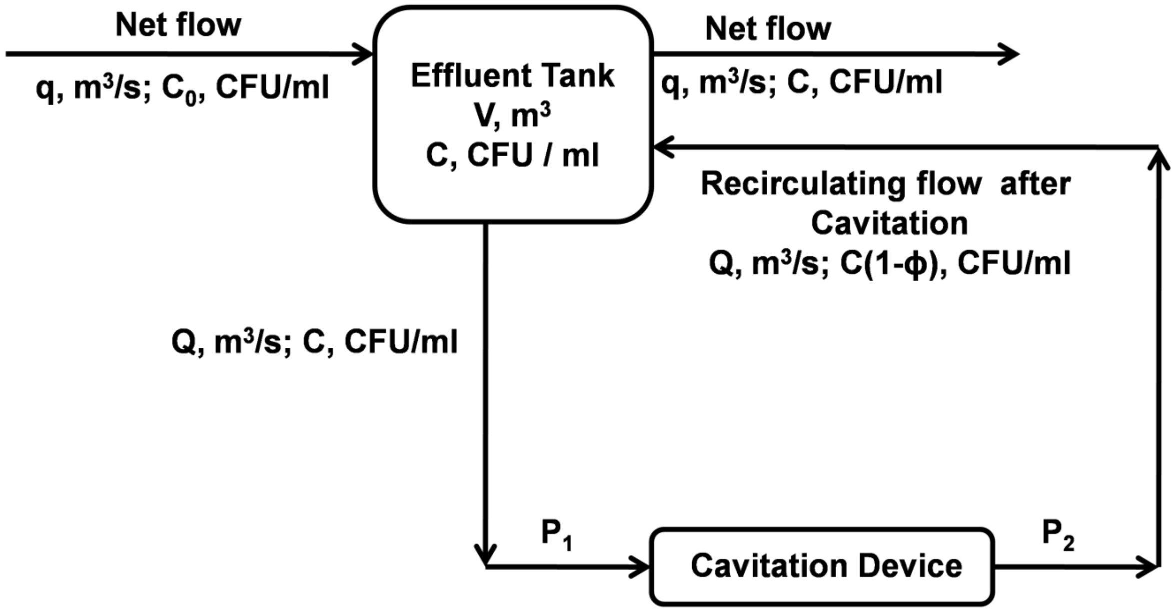


Figure 4.6: Schematic diagram for decontamination of water using cavitation

The kinetics of disinfection can be modelled in two ways: one is by conventional rate model and another is cavitation based model [43]. It was observed that the concentration of bacteria decreased exponentially with time and the kinetic data for disinfection of water can be fitted using Pseudo-first order equation in terms of k_G (growth rate of microorganisms) and k (disinfection rate of microorganisms). The mathematical model based on the physical description of cavitation process is closer to the real life operation and is also easy to solve using the experimentally obtained parameters such as flow rate (Q), volume (V) and concentration-time data. The value of number of passes is of practical importance since it determines the cost of operation and lower values are desirable. The value of per-pass disinfection factor can be simply obtained using Eq. 6.

tep	Conventional rate model	Cavitation based model
1	Assuming first order reaction $-\frac{\boldsymbol{dc}}{\boldsymbol{dt}} = \boldsymbol{kC}$ *k* is a rate constant	Pseudo-first order equation in terms of k_G (growth rate of microorganisms) , k (disinfection rate) $\boldsymbol{V}\frac{\boldsymbol{dc}}{\boldsymbol{dt}} = \boldsymbol{V}\,(\boldsymbol{k_G} - \boldsymbol{k})\boldsymbol{C}$
2	Integration of rate gives the pseudo first-order relationship $\ln\frac{\mathbf{C}}{\boldsymbol{C_0}} = -\boldsymbol{kt}, \boldsymbol{C} = \boldsymbol{C_0 e^{-kt}}$	The concentration of microorganisms C can be obtained by assuming the rates to be constant: $\boldsymbol{C} = \boldsymbol{C_0 e^{-(k-k_G)t}}$ where *C₀* is the initial concentration of bacteria (CFU/ml), t is the time for disinfection (min)
3	Not Applicable	The extent of disinfection in terms of per-pass disinfection factor (∅) and number of passes (n): $\boldsymbol{V}\frac{\boldsymbol{dC}}{\boldsymbol{dt}} = \boldsymbol{V}\,\boldsymbol{k_G}\,\boldsymbol{C} - \boldsymbol{Q}\,\emptyset\,\boldsymbol{C}\,;\ \boldsymbol{n} = \frac{\boldsymbol{Q}}{\boldsymbol{V}}\,\boldsymbol{t}$
4	Not Applicable	For the assumption of constant □and k_G, the concentration of microorganism at time t is estimated for the residence time of τ (V/Q). $\boldsymbol{C} = \boldsymbol{C_0 e^{-(\emptyset - k_G \tau)n}}$
5	$\boldsymbol{C} = \boldsymbol{C_0 e^{-kt}}$	Correlating the growth rate constant to doubling time, t_D as $k_G = (\ln 2/t_D)$ and assuming negligible growth of microorganism during the treatment time, the disinfection of water can be described as: $\boldsymbol{C} = \boldsymbol{C_0 e^{-kt}} = \boldsymbol{C_0 e^{-\emptyset n}}$
6	The effective disinfection rate constant (*k*) is: $\boldsymbol{k} = \frac{\ln(\boldsymbol{C_0}/\boldsymbol{C})}{\boldsymbol{t}}$	The effective disinfection rate constant (*k*) may be related to residence time (*τ*) and ∅ as: $\boldsymbol{k} = \frac{\emptyset\,\boldsymbol{n}}{\boldsymbol{t}} = \frac{\emptyset}{\boldsymbol{\tau}}$
7	The overall cavitation yield, $\boldsymbol{Y} = \frac{\boldsymbol{V}\,(\boldsymbol{C_0} - \boldsymbol{C})}{\Delta\boldsymbol{P}\,\boldsymbol{Q}\,\boldsymbol{t}}\ \boldsymbol{CFU/J}$	The overall cavitation yield, can be obtained as: $\boldsymbol{Y} = \frac{\boldsymbol{V}\,(\boldsymbol{C_0} - \boldsymbol{C})}{\Delta\boldsymbol{P}\,\boldsymbol{Q}\,\boldsymbol{t}}\ \boldsymbol{CFU/J}$
8	Not Applicable	For small values of ∅, $\boldsymbol{Y} = \frac{\emptyset\,\boldsymbol{C}}{\Delta\boldsymbol{P}}\ \boldsymbol{CFU/J}$
9	Rate of disinfection, R is: $\boldsymbol{R} = \boldsymbol{kC_{avg}}\ \boldsymbol{CFU/(ml\ s)}$ *C_{avg}* is average concentration; $\boldsymbol{C_{avg}} = \frac{\boldsymbol{C_0} + \boldsymbol{C}}{\mathbf{2}}$	The average disinfection rate over time 't_{op}' is: $\boldsymbol{R_{avg}} = \frac{\boldsymbol{C_0}\,(1-\boldsymbol{e^{-kt}})}{\boldsymbol{t_{op}}} = \frac{\boldsymbol{C_0}\,(1-\boldsymbol{e^{-\emptyset n}})}{\boldsymbol{t_{op}}}\ \boldsymbol{CFU/(ml\ s)}$

As discussed in our earlier work, per-pass disinfection factor based cavitation model is more realistic, as nature of geometry of the cavitation device can be reflected into per-pass disinfection. The mathematical treatment clearly indicates dependence of disinfection on residence time and less dependence on initial concentration compared to conventional reaction rate model.

The results of kinetics study for the conventional rate model and those using cavitation model are presented in Table 4.2, specifically for 15 minutes of operation, where differences in the initial rates are evident. Similar to our earlier findings [4], the values of rate of disinfection are very high indicating effectiveness of cavitation, in general and vortex diode, in particular. Thus, the results clearly establish strong dependence of rate of disinfection upon type of cavitating device. In this work, apart from different cavitating devices, we have also attempted to evaluate the performance under acoustic cavitation (using ultrasonic bath) and the rates of disinfection for the same are also listed in Table 4.2. Further, oil as an additive was evaluated for the improvement of the process. A number of interesting observations could be made in this regard.

1. The rates of disinfection in hydrodynamic cavitation are significantly/ order-of-magnitude higher compared to acoustic cavitation.
2. The rates of disinfection are higher using vortex diode as compared to orifice and orifice requires significantly higher pressures compared to vortex diode.
3. Low pH (4) gives substantially increased rates of disinfection.
4. Higher temperature, naturally and as expected, improves disinfection.
5. There is drastic effect of oil on disinfection behavior. While the two oils, namely clove and eucalyptus oil positively alter the cavitation behavior, the other two oils, cinnamon and castor oils adversely impact the disinfection behavior. This effect is also observed even in the case of acoustic cavitation, where more than 20 times increase in the initial rate of disinfection was observed by addition of clove oil.
6. The reasons for the variations in different oils can be explained on the basis of characteristics of oil and the constituent properties, as explained in the earlier section and also using the proposed mechanism.
7. Vortex diode is found to be superior compared to orifice even in the case of increased rates of disinfection by oil addition.

Table 4.2: Rate of disinfection for *S. aureus* (15 min)

Study	Parameter	Initial CFU/ml	% Disinfection	Rate of disinfection, CFU/(mL.s) (conventional model)	Rate of disinfection, CFU/(mL.s) (cavitation model)	Rate constant $(s^{-1})\times10^4$	Per-pass disinfection (Ø)
Effect of Pressure Vortex Diode	**ΔP, bar**						
	0.5	50000	32	18.0	17.8	4.3	0.0598
	1	35000	43	17.2	16.8	6.3	0.0622
	2	60000	39	26.4	25.9	5.5	0.0376
Effect of pH Vortex Diode (ΔP=1 bar)	**pH**						
	4	78500	71	70.5	62.4	14.0	0.1314
	7	68000	21	15.6	15.6	2.6	0.0249
	10	55000	18	11.2	11.1	2.2	0.0211
Effect of Temper-ature, (^{o}C) Vortex Diode (ΔP=1 bar)	**T, ^{0}C**						
	28	68000	21	15.6	15.6	2.6	0.0249
	40	88500	30	29.8	29.4	4.0	0.0388
	50	36300	70	31.4	28.1	13.3	0.1310
Effect of oil 0.1% (v/V) Vortex Diode (ΔP=1 bar)	**Oil**						
	Clove	35000	63	26.6	24.6	11.1	0.1106
	Eucalyptus	43800	74	41.7	36.2	15.2	0.1491
	Cinnamon	58000	30	19.5	19.3	4.0	0.0400
	Castor	73500	36	29.9	29.4	5.0	0.0497
Effect of Pressure Orifice (ΔP=2 bar)	**ΔP, 2 bar**	38000	32	13.5	13.3	4.2	0.0970
Effect of oil 0.1% (v/V) Orifice (ΔP=2 bar)	Clove Oil	25000	55	16.0	15.2	8.8	0.2061
Acoustic (15 min)		66100	3.18	2.3	NA	0.36	NA
Effect of oil 0.1% (v/V) Acoustic (15 min)	Clove Oil	62700	51	37.3	NA	8.0	NA

The differences in the rates for acoustic cavitation and hydrodynamic cavitation are quite understandable on the basis of the intensity of cavitation since large differences have been reported even within acoustic cavitation using ultrasonic bath and ultrasonic horn [14]. The temperatures also aid disinfection process and increased rates can be obtained at higher temperatures [31]. The conventional methodologies typically considered using the combination of different treatment methods. The oil as an additive can be one alternative to many of the hybrid techniques reported in the literature such as hydrogen peroxide treatment, ozone, ultrasonic cavitation coupled hybrid processes; implying uniform and intense cavitation effects in disinfection with possible health benefits for the oil characteristics apart from the conventional attributes of high efficiency and also ease of operation compared to ultrasonic cavitation, conventional hydrodynamic cavitation or hybrid methods.

The effect of temperature on per- pass disinfection factors for *S. aureus* is shown in Figure 4.7. For vortex diode and under ambient conditions, as the pressure increases from 0.5 bar to 2 bar, per-pass disinfection factors increase from 0.057 to 0.086 and subsequently energy dissipation rate also increases. However, similar trend is not found at higher temperatures (40 °C and 50 °C), as the pressure increase reduces per-pass disinfection factor partly due to the vapour cloud formation; large number of cavities lead to large vaporous bubbles which get carry-forward without collapsing [44, 45].

The impact of addition of natural oils on per-pass disinfection, especially in the initial rates, is shown in Figure 4.8 for vortex diode at the optimum pressure drop of 1 bar. The errors were largely below 1.5% for all sets, except for eucalyptus oil. The maximum error for eucalyptus oil was ~8%. It can be seen that per-pass disinfection factors for *S. aureus* are higher for clove and eucalyptus oil with cavitation than other oils. It is evident that in 15 min, cavitation with clove oil and cavitation with eucalyptus oil showed more than 100% increase in the per-pass disinfection as compared to cavitation alone. The benefits diminish with time and hence selection of best suitable oil and time of treatment is crucial. Thus, the results clearly highlight that the increased rates of disinfection and per-pass disinfection in hydrodynamic cavitation can be exploited to reduce the time of operation, consequently to reduce the cost of disinfection.

Although the initial rate of disinfection could be significantly increased using oil as an additive, more rigorous efforts are further required to establish the relationship of oil properties and its synergy with cavitation process so that appropriate guidelines can be developed for the selection of most suitable oil.

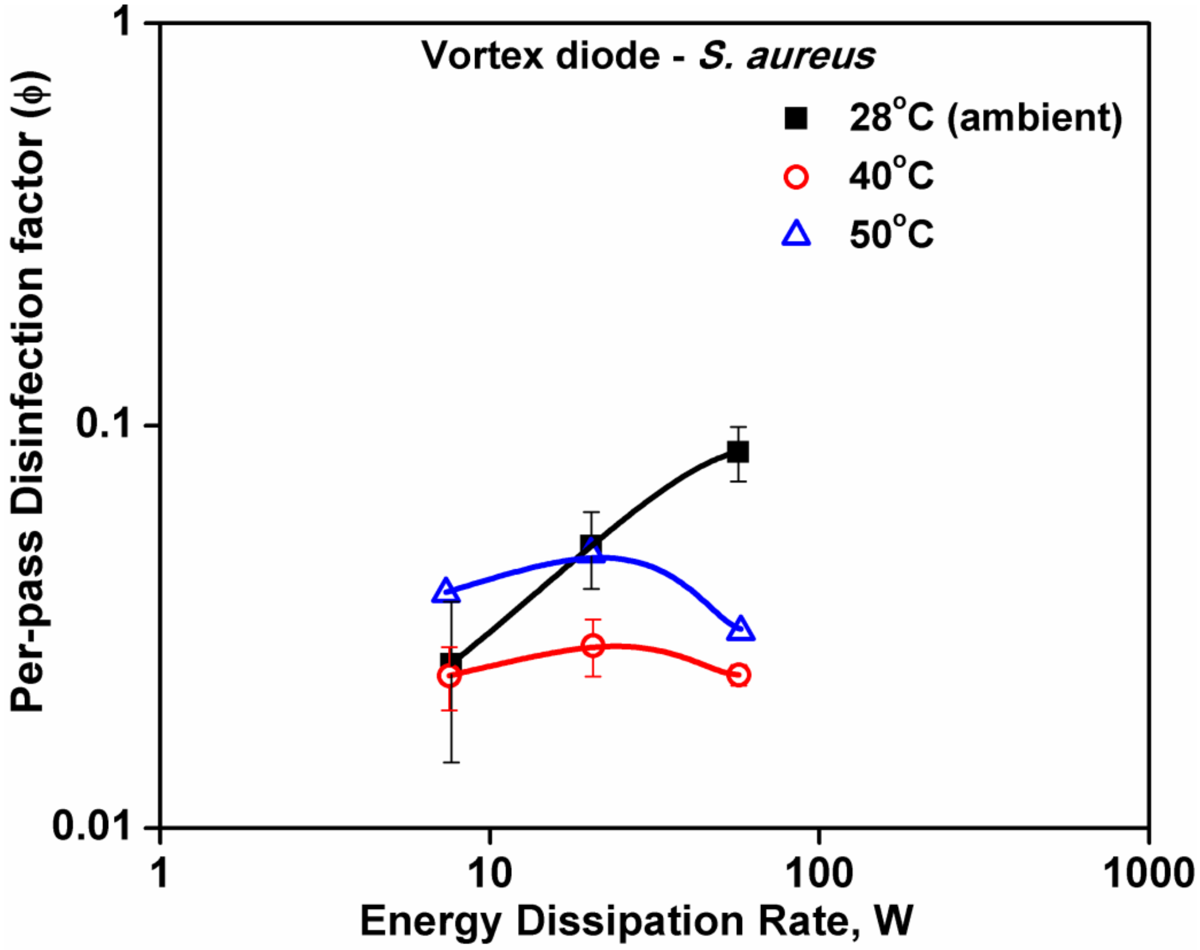


Figure 4.7: Effect of Temperature- Per- pass disinfection factors at 60 min

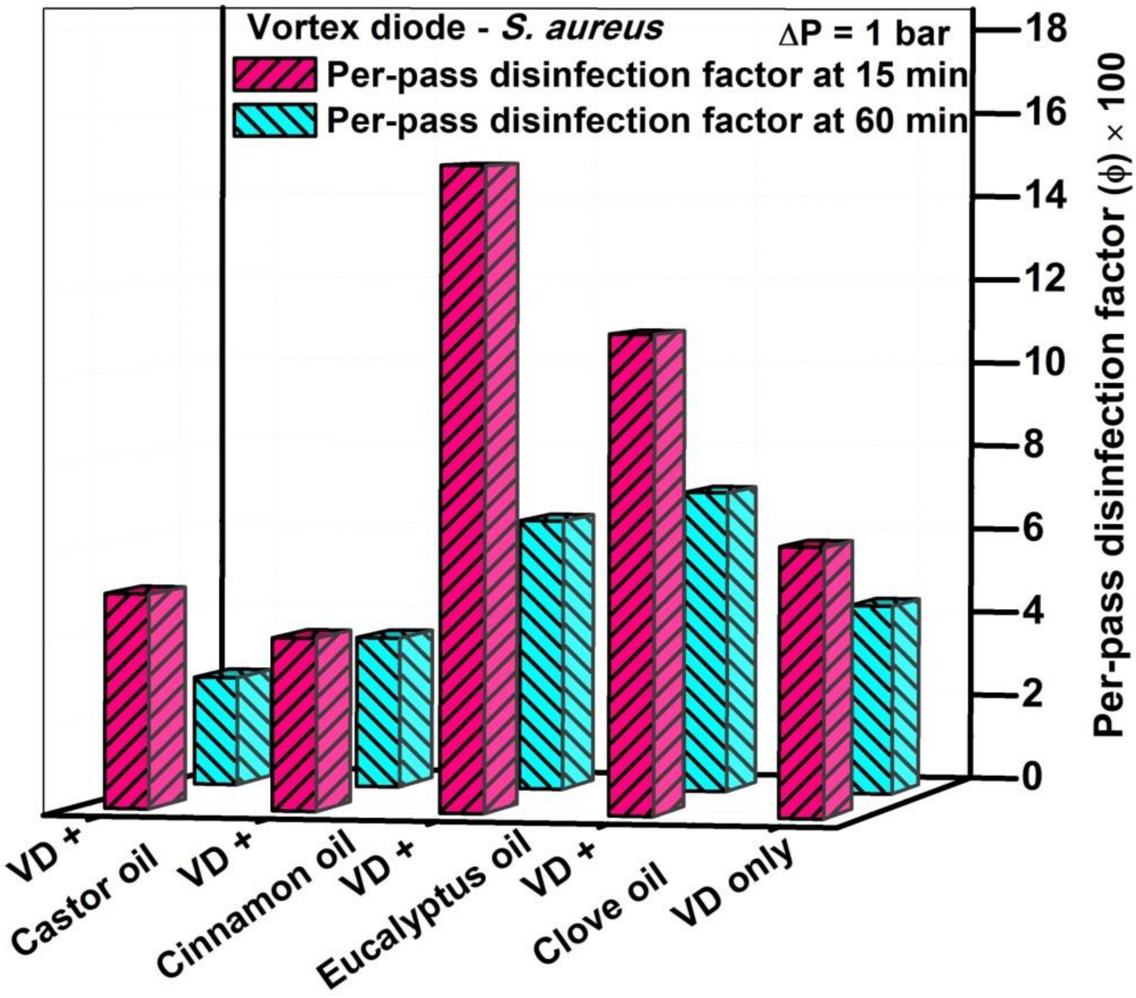


Figure 4.8: Effect of oil on per- pass disinfection (VD-Vortex diode)

4.3.7 Disinfection of water using hydrodynamic cavitation: A plausible mechanism

Oxidation process is known since long time for the destruction of bacteria, however their usage is limited due to major shortfalls. The conventional oxidation is a slow process and sometimes required additional catalyst to improve the removal rate. Also, the treatment is unsatisfactory for the complete killing of bacteria and rather only deactivates the bacteria. As per the EPA manual of water treatment, hydrogen peroxide is considered as a poor disinfectant. Thus, it would be prudent to find alternatives to existing many chemical disinfectants in this regard.

In the present study, cavitation with addition of natural oil was shown to achieve complete destruction of bacteria within shorter time period. The selection of natural oils is, however, not straightforward and a number of parameters are to be considered that would directly impact either the disinfection process or the cavitation process. Thus, in order to obtain synergetic effect of both cavitation and anti-microbial properties of natural oils, it is essential to envisage the possible mechanism of disinfection. Based on the results of the present study, a plausible mechanism for cell destruction is proposed and shown in Figure 4.9. The destruction of cells can be attributed to hydroxyl radicals generated during the cavitation resulting into oxidative damage of the cells. Localized heat conditions of cavity implosion can also damage the DNA. The main reason for cell death is cell disruption since once cell membrane and/or cell wall is severely damaged, the bacteria become dead without DNA and protein denaturation. It has been well reported that important constituents of microorganisms such as proteins, lipids, DNA and polysaccharides can be affected by oxidation. The reactive species such as •OH radicals can attack and oxidise double bonds and sulfhydryl groups of protein constituents and produce oxidative stress that creates unalterable consequences for the microorganisms [46, 47]. Moreover, the active compound present in the natural oil can react with the phospholipids of the cell membrane thereby altering its permeability and also denature cell protein. The denaturation of cell protein causes cell death [41].

To further support the mechanism, the difference in cell morphology of bacterial cell before and after the cavitation with oil treatment was investigated using SEM and TEM techniques (Figure 4.10). The results of FE-SEM clearly highlight the intact nature of the cells of *S. aureus* (0 min), round shaped and in a cluster form before treatment (Figure 4.10a) and their mutilated form after the treatment (60 min), where cellular morphology of bacteria is changed in terms of increased cell permeability, distorted cell membrane and creation of holes or wrinkles on bacteria (Figure 4.10b). These results were further reinforced by TEM analysis. The results of TEM analysis confirmed that at 0 min, the bacterial cell was intact as well as round shaped with clear cell membranes (Figure 4.10c), while after combined cavitation with oil process, the cells were seen unevenly distributed, condensed, loss of cytoplasm and leakage of cytoplasmic content (Figure 4.10d). Lu et al. [40] studied on antimicrobial activity of eucalyptus oil towards *Pseudomonas* sp., and stated that the antimicrobial effect of eucalyptus oil may be due to the active ingredient of oil that reacts with surface of bacterial cell and penetrate to plasma membrane leading to distortion of bacterial cell. The morphological changes and alteration of bacteria after oil treatment have been reported by several researchers [20, 40].

While, the antibacterial activity of various oils and reasons thereof are well reported in the literature, its synergetic effect in enhancing efficiency in combination with other processes such as cavitation are not well researched so far. The plausible mechanism as depicted in Figure 4.9 therefore is an attempt to qualitatively provide causes of cell damages, such as the membrane rupture due to extremely high stress produced during cavitation process, generation of extremely high temperatures during bubble implosion leading to the leakage of cytoplasmic matter apart from possible cell membrane rupture and DNA damage due to generation of active free radicals. The role of cavitation in disinfection in this regard is in accordance with that reported by Cerecedo et al. [20]. Palacios et al. [48] have reported *B. stearothermophilus* elimination by ultrasonic treatment and proposed that high pressures affected the permeability of protoplast membrane due to which dipicolinic acid, calcium and other low molecular weight substances get leaked and cell properties get modified which is in agreement with the present findings.

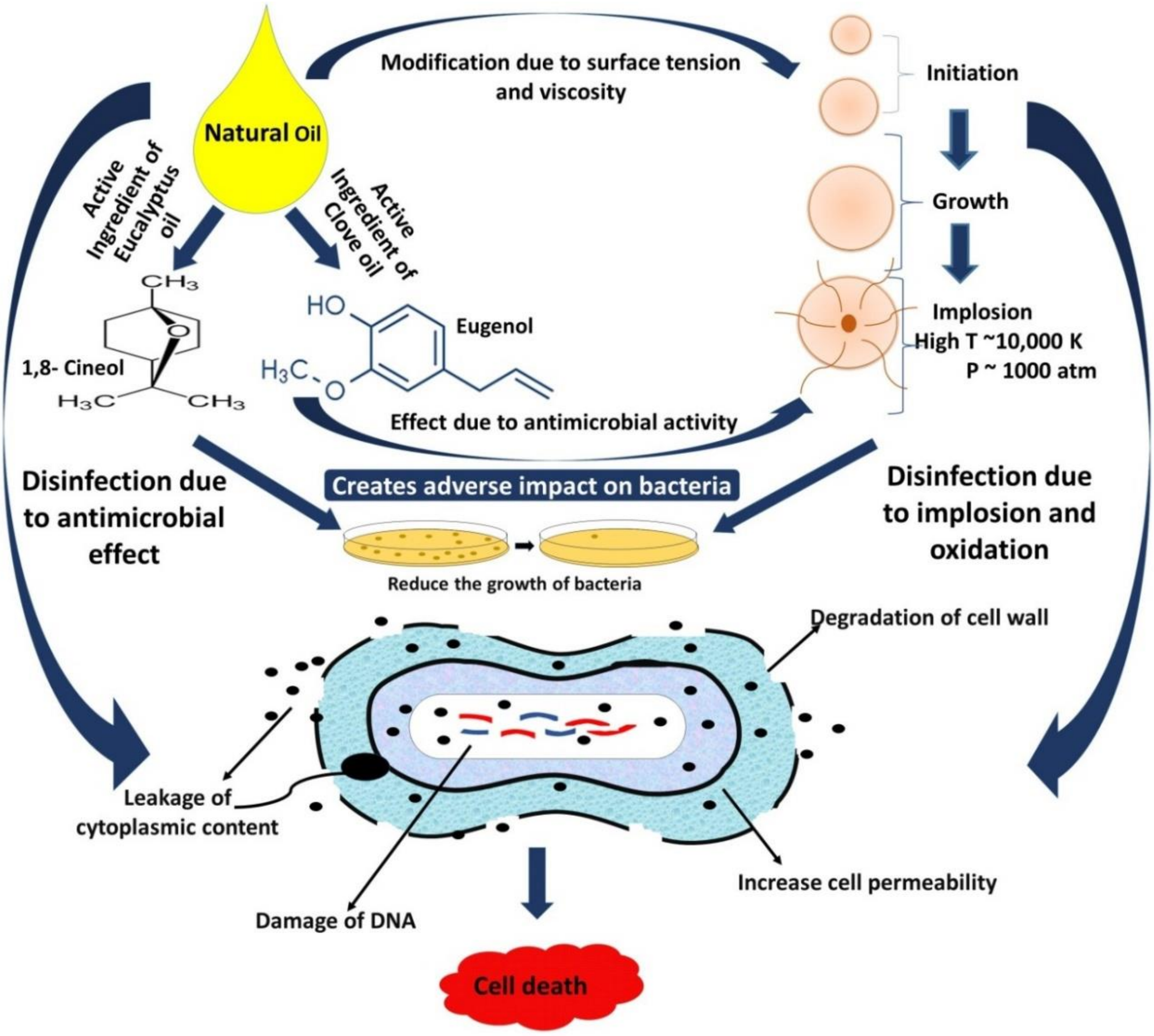


Figure 4.9: Plausible mechanism of disinfection using natural oils and cavitation

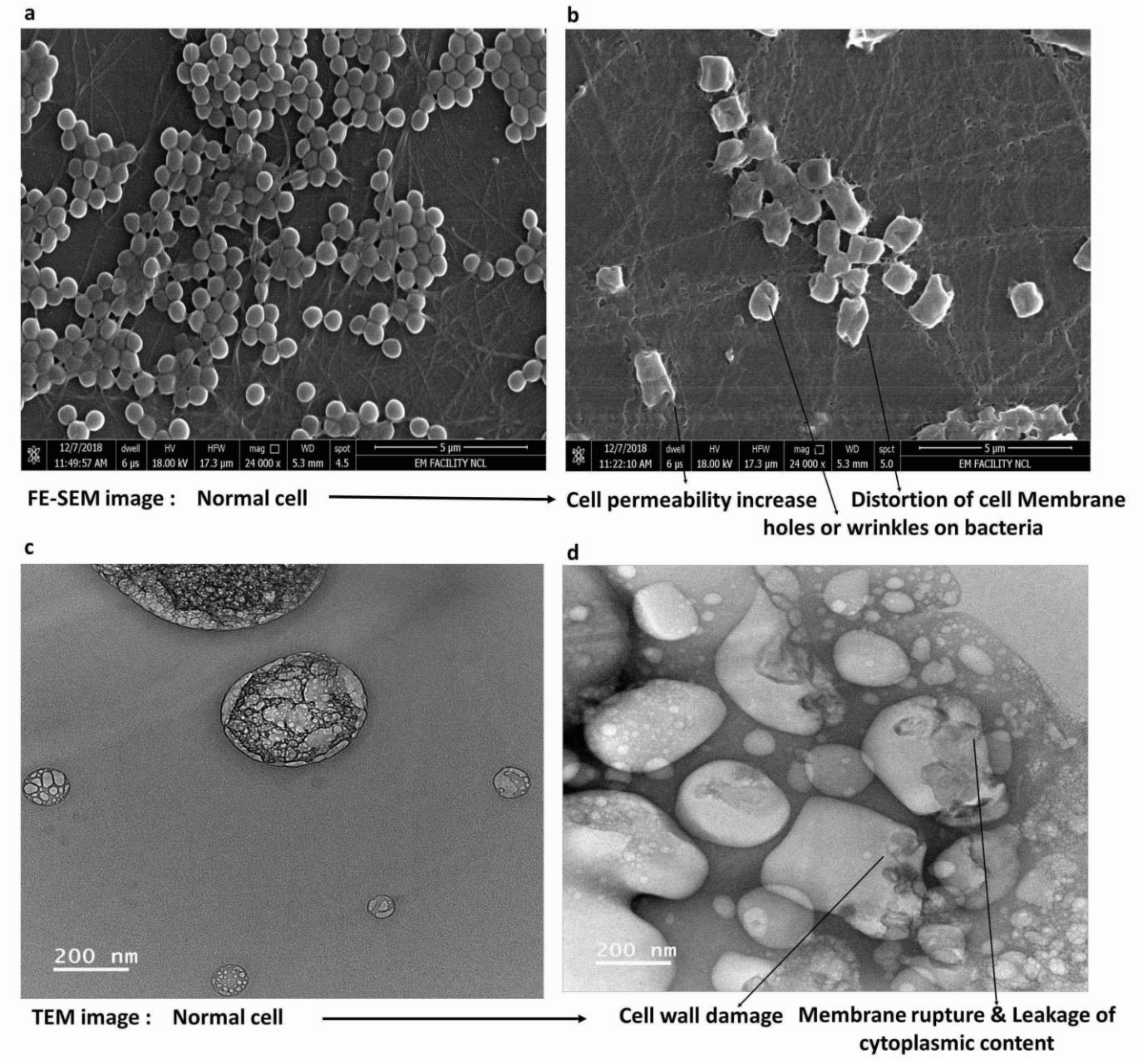


Figure 4.10: Effects of cavitation with natural oil on morphology of bacteria. FE-SEM image (24,000 X) (a) 0 min sample (b) 60 min of treatment (c) TEM image, 0 min (d) TEM image, 60 min of treatment

4.3.8 Comments on the practical application of the new method

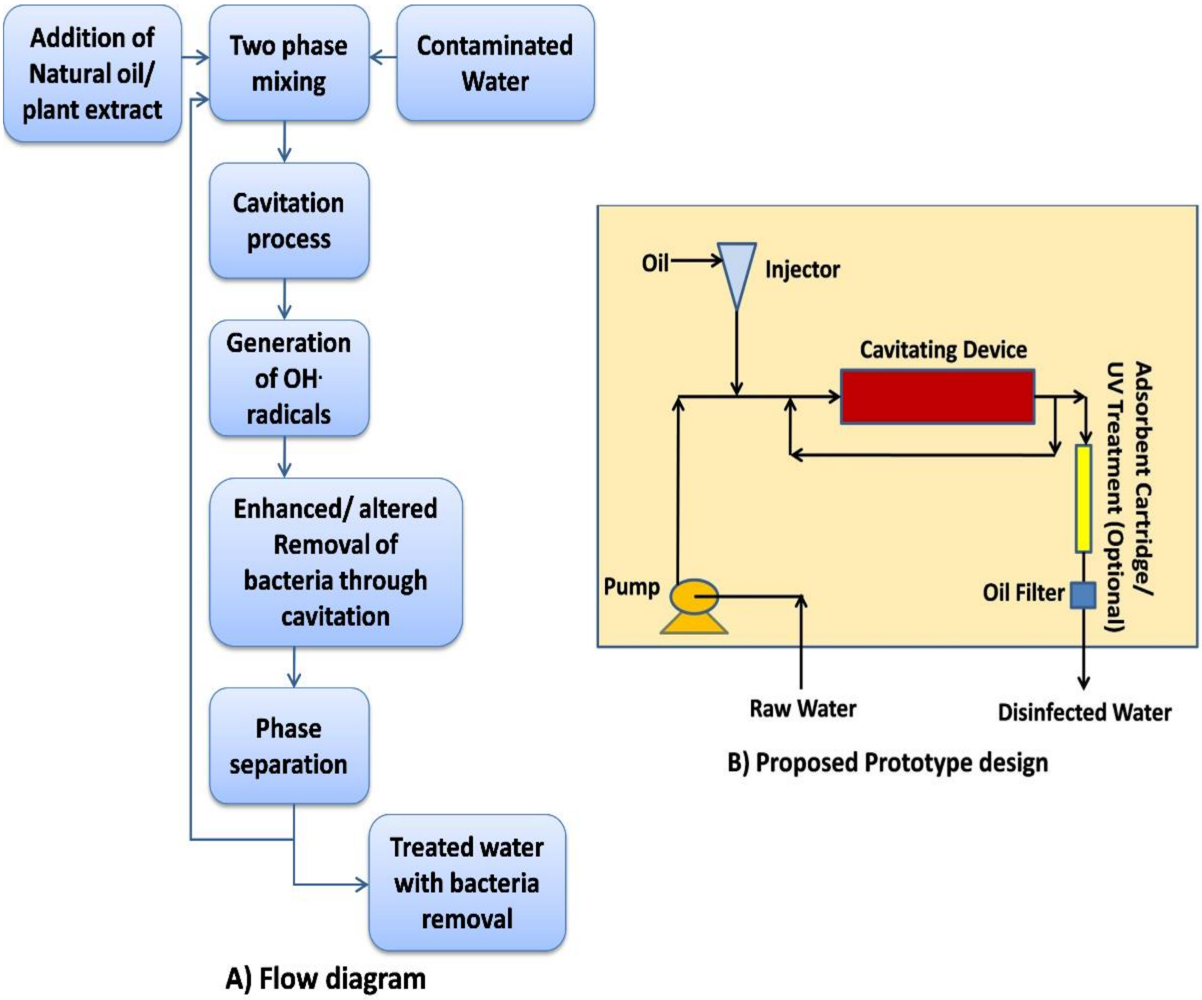
The cavitation process for disinfection of water is known and has been well reported in the literature, especially for acoustic cavitation and for hydrodynamic cavitation using conventional devices such as orifice, with and without process intensifications such as ozone, hydrogen peroxide addition, and so on. The success with these was, however, limited and as a result, practical application of such techniques is not available for either household applications or for large scale water treatment installations.

The results presented in this work are important from two counts. One, the hydrodynamic cavitation can eliminate the bacteria to the extent of 100% as desired by various norms. Secondly, the proof of concept in the form of addition of natural oils can significantly increase the rate of disinfection, thereby reducing the time of operation and consequently reducing the cost of operation. Although, the natural oil can be separated after use using standard methods, it may also be possible to exploit the health benefits of specific oils, with appropriate designs. Further, in such cases, it may also be useful to couple the process with other established methods such as adsorption for complete removal of bacterial contamination for cost optimization. It is necessary to investigate the effect of natural oils in detail to further enhance the performance of the developed process.

A typical flow diagram for the practical operation and conceived prototype design is shown in Figure 4.11. The process essentially has the following essential steps:

1. Creating a two phase system by contacting of oil phase with water/aqueous phase;
2. Creating of third vapor phase and conditions of in situ cavitation;
3. Allowing cavities to collapse so as to generate in situ hydroxyl radicals or hydrogen peroxide;
4. Allowing removal of bacteria from the contaminated water containing bacteria such as *E. coli*, *S. aureus* etc.
5. Separating the oil phase and aqueous phase after the process is completed;
6. Removing bacteria or having bacteria content altered as per desired limits
7. Recycling oil for further use.

In the case of partial destruction of bacteria using cavitation, the process can be suitable combined with other established such as adsorption, where suitable adsorbents effective for disinfection can be employed, e.g. silver nanocomposites, bio-nanocomposites and so on [8, 9]. It is believed that process integration using hydrodynamic cavitation and cavitating device-vortex diode has a potential to provide practical solution to disinfection of water so that the disadvantages of existing chemical disinfection processes can be circumvented.



A) Flow diagram

B) Proposed Prototype design

Figure 4.11: Flow diagram for disinfection using cavitation and proposed prototype

4.4 Conclusions

The present study, for the first time, clearly demonstrated the useful application of natural oils having antibacterial properties in combination with cavitation technology to enhance the efficiency of disinfection of water. Both gram-negative (*E. coli*) and gram-positive (*S. aureus*) bacteria can be effectively removed by optimizing the process parameters for hydrodynamic cavitation such as pressure, temperature and by use of suitable oil. It was shown that a very small percentage of oil (0.1%) can be sufficient to enhance initial rates of disinfection to the extent of 2 times for *S. aureus*, 5 times for removal of *E. coli* in the case of hydrodynamic cavitation using vortex diode and up to 17 times as compared to that in acoustic cavitation. The nature of oil modifies the cavitation behavior and hence a number of possible combinations can be anticipated in this manner. In the present study, clove oil was found to be the most effective natural oil in combination with cavitation as compared to eucalyptus, cinnamon and castor oil. Further, process is effective even at very high concentrations of bacteria, not reported so far. Practically 100% disinfection can be obtained using the hydrodynamic cavitation technology at very low pressure drop conditions, as low as 1 bar, especially for vortex diode as a cavitating device compared to orifice. A possible mechanism is proposed for the effect of oil and hydrodynamic cavitation in cell destruction through the rupture of cell wall, oxidative damage and possible DNA denaturation. The increased rates of disinfection using oils, where natural oils can be perceived as biocatalysts, along with reduced time and ease of operation, easy scale-up indicate potential to provide significant advantages in practical applications.

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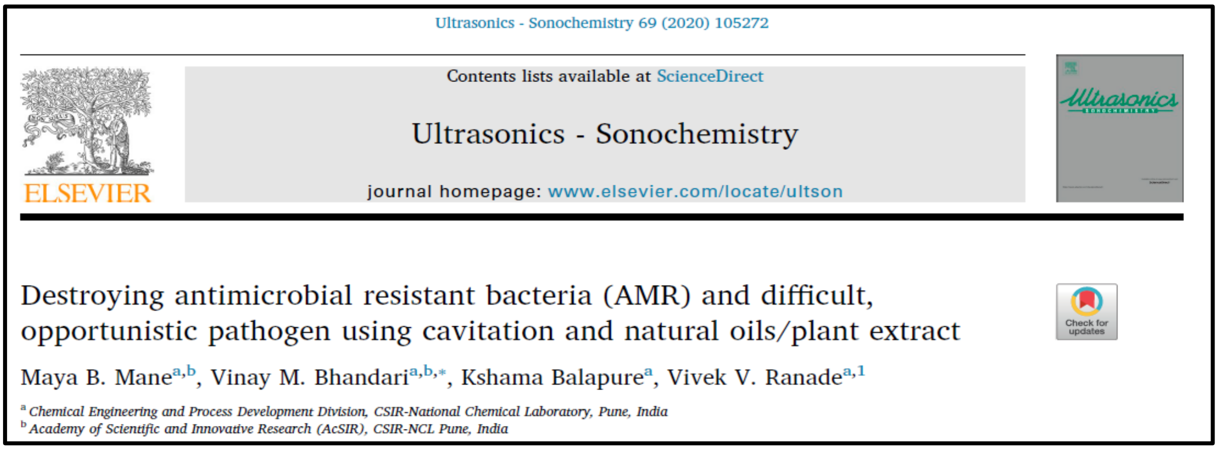

Ultrasonics - Sonochemistry 69 (2020) 105272

Contents lists available at ScienceDirect

Ultrasonics - Sonochemistry

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Destroying antimicrobial resistant bacteria (AMR) and difficult, opportunistic pathogen using cavitation and natural oils/plant extract

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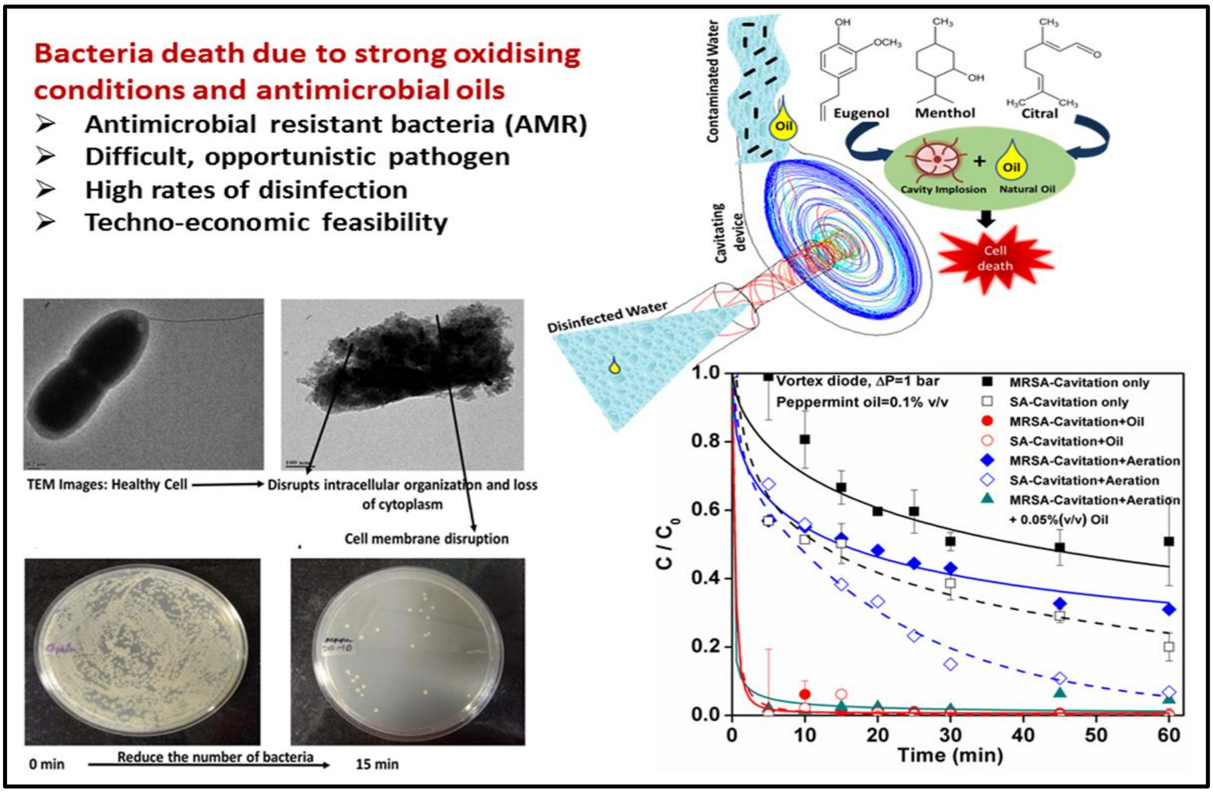
Chapter 5



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https://doi.org/10.1016/j.ultsonch.2020.105272

Chapter 5
Destroying antimicrobial resistant bacteria (AMR) and difficult, opportunistic pathogen using cavitation and natural oils/plant extract

Abstract

The present study reports, for the first time, a new and techno-economic strategy for effective removal of antimicrobial resistant bacteria (AMR) and difficult, opportunistic pathogen using cavitation and natural oils/plant extract. A hybrid methodology using natural oils of known health benefits has been discussed in combination with conventional physico-chemical method of hydrodynamic cavitation that not only provides efficient and effective water disinfection, but also eliminates harmful effects of conventional methods such as formation of disinfection by-products apart from reducing cost of treatment. A proof-of concept is demonstrated by achieving exceptionally high rates for practically complete removal of antimicrobial resistant (AMR) and relatively less researched, gram-negative opportunistic pathogen, *Pseudomonas aeruginosa* and gram-positive methicillin resistant, *Staphylococcus aureus* using a natural oil- Peppermint oil and two different cavitating reactors employing vortex flow (vortex diode) and linear flow (orifice) for hydrodynamic cavitation. More than 99% disinfection could be obtained, typically in less than 10 minutes, using vortex diode with operating pressure drop of 1 bar and low dose of 0.1% peppermint oil as an additive, depicting very high rates of disinfection. The rate of disinfection can be further increased by using simple aeration which can result in significant lowering of oil dose. The conventional device, orifice requires relatively higher pressure drop of 2 bar and comparatively more time (~ 20 min) for disinfection. The cost of the disinfection was also found to be significantly lower compared to most conventional processes indicating techno-economic feasibility in employing the developed hybrid method of disinfection for effectively eliminating bacteria including AMR bacteria from water. The developed approach not only highlights importance of going back to nature for not just conventional water disinfection, but also for eliminating hazardous AMR bacteria and may also find utility in many other applications for the removal of antimicrobial bacteria.

5.1 Introduction

Access to safe drinking water is one of the greatest challenge of 21st century [1], especially due to increased urbanization, industrialization, pollution, water scarcity/limited availability and changing climatic conditions. Antimicrobial resistance (AMR) is becoming a global crisis, threatening the future of drugs and also millions of lives worldwide [2]. Many resources of water are faecally contaminated, resulting nearly half million diarrhoeal deaths each year, including children below 5-year age. Apart from faecal contaminants *(Enterobacter*, *Klebsiella*, *Citrobacter*), different enteric viruses such as norovirus, calcivirus, cyanobacteria and algae also cause serious health problems [3]. Thus, disinfection of water is most critical issue for healthy life, especially for the developing countries. Disinfection of water also demands complete destruction or removal/inactivation of pathogenic microorganisms from drinking water/raw water/ground water to prevent recontamination of water in distribution system and maintain safest quality of water [4]. The most common bacteria reported for disinfection studies include gram-negative *E. coli* and gram-positive *S. aureus*. *E. coli* is an indicator bacteria that helps to know degree of fecal contamination in water and wastewater and therefore routinely used as a model bacteria for water disinfection. In recent years, bacteria that are resistant to antibiotics are causing concerns worldwide [5]. Presence of antibiotic resistant bacteria has been reported in untreated drinking water sources such as wells [6,7],[8], rivers, and lakes [9] and also in presumably safe water such as in tap/ bottled water [10]. According to WHO report, overuse and misuse of antibiotics in human and animal health is considered to be the main cause for accelerating the emergence and spread of AMR bacteria [11]. However, disinfection studies pertaining to antimicrobial resistant bacteria such as methicillin resistance *Staphylococcus aureus* and also difficult, opportunistic pathogen such as *Pseudomonas aeruginosa* have been sparsely reported, probably due to difficulty in its removal. *Pseudomonas aeruginosa* is a common nosocomial, opportunistic pathogen, mostly found in water/wastewater and hospitals that causes serious infections with a high mortality rate. It is resistant to various antibiotics and therefore considered as a harmful and dreaded pathogen [12]. It is one of the three critical bacteria species because of its adaptive antibiotic resistance [11],[13]. Since late 1980s, there has been a void in the discovery of new antimicrobial drugs for combating staphylococcal infections, which makes it imperative to develop techniques to destroy present day AMR bacteria [14]. The presence of such AMR bacteria in various water sources clearly indicate the urgent need for techno-economically feasible methodologies for destroying these and for mitigating the proliferation of AMR bacteria in drinking water systems.

Disinfection studies pertaining to gram-negative bacteria, *Pseudomonas aeruginosa* have been sparsely reported, probably due to difficulty in its removal. Armstrong [15] reported use of ionic copper for elimination of *P. aeruginosa* and could achieve up to 4 log reduction in longer duration of about 6h. Lineback et al. [16] found only limited disinfection using chemical route employing Hydrogen peroxide and sodium hypochlorite. Use of Nano-silica silver nanocomposites was also reported for effective disinfection [17]. Application of acoustic cavitation was not found to be effective [18], though use of hydrodynamic cavitation was reported with limited success even after employing for longer treatment times [19]. Recently, Jain et al. [20] and Mane et al. [21] discussed effective application of hydrodynamic cavitation methodology for the elimination of different bacteria such as *E. coli* and *S. aureus*; Mane and co-workers [21] introducing the concept of using natural oils in conjunction with cavitation techniques for disinfection and for increased rates of disinfection. However, not many disinfection studies on effective disinfection of *P. aeruginosa,* known to have adaptive antibiotic resistance, and also for antimicrobial resistant bacteria methicillin resistant *s. aureus* are reported so far. Kanchanapally et. al [22] suggested nisin peptide conjugated three dimensional (3D) porous graphene oxide membrane for the removal of methicillin-resistant *Staphylococcus aureus* (MRSA) pathogens from water. McKinney and Prude, [23] studied disinfection of MRSA, vancomycin-resistant *Enterococcus faecium* (VRE), *E. coli* and *P. aeruginosa* using UV with only limited success.

The disinfection of water for eliminating different types of microorganisms is typically carried out using a large number of different mechanical, chemical and biological/biochemical methods, either in isolation or in combination [21],[24],[25]. UV irradiation, Chlorination and ozonation are most commonly used methods, but majority of these have many limitations [26]. UV irradiation breaks down the molecular bonds of microbial DNA, leading to formation of thymine dimers that can destroy the bacteria, however, the technique is inefficient when bacteria has its own photo-reactivation repair mechanism [27]. Chemical methods of chlorination and ozonation, though provide ease of operation, can form toxic/ harmful by-products of carcinogenic nature and are therefore currently not considered to be a “healthy” practice or environment friendly. It was also observed that disinfection by-products in drinking water distribution systems might play role in increasing bacterial resistance. Moreover, chemical methods are not effective for those bacteria which form hidden flocs in biofilms and have high resistance to biocides [28]. The physical methods such as heating, radiation, microwave, filtration and plasma have many disadvantages in their practical application on large scale due to high cost and long treatment time [29],[1]. To overcome the limitations of physical and chemical methods and also to avoid production of harmful by-products, several new techniques have been proposed that include electrochemical, adsorption using newer nanocomposites, photocatalytic and copper-silver ionization, cavitation etc., of which use of novel magnetic nanocomposites for disinfection can certainly be found attractive if operational difficulties and scale-up issues can be appropriately addressed [30],[31].

As an alternative to the conventional physical and chemical processes, a physico-chemical method-cavitation, especially hydrodynamic cavitation, appears to be highly promising. Though a large number of studies were discussed on cavitation for disinfection in last two decades or so, not many commercial applications were reported. Cavitation is a physico-chemical technique employing suitable mechanism for formation, growth and collapse of cavities in a liquid that create suitable conditions of extreme temperatures (up to 10000K) and pressure (up to 5000 atm) at the points of implosion, resulting in generation of oxidising agents and as a result generating environment conducive for disinfection of bacteria [20],[21]. Both acoustic and hydrodynamic cavitation are suitable in this regard [32],[33,34],[35,36]. The performance of cavitation is influenced by different parameters such as pressure drop, temperature, pH, salt content, density, viscosity and surface tension apart from nature of the microorganism [21],[37]. Due to serious limitations of employing acoustic cavitation on a large scale, hydrodynamic cavitation appears to be most promising technique in this regard. Several different configurations and designs of hydrodynamic cavitation reactors have been proposed/ used. Balasundaram and Harrison, [38] compared effectiveness of multi-hole orifice design and single hole orifice for bacterial destruction. Increasing discharge pressure was shown to have positive effect on bacterial destruction in case of multi-hole orifice, whereas, there was negative effect in case venturi leading to lower inactivation rate. Badve et al. [39] and Pandit et al. [36] investigated effect of inlet pressure on water disinfection, and found that with increase in the pressure, destruction rate increases but only up to a certain point. Jain et al., [20] used newer type of cavitating device employing vortex flow, vortex diode and observed pressure impacting the disinfection performance depending on the nature of bacteria.

Moreover, the vortex diode required low pressure drop (1 bar), while orifice required higher pressure drop (2 bar or more) for complete destruction of bacteria. Hybrid approaches were also reported e.g. addition of H_2O_2 or ozone or by process integration with different physical methods such as UV [40]. However, most of the conventional methods are associated with many drawbacks mainly in terms of inefficient disinfection, slow rates, especially for different kinds of microorganisms and also high cost.

The use of natural oils [21] having antimicrobial property in the cavitation process is envisaged as a unique and also practical strategy that can address issues of high efficiency, increased rates of disinfection apart from also providing green process to eliminate AMR bacteria. A number of natural oils such as clove oil, cinnamon oil, eucalyptus oil, peppermint oil, tea tree oil can be highly useful in this regard. The selection of natural oils needs to be judiciously made to exploit functionalities for effecting disinfection and for additional health benefits.

The present study, for the first time, provides useful method for destroying antimicrobial resistant bacteria (AMR) and difficult, opportunistic pathogen using cavitation and natural oils or plant extract and also for enhancing and altering removal of bacteria by use of natural oils/plant extracts in cavitation with positive implications for possible commercial applications in the form of greener technology, especially for rural use. The study has specific relevance today due to the fact that, recently the World Health Organization (WHO) listed *P. aeruginosa* as one of the three critical bacteria species requiring new antibiotics development because of its adaptive antibiotic resistance [11],[41],[42,43]. The developed process does not require use of catalyst, harmful chemicals or does not have disadvantages of conventional chlorination processes and operates at nearly ambient conditions. Intensification of simple type such as aeration (sparging of air) has also been studied to further improve the process performance.

5.2 Materials and Methods

5.2.1 Cavitating devices

Two different types of devices, one employing rotational flow- Vortex diode and other employing linear flow-Orifice were used. The vortex diode (US9422952B2, 2016) used was similar to that reported in our earlier work having a nominal capacity of 1 m^3/h (fabricated locally; chamber diameter 66 mm, Throat diameter 11 mm, Material of construction- SS 316). The orifice includes a single circular hole, 3 mm diameter and 1 m^3/h capacity. The photograph of the experimental set-up and details with schematic are provided in our earlier publications[20,21,34].

5.2.2 Microorganisms

Microorganisms can be divided into two groups based on their cell wall composition gram-negative and gram-positive bacteria. Gram-negative bacteria have complex multi-layered structure of the cell wall whereas gram-positive bacteria have cell wall of thick single layer of peptidoglycan. In the present study, one gram-negative (*Pseudomonas aeruginosa* ATCC 15442), one gram-positive bacteria (*Staphylococcus aureus* ATCC-6538*)* and Methicillin resistance bacterium, *S. aureus* ATCC BAA-44 (Himedia), were used as model bacteria contaminants of each type. The first two organisms were obtained from NCIM- National Collection of Industrial Microorganism at CSIR, National Chemical Laboratory, Pune, India. MRSA is a Biosafety Level 2 (BSL 2) bacterium and appropriate guidelines for its use need to be followed [44]. For evaluating the efficacy of disinfection, both the cultures were grown individually in 50 mL Nutrient Broth (Himedia Nutrient HiVeg broth) and incubated at 37 °C, 200 rpm in an incubator-shaker for overnight. The overnight incubation ensures that bacterial population residing in broth medium is in robust stage of growth and not in saturation or death phase, since it is more difficult to kill the cells of robust stage.

5.2.3 Natural oils as bio-additive

Three different types of natural oil were used - Peppermint oil, Lemongrass oil and Tea tree oil. These were procured locally from Pune, Maharashtra, India. The detailed characteristics of different natural oils are given in Table 5.1.

Table 5.1: Characteristics of Natural oils

Sr. No.	Name of oil	Characteristics
1.	Peppermint oil (*Mentha x piperita*)[45]	**M.F.:** $C_{10}H_{20}O$ **M.W.**: 156.265 g/mol **Composition**: Menthol (29-60%), menthone (15-30%), methyl acetate (2-8.5%), menthofuran (1-7%), isomenthon (2-5.5%), limonene (1-4%), and germacrene D (0.5-3%) **Boiling Point:** 215 °C **Density**: 0.896-0.908 g/cc
2	Lemongrass oil (*Cymbopogon citrates*)[46],[47]	**M.F.:** $C_{51}H_{84}O_5$ **M.W.**: 777.2 g/mol **Composition**: Main constituents Citral (70%), Linalool (1.34%), Geraniol (5%), Citronellol, nerol (2.2%), Citronellal (0.37%), Linalylacetat, geranyl acetate (1.95%), α-Pinene (0.24%), Limonene (2.42%), Caryophyllene, β-pinene, β-thujene, myrcene (0.46%), β-Ocimene (0.06%), Terpenolene (0.05%), Methyl heptanone (1.5%) and α-terpineol (0.24%) **Boiling Point:** 224 °C **Density**: 0.887 g/cc at 25 °C
3	Tea tree oil (*Melaleucaalternifolia*)[48]	**M.F.:** $C_{28}H_{60}O_4P_2S_4Zn$ **M.W.**: 777.2 g/mol **Composition**: Terpinen-4-ol (35-48%), γ-Terpinene (14-28%), α-Terpinene (6-12%), 1,8-Cineol (traces-10%), terpinolene (1.5-5%), α-terpineol (2-5%), α-pinene (1-4%), p-Cymene (0.5-8%), Sabinene (traces-3.5%), limonene (0.5-1.5%), aromadendrene (0.2-3%), ledene (0.1-3%), globulol (traces-1%) and viridiflorol (traces-1%) **Boiling Point:** 165 °C **Density**: 0.898 g/cc at 25 °C

5.2.4 Experimental

The experimental procedure and experimental set-up was discussed in detail in our earlier reports and therefore is only briefly described here to avoid repetition [20,21]. The set-up included water storage tank of 50L capacity, high pressure pump, different cavitation devices and process control for the measurement and control of parameters such as pressure, temperature and flow rate. The hydrodynamic cavitation experiments were performed using two cavitation devices- vortex diode and orifice and by employing specific pressure drop conditions of cavitation, typically 1 bar for vortex diode and 2 bar for the orifice under controlled temperature conditions (~30-35 ºC). For model wastewater, a known concentration of bacteria was prepared in 20 L of water to get initial bacterial concentration ~10^4 CFU/mL. On the basis of preliminary work on natural oils, a concentration of just 0.1% by volume was used in each experiment, corresponding to 20 mL for the 20 L of synthetic contaminated water. The performance of cavitation was monitored by using bacterial viability test (Plate count method) - 10 mL of samples withdrawn from cavitation tank at periodic intervals, and 0.1 mL of culture spread on N. agar containing sterile Petri dish. After, 24 h of incubation, number of colonies were counted from each plate and represented as colony forming unit per milliliter (CFU/mL).

$$CFU/mL = \frac{Number\ of\ colonies\ on\ \text{N. agar plate}}{\text{volume plated (mL)}} \times dilution\ factor$$

For all the experiments, the average error was generally within ± 5% and reproducibility was confirmed for the experiments.

5.2.5 Evaluating cell destruction by FE-SEM and TEM analysis

To confirm the destruction of bacterial cells, different microscopic techniques such as Field Emission Scanning Electron Microscopy (FESEM, FEI-Nova NanoSEM-450) and TEM (Transmission Electron Microscopy Tecnai G2 20 S Twin; LaB6 filament as the electron source) were used. Morphological changes of bacterial cells before cavitation (0 min) and after cavitation (60 min of treatment) were confirmed by FE-SEM. For the sample preparation, bacterial culture was fixed with 4% (v/V) glutaraldehyde (prepared in 0.1 M phosphate buffer (pH 7.0)) and incubated for 1 h, subsequently washed with phosphate buffer (0.1 M) for 10 min. The fixed samples further dehydrated by using graded series of ethanol solutions (30, 50, 70, 90 and 100% ethanol) for 30 min. TEM analysis of initial and final samples were carried out for examining cell destruction during the process.

5.3 Results and Discussion

It is a common knowledge that for hydrodynamic cavitation, the most important process parameters include pressure drop, initial concentration of the contaminant apart from reactor geometry. In our earlier work [20,21], the comparison of acoustic cavitation, hydrodynamic cavitation and also impact of bacterial concentration for the two bacteria, *E. coli* and *S. aureus* was reported in detail. The present work, demonstrates elimination of difficult and "opportunistic pathogen", gram-negative *P. aeruginosa,* elimination of antimicrobial resistant bacteria, methicillin resistance *Staphylococcus aureus* and further improvises some of the findings reported earlier in this regard by comparing the results with *S. aureus*, where required to substantiate. Highly useful and important findings in terms of nature of bacteria, natural oils apart from nature of the reactor geometry are also discussed for a range of bacteria, oils and the two cavitating reactors- vortex diode and orifice.

5.3.1 Effect of pressure drop

Pressure drop (ΔP) is one of the most important parameter in hydrodynamic cavitation, which dictates not only the performance of cavitation process, but also major cost of the process. The flow rate and pressure drop data was reported earlier for the device [34]. Cavitation number is defined based on vapour pressure and throat velocity. However, cavitation number is relevant for cavitation devices using linear flows such as orifice or venturi where it is used to identify possible inception of cavitation. The cavitation numbers for orifice operated at 2 and 5 bar pressure drop are 0.75 and 0.35 respectively. Unlike these conventional devices, vortex based device used in the present work uses tangential velocity for generating low pressure regions. Therefore conventional cavitation number defined above is not relevant for vortex based cavitation devices. We have ensured that both the devices are operated in cavitating regime.

The disinfection was studied for the cavitating device- vortex diode and for the new bacteria, *P. aeruginosa* using three different pressure drop conditions, 0.5, 1 and 2 bar (the inception of cavitation is at ~0.48 bar and hence pressure drop of 0.5 bar represents lowest pressure drop for which cavitation takes place [21]). The results are shown in Figure 5.1. The experimental results on removal of *P. aeruginosa* show ~40% disinfection at ΔP of 1 bar. Further, increasing pressure drop to 2.0 bar, has not resulted in significant gains and the disinfection efficiency remained practically similar.

It is evident that the extent of disinfection for the *P. aeruginosa*, using the conventional hydrodynamic cavitation is quite less and not satisfactory from the practical application point of view. The results also clearly indicate the difficulty in the destruction of microorganism *P. aeruginosa.* Young et al., [49] stated that *P. aeruginosa* has a higher degree of cross linking compared to *E. coli* and *S. aureus*. In our previous findings, the results of *S. aureus* indicated substantially higher disinfection efficiency of ~89 which could be further enhanced to 97 % by increasing pressure drop from 1 to 2 bar. The disinfection behavior of different microorganisms depends on the cavitation device and degree of cell rupture. The limited destruction also implies need for exploring newer methodologies.

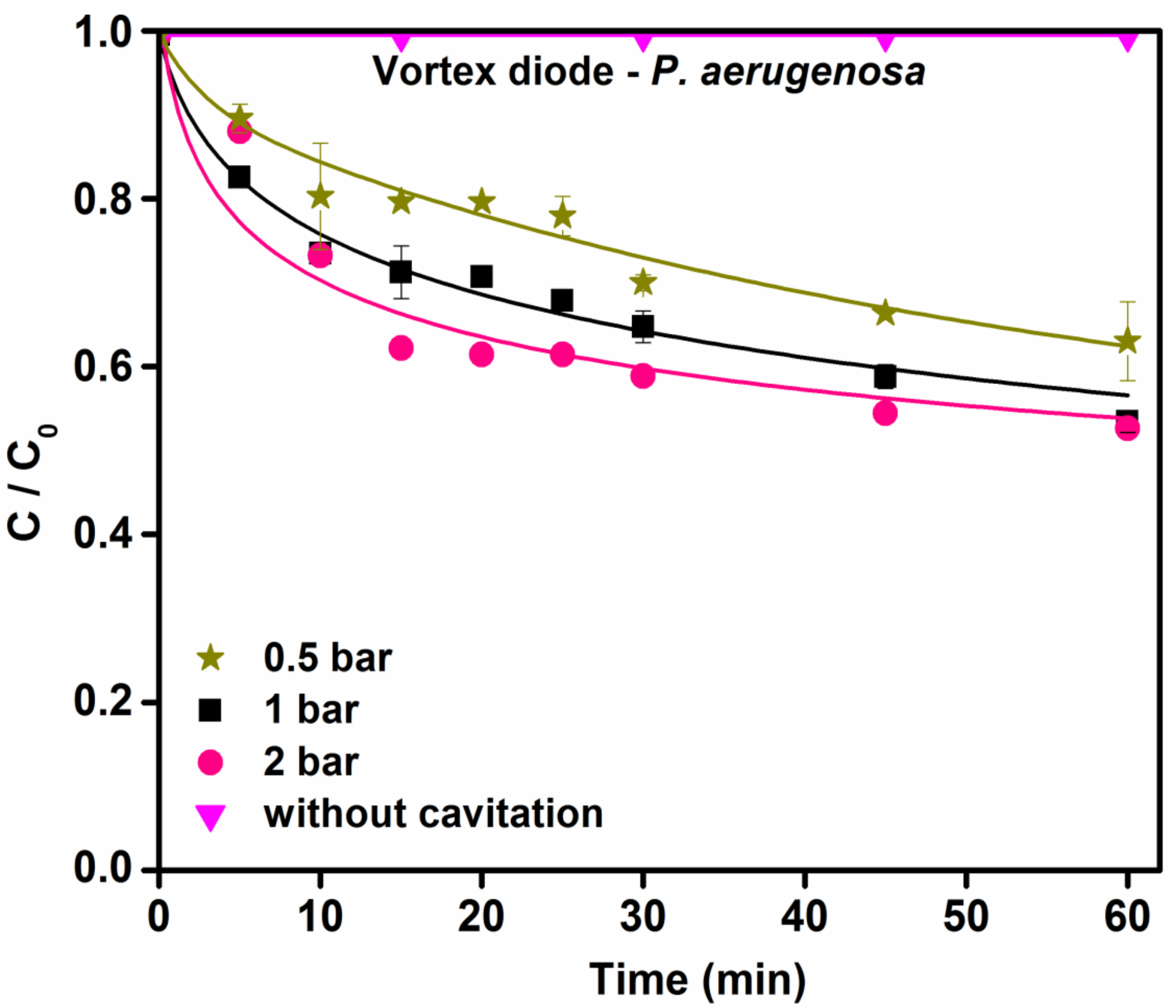

Figure 5.1: Effect of pressure drop on disinfection of *Pseudomonas aeruginosa*

5.3.2 Effect of bio-additives (natural oils) in hydrodynamic cavitation for elimination of pathogenic bacterial strains from water

It is instructive to develop methodology looking beyond the traditional methods including that of conventional cavitation to effectively circumvent the drawbacks pertaining to low efficiencies, longer time of treatment and high cost apart from possible formation of harmful disinfection by-products. The previous attempts were typically chemical modifications such as hydrodynamic cavitation with ozone and hydrogen peroxide.

The addition of bio-additives such as natural oil in hydrodynamic cavitation can be a newer and promising approach for disinfection [21]. A very small concentration of 0.1% (v/V) of natural oil was sufficient for disinfection. The effect of dose of the natural oil is one of the important parameter which is expected to depend on the nature of the oil. An optimum dose is required to achieve the complete disinfection of bacteria within shorter time period. In the present study, for the first time, highly effective natural oil, in the form of Peppermint oil, was found, that could practically provide >99% disinfection for various types of bacteria such as *S. aureus* (SA), Methicillin Resistant *S. aureus* (MRSA) and opportunistic/adapting bacteria *P. aeruginosa* typically in less than 10 minutes. Preliminary experiments using vortex diode as a cavitating device at 1 bar pressure drop for different dosage of peppermint oil (0.1 and 0.05 %) confirmed 0.1% v/V dose of oil as optimum since at 0.05 % of oil concentration, 94 % disinfection was observed within 60 min and nearly complete (>99%) disinfection within 10 min for 0.1 % dose.

5.3.3 Destroying difficult, opportunistic pathogen *P. aeruginosa*

The complete elimination of *P. aeruginosa* using hydrodynamic cavitation for vortex diode as a cavitating device is shown in Figure 5.2. It is evident that the hybrid method of combining natural oil and hydrodynamic cavitation is highly effective in disinfection of water. The extent of disinfection using cavitation alone is ~40% in 60 minutes, while with the hybrid method in combination with 0.1% peppermint oil; practically >99% disinfection was observed in about 10 min, an order of magnitude enhancement in the disinfection rate. The efficiency seen here is the highest compared to that reported in the literature so far. Mane et al. [21] had previously suggested clove oil as one of the highly effective oil for the elimination of *E. coli* and *S. aureus.*

In order to evaluate the comparative efficacy of peppermint oil, the experiments were also carried out by using clove oil (0.1%) for *P. aeruginosa* and the results are also compared in Figure 5.2. The clove oil too gave enhancement in the disinfection rate and ~60% disinfection was obtained in 60 minutes. Comparing the results, it is evident that peppermint oil is far superior and drastically increases the rate of disinfection. The reduced time of operation and close to complete disinfection clearly highlights the efficacy of the hybrid technology in practical/commercial applications, especially using peppermint oil and vortex diode.

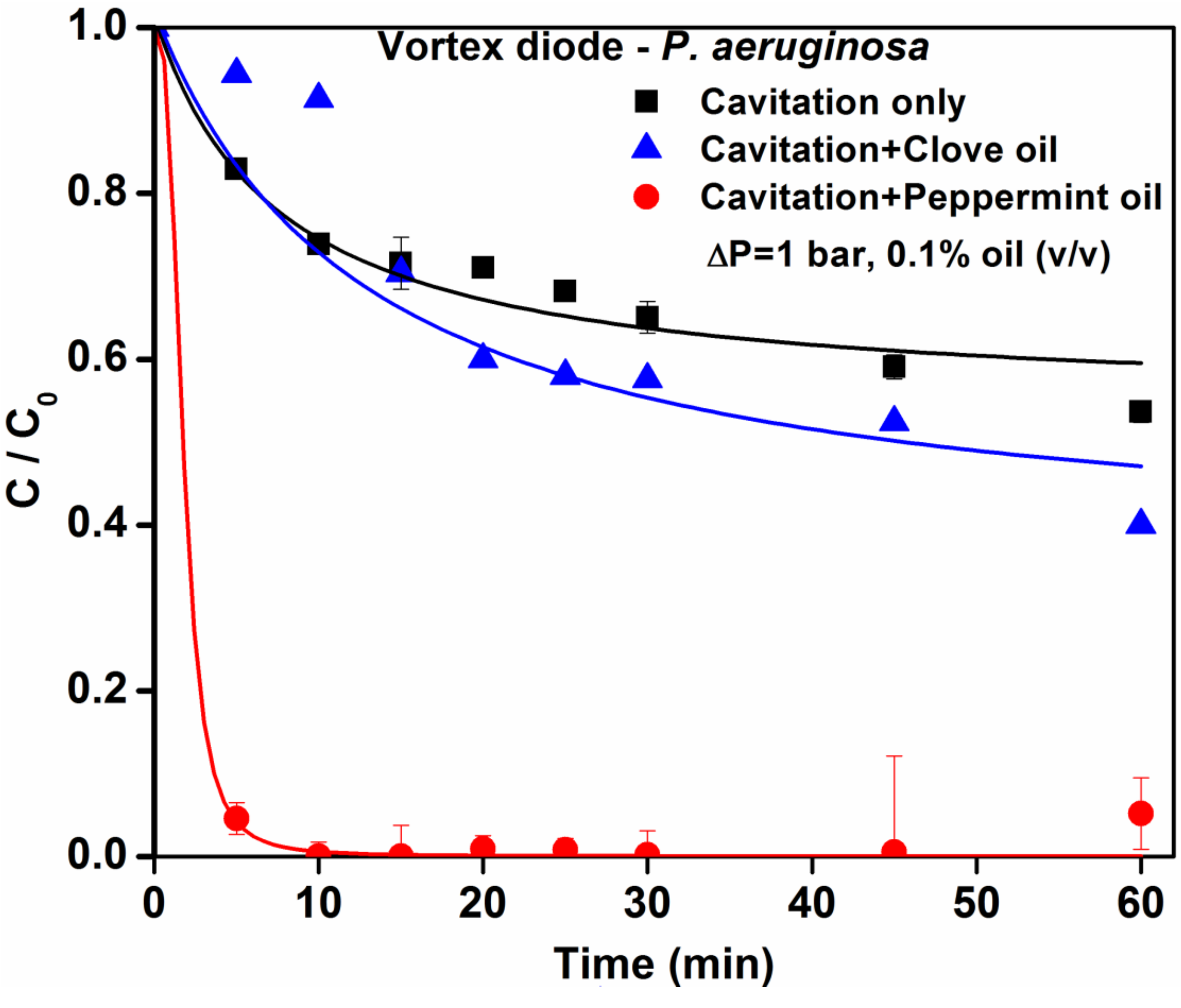

Figure 5.2: Effect of natural oil for disinfection of *P. aeruginosa*

The concept of cavitation using oil for disinfection was further validated using orifice as a cavitating device (Figure 5.3). The reactor geometry here employs linear flow for cavitation as against vortex flow in vortex diode. The results indicate ~30% disinfection using orifice at ΔP of 2 bar while the hybrid technique with 0.1% peppermint oil gave ~99.9% disinfection within 20 minutes. The difference in the disinfection behaviour due to change in the reactor geometry are clearly evident. While both the reactor types can achieve close to 100% disinfection by hybrid methodology using peppermint oil, the orifice requires substantially higher pressures compared to vortex diode implying higher cost of disinfection. Also, the time for complete disinfection is longer in orifice compared to vortex diode, again implying higher cost.

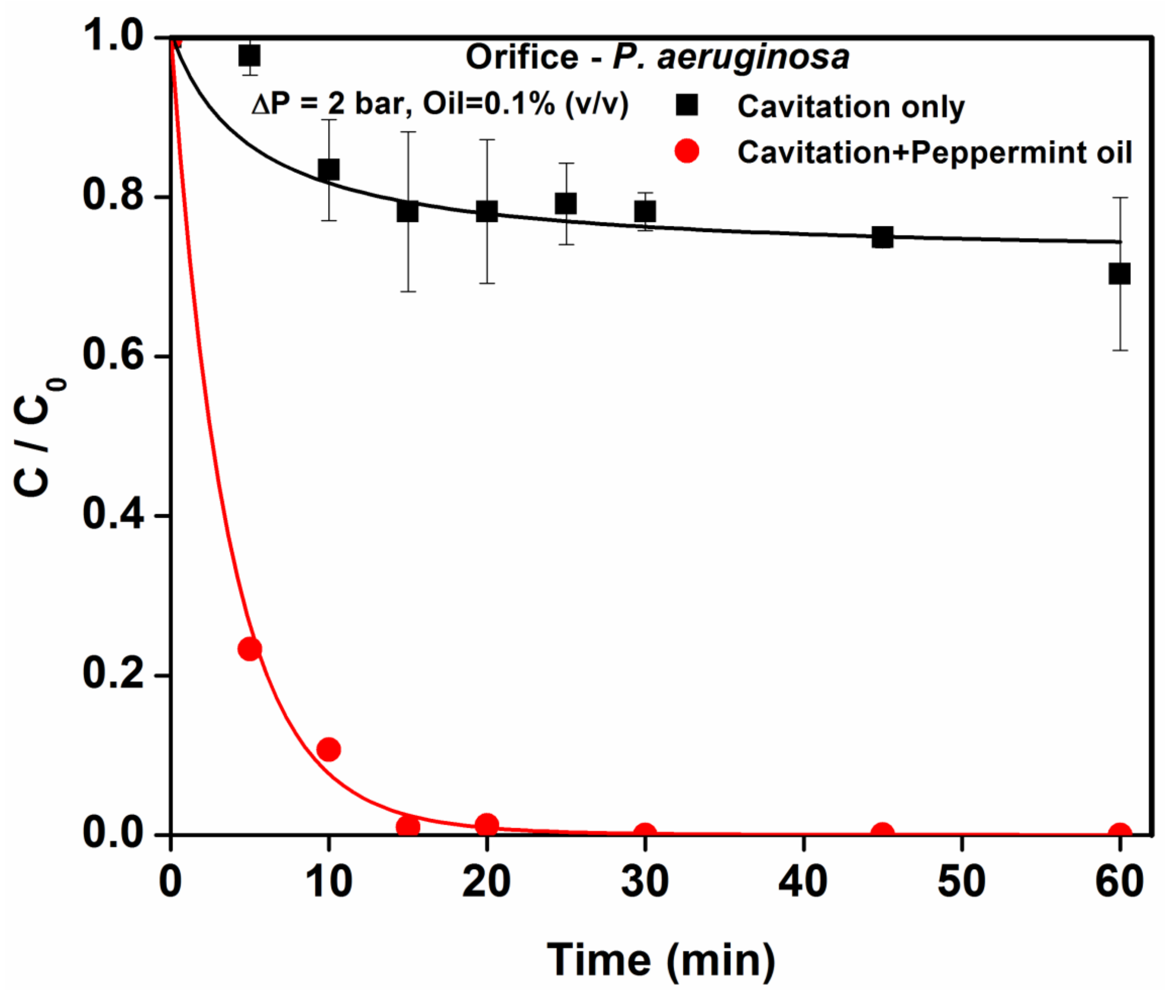

Figure 5.3: Effect of Reactor Geometry: Orifice/*P. aeruginosa*

A large number of natural oils are known to have antimicrobial properties. Our preliminary investigations indicated cavitation will not adversely alter properties of natural oils, the finding agrees well with recently reported data [50]. The use of natural oil not only alters the collapse of cavities but also helps to destroy the permeability of bacterial membranes by inherent antimicrobial property of active ingredient. Also, Peppermint oil contains menthol which significantly reduces virulence ability of *P. aeruginosa* [51].

It is instructive to evaluate the synergistic effect for the addition of natural oils in cavitation. The synergistic effect can be calculated using the following equation,

$$f = \frac{K_{HC+oil}}{K_{HC}+K_{oil}} \qquad (1)$$

Where, HC is the hydrodynamic cavitation and HC+oil is the hydrodynamic cavitation along with oil. For *P. aeruginosa*/peppermint oil, the synergistic index *f was* 6 and 5 for vortex diode and orifice respectively; values well above 1, confirming the synergistic effect.

5.3.4 Destroying AMR Bacteria: Methicillin Resistant *S. aureus*

After having established the efficacy of the hybrid methodology using peppermint oil for *P. aeruginosa*, it would be prudent to extend it further for the elimination of antibiotic resistant bacteria. Methicillin resistant *S. aureus* (MRSA) strain carries a mec gene, conferring the resistance to multiple antibiotics, which makes it resistance to methicillin, nafcillin, oxacillin, and cephalosporins. MRSA is the evolution of *S. aureus* (SA) into multi-resistant strains that makes is difficult to disinfection [52]. Investigations were carried out on destroying MRSA (shown by continuous lines in Figure 5.4 and Figure 5.5) and also elucidate comparative efficacy for SA (shown by dotted lines in Figure 5.4 and Figure 5.5) for the following:

1. Extent of disinfection using cavitation alone for both the bacteria
2. Extent of disinfection using cavitation and 0.1% peppermint oil (hybrid method)
3. A newer form of process intensification by means of simple aeration- again with and without oil, i.e. using conventional disinfection and hybrid disinfection process.

It is evident from Figure 5.4 that in the case of vortex diode as a cavitating device, the MRSA required significantly more time to disinfection compared to *S. aureus* in all the cases, viz. with only cavitation, cavitation + aeration and also in hybrid method with natural oil. The slower rates of disinfection in the case of MRSA clearly outline the difficulty compared to SA. The addition of 0.1 % peppermint oil drastically improves the disinfection efficiency in both of the bacteria- MRSA and *S. aureus,* an enhancement to the extent of ~200% which is phenomenal and not reported so far. It is also pertinent to note the time of disinfection using the hybrid method which is only 5-10 minutes for close to complete disinfection for any type of bacteria which obviously has positive commercial implications.

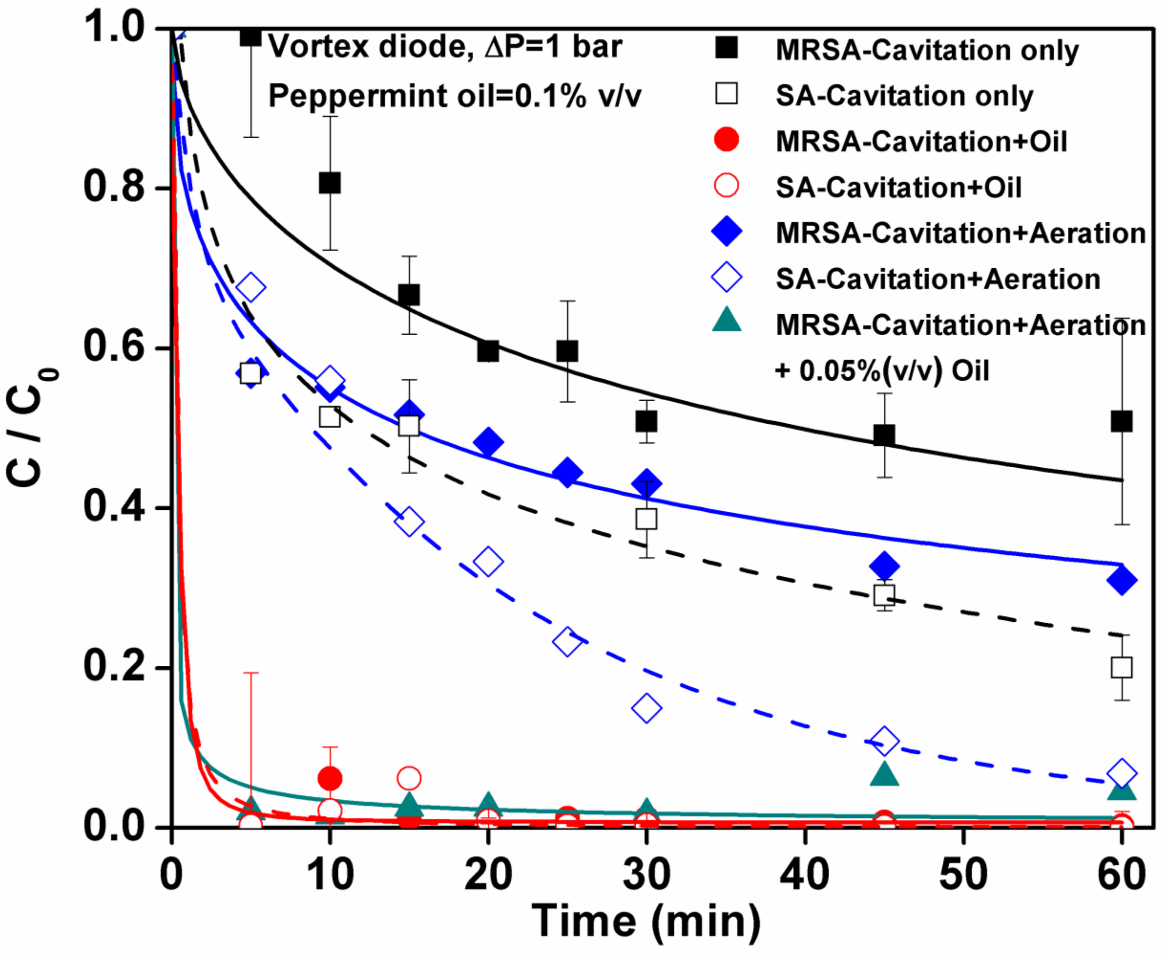

Figure 5.4: Destruction of bacteria using vortex diode: Comparison of MRSA and SA

Apart from the effect of nature of bacteria on rates of disinfection, the results of Figure 5.4 also clearly outline the differences in the disinfection behaviour because of aeration and because of dose of natural oil. It is essential to note that both aeration and addition of oil improve the disinfection behaviour over that of cavitation alone. A maximum benefit could be obtained, however, with addition of the natural oil and the positive effect of aeration can be exploited to reduce the requirement of natural oil. It can be seen that the requirement of peppermint oil can be reduced to nearly half (0.05%), if aeration is employed in the hybrid process of disinfection. The use of aeration in cavitation increases the shock wave impact, number of cavities and implosion inside the cavitation zone [53],[54]. Therefore, the aeration shows significant improvements possibly because of (1) enhanced dissolved oxygen - leading to enhanced generation of hydroxyl radicals (2) improved mixing of aqueous phase and oil phase and (3) altering compressibility of the medium. Thus, the increased rates of disinfection and reduction in oil dose can be attributed to the contributions of aeration as well as that due to antimicrobial properties of oil. A trade-off is, however, required for optimization between the operational cost due to aeration and savings due to oil requirement.

5.3.5 Effect of reactor geometry- Disinfection using orifice

The reactor geometry is expected to have significant effect on disinfection behaviour, and is crucial for techno-economic considerations. The reactor geometry directly affects the inception of cavitation and cavity implosion behaviour due to differences in the flow pattern [33,34],[55],[20]. In the present work, a single hole orifice, a cavitating device employing linear flow was compared with vortex diode, a cavitating device employing vortex flow. The disinfection behaviour, to establish the proof of concept in this regard, using orifice are given in Figure 5.5, mainly for SA. Two aspects are clear from the results- that the orifice requires significantly higher pressures (ΔP 2 bar) as compared to vortex diode (ΔP 1 bar) and also that the disinfection efficiency is higher in vortex diode compared to orifice. The MRSA destruction using orifice alone is only ~30% compared to that of 45% with only vortex diode; destruction of SA to the extent of ~65% using orifice while corresponding value for vortex diode is ~80% and finally ~99.9% destruction of SA in orifice in ~15 minutes compared to 5-10 minutes with vortex diode when hybrid process using natural oil (peppermint oil) is employed.

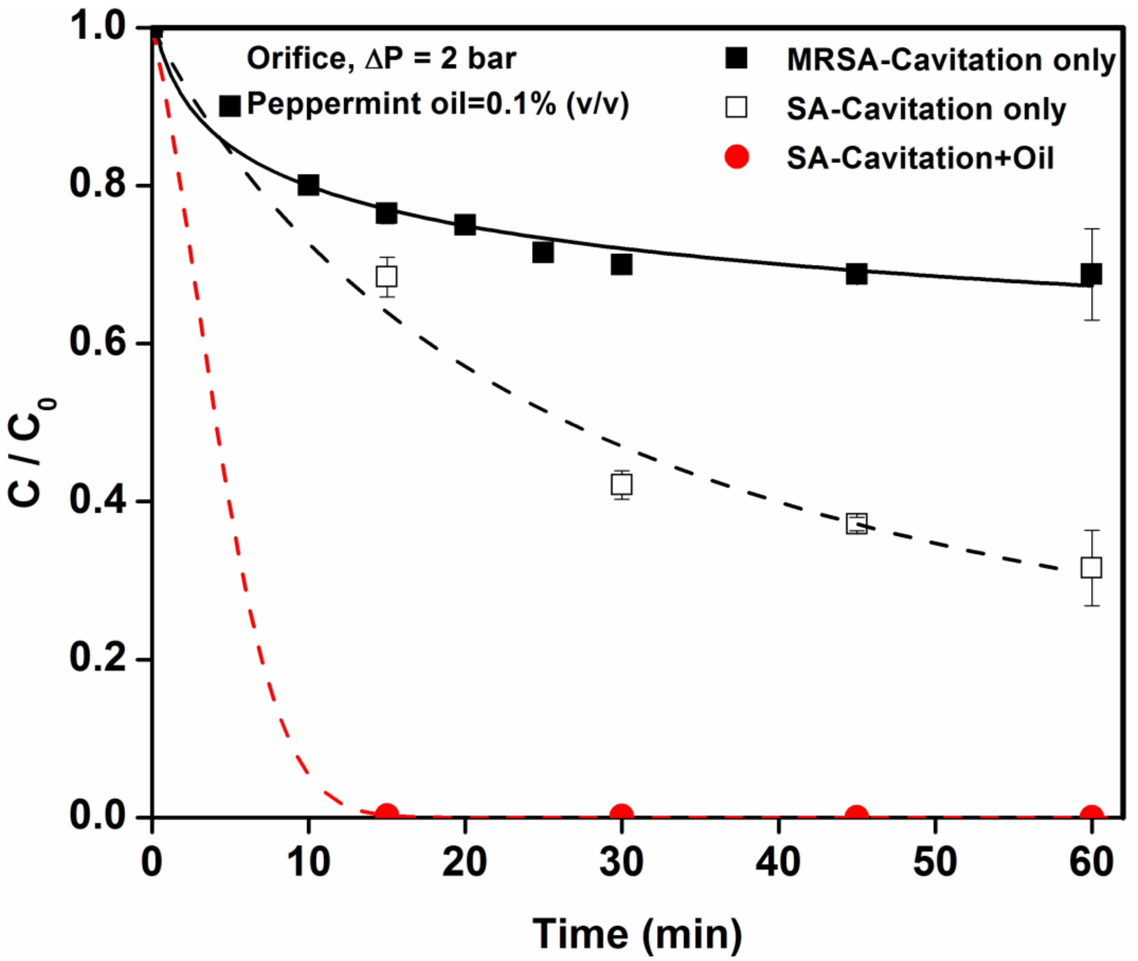

Figure 5.5: Destroying Methicillin Resistant *S. aureus* (MRSA) and *S. aureus* (SA) using Orifice

5.3.6 Nature of natural oils and disinfection

The importance of extract of medicinal plant/ natural oil derived from such plants, having antioxidant, antifungal and antibacterial properties, in disinfection has been widely recognised [45],[46],[47],[48],[56],[57],[58]. However, the studies are largely limited to using the zone of inhibition or only estimate antibacterial disk diffusion assay. Natural oils have the ability to kill the bacteria or retard the growth of pathogens because of the presence of natural active ingredients specific to the plant/oil. The antimicrobial activity of peppermint oil is believed to be mainly due to combined presence of compounds such as L-menthol, menthone, menthyl acetate and limonene [59]. The antibacterial activity of peppermint extract towards ten multi-drug pathogenic strains has been reported by [60]. Sujana et al. [61], reported that the leaf extract of peppermint contains effective active compounds which are responsible for disinfection of bacteria. Weak antimicrobial activity of peppermint oil for gram negative pathogens was mentioned in some studies [62],[63],[64]. In view of the above, the present hybrid process can be said to exhibit the "resonance effect" of both-antimicrobial activity of natural oils and also disinfection due to hydrodynamic cavitation that is hugely effective in the destruction of both gram-positive as well as gram-negative bacteria.

To illustrate the above aspect pertaining to nature of oil, the results using different natural oils are shown in terms of disinfection factor and for vortex diode as a cavitation device; ΔP of 1 bar and for 0.1% v/V for natural oil for the data of this work and also from that reported in the literature [21]. The per-pass disinfection factor, ϕ, in terms of rate constant (k), number of passes (n) and residence time (τ) is defined as:

$$\boldsymbol{k} = \frac{\emptyset\, \boldsymbol{n}}{\boldsymbol{t}} = \frac{\emptyset}{\boldsymbol{\tau}} \qquad (2)$$

Where, k is an apparent first order rate constant of disinfection. The per pass disinfection factor, ϕ, can be obtained by fitting the following equation to experimentally obtained disinfection data.

$$\emptyset = \frac{-ln\,(C_e/C_0)}{n} \qquad (3)$$

The parameters (effective rate constant and per pass disinfection factor) of Eq. (2) and (3) for different experiments reported in this work are listed in Table 5.2. The results clearly indicated that the use of peppermint oil in cavitation process in a very small concentration (0.1%) increases the rate and per-pass disinfection values by almost 20 times. The corresponding values of per pass disinfection factor (ϕ) are 0.7852 and 0.0371 for cavitation with oil and cavitation alone for vortex diode as a cavitating device. Similarly for orifice as cavitating device, ϕ values are 1.23 and 0.0647 for cavitation with oil and cavitation alone respectively. The orifice requires higher pressures to obtain similar extent of disinfection compared to vortex diode. The differences due to the nature/type of bacteria, characteristics of oil/oil constituents are clearly evident. Similarly, drastic effect of peppermint oil on reduction of antimicrobial resistance bacteria MRSA in hydrodynamic cavitation was observed; 3 times higher rates for hybrid process compared to only cavitation. The respective values of ϕ are 0.4919, 0.0713 for hybrid process and cavitation alone respectively. Further, aeration improves the performance of hybrid cavitation process and not only the cavitation behaviour is altered, but also quantity of oil gets reduced by half and ~3 times higher rates compared to the conventional cavitation process. The value of ϕ for advanced hybrid hydrodynamic cavitation process (vortex diode + aeration + 0.05% peppermint oil) is 0.4067 and for only cavitation is 0.0713. It is evident that the hydrodynamic cavitation with 0.1% peppermint oil and cavitation with 0.05% peppermint oil and aeration showed > 100% increase in the per-pass disinfection as compared to cavitation alone.

From Figure 5.6, it is evident that the nature of natural oil significantly affects the disinfection behaviour and therefore finding the most suitable natural oil is crucial from commercial application point of view. From the data of different oils, it can be seen that peppermint oil is the most effective natural oil compared to tea tree, clove, eucalyptus and lemongrass oil from the data of removal of *S. aureus*. The value of per-pass disinfection factor ϕ for peppermint oil is 31, significantly higher than tea tree oil (18), clove oil (11), eucalyptus oil (9), and lemongrass oil (5). The per-pass disinfection factor for cavitation alone is only 6. A grading of disinfection efficiency for various natural oils can be useful in the selection of natural oil in the hybrid process.

Table 5. 2: Rate of disinfection for *P. aeruginosa* and Methicillin Resistance *S. aureus*

Process	**% Disinfection**	**Rate of disinfection CFU/(mL.s)**	**Rate constant (s^{-1})×10^4**	**Per-pass disinfection (ϕ)**
Rate of disinfection for *P. aeruginosa* (15 min)				
Cavitation alone Vortex Diode, ΔP=1 bar	28	55.56	3.7	0.0371
HC + Peppermint oil Vortex Diode ΔP=1bar	99	144.33	79.7	0.7852
Cavitation alone Orifice, ΔP= 2 bar	22	7.44	2.74	0.0647
HC + Peppermint oil Orifice, ΔP=2bar	99	46.22	51.71	1.23
Without cavitation- Only Peppermint oil	20	NA	2.5	NA
Rate of disinfection for Methicillin Resistance *S. aureus* (MRSA) (15 min)				
Cavitation alone Vortex Diode, ΔP=1 bar	33	29.77	7.05	0.0713
HC + Peppermint oil Vortex Diode ΔP=1bar	98.7	88.89	48.83	0.4919
HC + aeration Vortex Diode, ΔP=1 bar	48	155.56	7.32	0.0733
HC + aeration + Peppermint oil, 0.05% Vortex Diode, ΔP=1bar	97	106.11	40.76	0.4067

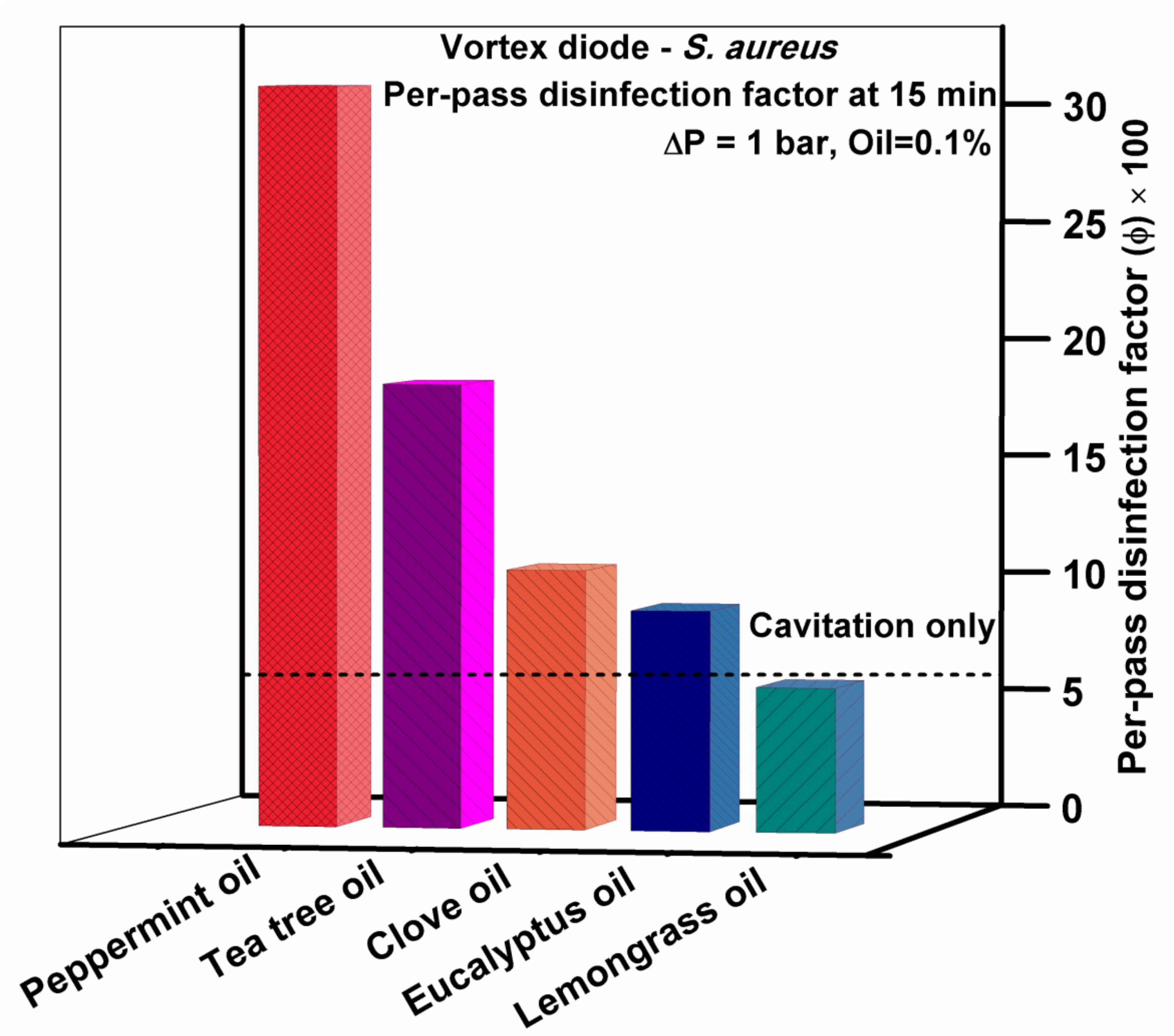

Figure 5.6: Comparison of natural oils in disinfection

5.3.7 Mechanism for disinfection using hydrodynamic cavitation and natural oils

A plausible mechanism of the hybrid process was discussed in our earlier work where it was shown that various physical/mechanical forces along with antibacterial properties of natural oils contribute to bacterial cell destruction[21]. The physical effects of cavitation include implosion of cavities creating hotspots and consequently damaging microorganism cells. The extreme temperatures during cavity implosion process can affect the intact nature of bacterial outer layer and make it more susceptible for further damage with reactive species [27],[65]. The chemical effect includes generation of active free radicals that can be oxidize the main constituents of bacterial cell such as proteins, lipids and DNA [4]. The biological effects include, antimicrobial activity due to the active ingredients present in natural oil (such as menthol, menthone and menthofuran in peppermint oil) having high antibacterial properties. The menthol is most active ingredient in this regard. Sing et al. reported that menthol has ability to affect the lipid fraction of bacterial plasma membrane, impacting the membrane permeability which induces the leakage of intracellular materials [66,67].

The results of the present study are also in agreement in this regard. Figures 5.7 and 5.8 show SEM and TEM images of the samples before and after the disinfection clearly providing visual inference in terms of cell destruction. The TEM analysis of *P. aeruginosa* indicates the intact and rod shaped bacterium before treatment (0 min), whereas after treatment (60 min) bacterial cell membrane and its intracellular organization has been disrupted. These results were further supported by FE-SEM analysis, which showed that at 0 min. bacterial cell was intact and in chain form and thereafter (60 min) was mutilated in terms of alternation in cell morphology (Figure 5.7). The FE-SEM analysis of MRSA shows the initial condition of 0 min, where the bacteria is seen round shaped with intact cell membrane and after the treatment (60 min), the shape of bacterial cell has been distorted as evident from hole formation and cell rupture (Figure 5.8). These results are further corroborated using TEM analysis where the initial spherical MRSA cells with smooth cell walls (0 min) get swollen and irregular in size and shape after the treatment. Moreover, discolouration of cytoplasm and leakage of cytoplasmic content was also observed. Swamy et al. [68] reported that the natural oil can destabilize the cellular structure of the cell, leading to breakdown of cell membrane integrity as well as increase cell permeability. Radaelli et al. [69] indicated that a food borne pathogen *Clostridium perfringens* was inhibited by the antibacterial action of peppermint oil. The natural oil may exhibit a different mechanism against different microbes depending on the inherent constituents [68]. Thus, it can be suggested that hydrodynamic cavitation using peppermint oil results in disinfection due to complete bacterial disintegration of *P. aeruginosa* and MRSA and the synergetic effect of oil in hydrodynamic cavitation is important.

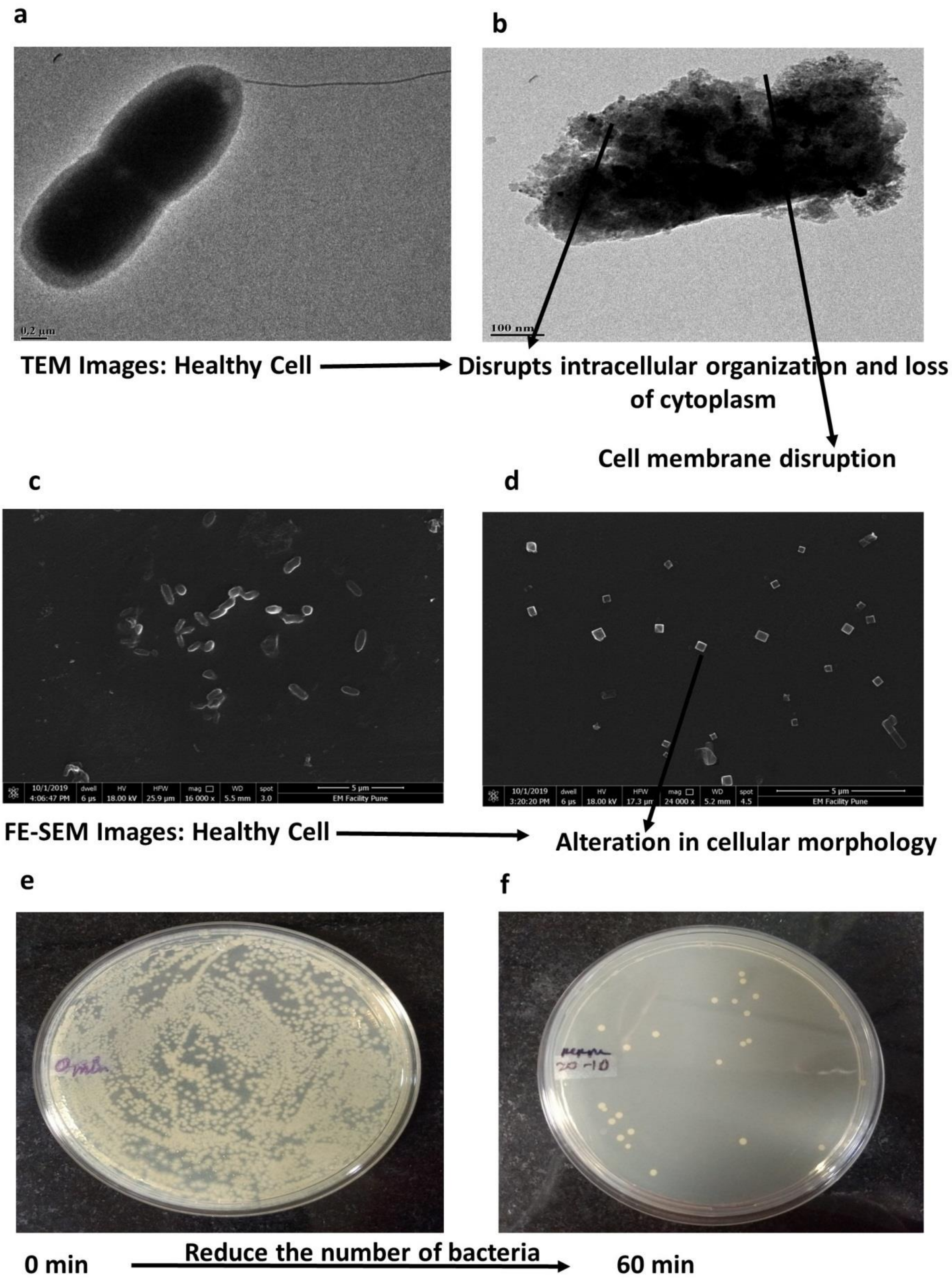

Figure 5.7: Elucidating disinfection through SEM and TEM characterization: *P. aeruginosa*

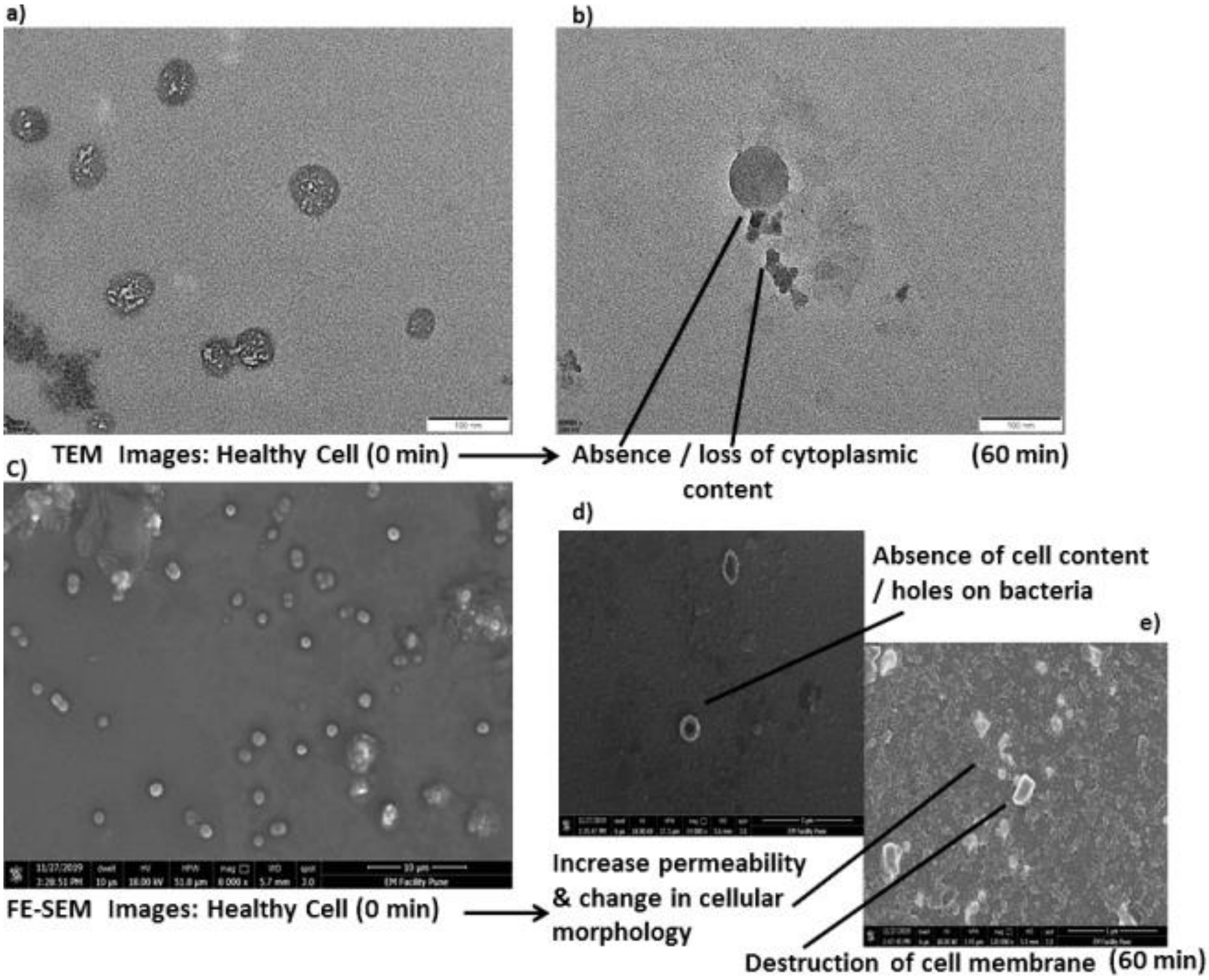

Figure 5.8: Elucidating disinfection through SEM and TEM characterization: MRSA

Figure 5.9 schematically depicts the role of the different constituents and hydrodynamic cavitation in water disinfection. The peppermint oil (Mentha piperita, L.) belongs to the Family Lamiaceae, primarily contains 0.1–1% of volatile oil, composed of menthol (29–48%), menthone (20–31%), menthofuran (6.8%) and menthyl acetate (3–10%). Other pharmacologically active ingredients include bitter substances, caffeic acid, flavonoids (12%), polymerized polyphenols (19%), carotenes, tocopherols, betaine, choline and tannins. It is widely used in food, pharmaceutical and cosmetics industries. Moreover, menthol as a raw material is used in toothpaste, toothpowder, confectionary, mouth fresheners, analgesic balms, cough drops, perfumes, chewing gums, etc. It is also used for a variety of health conditions and can be taken orally in dietary supplements or topically as a skin cream or ointment. Peppermint oil seems to reduce spasms in the digestive tract. Similarly, clove oil has advantages such as healing properties for toothaches and other tooth pains, improving blood circulation, reducing foul odor etc. It is also used for adding flavouring agent to the cough medicines. Eucalyptus oil is used to treat variety of diseases such as nasal congestion, asthma, arthritis etc. Thus, there could be several possible health benefits of using natural oil.

Most of the earlier work on cavitation focused on conventional devices such as orifice, venturi or on use of ozone, hydrogen peroxide etc., in isolation or in combination[70],[39],[36]. Further, disinfection efficiency was poor, in general and long treatment time was required. The hybrid process developed in this work not only demonstrates close to 100 % disinfection, but also demonstrates significantly shorter time periods and no use of harmful chemicals.

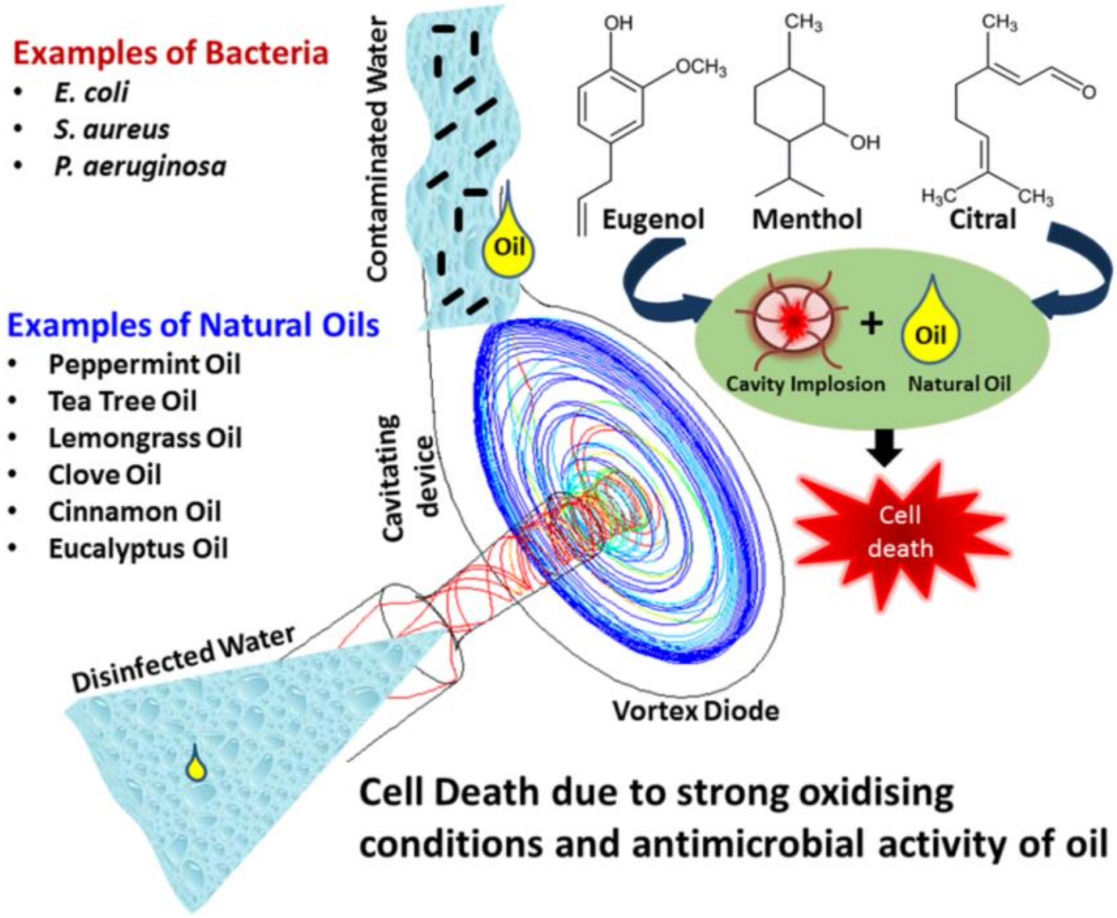

Figure 5.9: Schematic illustration of hybrid process and effect of natural oil

5.4. Cost considerations and evaluating techno-economic feasibility of the hybrid disinfection process

The cost calculations are presented in detail for the new hybrid process using the following representative data:

Bacteria: *S. aureus*
Volume: 20L
Reactor: Vortex diode,
Flow rate: 721.7 LPH, ΔP: 1 bar
Natural Oil: 0.1% peppermint oil (20 mL)
Initial concentration of bacteria = 312000 CFU/mL and in 5 min, 99.7% removal/ disinfection
Cavitation yield/volume treated (CFU/mL/J) $= \frac{(C_0 - C)}{(\Delta P \times Q \times t)}$ = 51.05 CFU/mL/J
The number of passes can be obtained as: $n = \frac{(Q \times t)}{V}$
For 1 bar of pressure drop, corresponding flow rate is 721.7 LPH. The number of passes needed for treatment (n) is 3.01

$$\text{Cost of treatment/m}^3\text{ of water} = \frac{n \Delta P P_E}{36\eta}$$

Assuming the cost of electricity as 10 Rs/kWh and efficiency of the multistage pump (η) as 0.66, the cost of treatment per m^3 of water is 1.28 Rs/m^3.

5.4.1. Techno-economic feasibility and possible real-life application

A tentative cost comparison of some of the useful methods using the data of this work and also from that reported in the literature is presented in Figure 5.10. As per the EPA (1996) [71], UV is a cheaper disinfection method as compared to chlorine and ozonation for small scale unit. The cost of UV for 40 and 140 mJ/cm^2 doses are \$ 0.05/m^3 and \$ 0.07/m^3 respectively, whereas, chlorination and ozonation (1 mg/L dose) require cost of \$ 0.75/m^3 and \$ 0.92/m^3 respectively. Though, UV is cost effective, it requires high dose for complete destruction of microorganisms and also need regular preventive maintenance to avoid fouling of the tubes. Moreover, UV is ineffective when colloidal and total suspended solids are present in water. According to

Environment Canada survey of Municipal Water and Wastewater (2004) [72], chlorination is largely used disinfection technique (93.38 %) as compared to Chloramines (3.67 %), Chlorine Dioxide (2.2%), UV and Ozone (5.9%). However, in recent years chlorination is not considered as an environment friendly, as it is associated with the formation of trihalomethanes and other halogenated by-products, which are carcinogenic in nature.

More recent disinfection techniques include high pressure homogenizer [3], high speed homogenizer [3], Ultrasonication (Ultrasonic horn, Ultrasonic bath) [3,40], membrane filtration[73] and hydrodynamic cavitation with or without process integration [3,35,36,40,74],[20,21]. Jyoti and Pandit, [3] reported operation cost of high pressure homogenizer as 3.9 $\$/m^3$, for high speed homogenizer with speed range of 1000–12,000 rpm as 0.48 $\$/m^3$ and for hydrodynamic cavitation as 0.83 $\$/m^3$. Cavitation with ozone, hydrogen peroxide, oxygen etc. was also reported to improve the treatment efficiency and reduce the cost of operation. For ~50% of disinfection in the case of ultrasonic horn alone, cost was calculated as 160 $\$/m^3$ which is higher than operation cost required for Ultrasonic bath (0.56 $\$/m^3$) with 75% disinfection, whereas hydrodynamic cavitation at 5.17 bar alone requires operating cost of 8 $\$/m^3$ [35,40]. Process intensification was carried out to reduce the cost of operation and the approximate costs are: Ultrasonic horn + 2 mg/L O_3 (10 $\$/m^3$); Ultrasonic bath + 2 mg/L O_3 (1 $\$/m^3$); Hydrodynamic cavitation (Orifice, ΔP, 5.17 bar) + 5 mg/L H_2O_2 (4.6 $\$/m^3$); Hydrodynamic cavitation (Orifice, ΔP,1.72 bar) + US flow cell, 40 kHz, (2 $\$/m^3$) and using 5 mg/L H_2O_2 (2.2 $\$/m^3$) [3,35,36,40,74]. However, there have been no reports of commercial implementation of many of the processes.

Membrane processes such as "ROAM plus" portable membrane which is made up of Polyethersulfone (0.02 µm pore size) has cost of < 1 $\$/m^3$ and ability to remove > 7 log coliform [73]. The problems such as fouling, biofilm formation and secondary waste generation are associated with membranes.

From Figure 5.10, it is evident that the proposed hybrid method for disinfection can provide green alternative and techno-economically feasible solution for disinfection of pathogenic bacteria. The hydrodynamic cavitation using vortex diode as a cavitating device alone has 0.22 $\$/m^3$ as cost of operation, whereas after process integration by addition of peppermint oil (0.1%) or with aeration, the cost can be drastically further reduced to only 0.036 $\$/m^3$ for complete disinfection of water. The hybrid hydrodynamic cavitation process requires lower pressure drop, ambient conditions and is easy to operate. A possible commercialization outline of the proposed hybrid process is schematically shown in Figure 5.11. A typical water treatment plant includes screening, coagulation, flocculation followed by filtration and finally disinfection processes. The hybrid water disinfection process by hydrodynamic cavitation can be integrated with the existing set-up for the supply of bio-contaminant free water.

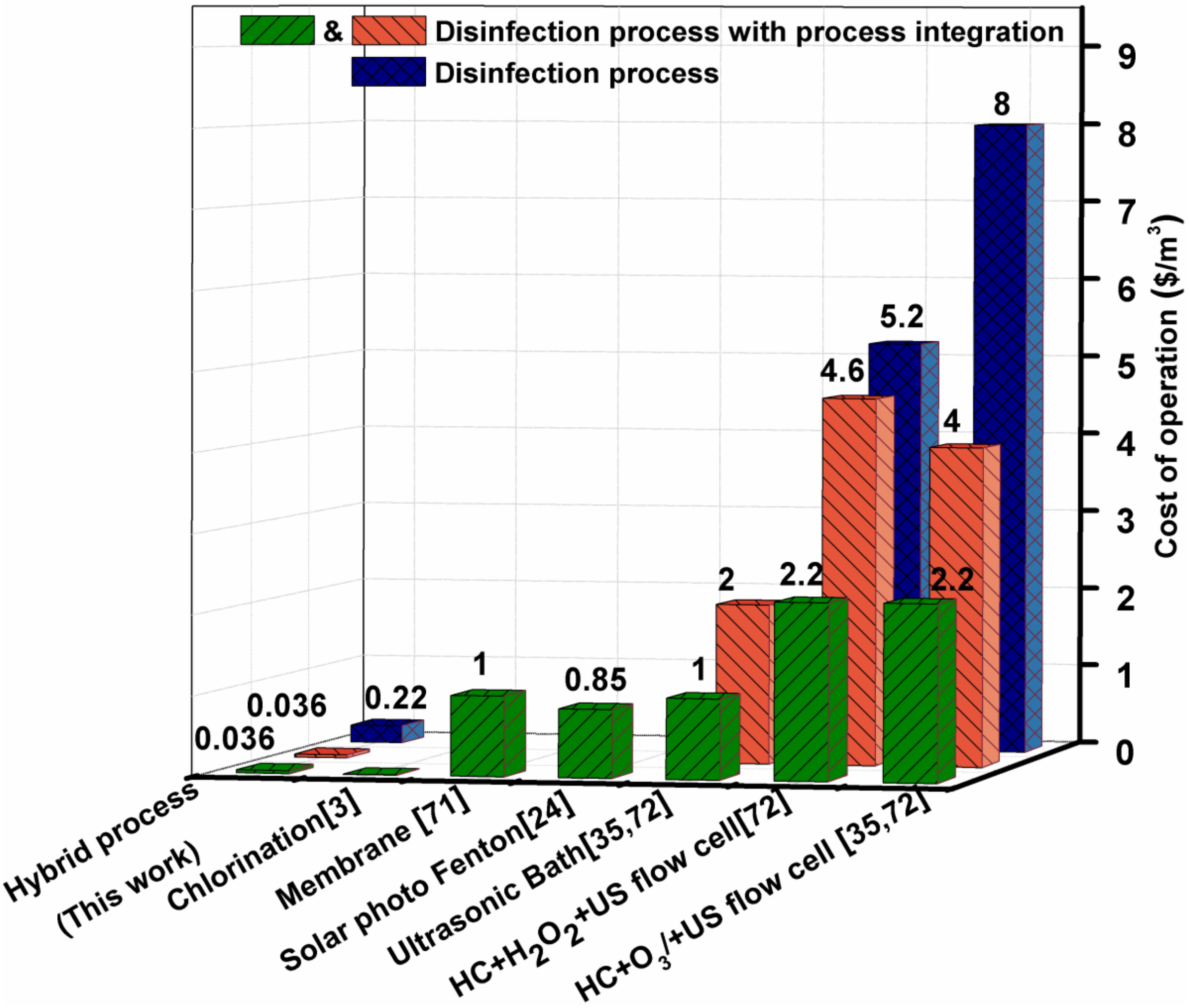

Figure 5.10: Cost comparison for various water disinfection processes

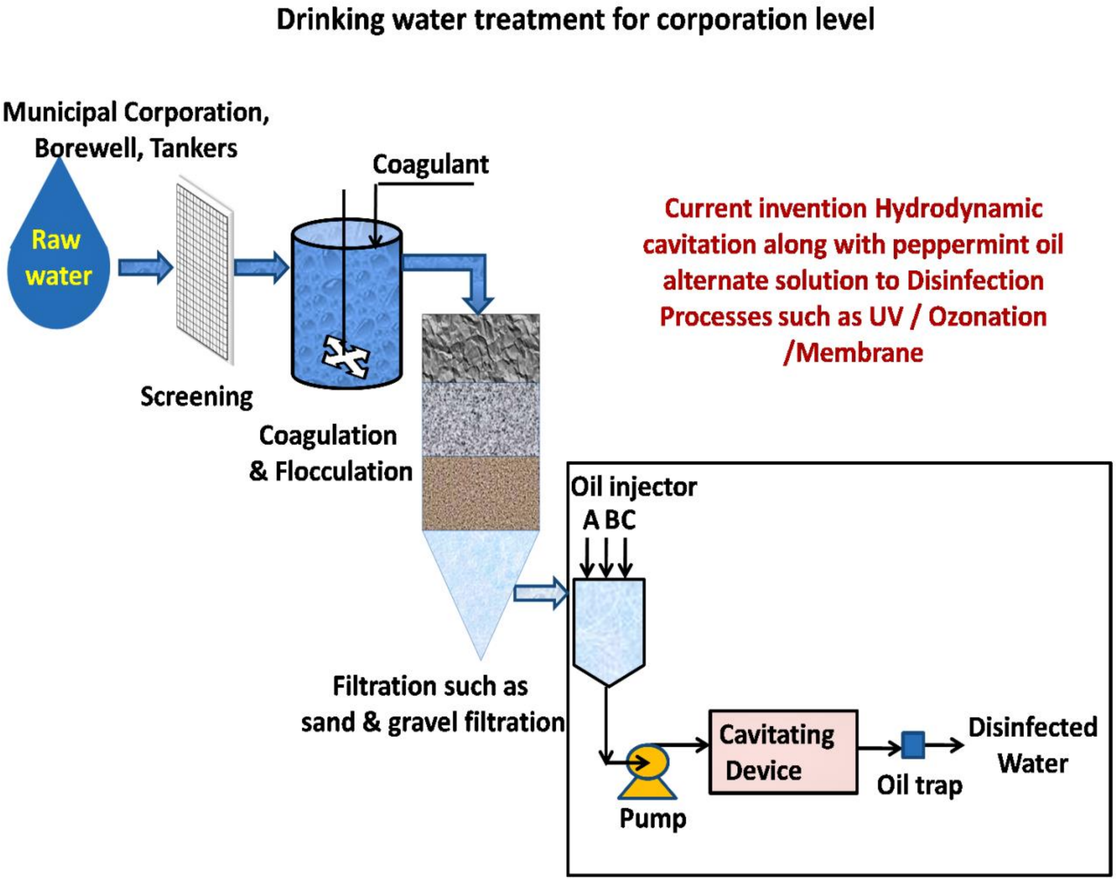

Figure 5.11: Flow diagram of hybrid disinfection process using natural oils

5.5. Conclusions

The present report on hybrid methodology employing hydrodynamic cavitation with natural oil-peppermint oil (0.1%) clearly highlights effective destruction of bacteria, antimicrobial resistant bacteria (AMR) and difficult, opportunistic pathogen. The specific findings include:

1. Exceptionally high rates of removal and effective destruction of antimicrobial resistant (AMR)-gram-positive methicillin resistant, *Staphylococcus aureus.*
2. Exceptionally high rates of removal and effective destruction for relatively less researched, gram-negative opportunistic pathogen, *Pseudomonas aeruginosa.*
3. Vortex diode as a cavitating device and natural oil-peppermint oil practically ensures complete removal within 10 min under mild operating conditions.
4. The hybrid process is also shown to be effective with other conventional cavitating devices such as linear flow based orifice.
5. Application of simple form of process intensification such as aeration was shown to further enhance the disinfection efficiency apart from possible lowering of oil dose.
6. The developed green process eliminates the use of harmful chemicals and can provide alternative to existing chemical processes such as chlorination.
7. The techno-economic evaluation indicated cost of the hybrid methodology to be significantly, order of magnitude, lower compared to the most conventional processes.

The above conclusions clearly indicate that the hybrid process can be easily adapted for the elimination of bacteria including AMR bacteria from water, thereby providing alternative water disinfection process for safe drinking water.

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Journal of Water Process Engineering 43 (2021) 102280

Contents lists available at ScienceDirect

Journal of Water Process Engineering

journal homepage: www.elsevier.com/locate/jwpe

Safe water and technology initiative for water disinfection: Application of natural plant derived materials

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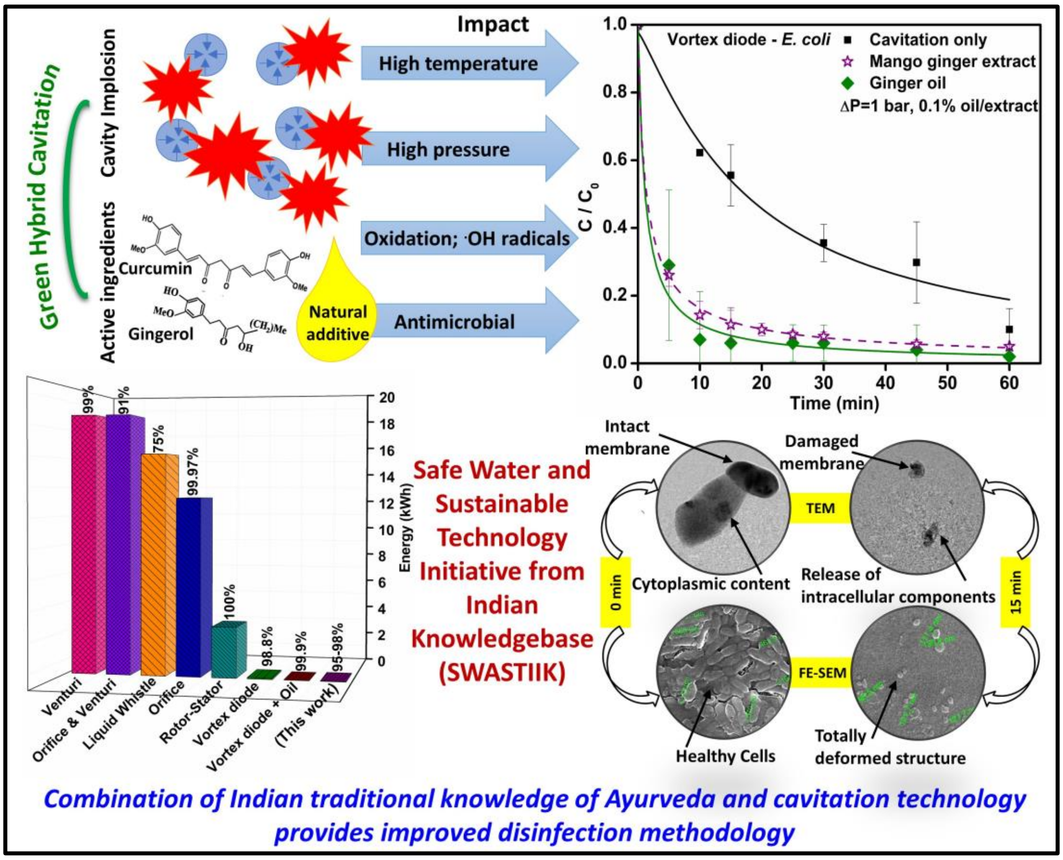
Chapter 6



Maya B. Mane, Vinay M. Bhandari, Vivek V. Ranade. Safe water and technology initiative for water disinfection: Application of natural plant derived materials. *Journal of Water Process Engineering* 43 (2021) 102280. https://doi.org/10.1016/j.jwpe.2021.102280

Chapter 6
Safe Water and Technology Initiative for Water Disinfection: Application of Natural Plant Derived Materials

Abstract

Safe drinking water is the necessity of life. The present study reveals use of natural resources such as plant extracts and natural oils for water disinfection. Differences between oil and water soluble additives were highlighted for plant extracts and insoluble natural oils. A hybrid hydrodynamic cavitation process was quite effective in both the cases and high rates of disinfection were achieved. Studies were reported using oils (ginger, turmeric, lavender, tulsi) and rhizome derived plant extracts such as ginger, turmeric and mango ginger, as additives in process intensification (0.1% v/V). A vortex based cavitation device (vortex diode, nominal capacity 1 m^3/h) was used with pressure drop of 1 bar. A high disinfection of 96% and 88% was obtained in 15 min for ginger oil and mango ginger extract respectively as compared to 44% using cavitation alone. Acoustic cavitation gave 94% and 30% disinfection with and without additive-Mango ginger extract. The FTIR analyses before and after cavitation, with ginger additive, showed no by-products formation and indicated gingerol as active component in disinfection. The per-pass disinfection values were also higher, up to 5 times than cavitation alone. Hybrid hydrodynamic cavitation using natural plant derived materials can offer a promising technology alternative in water disinfection.

6.1 Introduction

Availability of safe drinking water is an important issue today's context. Disinfection of water is essential for removing pathogenic microorganisms that are responsible for causing a number of water borne diseases as 88 % of diseases in the developing world are largely due to unsafe drinking water; about 842000 people die every year from diarrhea, especially children, due to unsafe drinking water, improper sanitization and hand hygiene [1]. Water scarcity in various parts of world also demand preserving drinking water sources by recycle and reuse of water, consequently demanding effective treatment methodologies. According to various norms, total coliform should be absent in drinking water [2]. Over the years, many different physical and chemical treatment methods are being used for disinfection of water and the most common is chlorination. The physical techniques for water disinfection are typically heating, filtration, microwave, UV irradiation, and plasma which generally have long treatment times, limited capacity and high cost. The chemical treatment method involves mainly chlorination and is widely used worldwide as the most preferred method for disinfection of water due to its effectiveness, ease of operation and low cost. However, formation of disinfection by-products (DBP) which are highly carcinogenic make chlorination process as not so environment and human friendly and in recent times is considered negatively, especially in many developed countries. The other possible technological alternatives are mainly adsorption, photocatalysis, membranes- Reverse Osmosis etc. Newer types of adsorbents in the form of bionanocomposites, especially that using antimicrobial properties of biomaterial and magnetic properties for easy separation can be promising from practical application point of view [3,4]. Similarly, photocatalytic disinfection using catalysts such as TiO_2 coupled with processes such as UV radiation can effect disinfection in short time [5]. Many of these are cost intensive, especially for higher volumes of operation and have fouling problems. It is therefore instructive to further evaluate and develop more techno-economically feasible alternative technologies for disinfection of water that would not have the disadvantages of chlorination and at the same time are cost-effective. Hydrodynamic Cavitation is reported as an effective technology for disinfection that does not generate any secondary disinfection byproducts. Hybrid technologies based on hydrodynamic cavitation such as by combining it with natural oils can be highly promising [6,7].

The fundamental aspects of cavitation process are relatively well known [8], though its implementation and different applications are not so straightforward. The process involves formation, growth and collapse of cavities using suitable cavitation devices. The collapse of cavities concentrates energy up to $1–10^{18}$ kW/m^3 which apart from playing direct role in disinfection, also assist in homolytic cleavage of water with generation of hydroxyl radicals and consequent oxidation damage to microorganisms effecting water disinfection. Thus, disinfection using cavitation typically includes combination of mechanical, thermal and chemical effects; mechanical effects in the form of shock waves, intense shear stress with high pressures (~ 5000 atm), thermal effects in the form of extreme temperatures (~ 10000 K) and chemical effects in the form of oxidation due to *in situ* generation of hydroxyl radicals (·OH) and such oxidizing species. The various forms of cavitation process are therefore exploited in different applications such as cleaning, water disinfection, wastewater treatment specifically for the removal of organic pollutants, removal of ammoniacal nitrogen and also recently in desulfurization of fuels for the removal of refractory sulfur compounds [6,7],[9],[10,11],[12,13].

From practical and technological view point, today, acoustic cavitation (AC) and hydrodynamic cavitation (HC) appear most promising for disinfection of water. The effects of AC or ultrasound on pathogenic bacteria were investigated by many, especially as small-scale operations. Gogate and coworkers found that intensity of cavitation decreased with increased distance from horn; negligible effect above 2-5 cm from tip [14]. In view of high cost, unsatisfactory thermal efficiency and limitations in scale-up, hydrodynamic cavitation is being considered as a more robust technology in this regard. HC offers ease of operation and different reactor designs/ variety of devices with/without moving elements. It can provide many a times simple design/construction, easy to scale-up and low cost solutions compared to acoustic cavitation reactor. In hydrodynamic cavitation reactors (HCR) using rotational mechanism, shear, shockwaves and heating are the main causes of disinfection. Milly et al. reported [15,16], a Shockwave Power Reactor converting electrical energy into thermal energy and increased temperature from 20 to 65.6 or 115 ^{0}C for complete pasteurization and sterilization of various fluids, foods such as calcium-fortified apple juice, tomato juice and skim milk. Rotor, driven by a simple milling cutter showed decreased ability of division of 75% for *E. coli* cells in 3 min [17]. Other advanced rotational HCR such as rotor and stator type device by Jyoti and Pandit [18], Cerecedo et al. [19], Sun et al. [20] and rotational generator by sarc et al. [21] were effective for various bacteria with high levels of disinfection. However, super cavitation and high thermal effects in these rotational HCR may lead to serious erosion problems, and coupled with low durability and higher costs, practical applications of these can be limited. Thus, it is imperative that newer forms of process intensifications for disinfection be explored using hydrodynamic cavitation employing cavitating devices without moving elements, simple in design, having ease of operation, mild process/operating conditions and at the same time accomplish equal or improved disinfection efficiencies for real life operations.

In HCR without moving elements, cavitation is induced when static pressure falls below saturated vapor pressure either due to geometrical constriction in linear flow or due to vortex flow. There are different types of cavitating devices that are reported mainly using linear flow based devices (orifice, venturi etc.) and vortex/rotational flow-based devices (vortex diode). The pressure/ energy requirement in linear flow devices is rather high. Loraine et. al. reported pump pressure of 345 kPa and 554 passes to achieve 99.999% of disinfection using a venturi reactor of 1.8 L water capacity [22]. Hybrid cavitation approaches using chemical process intensification are reported to enhance the performance of conventional cavitation devices such as venturi by addition of additional oxidizing agents such as H_2O_2 for increasing disinfection efficiency [21],[23],[24],[25],[26],[27]. The disinfection efficiencies were not satisfactory, in general, ranging from 24% to more than 90% for inactivation of *E. coli*. Satisfactory disinfection of 100% was reported with excessively high operating pressures of the order of 12 MPa in 30 min by using orifice plate with high operational cost [28]. Recently, vortex flow based cavitating device, vortex diode has been reported for water and wastewater treatment/pollution control [10,11], desulfurization [12,13]. Jain et. al reported inactivation of gram-negative and gram-positive bacteria, *E. coli* and *S. aureus,* by vortex diode with substantially higher disinfection than conventional cavitation devices such as orifice and requiring lower operating pressure [9]. Mane et al. developed a hybrid hydrodynamic cavitation process using natural oils having antimicrobial properties and could obtain practically complete disinfection within 10 minutes for different microorganisms [6,7]. The optimized conditions were pressure drop of 1 bar and additive natural oils in 0.1 % by volume. The approach was shown to be effective from common to antimicrobial resistant (AMR) bacteria and opportunistic difficult pathogen *P. aeruginosa;* with costs comparable to chlorination.

The use of plant extract coupled with cavitation technology for disinfection of water has not been discussed in the literature so far. The present study extends the philosophy of hybrid hydrodynamic cavitation technology beyond natural oils to other natural plant derived materials such as plant extracts, identify the differences in disinfection when the extract goes in water as a homogeneous mixture compared to heterogeneous oil water system reported earlier and evaluate the disinfection efficiencies for different oils and plant extracts. In view of the earlier reports in this regard, studies were carried out using comparable process conditions (Vortex diode, ΔP of 1 bar, 0.1 % of plant extract). The objective is to obtain insight into disinfection process to confirm no formation of disinfection by-products or intermediates and finally evaluate possible use of the natural plant materials for not just making water safe for drinking but also for additionally securing possible health benefits- A hybrid cavitation process that can be said to be Safe Water and Sustainable Technology Initiative from Indian Knowledgebase (SWASTIIK).

6.2 Materials and Methods

6.2.1 Cavitation Reactors

The hydrodynamic cavitation experiments were carried out by using vortex diode (VD) as a cavitating device. The design of vortex diode consists of a chamber of diameter 66 mm (throat diameter of 11 mm) with nominal capacity 1 m^3/h. Schematic of experimental set up and experimental details were discussed in our previous publications and only essential details are provided in the Experimental section [6,7]. The experiments were performed with typically 20L of contaminated water, with known microorganism, *E. coli* and known initial concentration at predetermined operating conditions of ΔP 1 bar, additives 0.1% v/V, unless otherwise specified. Samples were withdrawn at regular time intervals and analyzed for percentage disinfection.

Acoustic cavitation was carried out using UCP-20 Sonication Unit having ultrasound- 40 kHz frequency and 500 W of power.

6.2.2 Microorganisms

For ease of comparison with literature reports, a commonly used model microorganism, Gram-negative bacteria *Escherichia coli* (ATCC-8739) was used in the present study and was obtained from NCIM- National Collection of Industrial Microorganism at CSIR, National Chemical Laboratory, Pune, India. For disinfection study, bacterial culture was grown in 50 mL of N. broth solution, incubated at 37 ^{0}C in orbital shaker with speed of 200 rpm for overnight. After incubation logarithmic (or exponential) phase of bacteria are measured by UV-Vis spectrophotometer at 600 nm wavelength. This robust stage of bacteria of 50 mL added to the 20L of distilled water to obtain desired concentration (~10^4 CFU/mL).

6.2.3 Plant extracts and Natural oils as bio-additive

Different plant extract such as *Zingiber officinale* (Ginger) extract, *Curcuma longa* (Turmeric) extract and *Curcumin amada* (Mango ginger) extract were prepared in the laboratory using the plant materials procured from local sources, Pune, Maharashtra, India. Extraction was carried out without using any solvent (e.g. acetone, methanol, hexane) in simple home appliance-mixer followed by separation where inherent liquid phase from rhizomes is separated using centrifugation with 1000 rcf speed for 15 min. (ESCO centrifuge, Versati T1000 ESCO model - TCV-1500-B (T1000-MB-B).

The different types of natural oils used include *Zingiber officinale* (Ginger) oil, *Lavandula angustifolia* (Lavender) oil, *Ocimum tenuiflorum* (Tulsi) oil, *Curcuma longa* (Turmeric) oil and *Azadirachta Indica* (Neem) oil. These were procured locally from Pune, Maharashtra, India. The detailed characteristics of different natural oils and extracts are given in Table 6.1.

Table 6.1: Characteristics of Natural plant derived materials- oils and extracts

Sr. No.	Name of oil/ Extract	Chemical composition	Physicochemical properties- Oil	Reference
1	Neem	Hexadecanoic acid (78.25%), tetradecanoic acid (7.24%), Silane, triethylfluoro (3.96%), oleic acid (3.64%), octadecenoic acid (3.5%), and linoleic acid (1.39%) etc.	Density-0.91g/cc, Viscosity-58.94 cP, Surface Tension-40.69 dyne/cm	[29],[30]
2.	Lavender	1,6-octadien-3-ol,3,7-dimethyl (41.74%), Silane, triethyl fluoro (36.71%), bicyclo [1.2.2] heptan-2-one, 1,7,7-trimethyl (6.91%), eucalyptol (5.99%) , Methane sulfonyl chloride (5.67%) and 3-cyclohexene-1-methanol, a,a4-trimethyl(2.99%)	Density-0.883 g/cc, Viscosity-46.6 cP, Specific Gravity- 0.887	[29] [31] [32]
3.	Tulsi	Methyl eugenol (82.9%), eugenol (0.9%), β-Caryophyllen (4.1%), Borneol (2.4%), Germacrene D (2.3%), α-Copaene (1.9%), δ-Cadinene (1.1%), Germacrene A (0.7%), Linalool (0.5%), α-Elemene (0.5%), Cubebol (0.3%), α-Pinene (0.2%), Limonene (0.2%), β-Bourbonene (0.2%), α-Humulene (0.2%) etc.	Density-1.552 g/cc, Viscosity-26.75 cP, Surface tension-84.29 N/m	[33],[34]
4	Ginger	α-zingiberene (35-40%), β-sesquiphellandrene (11.5-13.5%), ar-curcumene (6.5-9%), camphene (5-8%), β-bisabolene (2.5-5.5%)	Density- 0.9104 - 0.9108 g/cc Viscosity-5 cP Surface Tension-30.9 Dyne/cm	[35] [36]
5	Turmeric	α-Turmerone (40.8%), zingiberene (16.9%), β-turmerone (14.1%), ar-turmerone (11.0%), and β-sesquiphellandrene (10.0%)		[37]
6	Mango ginger extract	Myrcene (88.6%), ocimene (47.2%), ar-turmerone (29.12%), (Z)-β-farnasene (21.9%), guaia-6,9-diene (19.8%), cis-β-ocimene (18.8%), cis-hydroocimene (18.79%), transhydroocimene (15.94%), α-longipinene (14.8%), α-guaiene (14.5%), linalool (13.37%), β-curcumene (11.2%) and turmerone (10.8%)		[38], [39]

6.3 Experimental

The experimental set up of hydrodynamic cavitation and experimental procedure was explained in detail in our earlier work [6,7] and hence only essential details are included here to avoid repetition. The experimental set up comprises a holding tank having 50 L capacity, a multistage vertical centrifugal pump (Model CNP make CDLF2-26, SS316, 1.2 m^3/h at 228 MWC, rating 3 kW (4 hp), 2900 RPM, discharge pressure 0–15 bar), vortex diode as a cavitation device and measurements and controls for flow, pressure and temperature. A 20 L volume of contaminated water with ~ 10^4 CFU/mL of initial concentration of bacteria was used for disinfection study. Bio-additives (Oil/ plant extract) were used with optimized concentration of 0.1% in the hybrid process. The samples were withdrawn from holding tank at periodic intervals of time and were analyzed by plate count method. For analysis, 100 µl of bacterial sample was spread over sterile N. agar petri dish. After incubation for 24-h, viable colonies were counted and measured as a colony forming unit per milliliter (CFU/mL).

$$CFU/mL = \frac{Number\ of\ colonies\ on\ N.agar\ plate}{Volume\ plated\ (mL)} \times dilution\ factor$$

The confirmation of cell destruction by cavitation was done by FE-SEM (Field Emission Scanning Electron Microscopy, FEI-Nova NanoSEM-450) and TEM (Transmission Electron Microscopy; Tecnai G2 20 STwin; LaB6 filament as the electron source) analysis. The samples before and after cavitation were analyzed for detailed morphological changes of bacterial cells to prove process efficacy. The functional groups of the natural oils and plant extracts, prior to cavitation and after cavitation, were characterized by Fourier transform infrared spectroscopy (Perkin Elmer’s Spectrum One FTIR Spectrometer)

6.4 Results and discussion

6.4.1 Cavitation using miscible plant extracts

Plant extracts derived from different parts of natural plants can provide useful alternative to the use of natural oils and can offer similar benefits along with good disinfection efficiency in the hybrid cavitation process described earlier for natural oils. A proof of concept is established here in this regard for the first time using different plants extracts from rhizomes such as turmeric extract, ginger extract and mango-ginger extract. For ease of comparison with similar natural oils, use of similar concentration, 0.1%, was made to evaluate disinfection efficiencies. In selection of the natural plant resources, medicinal properties of rhizomes of ginger, turmeric and mango ginger are well thought-out apart from their wide use in day to day life.

In order to establish the proof of concept, experiments were initially carried out using acoustic cavitation. Figure 6.1 shows the results of acoustic cavitation using mango-ginger extract. It was observed that even simple process of acoustic cavitation can yield more than 90% disinfection in 15 min.

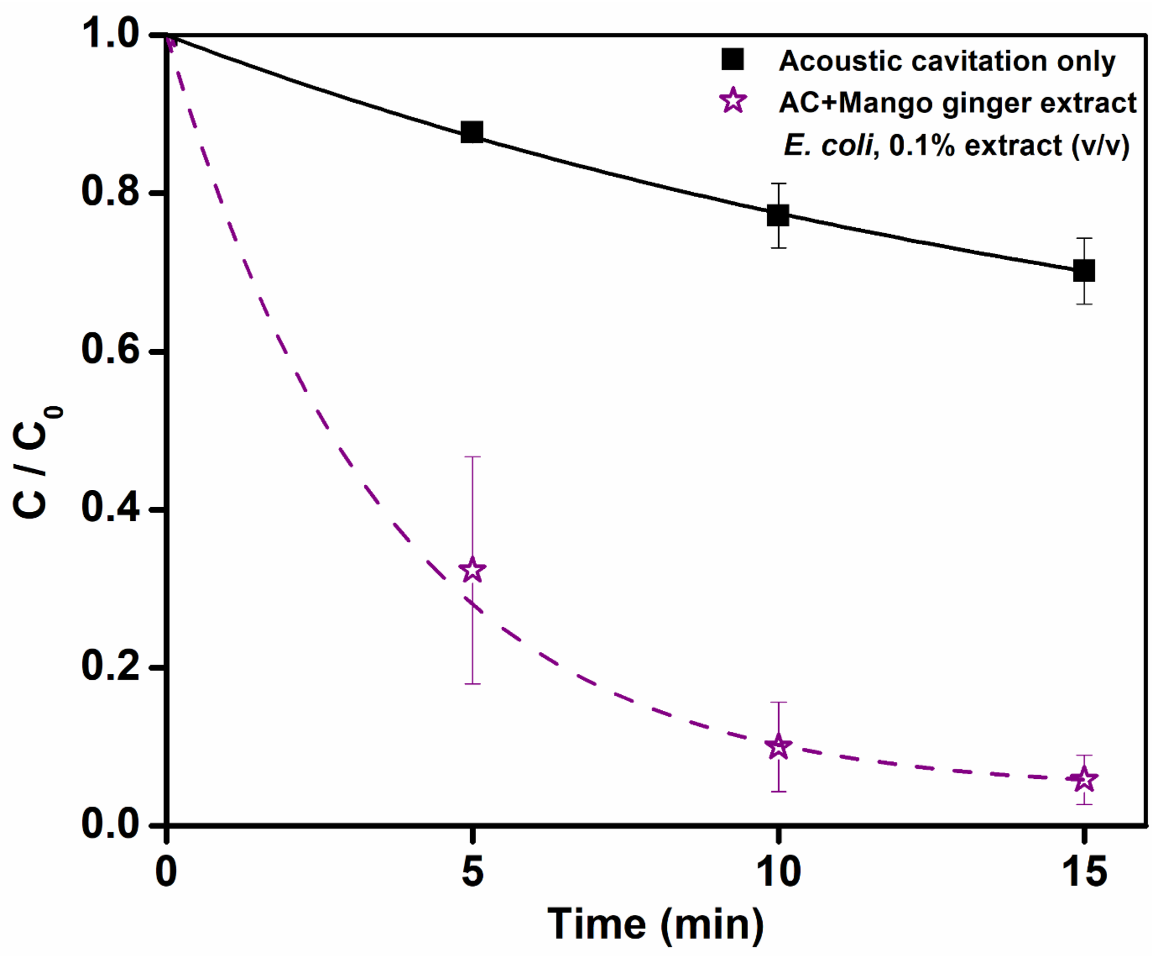


Figure 6.1: Disinfection efficiency using acoustic cavitation for Mango-ginger plant extract

Having established the disinfection efficacy of plant extract using acoustic cavitation, further experiments were carried out using hydrodynamic cavitation due to its commercial potential in terms of ease of operation and energy effectiveness. The results are presented in Figure 6.2. It can be seen that the disinfection efficiency for the mango-ginger plant extract is high, of the order of 90% in 15 min. For the other two extracts namely turmeric and ginger extract, the extent of disinfection was lower than that using cavitation alone similar to that observed with many natural oils. It is possible that the extraction efficiency for turmeric and ginger could be lower reflecting lowered content of the active ingredients as compared to mango-ginger. The roots of ginger, turmeric and mango ginger contain essential oils and other active ingredients such as curcuminoids. Hanif et al. [40] reported the essential oil yield of different plant extract by CO_2 supercritical fluid extraction and their antimicrobial properties, indicating % oil yield for rhizomes of *curcuma amada* as 6.38, roots of ginger as 5.59 and for *curcuma longa* as 3.56. It reveals higher antimicrobial activity for mango ginger than ginger and turmeric extract. The aqueous plant extract with cavitation gives higher disinfection for mango ginger- up to 95% disinfection in 60 min. This can be attributed to presence of higher curcuminoids and higher % of oil in mango ginger, than for ginger extract and for turmeric extract. The curcuminoids are lipophilic in nature and can reacts with phospholipids of the cell membrane and easily destroy the permeability of microorganisms.

Policegoudra et al. reported previously ignored component-difurocumenonol as active ingredient responsible for antimicrobial activity and nonpolar extracts of mango ginger by chloroform demonstrated higher inhibition zone for different Gram-negative bacteria such as *M. luteus*, *S. aureus*, *B. cereus, B. subtilis, L. monocytogenes* as compared to extraction obtained using hexane, ethyl acetate, acetone and methanol where negligible disinfection was obtained for *E. coli* [41]. The higher disinfection efficiency with mango-ginger extract may also be attributed to the presence of oil content in the extract and lipophilic curcuminoids and difurocumenonol.

The results with the plant extracts of this study in cavitation clearly demonstrate their potential application in water disinfection.

6.4.2 Synergistic effect

When working with hybrid methodology of cavitation, it would be prudent to evaluate synergistic effect of plant extract in hybrid cavitation method. Extraction of active ingredients from mango ginger rhizomes without addition of any solvent gave good disinfection efficiency of 80% without cavitation. The experiments using hybrid cavitation methodology with mango ginger extract exhibited higher rates of disinfection than cavitation and mango ginger individual effect (Figure 6.2). Proof of concept is established by carrying out experiments using acoustic cavitation with same small quantity of mango ginger extract, 0.1%. It was observed that acoustic cavitation with mango ginger exhibited ~95% disinfection which is higher than acoustic cavitation alone, of 30%.

The synergistic effect for plant extract is evaluated using the following Eq. (1).

$$\boldsymbol{f = \frac{K_{HC+oil/extract}}{K_{HC} + K_{oil/extract}}} \qquad (\mathbf{1})$$

Where, K is for rate constant in s^{-1}, HC and HC+oil/extract indicated for hydrodynamic cavitation and hydrodynamic cavitation along with natural essential oil/extract.

The value of $\boldsymbol{f}$ for mango ginger extract are 1.85 and 1.22, clearly indicating synergistic effect in hybrid process due to hydrodynamic cavitation along with mango ginger extract and acoustic cavitation along with mango ginger extract respectively. Similarly, for other extract such as ginger extract synergistic index is found less than 1 and therefore no synergistic effect found.

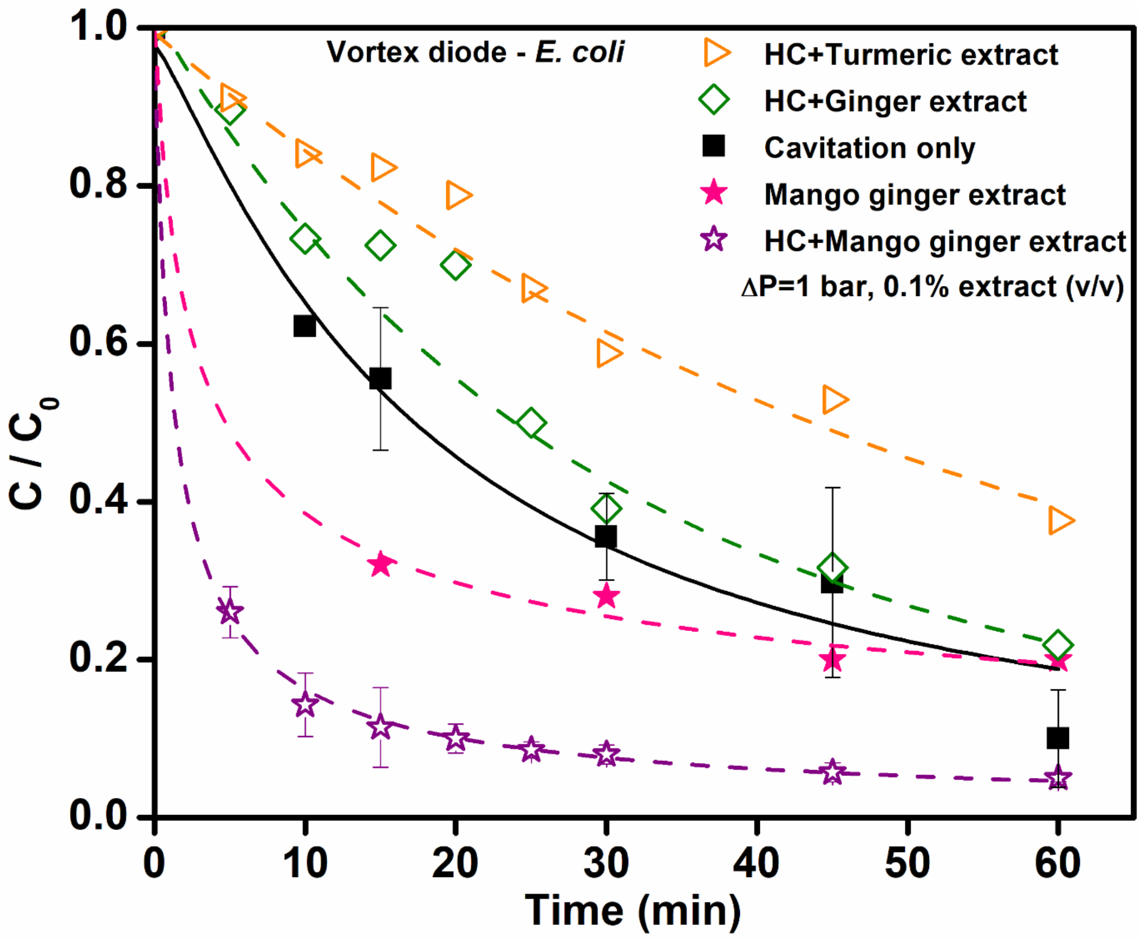


Figure 6.2: Disinfection efficiency for various plant extracts using hydrodynamic cavitation

6.4.3 Cavitation using immiscible oils

The use of immiscible natural oils as bio-additives in cavitation represents a complex heterogeneous system where oil phase is in addition to the conventional aqueous phase subsequently getting transformed into two phase - gas (e.g. water vapor/ air)-liquid (water) system during cavitation. The cavitation processes are known to generate emulsion and the type of cavitation, nature of cavitation device and such parameters dictate the extent of emulsion or micro-mixing, in general. Volatile organic compounds are the main components of essential oil that are expected to contribute in the process of disinfection and enhance the rates of disinfection as well. The present work describes the effect of various immiscible oils namely ginger oil, tulsi oil, turmeric oil, lavender oil and neem oil, not reported so far in this regard. Figure 6.3 shows the disinfection efficiency using these natural oils in the hybrid cavitation process using vortex diode as a cavitating device and using the same process parameters as discussed in previous section for plant extracts. It is seen that Ginger oil and Lavendor oil show significant increased efficiency of disinfection while the remaining oils perform negatively, with decreased efficiency.

Ginger is typically considered as a safe natural product to treat respiratory and gastrointestinal disease for many decades. It belongs to *zingiberaceae* family, perennial herb and because of its characteristic spicy aroma and taste, it is traditionally used as a spice in foods and beverages. In addition, it is an excellent source of many bioactive phenols such as gingerols, shogaols, and zingerones. It is reported that the antimicrobial activity of ginger essential oil (GEO) has higher inhibition zone for various bacteria, *Staphylococcus aureus* and *Listeria monocytogenes*, followed by *Pseudomonas aeruginosa* while some bacteria such as *Salmonella typhimurium, Shigella flexneri* and *Escherichia coli* were reported to be resistant to ginger essential oil [42]. Also, *S. aureus* has higher sensitivity for GEO than *E. coli*, as these bacteria commonly used for disinfection study [43]. Minimum inhibitory concentration of GEO for *S. aureus*, *Bacillus subtilis*, *E. coli* and *Penicillium spp.* exhibited the value of 8.69, 86.92, 173.84 and 869.2 mg/mL respectively [44]. *E. coli* required much higher inhibitory concentration of GEO compared with other microorganisms. In the light of the reported literature, it is evident from the present work that a small quantity of ginger oil along hydrodynamic cavitation exhibited excellent disinfection efficiency for *E. coli* (Figure 6.3).

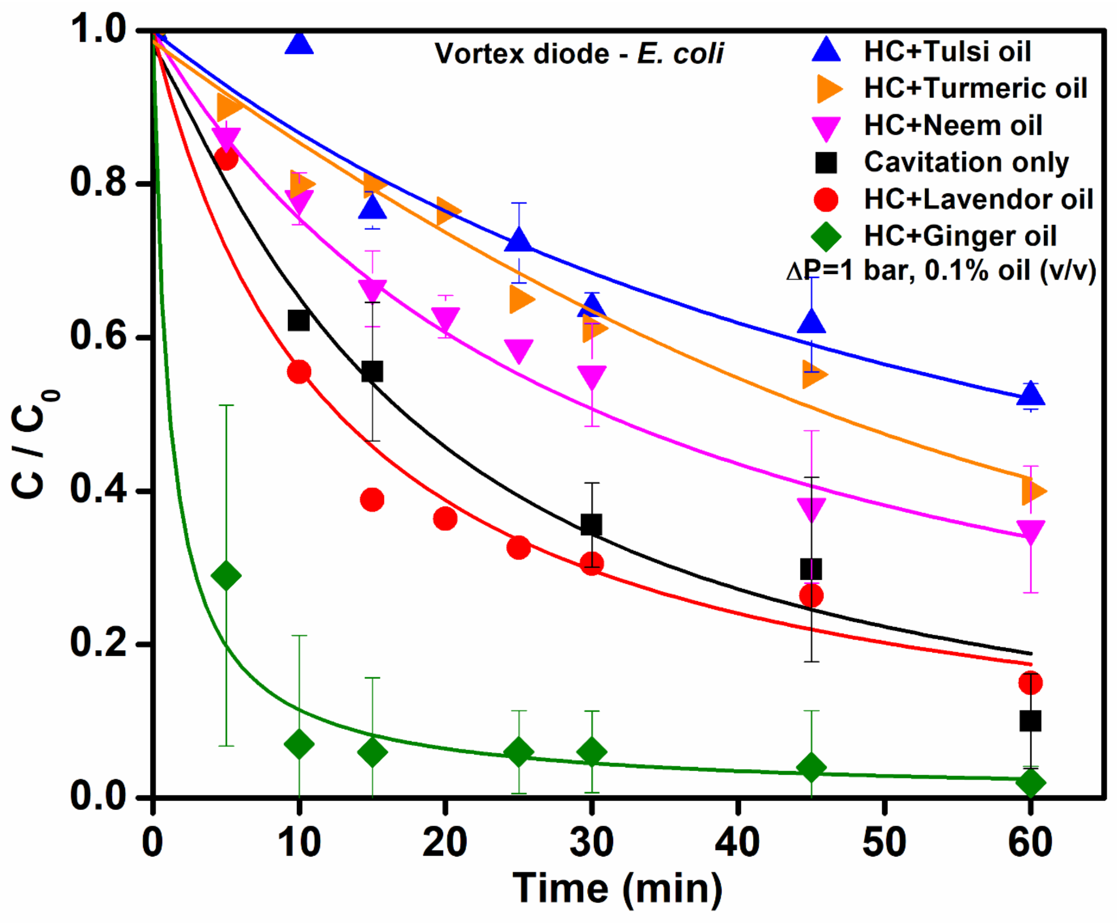


Figure 6.3: Disinfection efficiency for various natural oils using hydrodynamic cavitation

A more scrutiny to elucidate the disinfection effects reveals the role of bio-active components of ginger oil which include hydrophobic gingerol and hydrophilic polysaccharides. The Lipophilic gingerols have many pharmacological activities such as anti-oxidant, anti-inflammatory, antimicrobial, anticancer, anti-emetic, anti-metabolic syndrome, and neuroprotection [45]. Owing to lipophilic nature they are easily penetrable through cell membranes of microorganisms which may affect both the inner cellular components of cytoplasm and the external cell envelope. Consequently, these contribute to enhanced bacterial cell membrane permeability subsequently leading to loss of ions and leakage of cellular components. In some cases, presence of active ingredient of natural oils such as thymol, menthol, and linalyl acetate leads to higher antimicrobial activity [46]. The results of this work are also consistent with the reports of Kumari et al. [47] on antioxidant activity of essential oil and aqueous extract of ginger where essential oil was shown to exhibit higher antioxidant property due to the presence of high phenolic content (or major contents of monoterpenoids) than the aqueous extract of ginger (contains lower content of sesquiterpenoids). Also, similar to the findings of Baris et al. [48], hydrodynamic cavitation with ginger extract showed lower disinfection due to the presence of polar phenolics- components with low activity. It does not easily penetrate through cell membrane of microorganisms and may require higher dosage to obtain similar disinfection efficiency as that for cavitation with ginger oil. A high disinfection of 98% in 60 min with oil (0.1%) can be obtained using hybrid cavitation methodology.

It is possible that higher viscosity and surface tension of oils have adverse impact on cavitation. The hybrid process using neem oil and tulsi oil showed lower rates of disinfection, probably due to higher viscosity of these oils. The neem oil has viscosity of 37 cP [49], tulsi oil has viscosity 26.75 cP and surface tension 84.29 N/m [34], the ginger oil has low viscosity of 5 cP and surface tension of 30.9 dyn/cm. Higher values of viscosity and surface tension adversely affect the growth stage of bubbles, and increased the time of collapse [50]. There could be reduced collapse of bubbles, delay in collapse of bubble, or implosions of low intensity, producing less energy; all contributing to reduced disinfection efficiency in the hybrid process.

The antimicrobial activity of ginger oil is mainly due to the high percentage of eugenol (50.94%) as an active ingredient [36]. Considering easy availability of these medicinal plants and inherent health benefits associated with different plants, applying this traditional knowledge mainly from Ayurveda and advance oxidation technologies such as hydrodynamic cavitation can offer practical alternative to disinfection of water with possible health benefits of plant extracts.

Followings revealing observations can be made from Figures. 6.2 and 6.3 corresponding to hybrid cavitation technology operation of 15 min:

1. The rate of disinfection with ginger oil are higher, an order of magnitude, 2 times than cavitation alone and 3 times than cavitation with ginger extract.
2. Ginger oil showed higher degree of disinfection than ginger extract for the reasons explained above.
3. The Lavender oil exhibited higher rate of disinfection, of the order of 1.5 times higher than cavitation alone.

4. The turmeric oil and turmeric extract both showed nearly similar and lower extent of disinfection performance than cavitation alone.
5. The neem oil and tulsi oil showed lower efficiency similar to turmeric oil.
6. The rate of disinfection for mango ginger extract for both hybrid hydrodynamic cavitation and acoustic cavitation were significantly higher than cavitation alone. For hydrodynamic cavitation, the rates were 2 times higher and for acoustic cavitation, 3 times higher rate of disinfection could be obtained.

The synergistic coefficient for ginger oil is greater than 1, again confirming superiority of combined effects of natural oil along with cavitation. The results also indicate natural oils are more effective compared to plant extract in disinfection of water.

6.4.4 Kinetics of disinfection- Per-pass disinfection model of hydrodynamic cavitation

The kinetics of disinfection based on per pass disinfection factor is useful in understanding the disinfection behaviour[6,7]. The rate equations in this regard are elaborated below:

For the conventional model, the effective disinfection rate constant ($\boldsymbol{k}$), $\mathbf{s^{-1}}$ is defined as:

$$\boldsymbol{k} = \frac{\ln\left(\boldsymbol{C_0}/\boldsymbol{C}\right)}{\boldsymbol{t}} \tag{2}$$

Where, $\boldsymbol{C_0}$ and $\boldsymbol{C}$ are bacteria concentrations, initial and at any time $\boldsymbol{t}$ respectively, CFU/mL.

For per-pass disinfection model of hydrodynamic cavitation, the effective rate constant is defined as below ($\boldsymbol{k}$), s^{-1} and is related to residence time, $\boldsymbol{\tau}$

$$\boldsymbol{k} = \frac{\emptyset\,\boldsymbol{n}}{\boldsymbol{t}} = \frac{\emptyset}{\boldsymbol{\tau}} \tag{3}$$

Where, $\emptyset$ is per-pass disinfection factor and $\boldsymbol{n}$ is number of passes.

Per-pass disinfection model is more realistic and requires parameters like flow rate (Q), volume treated (V) operating pressure drop across cavitating device (P) and concentration-time data. The per-pass disinfection factor (∅) represents the significance of cavitating device.

$$\emptyset = \frac{-ln(C/C_0)}{n} \tag{4}$$

Also, number of passes ($\boldsymbol{n}$) is an important parameter used in cost calculations- lower the value of $\boldsymbol{n}$, lower is the cost of disinfection process. The number of passes can be obtained as:

$$n = \frac{Q \times t}{V} \tag{5}$$

Using the model, effective rate constant and per-pass disinfection factor can be calculated and these values are listed in Table 6.2. The pass disinfection factor (∅) for ginger oil in cavitation process is 5 times higher than cavitation alone and also 10 times higher than ginger extract as shown in Figure 6.4. The values of (∅) are 0.36, 0.07 and 0.036 for cavitation with oil, cavitation alone and cavitation with extract for vortex diode as a cavitating device. The per-pass disinfection factor (∅) for cavitation with mango ginger extract is 3.5 times higher than cavitation alone by using vortex diode as cavitation device. The value of (∅) for HC + Mango ginger extract is 0.243. The results for acoustic cavitation, cavitation with mango ginger extract also show consistent results. The variations in the values of (∅) because of the type of extract/oil, active components of extract/oil are clearly evident.

It can be seen that per-pass disinfection factors (∅) for *E. coli* are higher for ginger oil and mango ginger (MG) extract with cavitation than other oils and extract. It is also evident that in 15 min, increase in per-pass disinfection for cavitation with ginger oil is of the order of 500% and for mango ginger extract it is ~ 300% more as compared to cavitation alone. However, since 100% disinfection is desired, selection of oil and process integration is crucial. It is also to be noted that 0.1% extract represents substantially low dose as compared to corresponding oil dose of 0.1% and therefore, for higher disinfection efficiency, more than 0.1% of extract is desirable. The results clearly highlight utility of natural oil and plant extracts in enhancing the rates of disinfection.

Table 6.2: Rates of disinfection for *E. coli*

Hydrodynamic Cavitation (HC), Vortex Diode, ΔP=1 bar				
Process oil/extract=0.1%	**% Disinfection**	**Rate of disinfection CFU/(mL.s)**	**Rate constant (s^{-1})×10^4**	**Per-pass disinfection (ϕ))×100**
Cavitation alone	44	99	7.05	7
HC + Ginger oil	96	254.5	36	36
HC + Tulsi oil	23	12.3	3	3
HC + Neem oil	34	22	4.55	4.4
HC + Lavender oil	61	52.5	10.5	10.5
HC + Turmeric oil	20	22.3	2.5	2.45
HC + Mango ginger extract	88	94	24.1	24.3
HC + Ginger extract	27	18	3.6	3.6
HC + Turmeric extract	18	17	2.16	2.13
Without cavitation- Only Mango ginger extract	68	21	13	NA
Acoustic Cavitation (AC)				
Cavitation only	30	9	4	NA
AC + Mango ginger extract	94	108	31.5	NA

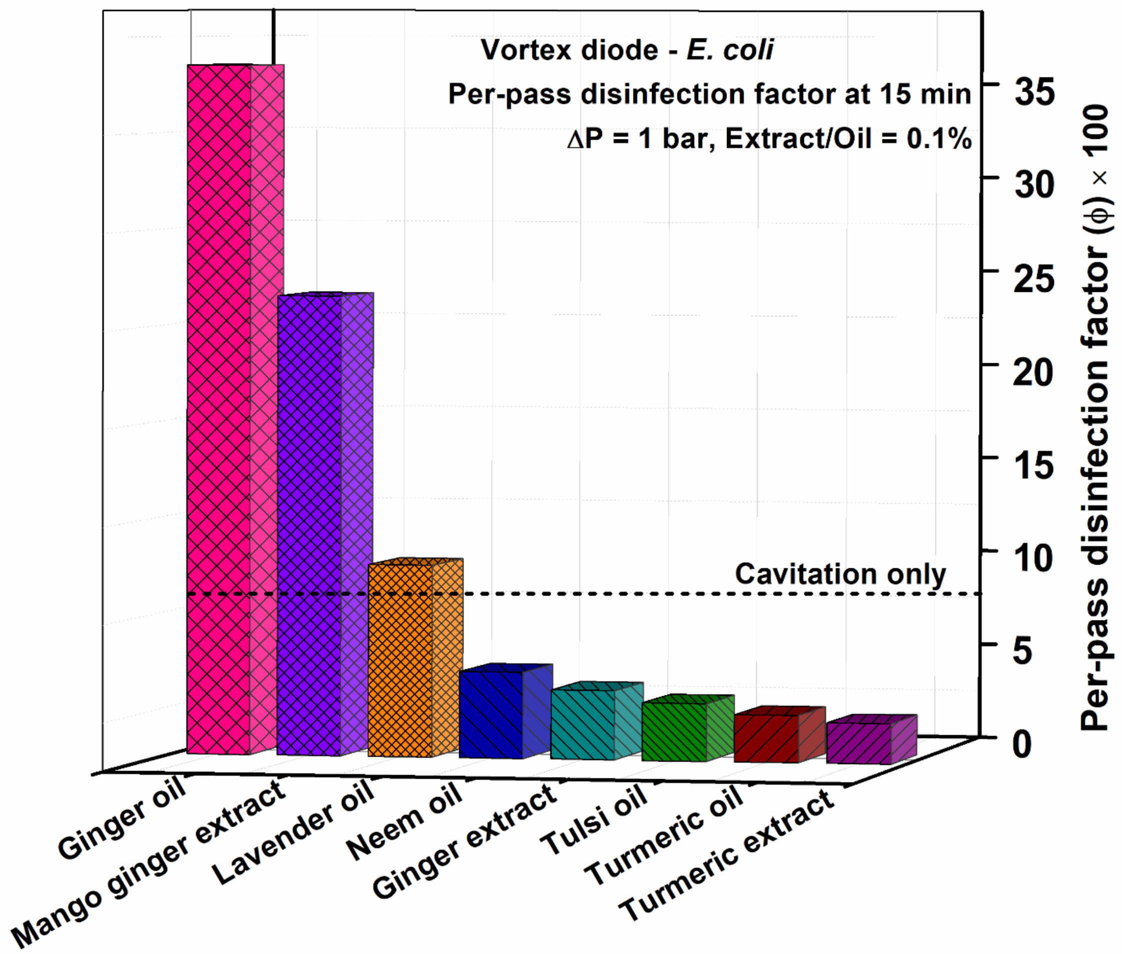


Figure 6.4: Comparison of per-pass disinfection factors

A comprehensive comparison of performance of different hydrodynamic cavitation reactors is presented in Table 6.3. Many reactors such as high pressure homogenizer, high speed homogenizer/mixer blender and hydrodynamic cavitation with orifice plate utilized for cell disruption [51,52],[53],[54]. Majority studies exhibited lower disinfection efficiency and required more time for disinfection, though the performance of can be enhanced by process intensification such as ozone (O_3), hydrogen peroxide (H_2O_2) or ultrasonic probe (US) or use of chlorine oxides. For example, orifice alone gave only ~40% disinfection and maximum of 75% using process intensification. Chlorination of some form, as part of process intensification, assists in reaching high levels of disinfection, however, disinfection by-products formation in such scenario is not well reported. The problems with rotor type devices are already well highlighted in earlier text. The present approach, showed a higher efficacy of hybrid cavitation with possible health benefits without forming any disinfection by-products, time saving, with less energy requirement.

Table 6.3: Comparison of different hydrodynamic cavitation methods used for disinfection

Cavitating Device	Operating conditions	% Disinfection	Ref.
Multiple hole orifice	P=5.17 bar ~100 *Faecal coliforms*/100 mL	5 mg/l H_2O_2 **9** (15 min), **21** (60 min) HC **38** (15 min), **92** (60 min) HC + 5 mg/l H_2O_2 **60** (15 min), **96** (60 min) HC (1.72 bar)+US (40 kHz) **60** (15 min), **80** (60 min) HC (1.72 bar)+US (40 kHz) +5 mg/l H_2O_2 **75** (15 min), **90** (60 min)	[23]
Ball type valve	P=5.17 bar ~100 *Faecal coliforms*/100 mL	2 mg/l O_3 **78** (15 min), **100** (60 min) HC **57** (15 min), **76** (60 min) HC + 2 mg/l O_3 **88** (15 min), **100** (60 min)	[55]
Liquid whistle Reactor	P=500 psi *E. coli* 10^8-10^9 CFU/mL	HC **22** (180 min) HC+O_3 **75** (180 min)	[26]
Orifice	P=2.5 bar *E. coli* 10^7 CFU/mL	**32.7** (120 min)	[25]
Orifice	ΔP=1-12 bar *E. coli* 10^7 CFU/mL	0.25-0.3 mg/l ClO_2 **>99** (3-6 min) HC + ClO_2 **99.99** (6 min)	[56]
Multiple hole orifice	0.45 MPa 2500–3000 CFU/mL	HC **67.3** (60 min) 0.5 mg/L ClO_2 **78.2** (60 min) 1.0 mg/L ClO_2 **~80** (60 min) 2 mg/L NaClO **~50** (60 min) HC+0.5 mg/L ClO_2 **~99** (60 min) HC+1.0 mg/L ClO_2 **100** (60 min) HC+2 mg/L NaClO **~79** (60 min)	[57]
Rotor-stator	*E. coli*	HC (4.3 L/min) **100** (14 min)	[20]
Vortex Diode	ΔP=10bar for O, ΔP=2bar for VD *E. coli*, 10^4 CFU/mL	Orifice **99** (60 min) Vortex diode **98** (60 min)	[9]
Venturi+ Plasma discharge	P=6MPa *E. coli* 10^7 CFU/mL	Silver wire **46** (1 treatment) HC + Silver electrode **98** (1 treatment)	[58]
Vortex diode	ΔP=1bar for VD *E. coli*, *S. aureus*, 10^4 CFU/mL	AC **3.18** (15 min) AC+0.1% clove oil **51** (15 min) Orifice **32** (15 min), **70** (60 min) Orifice+0.1% clove oil **55** (15 min), **92** (60 min) Vortex diode **~21-44** (15 min), **~84-90** (60 min) VD+0.1% clove oil **~63-86** (15 min), **92** (60 min)	[6]
Vortex Diode	ΔP=1bar for VD *S. aureus*, *Methicillin resistant S. aureus*, *P. aeruginosa*, 10^4 CFU/mL	HC **~21-33** (15 min), **~49-84** (60 min) HC+0.1% peppermint oil **~98-99** (5-10 min) HC+0.05% peppermint oil +aeration **~95-98** (5-10 min)	[7]
Vortex diode+0.1% natural oil	ΔP=1 bar *E. coli* 10^4 CFU/mL	*E. coli* HC **44** (15 min), **90** (60 min) HC+0.1% MG extract **88** (15 min)**, 95** (60 min) HC+0.1% ginger oil **96** (15 min), **98** (60 min)	**Present study**

6.4.5 Mechanistic understanding of the process

6.4.5.1 Philosophy behind selecting plant extract as an additive for hybrid cavitation

Curcuma amada, which is also known as a mango ginger or ambe haldi or aam haldi is traditionally used for medicinal purposes as a herbal medicine in Ayurveda, Unani medicine from centuries and in several food preparations. It is well reported that rhizome is rich source of essential oils, and containing more than 130 active ingredients with biomedical importance. It has antibacterial, insecticidal, antifungal and antioxidant properties [38]. The major chemical components with their biological activity include starch, phenolic acids, volatile oils, curcuminoids and terpenoids like difurocumenonol, amadannulen and amadaldehyde that are important from pharmacological point of view. Ramachandran et al. [59] reported mango ginger's anticancer potential and its action for Glioblastoma cells was reported where *curcuma amada* extract induces apoptosis in glioblastoma cells. Difurocumenonol, one of active component from mango ginger, is important for antimicrobial activity against Gram-positive and Gram-negative bacteria [41]. De et al. [60] reported presence of non-polar terpenes in Indian curcuma species e.g. *C. amada, C. aromatica, C. caesia, C. longa, and C. zedoaria*. Also, the lipophilic curcuminoid helps in killing microorganisms by inhibiting its cellular functioning. *C. amada* has a strong anti-microbial and other biological activity. The other active components may also enhance the disinfection or bactericidal activity by different mechanisms such as inhibition of cell wall synthesis, interference with the permeability of cell membrane, cause membrane disruption, modifying cellular constituents, and cell damage or cell mutation. Chandarana et al. [61] showed the antimicrobial activity of aqueous extract of *C. amada* against *E. coli, B. subtilis, S. aureus*. Many such plant extracts can prove to be useful from health benefits point of view, if appropriately used in the water treatment process and therefore the present study could provide starting point for elucidating use of plant extracts in hybrid cavitation process for water disinfection.

6.4.5.2 Functionality changes

The FTIR spectra of disinfection of water before and after cavitation with natural additives are presented in Figure 6.5 (a) (b) and (c). The different functional groups of natural additives with vibrational frequencies are clearly evident. The FTIR spectra of the oil phase of ginger oil, before and after hybrid cavitation, indicates similarity in wavenumber but difference in intensity of transmittance. The FTIR spectra for the aqueous phase indicated no change in the functional groups before and after hybrid cavitation. The IR band for O-H vibration of alcohol and carboxylic acid group represented in the range of 2500-3300 cm^{-1}, 1700-1750 cm^{-1} interval is for ketone group, the characteristic peak at 1430-1510 cm^{-1} wavenumber for C=C vibration ascribed to benzene group, 1375 cm^{-1} for C-O group, 987 cm^{-1} wavenumber indicated for =CH-H group and 883 cm^{-1} for para benzene functional group. All these functional groups are representing α-gingerol active component of ginger oil. The results of FTIR analysis before and after cavitation showed no indicative change suggesting no formation of byproducts or intermediates.

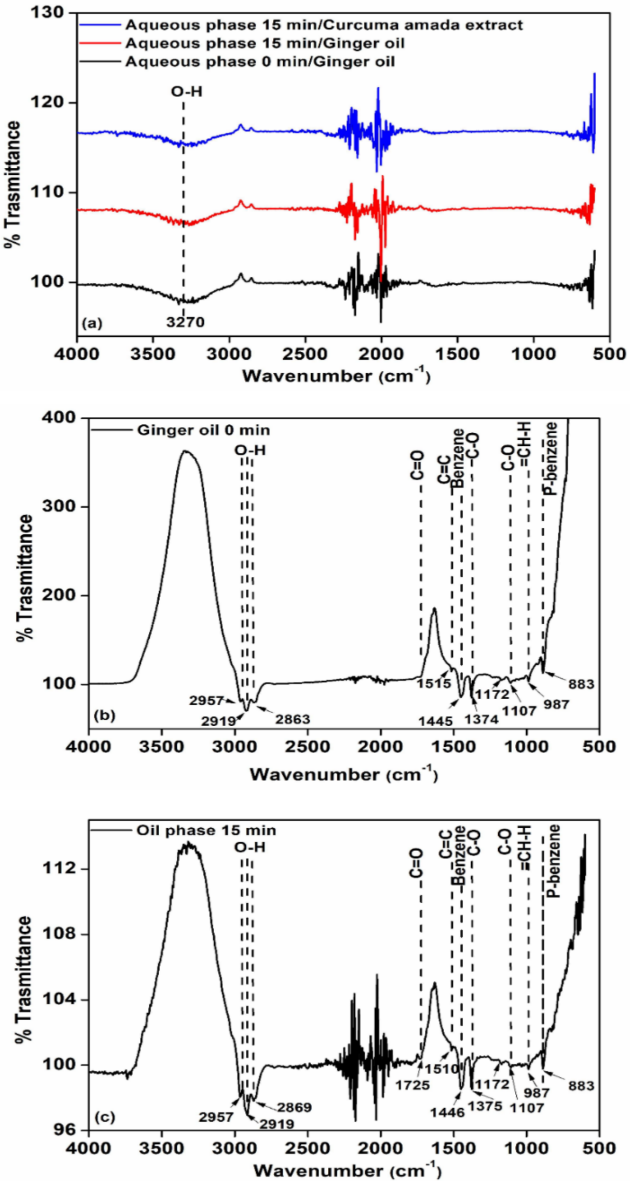


Figure 6.5: FTIR analysis before and after cavitation for the hybrid operation

6.4.5.3 Structural changes

A morphological analysis of bacteria before and after treatment was studied by TEM (Figure 6.6- a, b) and FE-SEM (Figure 6.6 c and d). TEM results indicate intact healthy *E. coli* cells with rod shape, homogenous, smooth surface and visible cytoplasmic contents that get damaged after 15 min of hybrid cavitation treatment. Significant change in shape, size and morphology was observed and damage in the form of cell membrane rupture and leakage of cytoplasmic content due to hybrid cavitation is clearly visible.

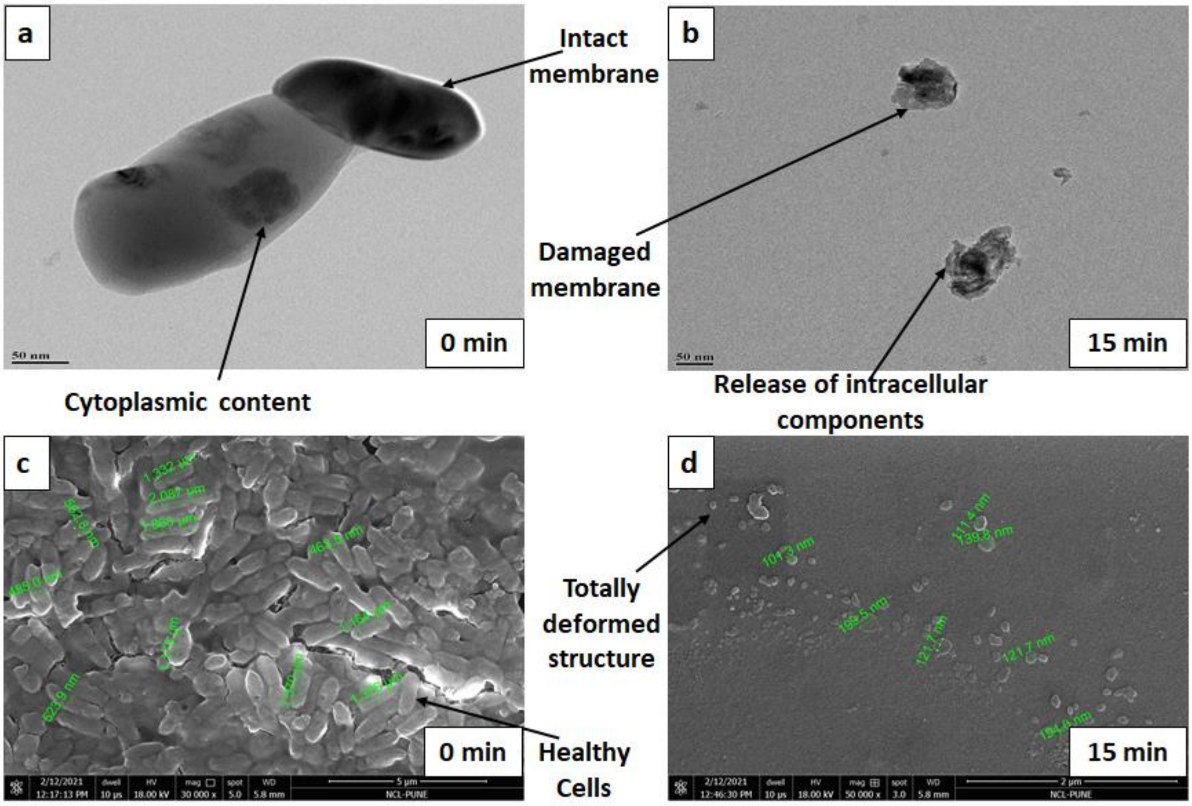


Figure 6.6: TEM analysis for establishing cell destruction

6.4.6 Possible mechanism of disinfection

From the literature studies, it can be deduced that the conventional cavitating devices such as orifice and venturi can impart severe surface damage to the microorganisms but considerably limited cell breakage/cleavage, thereby limiting the overall efficiency. The rotational devices largely effect cell cleavage, rough surface though size reduction and leakage of cytoplasm is not significant[24]. In the present work, hybrid cavitation led to loss of cytoplasm, reduction in size or totally deformed structure, size reduced from 1-2 µm to 100-200 nm as seen from Figure 6.6 (b) and (d). The combined effect of antimicrobial property of natural additives and hydrodynamic cavitation is evident in the form of increased efficiency. Figure 6.7 depicts this plausible mechanism of hybrid cavitation by highlighting contribution of different factors. The results are also consistent with those reported earlier with hybrid method [6,7]. Thus, the extreme conditions of temperature, pressure at the point of cavity implosion, high shear, oxidation or oxidative damage (action of highly reactive hydroxyl radicals) of sulfhydryl group and double bonds of protein components, etc. fragment the cellular content and cell membrane, damage DNA and protein and resulting into cell death. The active components of plant extract and essential oil both have lipophilic properties and permeate the cell wall as well as the cytoplasmic membrane, inducing a loss of membrane integrity in microorganisms [45]. The active component such as gingerol from ginger oil and curcuminoids and difurocumenonol from mango ginger extract can react with phospholipids of outer cell membrane thus altering the cell permeability and denature its protein thereby causes cell death.

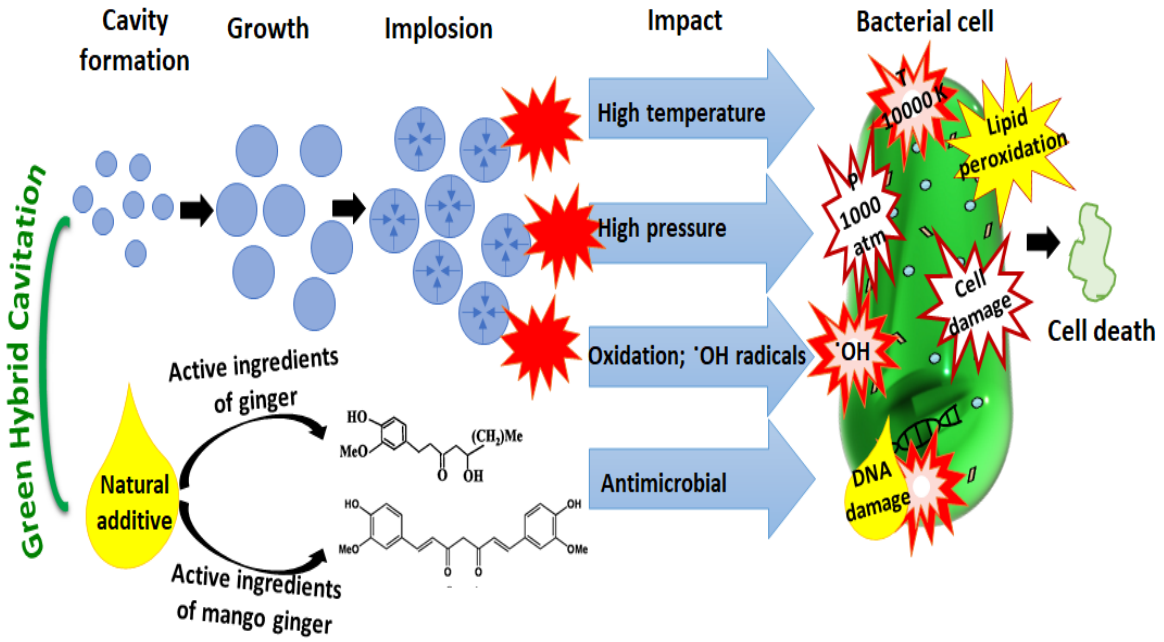


Figure 6.7: Plausible mechanism for destruction of E. coli by green hybrid cavitation process

6.4.7 Energy and cost considerations

The energy requirement is evaluated for different reactor configurations and is compared in Figure 6.8. Filho et al.[28] reported 99.97% of disinfection in 30 min with orifice as a cavitation device and copper coil in cooling system at a pressure of 10 MPa, requiring 12.28 kWh energy. Its disinfection performance is higher than that reported earlier by Chand et al. [26], Arrojo et al. [25] and Jancula et al. [62]. Chand et al. [26] reported disinfection efficiency of 75% using liquid whistle reactor with ozone and required energy of 15.3kWh, pressure of 500 psi and 3h of time of operation. Arrojo et al. [25] reported % disinfection of 91.1 for venturi and 32.7 for orifice in 2h under 18KWh energy. and Jancula et al. [62] reported 99% of disinfection with venturi with 350 kPa discharge pressure, 18 min of time with 18 kWh energy.

In recent reports on rotor-stator type of devices reported by sun et al. [63,64] obtained higher or similar disinfection efficiency of 100% of disinfection in 4-14 min of operation with rotational speed of 4200 rpm, 1.4 m^3/h and required low energy (0.748-3.48 kWh) compared with other rotational based hydrodynamic cavitation reactor reported by [65],[19] and conventional laminar flow based cavitation reactor. Sarc et al. [21] and Cerecedo et al. [19] reported 99.95% (9025 rpm, 150 min) required energy 0.7 kWh and 100% (2400 rpm, 7.8 min) required energy 0.65 kWh respectively. The drawback of the use of rotor and stator type of device is that with increase in the flow rate above 1.4 m^3/h and high rotational speed of 4200 rpm, the disinfection performance decreases; flow rate of 2.6 m^3/h showed no disinfection. Further, very high temperatures above 90 ^0C essentially indicate disinfection by way of boiling.

On the other hand, Jain et al. [9], utilizing rotational flow-based reactor, vortex diode reported more than 98% of disinfection with only 2 bar of pressure drop within 60 min of time of operation corresponding to only 0.0872 kWh energy requirement. Mane et al. [7] developed hybrid cavitation using natural oils that resulted in drastic reduction in time for disinfection with high disinfection efficiency and more than 99% of disinfection using 1 bar pressure drop for a very low 0.0025-0.005 kWh of energy requirement was obtained. In the present study, the disinfection efficiency for cavitation with ginger oil is 98% in 60 min of time with 0.03 kWh and first time reported the energy required for cavitation with mango ginger is 0.03 kWh with 95% (60 min) disinfection. However, since 100% disinfection is desired, more investigations on plant extracts are essential.

The hybrid cavitation methodology using vortex diode appears to provide substantial advantages and low cost. In addition, the vortex-based cavitation reactors are commercially available and have easy scale up [66]. Therefore, in view of the techno-economic feasibility, no harmful by-products and possible health benefits of plant extracts, the hybrid cavitation process can provide alternative solution to conventional disinfection methods.

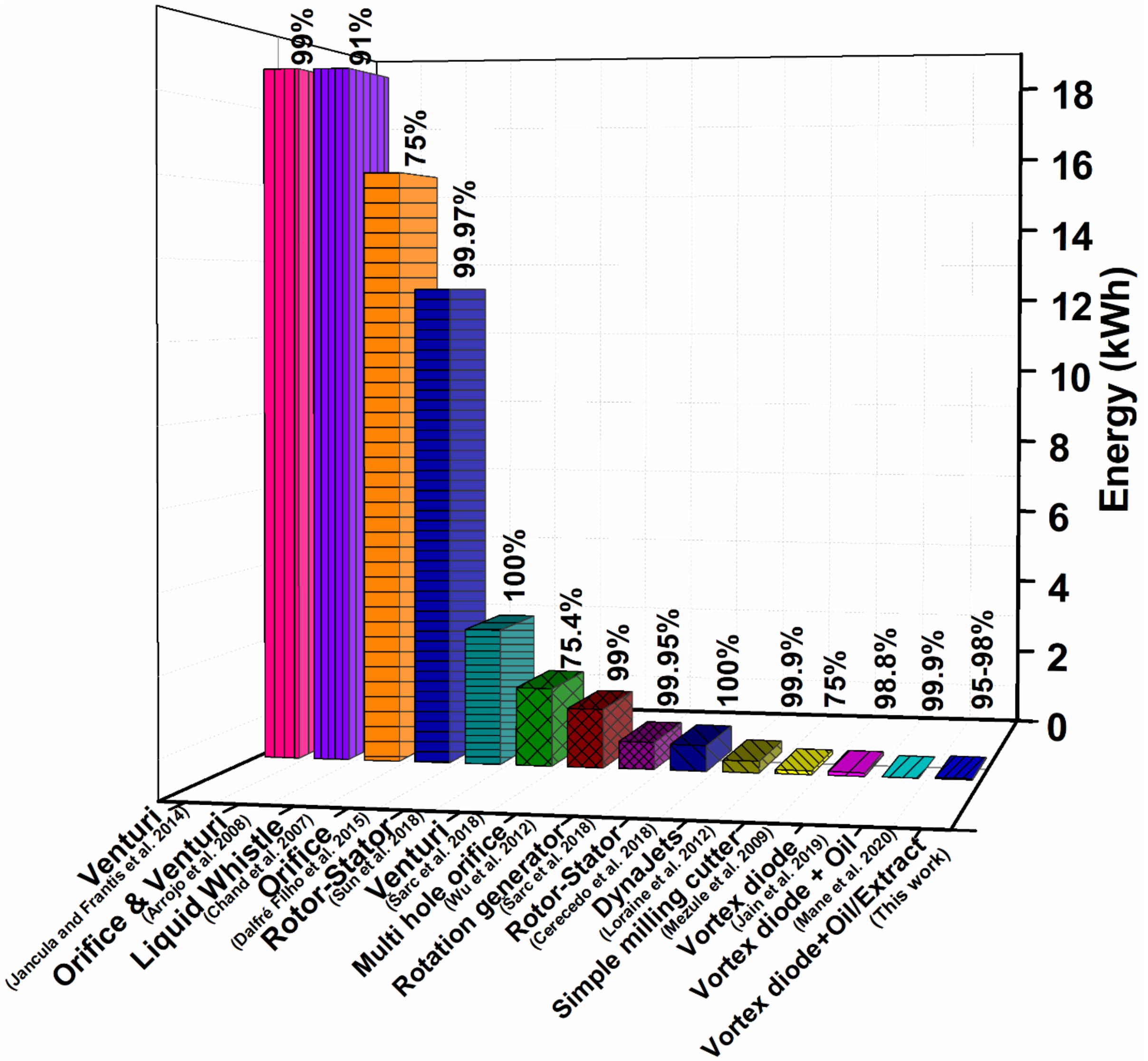


Figure 6.8: Comparison between energy required for different processes

The cavitation yield per volume treated (CFU/mL/J) can be obtained as:

$$\text{Cavitation yield/volume treated} = \frac{(C_0 - C)}{(\Delta P \times Q \times t)}$$

The cavitation yield per volume treated for hydrodynamic cavitation along with ginger oil and hydrodynamic cavitation along with mango ginger extract at time 15 min is 7.2 and 3.42 CFU/mL/J.

Further, the cost of treatment can be obtained using the following equation:

$$Cost\ of\ treatment/m^3\ of\ water = \frac{n\Delta P P_E}{36\eta}$$

Where, n is number of passes can be obtained as $n = \frac{(Q \times t)}{V}$

For vortex diode,

The flow rate (Q) measured at ΔP=1 bar is 720 LPH and volume treated is 20 L.

At 15 min of time of operation (t), the number of passes (n) obtained is 9. Assuming the cost of electricity is P_E is 10 Rs/kWh and pump efficiency (η) is 0.66, the cost of treatment per m^3 of water is 3.8 Rs/m^3 (0.052 \$/m^3).

In view of disinfection efficiency less than 100% using plant extract (0.1%), it is required that either the process can be evaluated at higher dose of plant extract or be combined with natural oils so that 100% disinfection can be realized. It may be noted that the cost of disinfection would get slightly modified, increased, in such eventuality. Since, this work only provides the proof of concept for the use of plant extracts with limited examples, many other plant extracts/ extraction methods/different plant parts need to be investigated where possibly high disinfection can be obtained.

6.5 Conclusions

The present study, for the first time, reports useful application of plant extracts in the hybrid cavitation process for disinfection of water and for providing possible health benefits. Followings are the main findings of the proposed green hybrid cavitation technology.

1. The process effectively eliminates gram negative *E. coli* at significantly higher rates.
2. Ginger oil was found to be effective natural oil and in case of plant extract, mango ginger extract was found to be most effective than other plant extracts.
3. A very small concentration of 0.1% of natural additive (both ginger oil and mango ginger extract) can effect disinfection, though increased amount of plant extract may be required for obtaining high disinfection efficiency.
4. The rate constant values can be improved to the extent of ~3 times for hydrodynamic cavitation with mango ginger extract, ~5 times for hydrodynamic cavitation with ginger oil and ~8 times for acoustic cavitation with mango ginger extract.
5. The lipophilic nature of antimicrobial active ingredient of natural additive is responsible for increased cell permeability and cell denaturation.
6. A plausible mechanism suggests synergistic effect of both natural additive and hydrodynamic cavitation and the rupture of cell wall/cell death can be due to various factors such as oxidation effect, high shear, localized heat/thermal effect and antimicrobial property of active constituents.
7. The energy requirement is significantly low indicating techno-economic feasibility.

The hybrid cavitation technology with plant extract or natural oils can be useful alternative to existing conventional processes for disinfection of water and more investigations into application of different plant extracts are required.

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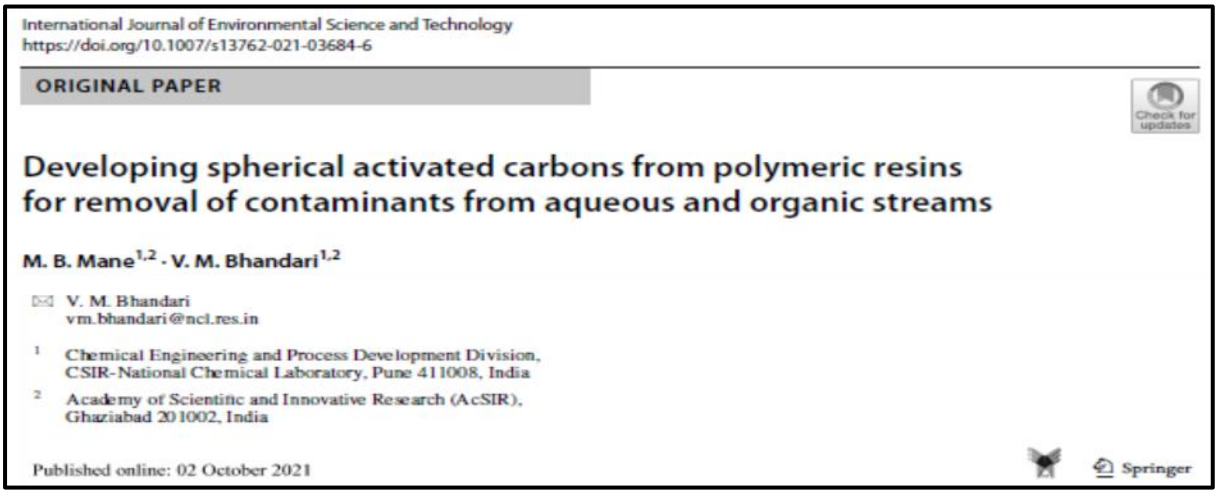
International Journal of Environmental Science and Technology
https://doi.org/10.1007/s13762-021-03684-6

ORIGINAL PAPER

Developing spherical activated carbons from polymeric resins for removal of contaminants from aqueous and organic streams

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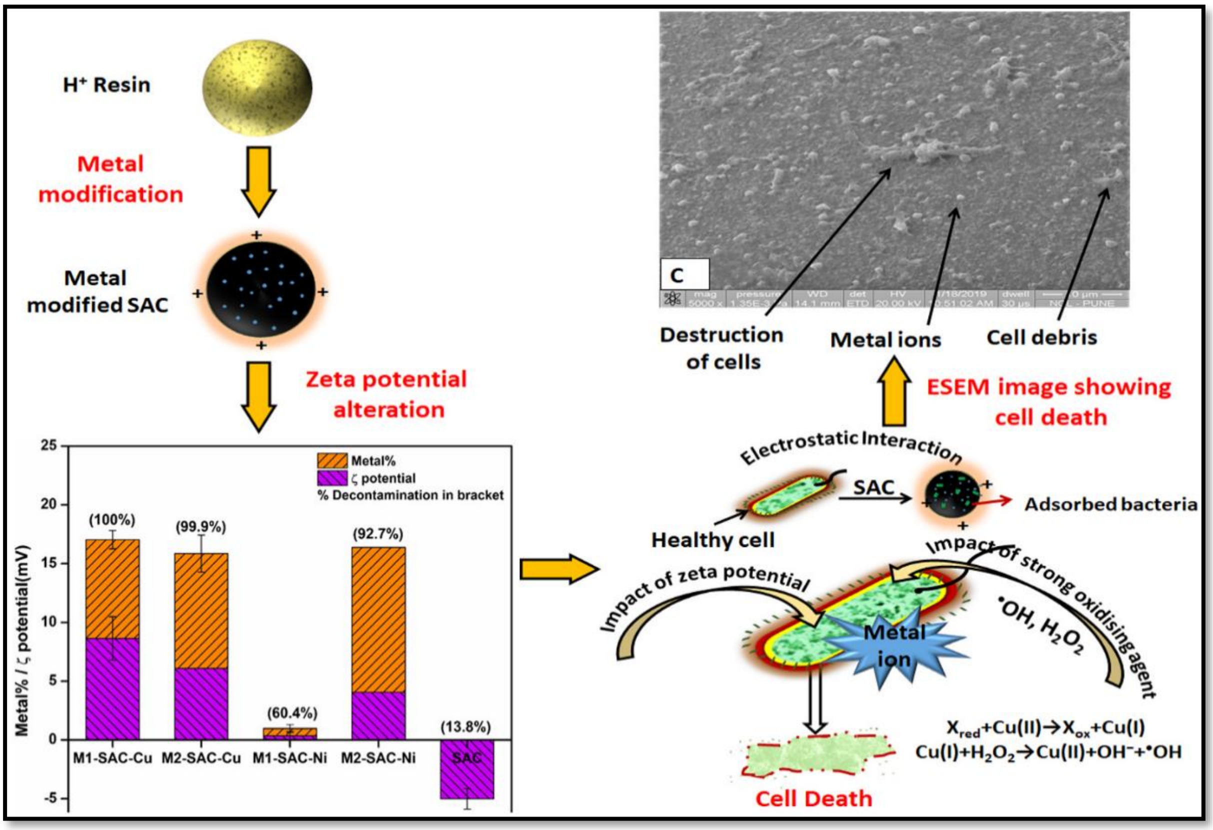
Chapter 7



Maya B. Mane, Vinay M. Bhandari. Developing Spherical Activated Carbons from Polymeric Resins for Removal of Contaminants from Aqueous and Organic Streams *International Journal of Environmental Science and Technology* (2021). https://doi.org/10.1007/s13762-021-03684-6

Chapter 7

Developing Spherical Activated Carbons from Polymeric Resins for Removal of Contaminants from Aqueous and Organic Streams

Abstract

Spherical activated carbons from polymer resin were developed with metal modifications, before/after carbonization using copper and nickel, for gradation of zeta potential (-5.01 to 8.64mV) and high metal loading (up to 12.3%). The materials provide improved removal of various contaminants from aqueous and organic streams- removal of bacteria from water and sulfur removal from fuel. The metal modified spherical activated carbons were highly effective for removal of both gram-negative, *E. coli* and gram-positive *S. aureus* bacteria. The copper modified spherical activated carbon could eliminate 99.9-100%, both bacterial content proving efficacy in water disinfection with a very high rate ~1.33×10^5 (CFU/ml.s). The zeta potential has significant impact with higher disinfection for high values; ~10-15% disinfection can be improved up to 100% for zeta potential changes from -5 to 8.6 mV. Kinetics of disinfection was studied by accounting for zeta potential in the conventional rate model and efficacy of both the models was compared. The fit of revised model was excellent. The spherical activated carbons can be useful for removal of slightly polar contaminants from organic streams and a high capacity of 12.8, 20 and 28 mgS/g for thiophene, benzothiophene and dibenzothiophene respectively. The developed materials can provide useful applications in the area of environmental pollution control.

7.1 Introduction

Activated carbons are probably the most widely used adsorbents worldwide for a variety of applications- ranging from colour removal to removal of specific chemicals/ metals/ pollutants and so on. In view of huge variations in terms of requirements and usage, most commercial adsorbents are available in various forms, such as powder, granules, spherical, fibres (including nanofibres) etc. and largely in modified form-either physical or chemical modification or both, to suit specific applications. The cost variation in most modified materials is also large, ranging from very cheap material to highly expensive advanced materials. The nature of activated carbon and its application mainly depends on its surface area, pore size/ pore size distribution, and surface properties. Further, nature of carbons is strongly dependent on the origin/source apart from the activation methodology or surface modification. For common applications, carbons with high surface area are generally suitable and can be used based on the commercial data available with the supplier. However, for specific applications pertaining to separations-process or effluent treatment, usually a tailor made adsorbent is required to meet the challenge. This has, therefore, directed research and development for variety of activated carbons with surface modification/ impregnation of metals/ morphology changes to accomplish not just the desired separation, but also for developing techno-economically feasible alternatives to meet precise separation needs. While, the conventional practice for making activated carbons employs natural sources, including naturally available waste, studies on spherical activated carbons, hybrid forms derived from polymers, are less researched compared to conventional carbons and also polymeric adsorbents.

Spherical activated carbon (SAC) can be prepared from synthetic source such as polymeric resins e.g. ion exchange resin. The SAC is expected to have high surface area, high micropore volume and desirable pore size distribution apart from inherent or add-on, functionalities to meet specific adsorption needs, high mechanical strength, wear resistance, provide low pressure drop and high bulk density [1]. The activated carbons can be derived from a large number of varied sources, can have excellent characteristics and can be modified in a number of ways for surface modifications or for addition of functionalities to meet adsorbent applications in aqueous or organic medium- extensively recognized as a versatile materials due to high surface area; wide range of porosity, tunable surface functionalities, stability in acidic medium & low cost. Ion exchange resins are most commonly used for water softening and water deionization. The polymeric resins have excellent surface area and pore structure which can be tailor-made. The ionised forms of polymeric resins have affinity towards ionic species while non-ionic polymeric adsorbents have preference to non-polar species. In the similar way, spherical activated carbons derived from polymeric resins can be useful tailor-made materials to meet demands of specific applications for the ionic or non-ionic application templates by suitable modification prior to carbonization or post-carbonization.

Activated carbons are hydrophobic in nature and metal modifications can suitably alter their applications for the removal of contaminants from both aqueous and organic streams. The framework can be used for housing various metals such as silver that provide disinfecting properties and biomass derived nanocomposites is an emerging research in this regard. Providing safe drinking water at an affordable cost is one of the most critical challenges, especially in developing countries. According to WHO report four out of every 10 people get affected by water borne diseases and United Nation suggests improving water quality as one of the Millennium Development Goals [2]. Water contaminated with fecal material harbours pathogens like *E. coli,* commonly accepted as biological indicator of fecal contamination of water. Apart from *E. coli* there are many other bacterial strains both gram-positive and gram-negative reported as causative agent of various water born disease outbreaks [2]. Chlorination is one of the most common practices used worldwide for drinking water decontamination. Chlorination, though cost effective has a major drawback in the form of generating disinfection by-products, many of these likely to be carcinogenic. Thus, chlorination is considered today as not environment friendly and is being discontinued in some countries. Physical methods like, electrochemical disinfection, ozone treatment are also reported to generate chlorine species and other DBP [3]. Advanced physicochemical method such as hydrodynamic cavitation is gaining more attention for complete removal of gram negative and gram positive bacteria and hybrid cavitation technology by using natural oils having antimicrobial properties as a destructive process by killing the bacteria was recently reported [4,5].

Decontamination by adsorption is significantly safer option in comparison to other chemical and physical treatment process [6],[7], where many a times, physical removal than destructive killing of the bacteria takes place. Yamamoto et al. reported that activated carbons have good affinity toward microorganisms and adsorbed large amount of bacteria [8]. Metals such as silver, copper have the disinfection capacity by killing the microorganisms. Silver nanoparticles, carbon nanotubes and sophisticated graphene are being studied extensively for disinfection of water [6],[9]. Biomass derived nanocomposites, especially using specific source such as *Cassia fistula* for the carbon and metal modifications using specialized techniques are recently reported for improved effectiveness and reduced cost due to low loading of the nanomaterials [10],[11]. These advanced methodologies have been proved largely in laboratory scale studies [12], however the large scale application of these material can increase the processing and operational cost many fold.

In order to understand the role of positive interfacial potential (zeta potential) in disinfection, we have attempted evaluating the antimicrobial impact of copper and nickel by employing copper and nickel modified spherical activated carbons against gram-positive and gram-negative bacteria and found significant disinfection efficiency against pathogenic bacteria in comparison to unmodified SAC with negative zeta potential. The study therefore highlights simple alteration of surface potential leading to significant changes in microbial viability through either physical rupture of cell membrane by depolarization or by enhanced reactive oxygen species (ROS) production. To the best of our knowledge, the kinetics of adsorptive disinfection based on surface potential or zeta potential has not been reported till date. It is also instructive to modify the conventional rate model by accommodating the effect of zeta potential for better fit compared to the conventional rate model.

Contaminant removal from organic streams such as removal of slightly polar sulfur from fuels for ultra-low sulfur fuel is now necessary requirement for petroleum refineries in most countries due to stringent restrictions on the emission of SO_x from combustion of liquid fuels like diesel and petrol. Near zero levels of sulfur are also essential to avoid poisoning of the catalyst in the fuel cell applications [13]. Adsorptive desulfurization can be an useful cost-effective alternative in deep desulfurization application compared to conventional hydrogen based or oxidative operations apart from emerging forms such as biodesulfurization, extractive desulfurization etc. A wide variety of adsorbents have been used for deep desulfurization starting from Activated Carbon [14],[13], alumina, silica based sorbents [15], zeolites [16], metal oxides [17], metal–organic frameworks [18–20], and metal-exchanged and -impregnated activated carbon, zeolite, and mesoporous materials. Hernandez et al. [21] showed that the activated carbon with nickel gave high capacity than activated carbon. Similar results were obtained by Selvavathi et al. [22], Kim et al. [23] and Li et al. [24] also indicated high capacity and selectivity for refractory sulfur compounds on nickel dispersed activated carbon compared to metal dispersed silica, alumina, zeolite and molecular sieve. The incorporation of transition metals such as Ni, Cu, Ag, Zn have the capability to enhance the adsorption of sulfur species from liquid fuels through π-complexation [25,26],[27] and metal-sulfur interaction [28–30]. It is apparent that Ni and Cu have better affinity for refractory sulfur compounds than many other metals. Though a large number of modified carbons were reported for sulfur removal, the capacities and/ or selectivity were not satisfactory, apart from problems with regeneration. The quest for new materials and material modifications is thus imperative to provide improved capacities for sulfur removal at reduced costs[31].

The objective of the present study is to develop different modified spherical activated carbons derived from polymeric ion exchange resin for applications in contaminant removal from aqueous and organic streams. Two specific forms of material modifications, using transition metals nickel and copper, are studied using different forms of carbonization of polymeric resin-before and after metal modification and for obtaining substantially high metal loading apart from varying the zeta potential. The developed materials were evaluated for disinfection of water and desulfurization of fuels - in both, the role of metal modification is most critical. In water disinfection, removal of bacteria, gram-negative *E. coli* and gram-positive *S. aureus*, was studied to obtain specific insight into the extent of disinfection based on zeta potential of the modified material while removal of refractory sulfur compounds such as thiophene (T), benzothiophene (BT) and dibenzothiophene (DBT) in n-octane was investigated. The results are expected to provide further directions in material developments/ modifications, especially for newer applications in sulfur removal and in water and wastewater treatment. The research has been carried out at CSIR-National Chemical Laboratory, Pune, India during 2016-19.

7.2 Materials and Methods

7.2.1 Materials

For disinfection studies, a reference strain of *Staphylococcus aureus* (ATCC-6538) and *E. coli* (ATCC-8739) was collected from National Collection of Industrial Microorganism (NCIM), CSIR-National Chemical Laboratory (CSIR-NCL), Pune.

All the chemicals were AR grade and were obtained from companies of repute; n-octane (99%, Loba), thiophene (≥99%, Aldrich), 1-benzothiophene (≥95%, Fluka), dibenzothiophene (98%, Aldrich), Nickel (II) chloride hexahydrate (≥98%, Sigma Aldrich), Cu $(NO_3)_2.3H_2O$ (≥99%, Sigma Aldrich). A strong acid cation exchange resin, T42H (Thermax Ltd., India) was used as a precursor. Metal modifications were carried out using nickel and copper salts.

7.2.2 Preparation of Spherical Activated Carbon (SAC)

Table 7.1 shows physical properties of cation exchange resin T42H as obtained from the manufacturer. The different types of spherical activated carbons were prepared using two different methods of material modification on the basis of process for incorporation of the metal.

Table 7.1: Physical properties of cation exchange resin T42H

Parameter	Tulsion T42H
Manufacture	Thermax Ltd., India
Ionic group	H^+ strong acid cation exchange resin
Particle size distribution	0.3 to 1.2 mm
Physical form	Amber colour spherical beads
Dry weight exchange capacity	4.7 meq/g
Moisture content	45%
Stability Maximum Temperature	140^0C
pH range	1-14
Matrix structure	Polystyrene copolymer

7.2.2.1 Method-1: SAC- Material modification prior to carbonization

The resin was pretreated, prior to carbonization or metal modification, using the standard procedures of washing with distilled water, and two cycles of cation/ anion exchange [32]. The dry weight capacity of the resin was found to be 4.7 meq/g. Metal modification of the resin was done by exchanging H^+ ion of resin with Ni^{2+} ion of 0.5M Nickel chloride hexahydrate solution and Cu^{2+} ion of 0.5M Cupric chloride Nitrate solution respectively using column technique. Complete conversion to Ni^{2+} form or Cu^{2+} form was ensured. The metal modified resins are referred as Ni-T42H and Cu-T42H.

The spherical activated carbons using this method were produced by carbonizing the metal modified resins in an inert atmosphere of nitrogen in a temperature-programmed horizontally aligned electrical tube furnace (Nabertherm, Germany). On the basis of preliminary studies on different temperatures, all the modified carbons were made using the carbonization temperature of 600 ^{0}C and carbonization time of 3h (ramping to 600 ^{0}C at the rate of 5 ^{0}C/min and constant temperature for 3h in the presence of nitrogen at the flow rate of 100 L/hr). The different types of activated carbons are referred to as SAC, M1-SAC-Ni and M1-SAC-Cu, where M1 refers to Method 1 or material modification 1 of SAC before carbonization.

7.2.2.2 Method-2: SAC- Material modification after the carbonization

In method 2, the metal modification was carried out after the production of spherical activated carbon using the process as described above- by carbonizing the polymeric resin in an inert atmosphere of nitrogen in a temperature-programmed horizontally aligned electrical tube furnace (Nabertherm, Germany) at 600 ^{0}C for 3 h. A known quantity of spherical activated carbon (5g/100ml) was dispersed in 1M Nickel chloride hexahydrate. The mixture was stirred well, pH adjusted to alkaline pH of 9 by drop wise addition of 1M NaOH. The solution was then heated under reflux at 150 ^{0}C for 4h under nitrogen atmosphere. The modified SAC was washed with distilled water and centrifuged to remove excess metal salt. The product was dried and then reduced under a nitrogen flow at 600 ^{0}C for 3 h in the tube furnace to complete metal modification process. For copper modification, the same procedure was followed using 1M cupric nitrate solution. The two types of metal impregnated spherical activated carbon are referred as M2-SAC-Ni and M2-SAC-Cu, where M2 refers to Method 2 or material modification 2 of SAC preparation and modification after the carbonization.

7.2.3 Material characterization

The morphologies of the carbon samples and elemental analysis were studied by Environmental Scanning Electron Microscope (ESEM) (FEI Quanta 200 3D dual beam having a resolution of 3 nm at 30 kV with tungsten filament (W) as the electron source under vacuum mode) and transmission electron microscope (TEM) (FEI, Tecnai G2 20 S-Twin having LaB6 filament as the electron source) equipped with an energy dispersive X-ray spectrometer (EDS) (EDAX, AMETEK) used for finding the elemental composition as well as selected area electron diffraction (SAED) pattern and detailed morphological study. The BET surface area, pore diameter and pore volume are determined by Autosorb-1 (Thermo Scientific) using nitrogen adsorption. Barrett-Joyner-Halenda (BJH) method was used to determine the cumulative pore volume and average pore diameter. The pyrolysis process was investigated by thermo gravimetric analysis (TGA) and differential scanning calorimeters (DSC) analysis (Mettler Toledo TGA/SDTA851e model). Powder X-ray diffraction patterns of carbon samples were recorded using X'Pert Pro PAN analytical XRD with Cu Kα radiation (λ=1.542 Å) in 2θ range of 10-80^0. The functional groups of the activated carbon were characterized by Fourier transform infrared spectroscopy (FTIR-2000, Perkin Elmer). The nickel and copper concentrations was measured by means of an atomic absorption spectrophotometer (Thermo Fisher Scientific iCE 3300). The zeta potential was measured by 90 Plus nanoparticle size and zeta potential analyzer (Brookhaven Instruments, USA).

7.2.4 Experimental

7.2.4.1 Water disinfection studies

In the present study, the five different SACs (SAC, M1-SAC-Ni, M1-SAC-Cu, M2-SAC-Ni and M2-SAC-Cu) were tested for antimicrobial property against *E. coli* and *S. aureus* using 0.5% of adsorbent loading and 20 ml of bacterial solution.

For the experiment, a loop of bacterial colony was inoculated in the 50 ml of nutrient broth solution. The flask was incubated at 37 ^{0}C with constant shaking at 120 rpm (Spectralab orbital shaker Incubator). The optical density of culture was reached to 2.5 at 600 nm (1 O.D = 1 × 10^9 cells/mL). The known concentration of bacteria was diluted and 20 ml of bacterial suspension having cellular concentration of ~ 10^7 was used for further experiments. Spherical activated carbon adsorbent was kept suspended in a flask containing nutrient medium inoculated with bacteria. 100µl of sample from the reaction flask was drawn after 2h to spread on nutrient agar plate. After a period of 24h of incubation and 37 ^{0}C of temperature, the number of colonies on the plates was counted. The colony forming unit (CFU) was calculated by using following equation,

$$CFU = \frac{Number\ of\ colonies \times Dilution\ factor}{Volume\ incubated}$$

Where the dilution factor is the reciprocal of the dilution in which the plate count was taken and volume incubated was 100µl.

Antibacterial efficiency of the materials was represented as percentage of decontamination of bacteria which was calculated using the initial bacterial count (CFU/ml) at the time of incubation and the final bacterial count after 2h of incubation with materials.

7.2.4.2 Adsorptive desulfurization studies

Adsorption equilibrium studies were carried out using model fuels of thiophene, benzothiophene and dibenzothiophene in n-octane solvent having known predetermined initial sulfur concentration and adding known amount of adsorbents, equilibrating for a period of 16 h, at ambient conditions (28±1 ^{0}C). The activation of the adsorbent was carried out at a temperature of 200 ^{0}C for 4 h prior to use. The analysis of the initial and residual sulfur concentration after adsorption was done by using Total sulfur analyser TN-TS 3000 (Thermo Electron Corporation, Netherlands) and Gas chromatograph (Agilent 7890A) equipped with CPSil 5CB for sulfur as column (30 m x 320 µm x 4 µm) in conjunction with flame photometric detector (FPD) with Helium as a carrier gas, flow rate of 2 ml/min, split ratio of 10:1, Injector temperature of 250 ^{0}C, injection volume of 0.2µL and total analysis time of 25 min. The oven temperature was ramped at 20 ^{0}C/min from 40 ^{0}C to 100 ^{0}C and at 60 ^{0}C/min from 100^{0}C to 230 ^{0}C. Reproducibility of the experimental results was checked and was found satisfactory.

Adsorption equilibrium studies were typically carried out using adsorbent dose of 0.1 g and 20 ml model fuel containing known concentration of sulfur in n-octane (sulfur from Thiophene, Benzothiophene and Dibenzothiophene) in the concentration range of 50-500 ppm. Samples were equilibrated using Spectralab HM8T orbital shaker with a shaking speed of 120 rpm at ambient conditions for minimum 8h to 24h. The sulfur content was analysed before and after the equilibrium. The amount adsorbed per gram of adsorbent at equilibrium (q_e, mg/g) was calculated by using the following equation:

$$q_e = \frac{(C_0 - C_e) \times V}{m}$$

Where C_0 and C_e (mg/L) are the initial and equilibrium concentrations of sulfur, respectively; V (L) is the volume of solution and m (g) is the weight of adsorbent.

7.3 Results and Discussion

The results on the characterization of the materials are discussed first along with the implications for the two applications- water disinfection and sulfur removal from fuels.

In order to make proper spherical activated carbons by carbonization of polymer resins, it is essential to know the thermal behaviour of the polymer and degradation. Figure 7.1 depicts TGA curves of the strong acid cation exchange resin T42H (Figure 7.1a), its nickel exchanged form (Figure 7.1b) and copper exchanged resin (Figure 7.1c), in the temperature range from room temperature to 900 ^{0}C in presence of nitrogen. The polystyrene ion exchange resin gets thermally decomposed in two stages as seen from the major weight loss behaviour. A low temperature thermal decomposition up to 300 ^{0}C includes water loss at ~100 ^{0}C and loss of ion exchange group with the lowest bond energy i.e. sulfonic acid group (~260 kJ/mol) having decomposition temperature 200-300 ^{0}C. The stable line indicates stabilization in new structure after initial decomposition until high temperature where complete polymer structure collapses. The second stage of decomposition incorporates high temperature thermal decomposition above 300 ^{0}C wherein straight chain moiety of the polymer matrix (~330-370 kJ/mol) having decomposition temperature 350-400 ^{0}C gets decomposed and finally the benzene ring moiety (~480 kJ/mol) having decomposition temperature 380-480 ^{0}C is decomposed [33],[34]. The thermal behaviour of resin in Figure 7.1 (a) and (b) is quite similar, however, Figure 7.1 (c) indicates significant difference due to the influence of copper on thermal degradation process of the resin, largely through its catalytic action which enhances the thermal degradation of resin also making more porous structure.

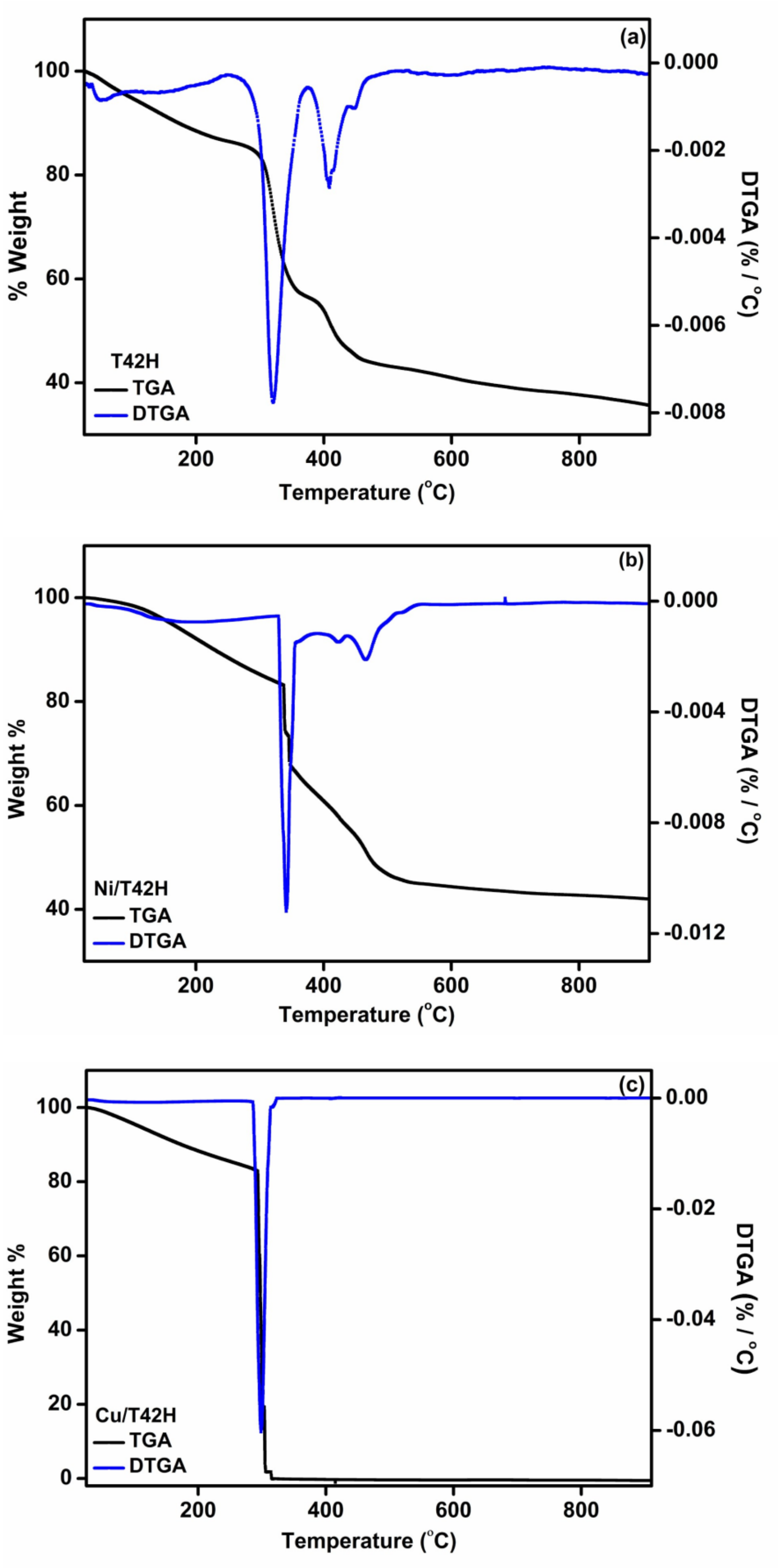
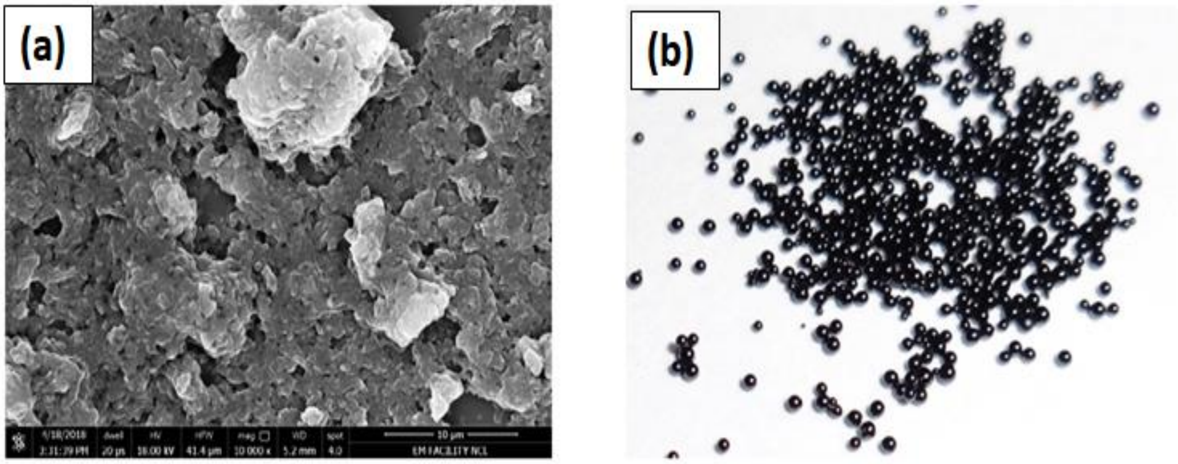


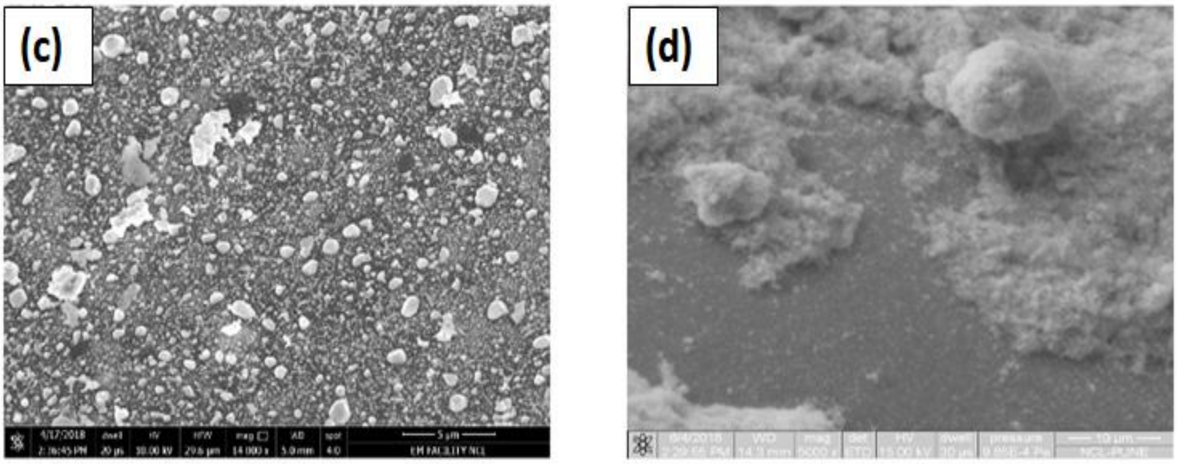
Figure 7.1: TGA analysis: (a) Resin T42H (b) Nickel exchanged resin Ni-T42H (c) Copper exchanged resin Cu-T42H

The surface morphology has important role in developing the newer materials. The metal incorporation is confirmed by the ESEM and FESEM images which clearly indicated the presence of copper and nickel metal ions (Figure 7.2). The spherical activated carbon, without any modification showed simple morphology with few cavities on the surface revealing the large amount of mesoporosity (Figure 7.2 (a)). Figure 7.2(b) is a digital photograph of spherical activated carbon (SAC), showing good spherical shape with smooth surface. The modified adsorbents have heterogeneous surface with rough texture and wide range of porosity due to presence of metal and thermal/physicochemical treatment. The presence of elements such as C, O, Ni or Cu in SACs from EDX analysis indicated small to large variations in different types of spherical activated carbons. The Atomic Absorption Spectrophotometer results on the metal content indicated presence of nickel to the extent of 0.63 and 12.3% in M1-SAC-Ni and M2-SAC-Ni respectively as compared to initial nickel modified resin containing 5.11% Ni. Similarly, the modified SACs were found to have copper content of 8.4 and 9.8% in M1-SAC-Cu and M2-SAC-Cu respectively as compared to copper modified resin containing 8.8% Cu. It is evident that the M1 modification methodology (ion exchange prior to carbonization) for Nickel indicated significantly lower metal content in the modified form whereas, for copper loading, both M1 and M2 methods gave somewhat similar metal loading, though, again here ion exchange prior to carbonization failed to provide more metal incorporation into the matrix compared to post carbonization metal modification of the resin.

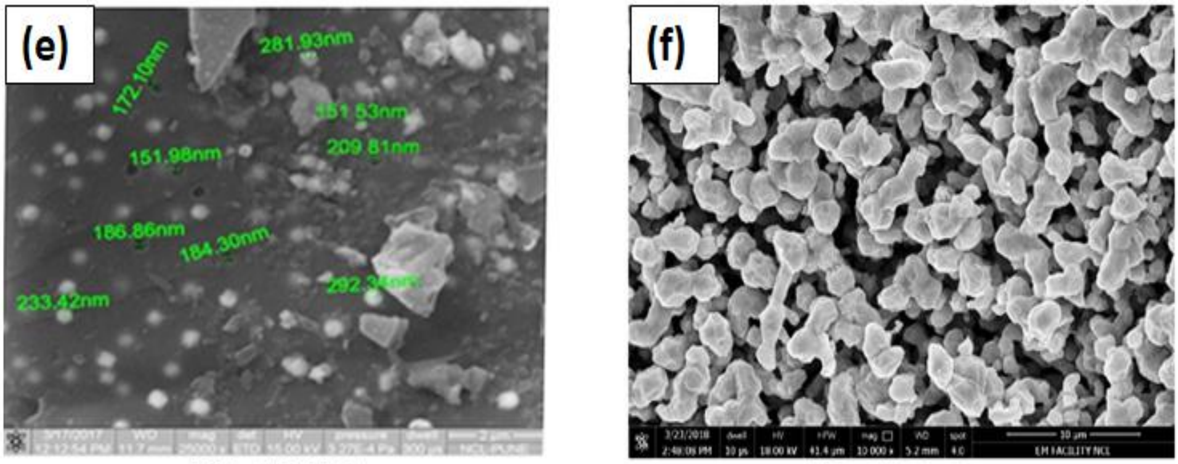
The results of ESEM EDX for different Spherical activated carbons confirmed the differences due to the two methods of metal incorporation as seen from the morphology of the surface and different inherent metal content. The high temperature of carbonization is important in surface modification for the reasons of pore volume changes. The morphology of M1-SAC-Cu (Figure 7.2(e)) shows white dots of copper in the nanometer (nm) range evenly distributed in spherical activated carbon matrix although this type of metal incorporation was not observed in the case of M1-SAC-Ni (Figure 7.2(c)). Therefore, the selection of metals is important for modification through ion exchange process. For metal modification after carbonization of the resin, formation of heterogeneous surface in place of plain surface of SAC was observed which implies more favourable metal bonding on the rough surface as shown in Figures 7.2(d) and 7.2(f). The extent of metal loading has important bearing in adsorption process and in disinfection of water.



SAC



M1-SAC-Ni M2-SAC-Ni



M1-SAC-Cu M2-SAC-Cu

Figure 7.2: Material Characterization: (a) ESEM: SAC, (b) Photograph of SAC, (c) ESEM: M1-SAC-Ni, (d) ESEM: M2-SAC-Ni, (e) ESEM: M1- SAC-Cu and (f) ESEM: M2-SAC-Cu

For the adsorbents, the surface area and pore characteristics are crucial from the point of view of both equilibrium capacity and for rates. It was observed (Table 7.2) that copper modified spherical activated carbons M1-SAC-Cu, M2-SAC-Cu have higher BET surface area (393.3 m^2/g and 150.2 m^2/g respectively) in comparison with the surface area of nickel modified spherical activated carbons M1-SAC-Ni, M2-SAC-Ni (6.2 m^2/g, 117.2 m^2/g respectively) and unmodified spherical activated carbon SAC (65.0 m^2/g). All spherical activated carbons have an average pore diameter, more or less uniform ~1.5 to 5 nm, on the lower side in the range of 2 to 50 nm, corresponding to mesoporous structure. The high metal content in the modified materials apart from surface characteristics are important for removal of pollutants.

Table 7.2: Surface characteristic and porosity of developed adsorbents

Adsorbent	**Surface area (m^2/g)**	**Average pore diameter (nm)**	**Total pore volume (cc/g)**
SAC	64.983	4.016	0.0652
M1-SAC-Cu	393.262	1.473	0.145
M1-SAC-Ni	6.209	3.2	0.008
M2-SAC-Cu	150.167	5.014	0.188
M2-SAC-Ni	117.177	5.008	0.146

The N_2 adsorption-desorption isotherms along with Barret–Joyner—Halenda (BJH) pore size distribution plots are shown in Figure 7.3. The isotherm of SAC displays type I pattern with absence of hysteresis loop according to IUPAC classification and is a highly microporous. All other modified spherical activated carbon show typical IUPAC type IV pattern with the presence of a H4 type of hysteresis loop and are associated with narrow slit like pores in the sample with significant amount of mesopores [35,36].

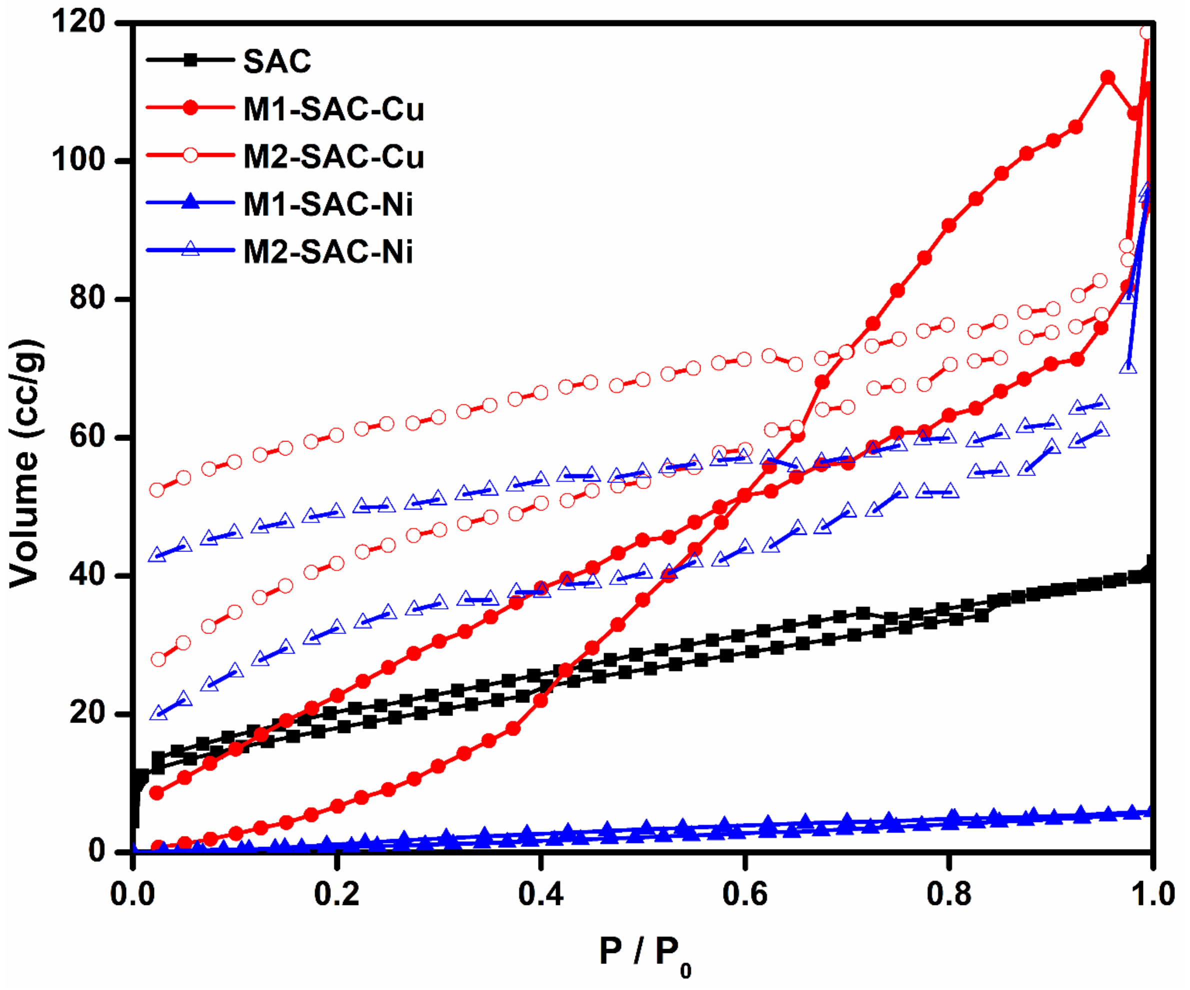


Figure 7.3: Nitrogen adsorption–desorption isotherms of Spherical Activated Carbons

The Fourier transform IR spectroscopy (FTIR) analysis of different materials are presented in Figure 7.4. The results provide identification of functional groups in the materials before and after modification process.

As seen from Figure 7.4, the peaks from 675 to 1000 cm^{-1} indicate C-C stretching vibration. The peak at 525 cm^{-1} indicates Cu-O stretch of strong bonding between the metal ions and the oxygen containing functional groups [37]. High intense bands between 1000 and 1260 cm^{-1} indicate C-O stretching of alcoholic, ether and carboxylic groups. The peaks at 2220 cm^{-1} and 3021cm^{-1} can be attributed to C-H and O-H groups stretching vibration. The broad absorption band at around 3104 cm^{-1} corresponds to O-H stretching vibration of the surface hydroxyl groups. The stretching band of C=C at 1542 cm^{-1} indicates presence of aromatic ring. The peak at 1122 cm^{-1} indicates C-O stretching of COOH and O-H stretching of alcoholic, phenolic and carboxylic groups. The absorption peaks at ~400-870 cm^{-1} indicates Ni-O and Ni-O-H stretching of strong bonding between the metal ions and the oxygen containing functional groups [38].

FTIR spectra showed that copper and nickel modified spherical activated carbon have presence of oxygen containing functional groups (OH, COOH, C-O, Ni-O, Cu-O etc.) which can play an important role in water disinfection and sulfur removal.

XRD result of SAC (Figure 7.5) showed a combination of amorphous and crystalline surface of two broad peaks of carbon at C (002) and C (101) planes (JCPDS Card No. 75-1621) at 21.9^0. There is presence of Nickel oxide and nickel ions in nickel-doped spherical activated carbon samples which is confirmed by intense and prominent peak of Ni at 010, 111, 200 and 220 planes (JCPDS card no. 88-2326) for M1-SAC-Ni and M2-SAC-Ni and small intensity peak of NiO at 220 (JCPDS card no. 44-1159) indicated Ni partly converted into NiO during activation/carbonization. The intense peak of Cu in M1-SAC-Cu sample at 111, 200 and 220 planes (JCPDS card no. 85-1326) and CuO peaks of M2-SAC-Cu predominately indicated at 111, 111, 112, 202, 020, 202, 113, 311, 220, 311 and 222 planes (JCPDS card no. 80-1916).

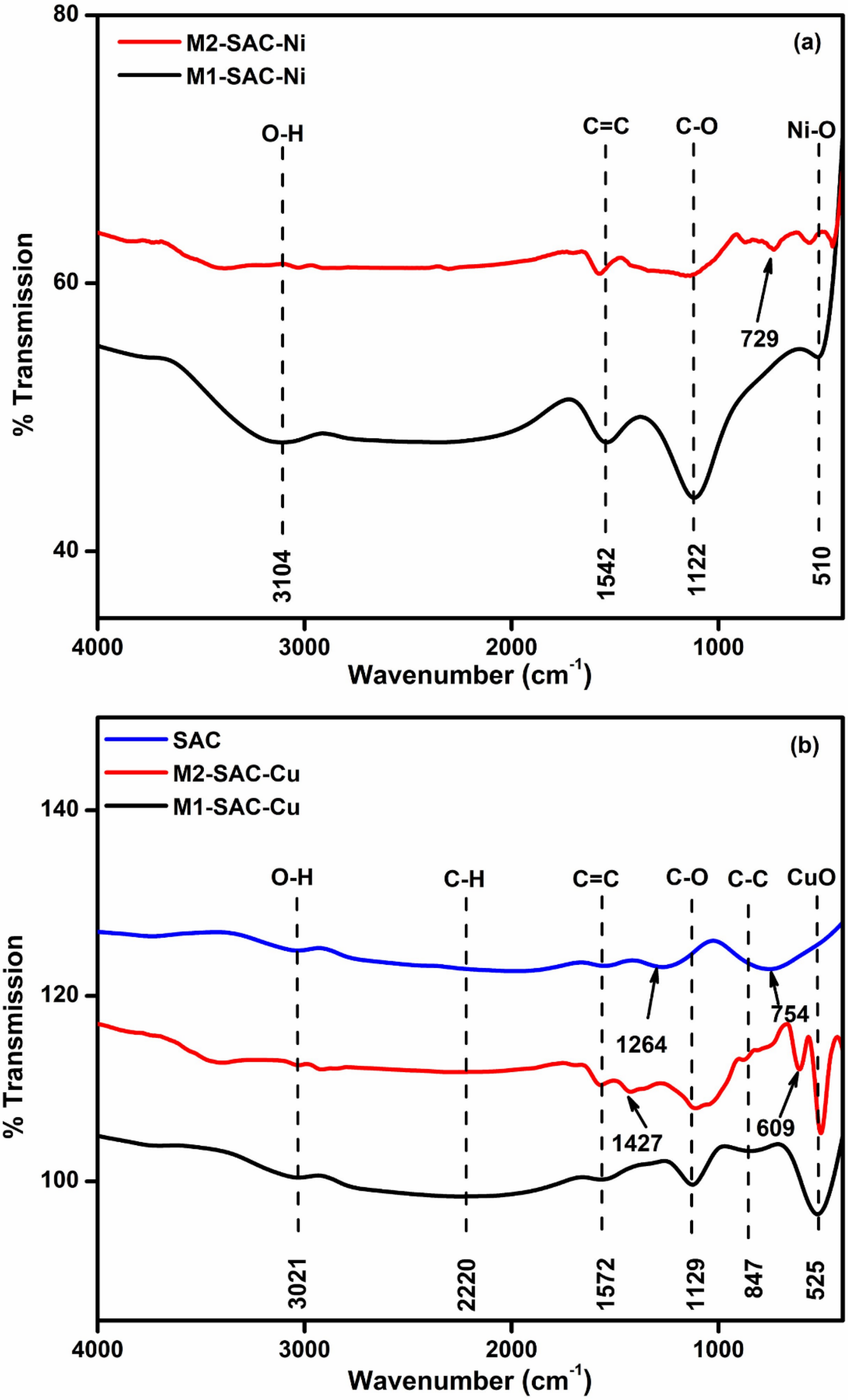


Figure 7.4: Fourier transform infra-red (FTIR) Analysis: (a) M1-SAC-Ni and M2-SAC-Ni (b) SAC, M2-SAC-Cu and M1-SAC-Cu

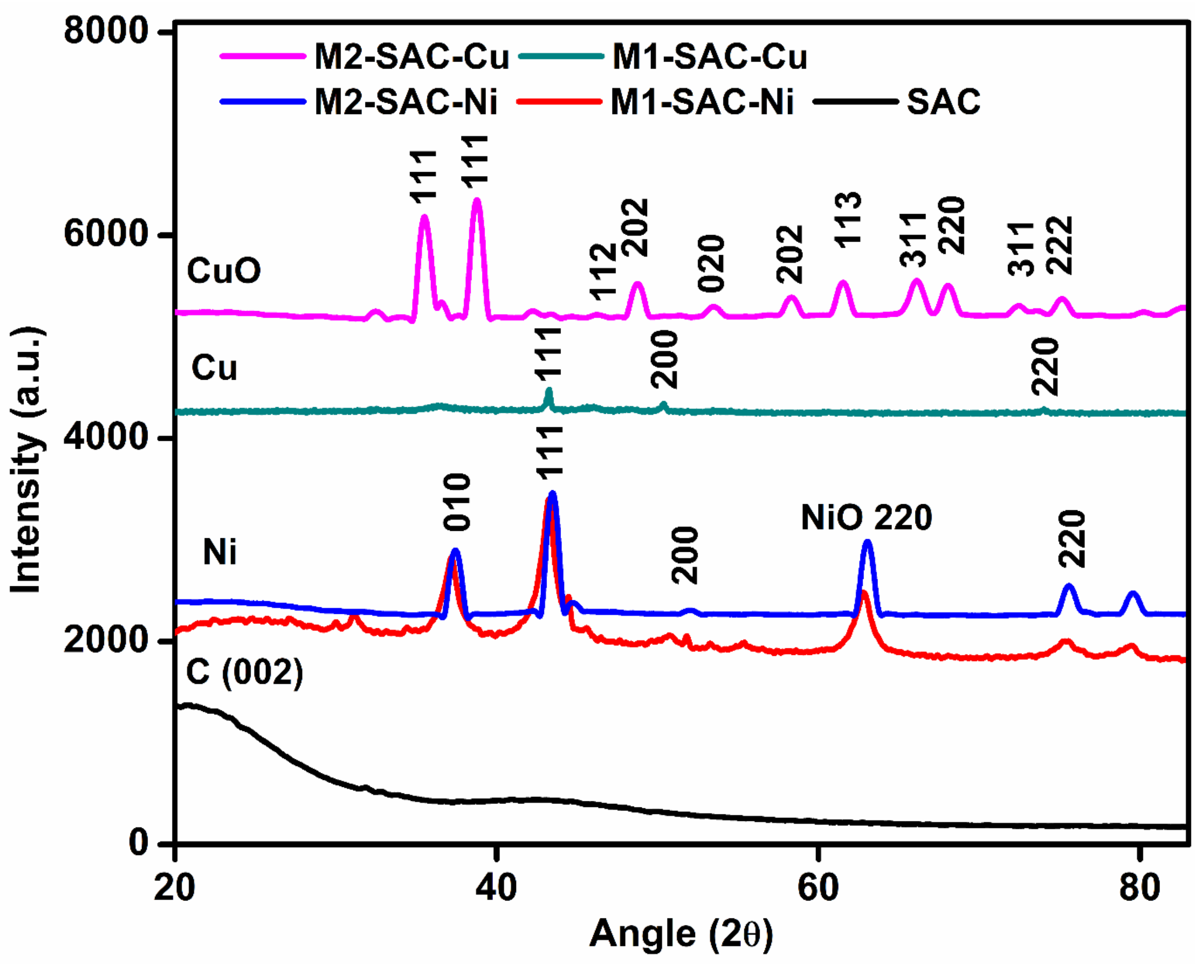


Figure 7.5: XRD analysis of spherical activated carbons

7.3.1 Evaluating spherical activated carbons for disinfection of water

Metals such as copper and silver are known to assist in disinfection of water. Based on the knowledge, many metal nanomaterials, nanocomposites or metal modified adsorbents have been reported, many of which have limitations in terms of efficiency, ease of operation, handling and therefore not suitable for large scale operation. Spherical activated carbons, using metal modifications, can be used similar to that of ion exchange resins for water treatment and hence are suitable for commercial applications provided issues with respect to efficiency of disinfection are addressed. The objective is to remove pathogenic bacteria not by way of only adsorption but by eventually destroying them to make water safe for drinking-the desired limit of total coliforms organisms in the drinking water is zero.

The metal modified SACs act in different ways in disinfecting water. There is inhibition to microbial multiplication by nickel and copper ions present in metal modified SACs through charge neutralization of –SH groups present in the cell wall. The studies on antimicrobial activity of different metal modified SAC revealed effective removal of *E. coli* and *S. aureus*.

The extent of decontamination for the two microbial contaminants, *E. coli* and *S. aureus* in terms of reduction of bacterial colonies of CFU/ml after 2 h of adsorption treatment using SACs is shown in Figure 7.6. It was observed that copper modified SACs were most effective with close to 100% decontamination for both *E. coli* and for *S. aureus* (100% and 99.93% for M1-SAC-Cu and M2-SAC-Cu respectively for *E. coli* and 99.8% for *S. aureus*). The excellent performance of the developed materials is attributed to copper and its high loading on the surface that provides effective interactions. Further, an interesting factor in terms of high positive zeta potential (~8.64mV) is believed to be responsible for the significantly increased efficiency in disinfection. The copper modified SACs inhibit the metabolism and/or damage the protective membrane of the cell wall consequently resulting in cell death. The nickel modified adsorbents have comparatively lower efficiencies and M2-SAC-Ni demonstrated disinfection efficiency of ~93% for *E. coli* and ~76% for *S. aureus*, whereas M1-SAC-Ni had only ~60 % disinfection with *E. Coli* and ~65% disinfection for *S. aureus* possibly due to low Ni content apart from lower values of zeta potential (0.35mV). The SAC without any modification showed a very little disinfection to the extent of ~14% for *S. aureus* and ~10% for *E. coli* and had negative zeta potential (-5.01 mV).

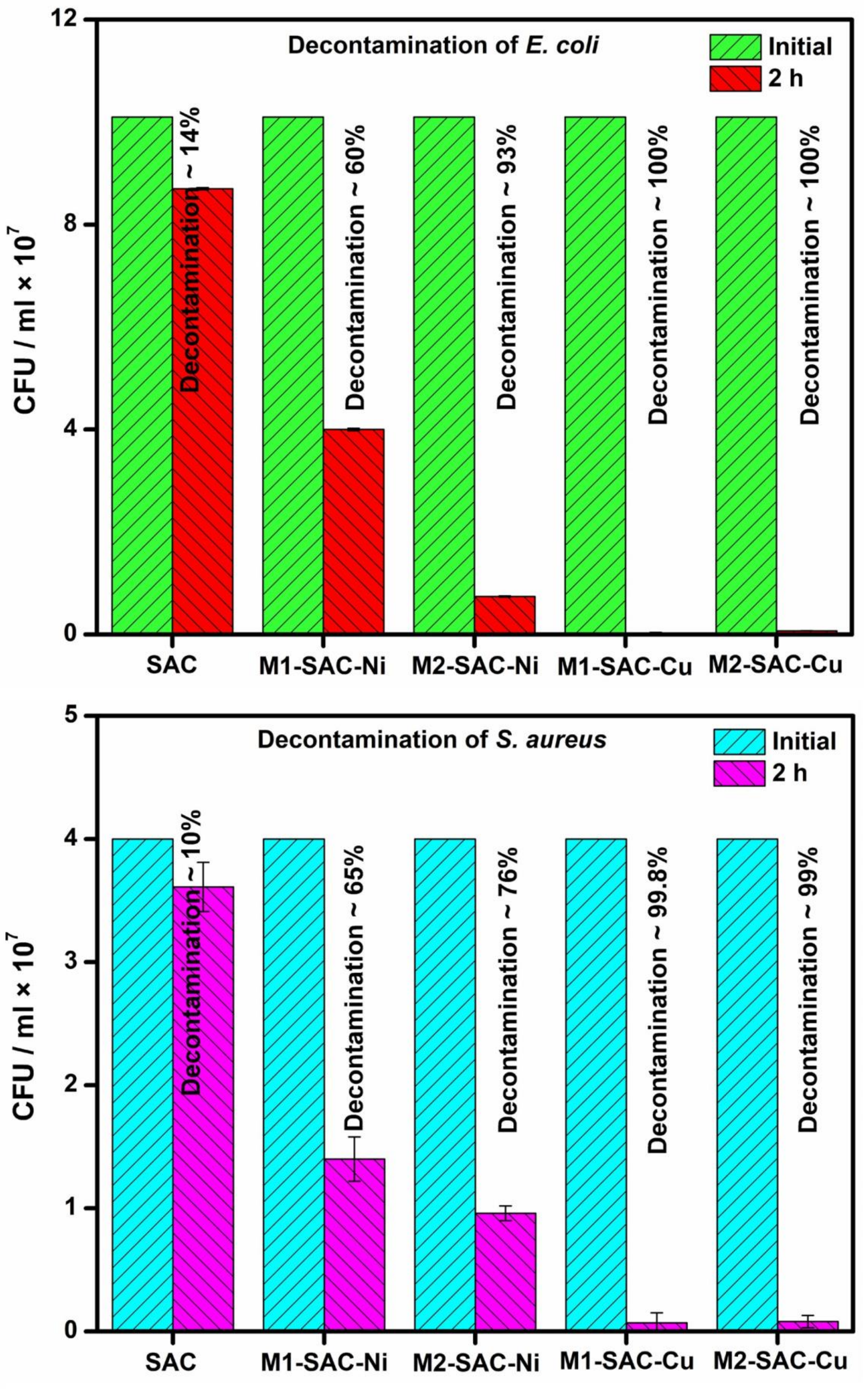


Figure 7.6: Disinfection performance of different adsorbents

7.3.2 The role of zeta potential in disinfection

The surface charge of the bacteria, viruses has often been interpreted by the zeta potential measurements. Zeta potential (ζ), here, can be expressed as an electrochemical property of the surface of bacterial cells or particle/nanoparticles which represents the surface charge or potential at the shear plane of the electrical double layer on all sides of a cell or particle/nanoparticles in solution and is measured in millivolts [39]. The electrostatic interaction between the surface charge of cells and ions of opposite charge is an important aspect of disinfection [39]. In general, the net surface charge for most bacteria is negative and is balanced by oppositely charged counter ions present in the surrounding media. The interaction between the bacterial surface and various disinfecting agents of the type metal or specific functionality on the adsorbent matrix begins due to electrostatic interactions, impacting zeta potential and may subsequently alter cell surface permeability leading to cell death.

Arakha et al. (2015) reported the average zeta potential values for the untreated *E. coli* and *S. aureus* as −23.6 and −18 mV, respectively and evaluated effect of both positive and negative zeta potential ZnO nanoparticles on bacterial cell suspension. The positively charged ZnO nanoparticles (ζ 12.9mV) were found to interact effectively with the negative bacterial membrane and the effect was dependent on the concentration of ZnO nanoparticles (250-500 µg/mL) and time (8-9 h for 250 µg/mL and 4-5 h for 500 µg/mL) for the destabilization of the membrane [40]. Similarly, it was reported that ZnO nanofluids (0.25 g/L) with 9.4 mV zeta potential can affect 86% disinfection in 10h [41]. A large number of such nanoparticles were researched for disinfection of water [42],[43],[40]. Weak antimicrobial activity of the negative value of zeta potential of AC is enhanced by treatment with silver bromide in silver nitrate solution and higher antimicrobial activity for Ag-AC also noted [42]. The zeta potential values are higher for nanoparticles alone than nanoparticle modified adsorbent. The antibacterial activity can be correlated to the zeta potential. Apart from disinfection application, the effect of zeta potential on removal of different pollutants such as dyes and pesticides was reported in the literature [44,45],[46]. Garg et al.[46] suggested enhanced imidacloprid degradation due to positive zeta potential in neutral pH compared to other pH conditions.

In the present study, a small dose of 0.5% of adsorbent was found sufficient to alter the zeta potential in both *E. coli* and *S. aureus*, and 100% decontamination was obtained within 2 h. In view of the literature reports as above, the present study has exhibited significant enhancement in values of zeta potential of SAC after metal modification; consequently, in the antimicrobial activity of metals such as copper and nickel. As a result, complete disinfection could be obtained due to higher values of zeta potential for both gram-negative as well as gram-positive bacteria. The zeta potential measurement for all adsorbents was carried out in neutral pH 7.

From Figure 7.7, it is evident that the nature of metal modification significantly impacts the decontamination behaviour and therefore finding the most suitable metal modification is crucial from commercial application point of view. From the data on different metal modified SACs, it can be seen that copper modified SAC is the most effective adsorbent compared to nickel modified adsorbents or unmodified SAC. The value of zeta potential ζ in mV for M1-SAC-Cu is 8.64, significantly higher than M2-SAC-Cu (6), M1-SAC-Ni (0.35), M2-SAC-Ni (4.06) and unmodified SAC (-5.01). Thus, higher value of zeta potential/surface tension implies increased disinfection efficiency.

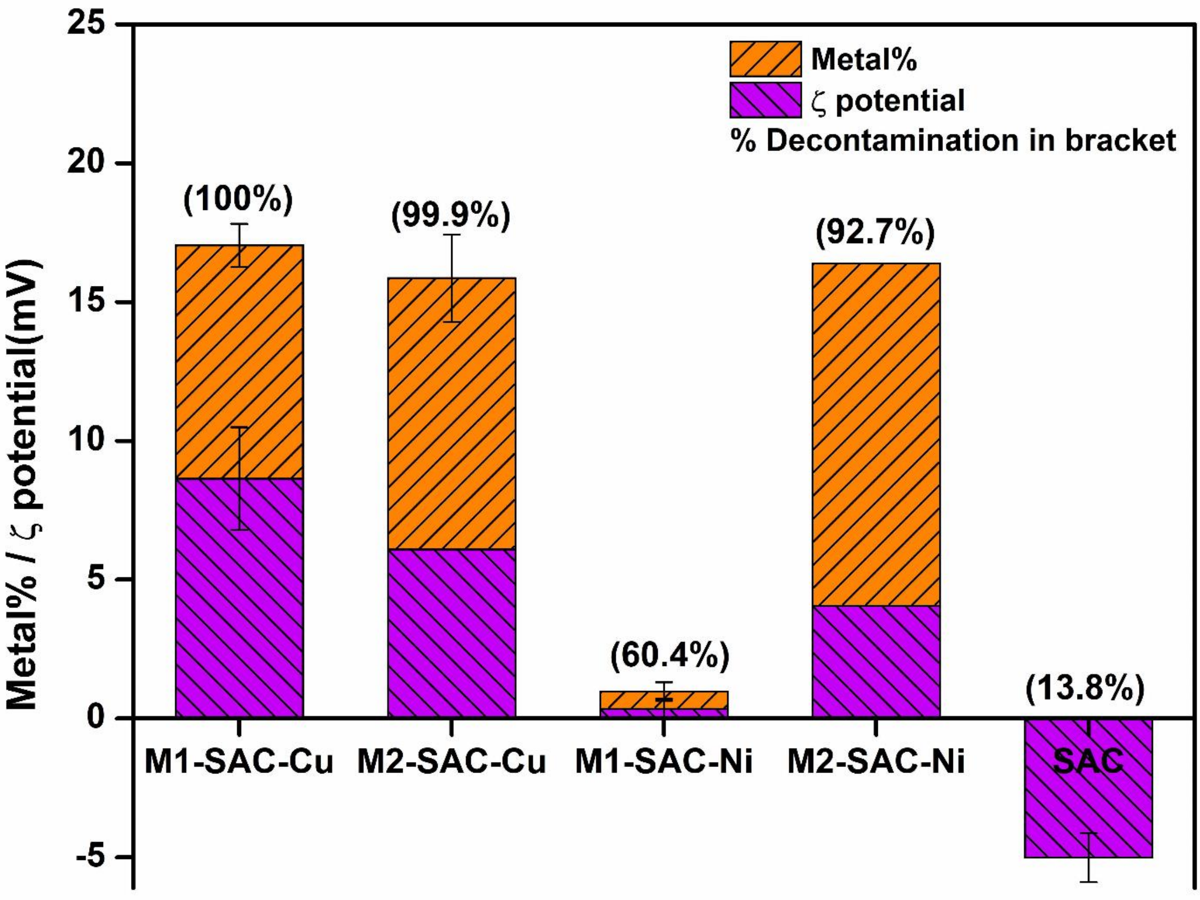


Figure 7.7: Zeta potential corresponding to metal % for different adsorbents and *E. coli* removal

The results of modified spherical activated carbons in this work have potential to provide techno-economic alternative, especially compared to various nanomaterials and nanocomposites reported for disinfection of water. Carbon nano structures such as SWCNT and MWCNT have strong inhibitory action in short exposure time on soil microbial activity and to enhance the effectiveness of CNT, the CNTs are modified by different metals or metal oxides [47]. It was also reported that the TiO_2/MWNTs/Si surface (annealed at 400 ^{0}C) displayed great photo-catalyst activities and killed virtually all *E. coli* cells upon contact (in 60 min) [48]. Further, the functionalized CNT–ZnO inactivated 100% of *E. coli* cells within 10 min of UV-visible light illumination, while the un-functionalized CNT–ZnO could inactivate only 63% of the microorganisms under the same conditions under the visible light illumination [49]. A number of different transition metal modified adsorbents such as Fe, Al, Ag, Mg etc. have been studied for disinfection of bacteria. Though, silver is a promising metal in this regard and is widely reported since it can eliminate microbes in less time, according to WHO [50], silver is not recommended as a primary disinfectant in drinking water supplies. Compared to many metals, the present work showed effective and complete elimination in 2 hours and with only 0.5% adsorbent loading (Table 7.3).

It is evident that there are no systematic studies on the evaluation of progression in the zeta potential values for materials, spherical activated carbons or for its application in the water disinfection. Some of the comparable work in this regard is listed in Table 7.3 for different materials which clearly highlights the consistent and important results of this work pertaining to material development, systematic evaluation of the effect of zeta potential and possible application potential in the real life, in terms of starting material (polymeric resin waste), material development (Spherical activated carbons), modification methodology apart from recommendations for most suitable material for disinfection.

Table 7.3: Comparison of % disinfection for various adsorbents

Bacteria/ Initial Concentration	**Adsorbent**	**% disinfection**	**Ref.**
E. coli; 10^7 CFU/mL.	AC: Modification using aluminium hydroxyl chloride; nano AgBr- AC	99.99% > 6 log reduction	[42]
E. coli 10^3 CFU/mL	Plasma treated AC impregnated with silver Nanoparticles	~100% in 10min for plasma/AC-Ag in 60 min for untreated AC-Ag	[51]
E. coli and *S. aureus* 100 CFU/mL	Spherical activated carbon coated with zinc oxide	100% in 24 h	[8]
E. coli 10^4 CFU/ml	Ag/AC by wet impregnation	~100% in 25 min	[52]
E. coli and *S. aureus* 10^6-10^7 CFU/mL	Mg/SAC at 1000^{o}C	in 6 hr for *E. coli* ~70% for *S. aureus* ~25%	[53]
E. coli 2 × 10^7CFU/mL	Ag/zeolite	~99-100% in 40 min	[54]
E. coli 10^7 CFU/mL	Fe nanoparticles (NP) Nanocomposite NC-450; (SPION + CF) NCm1;(SPION + CF + C. butter)	NC-450 59% NCm$_1$ 82% NP 91% in 1h	[11]
E. coli 10^7 CFU/mL	Fe nanoparticles (NP), Nanocomposite NC-ALV-450 and NC-OCT-450 10 mg/mL	NP 91% NC-ALV-450 90% NC-OCT-450 96% in 1h	[10]
E. coli and *S. aureus* 10^7 CFU/mL	SAC, M1 and M2-SAC-Ni, M1 and M2-SAC-Cu 5 mg/mL	SAC 14% M1-SAC-Ni 60% M2-SAC-Ni 93% M1-SAC-Cu 100% M2-SAC-Cu 100% in 2h for *E. coli* SAC 10% M1-SAC-Ni 65% M2-SAC-Ni 76% M1-SAC-Cu 100% M2-SAC-Cu 100% in 2h for *S. aureus*	This Work

7.3.3 Kinetics of disinfection

A revision of model based on zeta potential (ζ) for adsorption is attempted in this work and the same is applied for evaluating representative kinetic data of the present study.
The kinetics of disinfection using the conventional rate model requires:

Pseudo-first order equation

$$\boldsymbol{\frac{dC}{dt} = -kC} \qquad (1)$$

Where $\boldsymbol{k}$ is disinfection rate constant

The concentration of microorganisms C can be obtained by assuming $\boldsymbol{\zeta = \zeta_0}$,

$$\boldsymbol{ln\left(\frac{C}{C_0}\right) = -kt} \qquad (2)$$

Modified Model:

Since zeta potential changes with respect to time, the modified rate model requires:

$$\boldsymbol{\frac{d(C\zeta)}{dt} = -kC\zeta} \qquad (3)$$

and,

$$\boldsymbol{ln\left(\frac{\zeta}{\zeta_0}\right) + ln\left(\frac{C}{C_0}\right) = -kt} \qquad (4)$$

Where, $\boldsymbol{C_0}$ is the initial concentration of bacteria (**CFU/ml**), t is the time for disinfection (**min**), ζ_0 is zeta potential at time **t=0** and ζ is zeta potential at any time **t**.

The values of the rate constants and rates of disinfection using the conventional model and modified rate model are provided in Table 7.4 (Initial CFU/ml, 10.1×10^7) for the initial solution zeta potential value of -17.01 mV and after disinfection with modified activated carbons M1-SAC-Ni and M1-SAC-Cu, zeta potential values of solution are -15.36 mV and -8.81 mV respectively.

Table 7.4: Rates of disinfection using conventional and revised model

Adsorbent	% Disinfection	Rate constant, k (s^{-1}) × 10^4	Rate of disinfection CFU/(ml.s) (conventional model)	Rate constant, k' (s^{-1}) × 10^4	Rate of disinfection CFU/(ml.s) (zeta potential model)
SAC	13.9	0.2	1948		
M1-SAC-Ni	60.4	1.29	9069	1.43	10068
M2-SAC-Ni	92.7	3.63	19674		
M1-SAC-Cu	100.0	25.6	129270	26.54	133884
M2-SAC-Cu	99.9	10.06	50860		

The fit of the rate models are shown in Figure 7.8. The conventional rate model showed a large deviation from the experimental data and the deviation is predominant for M1-SAC-Cu. In contrast to conventional rate model, the zeta potential rate model fits well. It was observed that the values of zeta potential impact the prediction of the rates by about 11% in the case of M1-SAC-Ni and 3.6 % in the case of M1-SAC-Cu. The revised kinetic model incorporating zeta potential clearly highlights importance of its application as against conventional model. Arakha et al. [40] reported that there is decrease in zeta potential value of bacterial solution corresponding to decrease in percentage bacterial cell viability in their study on effect of bacterial cell viability and surface zeta potential of *B. subtilis* and *E. coli* cells; observing decrease from ~-19 to -9 mV for *B. subtilis* and for *E. coli* from -24 to ~-8.5 mV. Thus, the kinetics need to incorporate effect of zeta potential, in general, for accurately predicting rates of disinfection, especially where significant difference exists in zeta potential values.

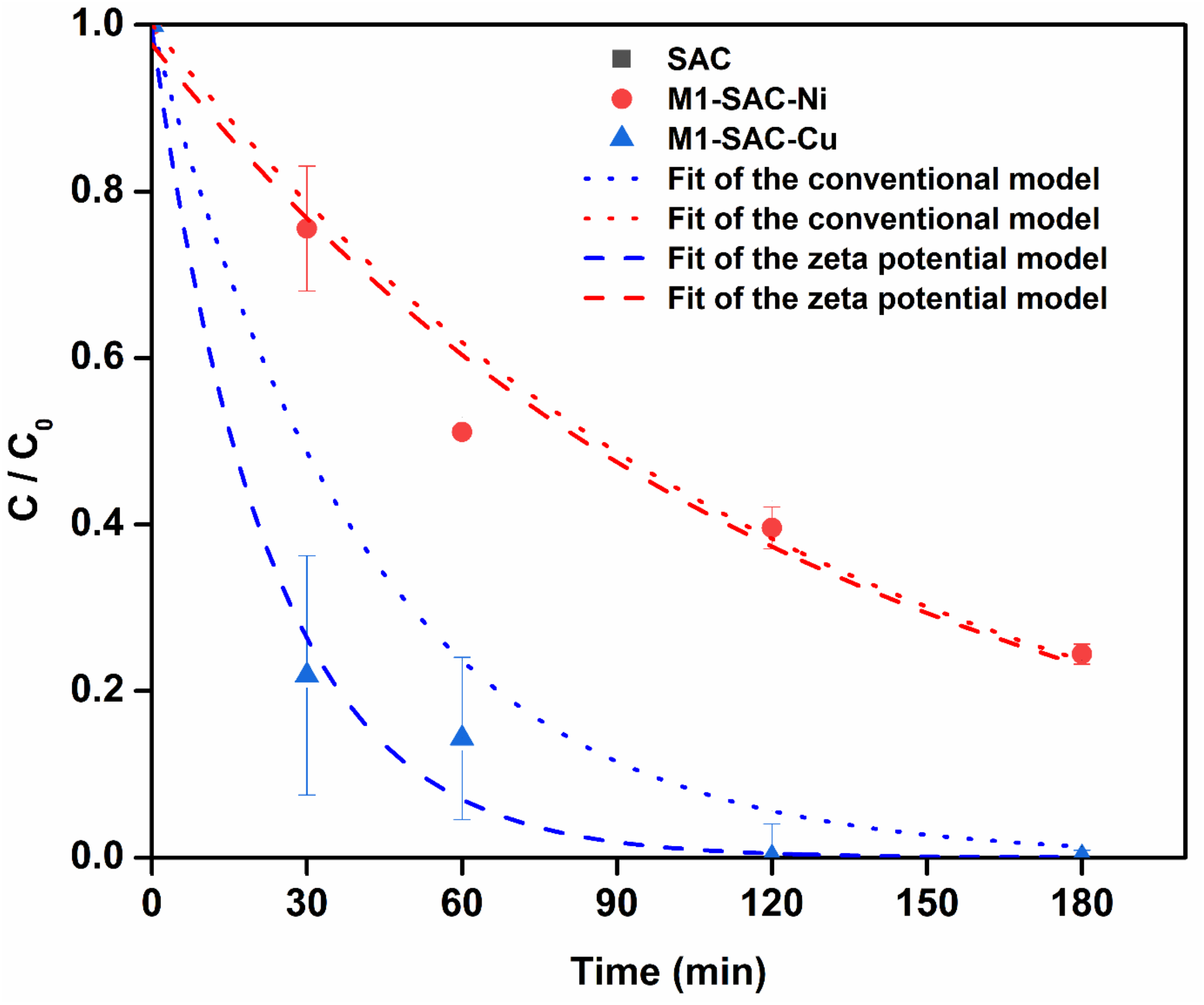


Figure 7.8: Effect of adsorbent and conventional rate model vs zeta potential rate model

7.3.4 Mechanism of disinfection

In order to completely destroy the bacteria, the following factors are believed to contribute in the disinfection process:

1. Zeta potential effect: Disruption of membrane integrity by powerful electrostatic forces between microbial outer surface and adsorbent, leading to oxidation of the membrane.
2. Generation of the reactive oxygen species due to interaction of metal ions and oxygen functional group present on the adsorbent which may directly harm bacteria and/or indirectly prompt DNA destruction.

3. Presence of metallic particles that are introduced into adsorbent can contribute through their antibacterial activities.

A possible disinfection mechanism for the modified spherical activated carbons prepared from two different pathways is shown in Figure 7.9.

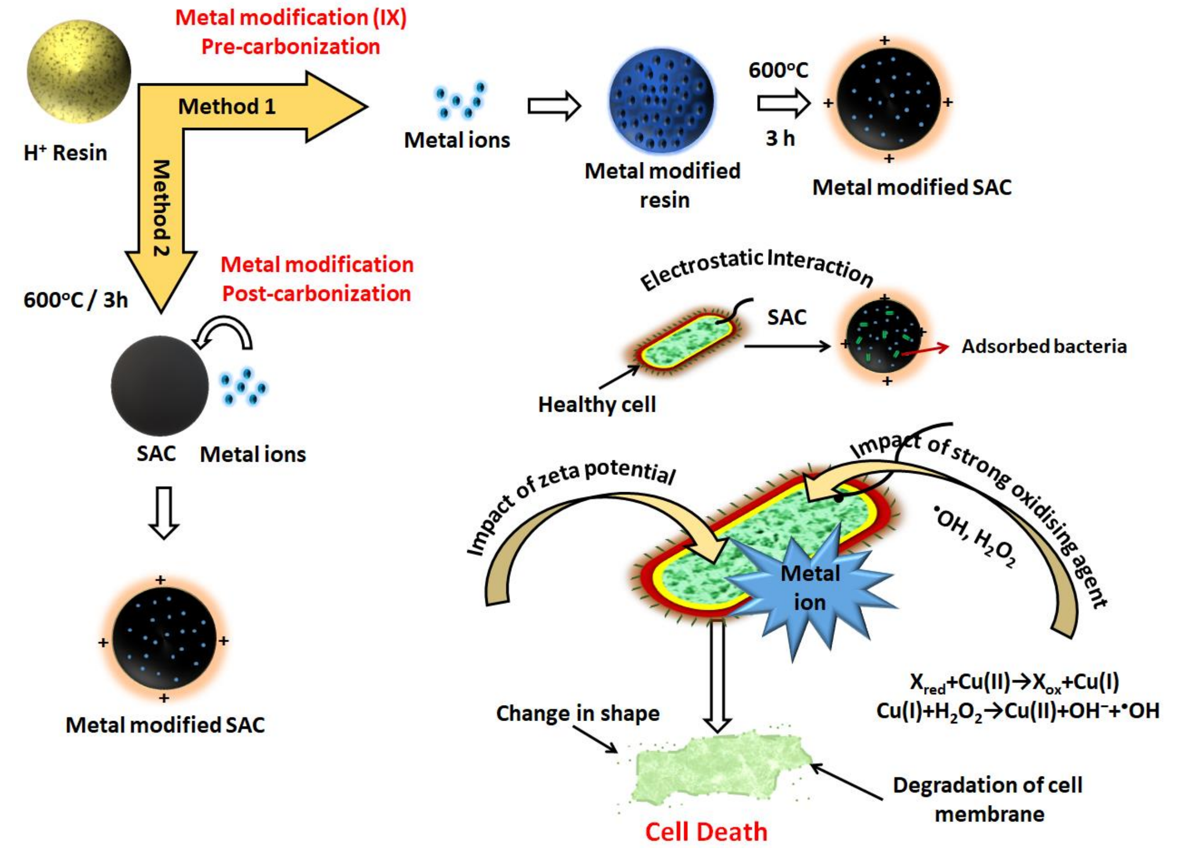


Figure 7.9: Possible mechanism of disinfection

The interface in adsorption needs to develop a potential that will result in physical rupture of membrane (membrane depolarization). The chemical effects include enhanced reactive oxygen species (ROS) production (at the interface or inside the bacteria). These ROS are ·OH radicals or strong oxidising agent such as H_2O_2 /active free radicals that enable oxidation of main constitutes of cell membrane such as proteins, nucleic acid, lipid or DNA. Fernandes et al. reported that alteration of zeta potential by increased dielectric constant or by changing the composition of the medium by supplying maximum amount of oxygen, hydrogen peroxide may often lead to agglutination of bacterial cells [55]. The other effects include antimicrobial activity of the metals such as copper or silver. Copper modified adsorbents/nanoparticles/surfaces provide cationic surface with strong bactericidal activity and are widely used as disinfectants [50],[56]. The antibacterial properties and mechanism of the antibacterial action of such metal modified adsorbents have been widely discussed in the literature for nanoparticles, but not for spherical activated carbons. SAC modifications may provide pathways for preparing adsorbents with enhanced antimicrobial, antiviral properties. As most bacteria, viruses have a negative charge in neutral solutions [57], the negatively charged surfaces of SACs are required to be functionalized with various metals or other modification to render them positive for enhanced disinfection efficiency.

The above mechanism is partly substantiated from the results of surface morphology of different SAC and modified SACs before and after the decontamination (Figure 7.10). It can be seen that there is adhesion/adsorption of bacteria on SACs. The *E. coli* and *S. aureus* bacteria before adsorption are seen with intact cell morphology (Figure 7.10 (a) and (d)) and subsequent to adsorption by Nickel modified SACs (Figure 7.10 (b) and (e)) reveal change in shape due to increase in cell permeability. Further, the destruction of the cell membrane in copper modified SACs is clearly evident from Figure 7.10 (c) and (f), due to the strong antimicrobial property of copper apart from interaction of strong oxidising agents. The active sites/active metal ions of SACs promote electrostatic adsorption of the bacteria on the surface of SACs which promotes active interactions/reaction with bacteria through different actions leading to destruction of cells. The overall mechanism therefore predominantly includes oxidative damage of cells through reaction- e.g. Cu(II) to Cu(I) of M1 and M2-SAC-Cu with generation of strong oxidising agents such as $^{\cdot}OH$ radicals and H_2O_2, initiating oxidation process with cell content. The oxidation of the nucleic acids, lipids and proteins results in further damage to the cell, leading to cell death. Figure 7.10 (f) verifies presence of cell debris due to the cell damage after adsorption of bacteria over M1-SAC-Cu. Figure 7.10 (c) and (f) confirm absence of bacteria cell and complete decontamination of bacteria by M1 and M2-SAC-Cu. Thus, the copper modified adsorbents are seen as more effective in the process of complete elimination of bacteria.

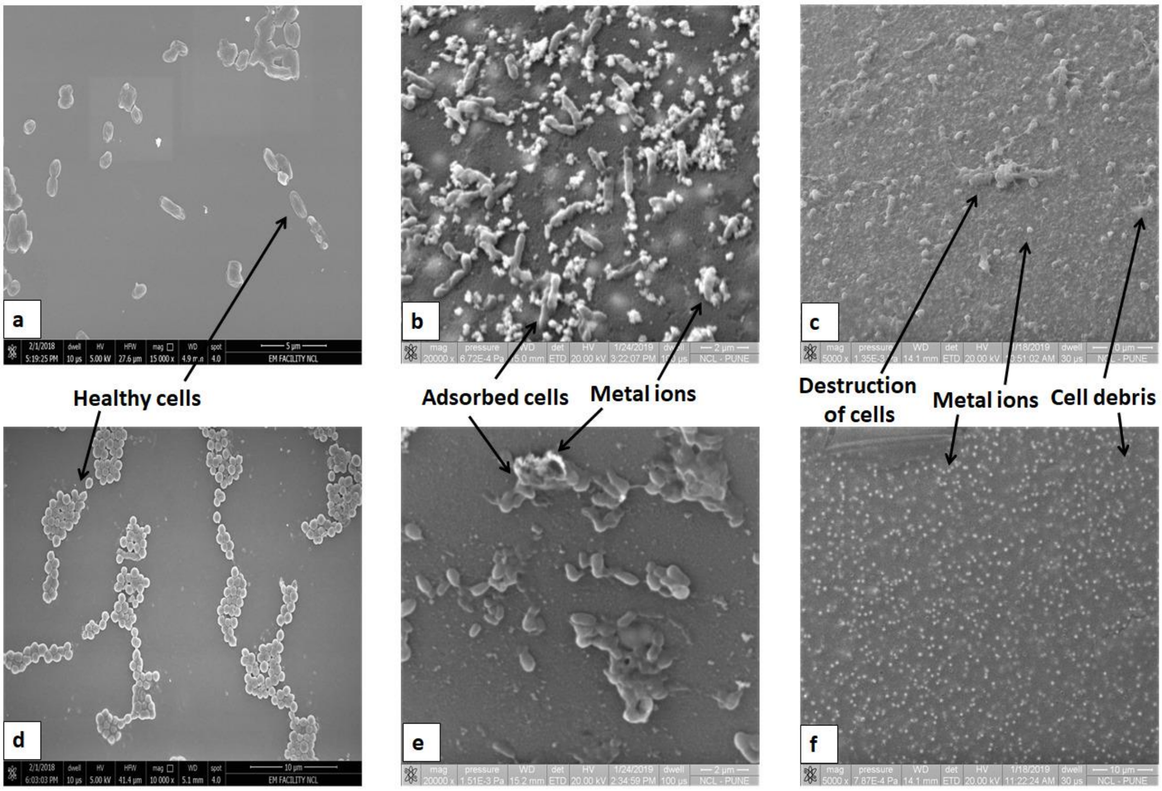


Figure 7.10: Surface morphology before and after disinfection (a) *E. coli* (0 min); (b) M2-SAC-Ni/ *E. coli*; (c) M1-SAC-Cu/ *E. coli* (d) *S. aureus* (0 min); (e) M1-SAC-Ni/ *S. aureus*; (f) M1-SAC-Cu/*S. aureus*

7.3.5 Evaluating spherical activated carbons for adsorptive deep desulfurization

There have been numerous reports on various forms of activated carbons and metal modified carbons for the removal of different sulfur compounds from fuels. In general, ordinary activated carbons have poor capacity for the refractory sulfur compounds while there has been substantial increase in the adsorption capacity for modified carbons, especially for metal modified carbons - specific metals such as copper and nickel. In order to evaluate the efficacy of the developed spherical activated carbons and also to differentiate the two methods of metal modification for the ion exchange polymers, the developed materials were studied for the removal of three refractory sulfur compounds- thiophene (T), benzothiophene (BT) and dibenzothiophene (DBT). The equilibrium plots for the adsorption of T, BT and DBT on various SACs are shown in Figure 7.11. The following observations clearly identify the differences in not only these materials, but also for the difference in the method of metal modification in the case of polymeric ion exchange resins.

1. All the spherical activated carbons have reasonably good capacity for the sulfur removal and the adsorption capacity is somewhat higher than many of the materials reported in the literature for commercial/ synthesized modified carbons.
2. The copper modified spherical activated carbons (both M1 and M2-SAC-Cu) were found to be more effective and the selectivity was of the order: DBT > BT > T.
3. It was observed that the copper modified spherical activated carbon using ion exchange modification method (M1-SAC-Cu) was highly effective for all sulfur compounds (T, BT and DBT) and a high capacity of 28 mgS/g for DBT, 20 mgS/g for BT and 12 mgS/g for T could be achieved.
4. The nickel modification is comparatively less effective though capacity for thiophene, is reasonably high, ~5-12 mgS/g adsorbent. Although the capacity is not commensurate with high Ni loading, it is higher compared to many commercial sulfur specific adsorbents and other adsorbents [58],[13].

The high capacity and selectivity for sulfur can be attributed mainly to the nature of metal species, higher surface area and electrostatic attraction for the sulfur moiety. For thiophene, where the capacity is comparatively less, the impact of metal appears to be insignificant. The increased effectiveness using ion exchange prior to carbonization is in contrast with the conventional methods of metal impregnation on the surface of activated carbon. It is also evident that mere high metal content in the adsorbent is not the only important contributions in the sulfur removal since both M1-SAC-Cu and M2-SAC-Cu have similar copper content and only M1-SAC-Cu has higher capacities for different sulfur compounds. The order of magnitude difference here could be attributed to Cu form in M1 modification compared to stabilized CuO form in M2 modification.

It is also to be noted that the spherical activated carbons reported in the literature had much lower capacity than that reported in the present study. The surface area, nature of metal, metal content and oxygen containing functional groups are thought to have combined effect through interactions such as π-π or π-H interaction of π electrons of thiophenic aromatic sulfur compounds with the carbon surface [59],[60]. Table 7.5 provides comparison of the adsorptive desulfurization capacity for the materials of this work with some of the reported data on similar studies in the literature. It is evident that modification of the materials is essential for obtaining reasonably good capacity, especially for refractory sulfur compounds. Further, metal modification is particularly attractive in all the types of the materials. However, it is also seen that not very high capacities could be obtained for all types of sulfur moieties and typically the highest capacity for the sulfur is up to 25-30 mg/g for single metal modification which can be further increased up to 40 mgS/g using double metal modification approach or metal and chemical modification strategy [31]. By and large, for reportedly cost-effective materials such as conventional activated carbons and biomass derived adsorbents, the capacity is typically much less than 10 mg/g, far from being satisfactory [61]. Thus, the spherical activated carbons of this study derived from used polymeric resin can offer the benefit of cost as well as good sulfur removal capacity.

Table 7.5: Comparison of sulfur adsorption capacity of various carbons from liquid fuels

Adsorbent	**Sulfur compound**	**Capacity mgS/g**	**Ref.**
MnO-10%/AC	T, BT, DBT	T 4.5, BT 5.7 and DBT 11.4	[58]
Biomass derived AC	T, BT, DBT	T 4.5, BT 3, DBT 7.5	[61]
Resin derived AC and KOH activation	DBT	~180	[62]
Activated carbon	BT, DBT	~0.5-1	[63]
Carbon nonofiber Ni-CNF/ACB	T, DBT	DBT 8.2, T 88.2	[35]
Ni/ACB	T, DBT	DBT 27.3, T 85	[35]
Zn/GAC	DBT	14	[64]
AC	T, BT, DBT	T 4.16, BT 11.52, DBT 16.32	[65]
AC, Acid modified AC, Ni/AC	DBT, MDBT, DMDBT	0.5-1.5	[22]
AC	T	0.96	[66]
Double metal modifications TAC-Ni-Cu-Acoustic cavitation TAC-Ni-Cu CFP-Ni-Cu	T, BT, DBT	 4.3, 31.6, 38 ~2, 12, ~33 ~4, ~13	[31]
SAC M1-SAC-Ni M2-SAC-Ni M1-SAC-Cu M2-SAC-Cu	T, BT, DBT	8.0, 4.4, 2.6 5.2, 5.0, 3.4 12.4, 5.4, 4.2 12.8, 20.0, 28.0 3.0, 5.2, 15.7	This work

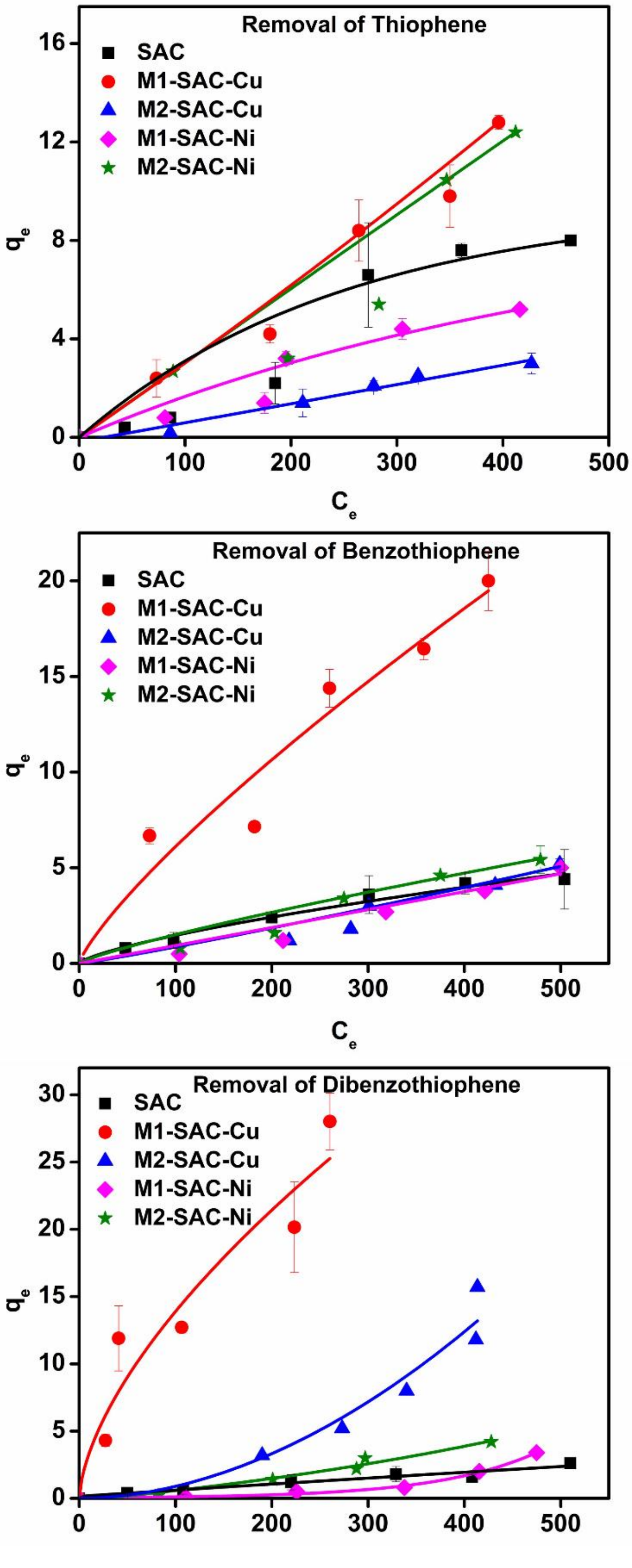


Figure 7.11: Adsorption isotherm for removal of refractory sulfur compounds

7.4 Conclusions

The present research identifies two different methodologies of preparation of spherical activated carbons using polymeric ion exchange resin (waste) as a starting material- one through exchanging of metal ions on resin matrix and other metal impregnation on carbonized form of spherical activated carbon. The spherical activated carbons, especially using metal modifications were highly effective in disinfection of water and in sulfur removal from organic fuels. The important findings include:

1. A significantly high metal loading in general was obtained in most SACs.
2. The metal-modified spherical activated carbons were highly effective in the removal of both gram-negative, *E. coli* and gram-positive *S. aureus* bacteria.
3. The copper-modified spherical activated carbons completely destroy (100%) both bacterial content proving efficacy of the developed materials.
4. The excellent disinfection behaviour can be attributed to metal modification and associated surface charge destroying cell membrane of bacteria and to the high values of zeta potential.
5. The graded variation in zeta potential clearly highlights implications of materials having high zeta potential-the higher the potential, higher is the disinfection ~10-15% disinfection can be improved up to 100% for zeta potential from -5 to 8.6 mV.
6. Kinetics of disinfection can be better represented by accounting for zeta potential effect in the conventional mathematical model. The fit of revised model was excellent, and a very high rate of disinfection, 1.33×10^5 (CFU/ml.s) was obtained using copper-modified spherical activated carbon.
7. The spherical activated carbons after metal modifications largely improve the sulfur removal capacity apart from altering the selectivity for thiophene, benzothiophene and dibenzothiophene. A high capacity of 12.8, 20 and 28 mgS/g was obtained in copper-modified SAC for thiophene, benzothiophene and dibenzothiophene respectively.
8. The metal modification of polymeric resins can be useful in utilization of resin waste; starkly different from conventional carbon sources, providing more degrees of freedom in material modifications.

The spherical activated carbons and metal modifications apart from possible cost effectiveness compared to similar conventional adsorbents or nano-adsorbents can provide suitable methodologies for developing tailor made adsorbents to meet specific demands and for useful applications in the area of environmental pollution control.

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Chapter 8
Summary

Chapter 8

Summary

The present work has resulted in the development of one newer form of hybrid technology for disinfection of water- SWASTIIK, Safe Water and Sustainable Technology Initiative from Indian Knowledgebase. SWASTIIK has the potential to provide techno-economical alternatives to the existing chemical methods of disinfection- chlorination. This novel hybrid cavitation process was successfully demonstrated for enhancing and altering the rates of disinfection by use of natural oils having antimicrobial properties, derived from plants. The effectiveness of hybrid methodology and process integration approach was demonstrated at a pilot plant scale of 1 m^3/h capacity and for various types of common gram-negative bacteria, common gram-positive bacteria apart from for destroying antimicrobial resistant bacteria (AMR) and difficult, opportunistic pathogen. Application of plant extract was also successfully demonstrated in this regard along with cavitation in SWASTIIK technology to produce safe drinking water. The natural oils and plant extracts used in the present research were selected from Indian knowledgebase, Ayurveda, and those that find regular use in most of Indian household cooking, in an attempt to also envisage/foresee possible health benefits that could be derived apart from producing safe water.

Development of materials and material modification were also explored in the form of metal modifications, through two different routes, in Spherical Activated Carbons (SACs) to improve efficiency of newer materials for both disinfection of water and another important environmental application- adsorptive desulfurization of fuel.

The important findings of this study include:

Water Disinfection by SWASTIIK

1. Natural oils having antibacterial properties, such as clove oil, peppermint oil, in combination with cavitation technology can enhance the efficiency of disinfection of water significantly as compared to conventional hydrodynamic cavitation.

2. Both gram-negative and gram-positive bacteria can be effectively destroyed.
3. Optimization of process parameters indicated an optimum pressure drop of 1 bar at ambient temperatures. Optimum concentration of natural oils was indicated as 0.1 % by volume.
4. Vortex diode was found to be far superior to conventional device such as orifice. Thus, vortex flow for generating cavitation is more useful in terms of reduced energy requirement since the pressure requirement for the vortex diode was order of magnitude lower than that required for orifice for the similar disinfection efficiency.
5. The nature of bacteria is also important in dictating the disinfection performance. However, the developed hybrid methodology, SWASTIIK, was found to effectively destroy all types of microorganisms such as gram-negative *E. coli*, gram-positive, *Staphylococcus aureus*, antimicrobial resistant bacteria (AMR) gram-positive methicillin resistant, *Staphylococcus aureus* and difficult, gram-negative opportunistic pathogen *Pseudomonas aeruginosa*.
6. Exceptionally high rates of removal could be obtained using hybrid methodology compared to conventional hydrodynamic cavitation for the effective destruction of all types of microorganisms. The initial rates of disinfection were enhanced to the extent of 2 times for *S. aureus*, 5 times for removal of *E. coli* in the case of hydrodynamic cavitation using vortex diode and up to 17 times as compared to that in acoustic cavitation.
7. The nature of oil modifies the cavitation behavior and hence a number of possible combinations can be anticipated in this regard. Vortex diode as a cavitating device and natural oil-peppermint oil was found to be the best combination in the present study that practically ensures complete removal within 10 minutes under mild operating conditions. However, it is also possible to further enhance the rates of disinfection through combination of different natural oils or plant extracts.
8. Process intensification in the form of aeration was shown to further enhance the disinfection efficiency apart from possible lowering of oil dose. The present study showed that aeration could reduce the requirement of oil by 100% for similar disinfection efficiency, in the case of peppermint oil.
9. Application of plant extracts in the hybrid cavitation process also effectively eliminates bacteria at significantly higher rates. Mango ginger extract was found to be most effective in water disinfection in the present study. A very small concentration of 0.1%

of natural additive, mango ginger extract, can effect disinfection, though increased amount of plant extract may be required for obtaining high disinfection efficiency.

10. The rate constant values can be improved to the extent of ~3 times for hydrodynamic cavitation with mango ginger extract, ~5 times for hydrodynamic cavitation with ginger oil and ~8 times for acoustic cavitation with mango ginger extract.
11. A plausible mechanism suggests synergistic effect of both natural additives and hydrodynamic cavitation and the rupture of cell wall/cell death can be due to various factors such as oxidation effect, high shear, localized heat/thermal effect and antimicrobial property of active constituents.
12. The lipophilic nature of antimicrobial active ingredient of natural additive was believed to be responsible for increased cell permeability and cell denaturation.
13. The cost of operation of SWASTIIK technology was 0.036 $\$/m^3$ for complete disinfection of water, lower than other disinfection processes such as chlorination (0.042 $\$/m^3$), membrane separation (1 $\$/m^3$), solar photo Fenton (0.85 $\$/m^3$).
14. The techno-economic evaluation indicated cost of the hybrid methodology to be significantly, order of magnitude, lower compared to the most conventional processes. The energy requirement is significantly low indicating techno-economic feasibility.
15. The developed green process eliminates the use of harmful chemicals and can provide alternative to existing chemical processes such as chlorination.

Newer Adsorbents/ Material Modifications and applications in Disinfection and desulfurization

1. The present research identifies two different methodologies of preparation of spherical activated carbons using polymeric ion exchange resin as a starting material- one through exchanging of metal ions on resin matrix and other metal impregnation on carbonized form of spherical activated carbon. A significantly high metal loading in general was obtained in most SACs.
2. The spherical activated carbons, especially using metal modifications were highly effective in disinfection of water and in sulfur removal from organic fuels.
3. The metal modified spherical activated carbons were highly effective in the removal of both gram-negative, *E. coli* and gram-positive *S. aureus* bacteria. The copper modified

spherical activated carbons completely destroy (100%) both bacterial content proving efficacy of the developed materials.

4. The excellent disinfection behaviour of newer adsorbents can be attributed to metal modification and associated surface charge destroying the cell membrane of bacteria and to the high values of zeta potential.
5. The graded variation in zeta potential clearly highlights positive implications for materials having high zeta potential-higher the potential, higher is the disinfection ~10-15% disinfection can be improved up to 100% for zeta potential from -5 to 8.6 mV.
6. Kinetics of disinfection can be better represented by accounting for zeta potential effect in the conventional mathematical model. The fit of revised model was excellent and a very high rate of disinfection, 1.33×10^5 (CFU/mL.s) was obtained using copper modified spherical activated carbon.
7. The spherical activated carbons after metal modifications largely improve the sulfur removal capacity apart from altering the selectivity for thiophene, benzothiophene and dibenzothiophene. A high capacity of 12.8, 20 and 28 mgS/g was obtained in copper modified SAC for thiophene, benzothiophene and dibenzothiophene respectively.
8. The findings of this research on newer spherical activated carbons, metal modification of polymeric resins can be useful in utilization of resin waste; starkly different from conventional carbon sources, providing more degrees of freedom in material modifications. The spherical activated carbons, metal modifications apart from possible cost effectiveness compared to similar conventional adsorbents or nano-adsorbents can provide suitable methodologies for developing tailor made adsorbents to meet specific demands and for useful applications in the area of environmental pollution control.

Overall, the present research has resulted in development of a new technology for disinfection of water, believed to be at Technology Readiness Level (TRL) of 4-6.

Scope for Future Work

The work pertaining to the development of “Safe Water and Sustainable Technology Initiative from Indian Knowledgebase”, in the present study, is a new concept and needs to be further strengthened by generating database on the materials and by way of process integration.

We have used the commonly known Ayurvedic plants/plant derived materials for water disinfection such as clove oil, peppermint oil, ginger oil etc. These are used in daily household preparations (India) and therefore, were selected considering the priorities for safe water and possible “healthy” water. However, it is quite possible that there could be hundreds of such plant derived materials from Ayurveda which can potentially have high medicinal effectiveness and more utility for disinfection of water especially the plants/materials found in Himalayan region/North’s East parts of India. Therefore, rigorous screening and research for such materials is required for fine tuning SWASTIIK technology for deriving benefits for human life. The process can replace/ integrate with the conventional chlorination process that is used in the Indian water treatment plants. In future, efforts are required to conduct trials for its real life implementation in the water treatment plants.

The process also has a potential for household applications for *in situ* generation of safe and healthy drinking water in homes. It is essential to develop compact units that can be installed at homes of people for providing safe disinfected water. Apart from it, in the current COVID-19 scenario which highlighted need for increased immunity among people, efforts can be made to utilize, not just one, but combinations of different natural oils for boosting the immunity by way of drinking water (similar to the practice of drinking cinnamon tea in some Asian countries). The home appliance can come with different “Natural Oil Cartridges” for the specific needs of people in this regard.

Newer materials are required in adsorption which is an excellent technology for final polishing, in water treatment or pollution control. Many newer materials can be developed in this regard, using the philosophy presented in this research, especially in the form of Nanocomposites where inherent disinfection properties of material/metals mentioned in Ayurveda such as silver, copper etc. can be effectively incorporated. Adsorption is an excellent process integration in this regard.

Abstract

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Year of Submission: 2021
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Title of the thesis: Studies in newer methodologies and materials/ material modifications for environmental, pollution control applications specifically for water treatment and desulfurization

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Safe and clean environment is most essential for the ecosystem and Water and Air are two most critical components. The present research addresses two specific studies in this regard; one pertaining to the safe water and other pertaining to clean air, Disinfection of water and Desulfurization of transportation fuels. Safe drinking water is necessary to prevent occurrence of large number of waterborne diseases and to save millions of lives, one of the most priority subjects for developing country like India. The main objective of this research is to develop methodology which provides safe and healthy drinking water at low cost with substantial ease of operation, scale-up and without harmful disinfection by-products. The study is an attempt to improvise the hydrodynamic cavitation methodology for effective disinfection of water and also to suggest prototype development for practical application. The enhancement in the disinfection efficiency was evaluated specifically for the effect of pressure, temperature, pH, microbial inoculum size and also on effect of different additives for the two model microbial strains, gram-negative (*Escherichia coli*) and gram-positive (*Staphylococcus aureus*). Also, complete removal of antimicrobial resistant (AMR) and relatively less researched, gram-negative opportunistic pathogen, *Pseudomonas aeruginosa* and gram-positive methicillin resistant, *Staphylococcus aureus* was studied. The efficacy of the hydrodynamic cavitation was evaluated for the two types of flows/cavitation devices – linear flow in the case of orifice and vortex flow for vortex diode. The present study, for the first time, reports possible use of different natural oils such as castor oil, cinnamon oil, eucalyptus oil, clove oil, lemongrass oil, peppermint oil etc. in conjunction with hydrodynamic cavitation. Exceptionally high rates were obtained for practically complete removal of all types of bacteria, within less than 10 minutes. The nature of oil modifies the cavitation behaviour and an order of magnitude enhancement in the cavitation rate was observed for the oils such as eucalyptus, clove oil and peppermint oil, for a very small concentration of 0.1%. Process intensification using simple aeration can further increase the rates resulting in significant lowering of oil dose. The use of natural resources such as plant extracts (ginger, turmeric, mango ginger etc.) was also successfully reported in disinfection for the first time. Differences between oil and water soluble additives were highlighted. The increased rates of disinfection using oil/extract can drastically reduce the time of operation and consequently reduce cost of disinfection. A possible mechanism is proposed for the effect of oil/extract and hydrodynamic cavitation in cell destruction through the rupture of cell wall, oxidative damage and possible DNA denaturation. A cavitation model using per pass disinfection was used to correlate the data. The developed methodology, Safe Water and Sustainable Technology Initiative from Indian Knowledgebase, SWASTIIK, has the potential to provide viable alternative to chemical disinfection methods and operating cost of only 0.036 $\$/m^3$ was estimated (~Rs. 2.5/ m^3 or 0.25 Paise per liter). Synthesis, design and development of new materials for disinfection of water and desulfurization of liquid fuels was also investigated for the role of adsorbent modifications. Spherical activated carbons from polymer resin were developed with metal modifications, using copper and nickel, for gradation of zeta potential (-5.01 to 8.64mV) and high metal loading (up to 12.3%). The materials provide improved removal of various contaminants from aqueous and organic streams-removal of bacteria from water and sulfur removal from fuel. Overall, the present research has resulted in development of a new technology and methodologies for disinfection of water.

Details of publications, emanating from the thesis-work

List of publication(s)

1. **Maya B. Mane**, Vinay M. Bhandari, Kshama Balapure, Vivek V. Ranade. A novel hybrid cavitation process for entering and altering rate of disinfection by use of natural oils derived from plants. *Ultrasonics - Sonochemistry* 61 (2020) 104820. https://doi.org/10.1016/j.ultsonch.2019.104820

2. **Maya B. Mane**, Vinay M. Bhandari, Kshama Balapure, Vivek V. Ranade. Destroying antimicrobial resistant bacteria (AMR) and difficult, opportunistic pathogen using cavitation and natural oils/plant extract. *Ultrasonics - Sonochemistry* 69 (2020) 105272. https://doi.org/10.1016/j.ultsonch.2020.105272

3. **Maya B. Mane**, Vinay M. Bhandari, Vivek V. Ranade. Safe Water and Technology Initiative for Water Disinfection: Application of Natural Plant Derived Materials. *Journal of Water Process Engineering* 43 (2021) 102280. https://doi.org/10.1016/j.jwpe.2021.102280

4. **Maya B. Mane**, Vinay M. Bhandari. Developing spherical activated carbons from polymeric resins for removal of contaminants from aqueous and organic streams. *International Journal of Environmental Science and Technology* (2021). https://doi.org/10.1007/s13762-021-03684-6

Patents

1. Vinay M. Bhandari, **Maya B. Mane**, Kshama Balapure, *A novel process for enhancing and altering removal of bacteria by use of natural oils derived from plant or extract in cavitation*. Patent Filed-20/07/2019 (201911021646).

2. Vinay M. Bhandari, **Maya B. Mane**, Kshama Balapure, *Destroying antimicrobial resistant bacteria (amr) and difficult, opportunistic pathogen using cavitation and natural oils or plant extract*. Patent Filed-24/12/2019 (202011004159).

Conferences/Seminars

1. **Maya Mane**, Vinay Bhandari, LS Gayatri. Newer spherical activated carbon materials and material modifications for deep desulfurization of fuels. *'21st CRSI National Symposium in Chemistry'* held at CSIR-IICT, Hyderabad during 14-16 July, 2017.

   Abstract-The present work reports newer materials and materials that can be highly useful for deep desulfurization of transportation fuels. Spherical activated carbons were prepared using cation exchange resins as starting materials and were further modified using copper and nickel metal modifications. A very high metal loading on the activated carbons as compared to conventional metal modifications was obtained. The developed materials were characterized using XRD, AAS, FTIR, ESEM and for surface area and pore size/ distribution. The FT-IR results revealed that phenols and carboxylic acids were the major functional groups found on the surface of the prepared AC and there was presence of nickel and copper metal as in the form of oxides NiO, CuO and Cu_2O by XRD. Deep desulfurization of synthetic fuels was studied for the removal of refractory sulphur compounds such as benzothiophene and dibenzothiophene. A very good sulphur removal capacity of ~28 mg/g was obtained for copper modified adsorbent for the removal of refractory sulphur compound. The results of this work could provide more insight into the development and activation of activated carbons, metal modification of carbons and application in desulfurization specifically for effective removal of refractory sulphur compounds, an important application form environmental pollution control point of view.

2. **Maya B. Mane**, J. Jena, Vinay M. Bhandari, LS Gayatri. Spherical activated carbon adsorbents with metal modification for disinfection. *'National Science Day Symposium'* held at CSIR-NCL, Pune during 26-27 Feb, 2018.

   Abstract- The present work reports newer materials and material modifications for industrial effluent treatment, in general, and disinfection, in particular. Spherical activated carbons were prepared using cation exchange resin as a starting material and were further modified using copper metal impregnation. The materials were characterized using XRD, AAS, FTIR, ESEM and BET surface area. The FT-IR results revealed that phenols and carboxylic acids were the major functional groups and there was presence of nickel and copper metal as oxides NiO, CuO and Cu_2O. Disinfection of synthetic wastewaters containing Gram positive (*Staphylococcus aureus*) and Gram negative (*E. Coli*) was studied. SACs were found to have antibacterial activity against both Gram positive and Gram negative bacteria. Practically complete disinfection of *E. Coli* was obtained for copper modified adsorbents, even at low copper loading though, higher loading was required against *S. aureus*. The results indicated metal modification as essential feature for application in disinfection.

3. **Maya B. Mane**, Vinay M. Bhandari, J. Jena, T. Sinha. 'Newer spherical activated carbon adsorbents for disinfection and industrial effluent treatment' *'8th DAE-BRNS biennial Symposium on Emerging trends in separation science and technology (SESTECH 2018)'* held at BITS Pilani, Goa Campus, Goa from 23-26 May,2018.

Abstract-The present work reports newer materials and material modifications that can be highly useful for industrial effluent treatment, in general, and disinfection, in particular. Spherical activated carbons were prepared using cation exchange resin as a starting material and were further modified using copper metal impregnation. The developed materials were characterized using XRD, AAS, FTIR, ESEM and for surface area (Fig.1). The FT-IR results revealed that phenols and carboxylic acids were the major functional groups found on the surface of the prepared AC and metals-nickel and copper, in the form of oxides NiO, CuO and Cu_2O. Disinfection of synthetic wastewaters containing Gram positive (*S. aureus*) and Gram negative (*E. Coli*) was studied (Fig.2). SACs were found to have antibacterial activity against both Gram positive and Gram negative bacteria. Practically complete disinfection of *E. Coli* was obtained for copper modified adsorbents, even at lower loading though, higher loading was required against *S. aureus*. It was also observed that the copper modification has huge impact on the disinfection ability of the original spherical activated carbon adsorbent, implying metal modification as an essential requirement in this case. Further, with the variation in the processing parameters such as temperature of the carbonization and adsorbent loading the materials can be appropriately tailored for wastewater treatment. The results of this work could provide more insight into the development and activation of spherical activated carbons, metal modifications and application in

wastewater treatment/ disinfection, important form environmental pollution control point of view.

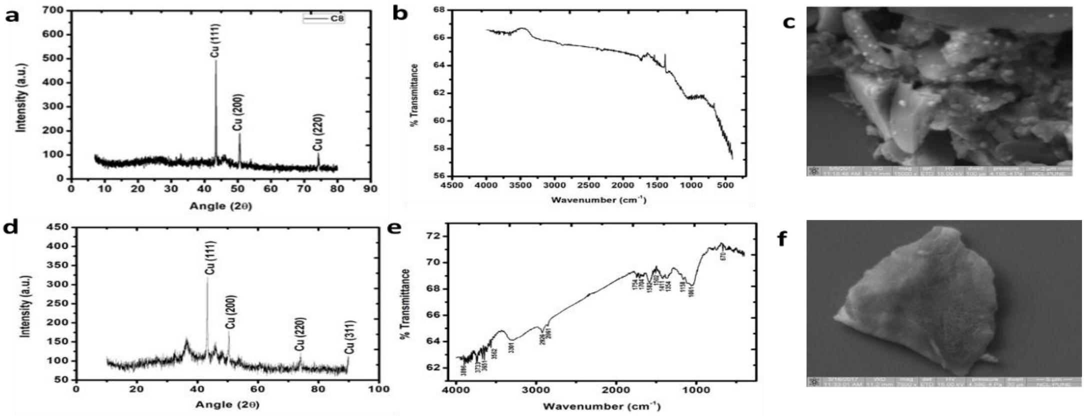

Fig.1. Characterization (a) XRD (b) FTIR (c) SEM image of C8; (d) XRD (e) FTIR (f) SEM image of C2

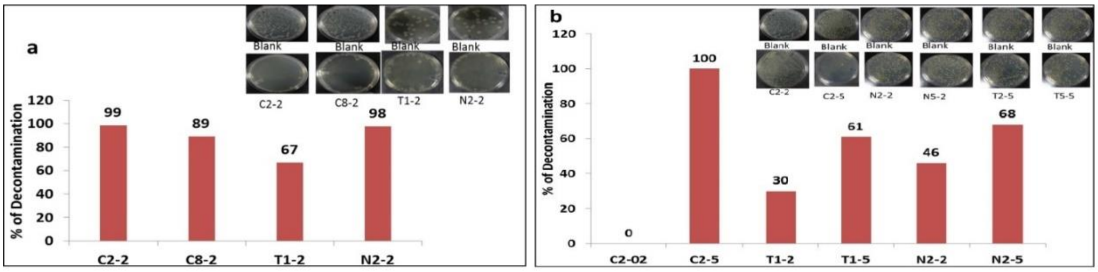

Fig.2 (a) Antibacterial activity of C2 and C8 (a) *E. Coli* (b) S*taphylococcus aureus*

Key words: Adsorption, Pollution control, Wastewater, Bacteria, Decontamination

4. **Maya B. Mane**, K. Balapure, Vinay M. Bhandari, Kinetics of disinfection using vortex flow of vortex diode in hydrodynamic cavitation. '*National Symposium on Chemical Reaction Engineering'* held at CSIR-NCL, Pune during 17-18 Dec, 2018

Abstract- The acoustic cavitation is well known process use for removal of bacteria from water and waste water. However, the use of hydrodynamic cavitation as a single method or in combination with other method like ultrasound has been employed recently. The kinetics and mechanism of disinfection of water and waste water via hydrodynamic cavitation has not been reported elsewhere. In present study we have study removal of Gram positive bacteria *S. aureus* by using hydrodynamic cavitation and vortex diode as a cavitating device. The effect of different parameters on hydrodynamic cavitation like pressure drop, temperature and pH also studied. We have

successfully developed a mechanism and kinetics for disinfection of water and waste water. The path for use of hydrodynamic cavitation for disinfection of water and waste water is still long but current results have shown great potential for water and waste water cleaning.

5. **Maya B. Mane**, Kshama Balapure, Vinay M. Bhandari, Exploring Green Technologies: Newer materials and methods for disinfection of water*, 'International Conference on materials for the millennium MATCON 2019'* held at cochin university of science and technology, kochi during 14-16 March, 2019.

   Abstract- Water quality is one of the most critical parameter worldwide gauging standards of human life since a wide range of fatal diseases to human beings as well as to animals can be attributed to contaminated water. The present work reports newer materials in the form of modified adsorbents/nanomaterials and a newer method of hydrodynamic cavitation with vortex diode that can be highly useful for disinfection of water. Spherical activated carbons prepared from carbonization of resin and subsequent metal modifications using copper and nickel metals exhibited excellent antimicrobial properties implying effective removal of Gram positive and Gram negative bacteria. The developed materials were characterized using XRD, AAS, FTIR, ESEM and for surface area. The presence of phenols, carboxylic acids as major functional groups and metal modification was found to contribute mainly in the disinfection mechanism. Removal of both Gram positive (*S. aureus*) and Gram negative (*E. coli*) was studied. Apart from adsorptive disinfection, a newer method of hydrodynamic cavitation with vortex diode as a cavitating device was investigated in detail for elimination of bacterial contamination. The vortex diode employs vortex flow for effecting cavitation and a very high efficiency of disinfection (~100%) was obtained at low pressure drop of 0.5 to 2 bar, indicating disinfection at significantly low energy consumption or at lower cost of operation compared to conventional methods. The results have potential and implications for household use or for application in water treatment plants for eliminating water borne bacteria responsible for variety of diseases, thereby making safe drinking water available to the society.

6. **Maya B. Mane**, Kshama Balapure, Vinay M. Bhandari, Hybrid Cavitation Process using Natural Oils for Disinfection of Water, *'International Conference on Eco-health & Environmental Sustainability, ICEES-2020'* organized by Navrachana University, Vadodara in association with University of Calgary, Canada during February 24-26, 2020.

Abstract- The World Health Organization (WHO) estimates that more than 3.4 million people die every year from waterborne diseases caused by bacterial contamination of water and the problem is especially relevant in Indian context. The present study provides an easy to implement and cost effective hybrid hydrodynamic cavitation technology for disinfection of water. Addition of natural oils having antimicrobial properties along with health benefits is shown to drastically enhance the disinfection rates. Effect of pressure, temperature, pH, microbial inoculum size and also effect of different additives for the two model microbial strains, Gram-negative (*Escherichia coli*) and Gram-positive (*Staphylococcus aureus*) was extensively studied for two types of cavitation devices – linear flow in the case of orifice and vortex flow for vortex diode. Practically 100% disinfection could be obtained using the hybrid process. The vortex diode requires significantly lower pressure drop (1 bar) compared to orifice (>2 bar) for the similar extent of disinfection, indicating role of reactor geometry in disinfection. Different natural oils such as castor oil, cinnamon oil, eucalyptus oil and clove oil were used in conjunction with hydrodynamic cavitation. Eucalyptus and clove oil, in concentration of 0.1%, increased the disinfection rate drastically, to the extent of 2-4 folds, implying substantially reduced time of operation and also cost of disinfection compared to cavitation alone. The mechanism of disinfection using oil and hydrodynamic cavitation indicates cell destruction through the rupture of cell wall, oxidative damage and possible DNA denaturation. A mathematical model is developed to provide insight into the disinfection process. It is suggested that increasing efficiency using natural oils, possible health benefits, ease of operation, low cost and easy scale-up can have significant advantages in practical applications.

Key words: Wastewater treatment, Disinfection, Cavitation, Oil, Antimicrobial

7. **Maya B. Mane**, Vinay M. Bhandari. Hybrid hydrodynamic cavitation technology for disinfection of water using natural additive. '*Advances in Chemistry and Chemical Engineering 2021 (ACCE2021)*' organized by Department of Chemical Engineering, Sardar Vallabhbhai National Institute of Technology, Surat during April 16–17, 2021.

Abstract- The scarcity of water is a major issue in developing countries like India and available water for drinking purpose has quality issue, present of microbiological pollutant increases of disease like cholera, typhoid, diarrhea etc. The several Environmental Protection Agencies has set permissible limits for *E. coli* or thermotolerant coliform bacteria must not detected in 100 mL of sample. The use conventional chemical method; chlorination is banned in most of the European countries due to formation of carcinogenic disinfection by-products (DBPs). Whereas, the physical treatment methods such as membrane technology, UV or RO are cost intensive. So, there is need for development of newer or modification of existing disinfection technologies and Hydrodynamic Cavitation (HC) is a practical option. To obtained complete disinfection of water the process integration to hydrodynamic cavitation with the help of chemical or physical means can be done such as use of oxidants (e.g. hydrogen peroxide, ozone), use of chemical disinfectant (e.g. sodium hypochlorite), use of physical methods (e.g UV, plasma). These hybrid disinfection approaches are time consuming and has by-product formation issue. So, our objective is to develop indigenous technology for disinfection of water using Indian traditional knowledge of Ayurveda the use of natural oil or plant extract with modern hydrodynamic cavitation technology. A small quantity (0.1%) of different types of natural oil such as ginger oil, lavender oil, tulsi oil, etc., and natural extracts such as mango ginger, ginger extract etc., were used in combination with cavitation. A simple and easy extraction technique of pressing (expression) extraction was applied without using any solvent and aqueous phase of extract further utilized. The vortex flow-based device, vortex diode was used at a pressure drop of 1 bar for all experiments. The ginger oil with cavitation gave 96% of disinfection which is higher than cavitation alone of 44% and similarly, for mango ginger with cavitation showed 88% disinfection efficiency higher than cavitation alone for 15 min. For proof of concept, the mango ginger with cavitation was performed on acoustic cavitation and 94% disinfection, higher rate of disinfection achieved with compared to acoustic cavitation only of 30%.

The FTIR analysis were carried to identification of function group prior and after cavitation. It is found out for ginger oil with cavitation experiments, there is no change in functional group of oil phase in before and after hybrid cavitation, presence of gingerol active component is identified and no any by-product formation in both aqueous and oil phase. So, the insoluble natural oil can be recycled and reuse for further cavitation operation. Due to absence to any harmful by-products, this promising approach is alternative process for conventional chlorination cavitation technology.

Achievements

1. **Best Poster Award with Citation** for the paper entitled Newer spherical activated carbon materials and material modifications for deep desulfurization of fuels in 21st CRSI National Symposium in Chemistry 2017, Hyderabad.

2. **SERB-IGCW 2019 Green Chemistry Award-Top Three Nominee certificate in Knowledge Community Students** for Innovation for outstanding case studies incorporating the Principles of Green Chemistry and Engineering into Chemistry routes, Chemical designs and Manufacturing Practices; and steps taken towards pollution prevention while meeting the triple bottom line of People, Profit and Planet.

3. **Best Oral Presentation Award with Trophy** for the paper entitled Hybrid Cavitation Process using Natural Oils for Disinfection of Water in at International conference on Ecohealth and Environmental Sustainability (ICEES-2020), Gujrat.

4. **Director's Commendation Award with Citation** for Research Publication in Chemical Engineering/Technology-2020 for the paper entitled Destroying antimicrobial resistant bacteria (AMR) and difficult, opportunistic pathogen using cavitation and natural oils/plant extract, CSIR-NCL, Pune

5. **Publicity received for research and Development**

   DD News http://ddnews.gov.in/sci-tech/modern-technology-indian-traditional-knowledge-combines-bring-safe-healthy-drinking-water

Rajya Sabha TV https://youtu.be/2qfy3iR4MWI

DST PIB https://pib.gov.in/PressReleasePage.aspx?PRID=1723634

https://pib.gov.in/PressReleaseIframePage.aspx?PRID=1723594

Digital India https://twitter.com/indiadst/status/1399956079543418881?s=24

https://www.livemint.com/news/india/csirncl-lab-leverages-ayurveda-for-safe-drinking-water-technology-11622617458721.html

https://www.google.com/amp/s/indiaeducationdiary.in/modern-technology-and-indian-traditional-knowledge-combine-to-bring-safe-healthy-drinking-water/

http://ibgnews.com/2021/06/02/modern-technology-and-indian-traditional-knowledge-combine-to-bring-safe-healthy-drinking-water/amp/

https://www.foodtechbiz.com/food-safety-and-traceability/modern-technology-ayurveda-unite-to-bring-safe-drinking-water

https://www.gaonconnection.com/bat-pate-ki/modern-technology-and-indian-traditional-knowledge-combine-to-bring-safe-and-healthy-drinking-water-49289

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Ultrasonics - Sonochemistry 61 (2020) 104820

Contents lists available at ScienceDirect

Ultrasonics - Sonochemistry

journal homepage: www.elsevier.com/locate/ultson

A novel hybrid cavitation process for enhancing and altering rate of disinfection by use of natural oils derived from plants

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ARTICLE INFO

Keywords:
Wastewater treatment
Disinfection
Cavitation
Oil
Antimicrobial

ABSTRACT

The present study is an attempt to improvise the hydrodynamic cavitation methodology for effective disinfection of water and also to suggest prototype development for practical application. The enhancement in the disinfection efficiency was evaluated specifically for the effect of pressure, temperature, pH, microbial inoculum size and also on effect of different additives for the two model microbial strains, gram-negative (*Escherichia coli*) and gram-positive (*Staphylococcus aureus*). The efficacy of the hydrodynamic cavitation is evaluated for the two types of flows/cavitation devices – linear flow in the case of orifice and vortex flow for vortex diode. The vortex diode requires significantly lower pressures, 50% lower as compared to orifice for the similar extent of disinfection. While the bacterial disinfection at high temperature is known, the usefulness of hydrodynamic cavitation is especially evident at ambient conditions and the process is effective even at very high concentrations of bacteria, not reported so far. The reactor geometry also has significant effect on the disinfection. The present study, for the first time, reports possible use of different natural oils such as castor oil, cinnamon oil, eucalyptus oil and clove oil in conjunction with hydrodynamic cavitation. The nature of oil modifies the cavitation behavior and an order of magnitude enhancement in the cavitation rate was observed for the two oils, eucalyptus and clove oil for a very small concentration of 0.1%. The increased rates of disinfection, of the order of 2–4 folds, using oil can drastically reduce the time of operation and consequently reduce cost of disinfection. A possible mechanism is proposed for the effect of oil and hydrodynamic cavitation in cell destruction through the rupture of cell wall, oxidative damage and possible DNA denaturation. A cavitation model using per pass disinfection was used to correlate the data. The increased efficiency using oils and possible benefits of the developed process, where natural oils can be perceived as biocatalysts, can have significant advantages in practical applications.

1. Introduction

The quality of water has been a major concern worldwide and Asia is one of the worst affected region facing the problem of water contamination with pathogenic bacteria [1]. In addition, scarcity of drinking water also has become a major issue worldwide due to increased human population and industrialization. The scarcity of water can be alleviated to a certain extent by recycling and reusing the water. However, environmental pollution due to industrial effluents/sewage water /biological pollutants impacts the quality of water. The biological pollutants are known to cause various water-borne diseases such as amoebiasis, shigellosis, cholera, typhoid fever, Hepatitis A or E and so on [2], consequently reflected in increasingly more number of deaths because of consumption of unsafe drinking water. Thus, there is an urgent need to formulate newer methodologies that are easy to implement and can generate safe drinking water. According to various norms, the desired total coliforms organism in drinking water should be zero. To comply with this stringent regulation, it is necessary to develop an efficient, green and viable technology for water treatment [3].

Though a number of conventional treatments such as chemical and physical water disinfection methods have been used for microbial decontamination, most of these have limitations/ drawbacks resulting into inadequate efficacy translating into limited applicability [4,5]. The conventional physical methods include heating, radiation, microwave, filtration, UV irradiation and plasma. Many of these, though effective, have scale-up problems, high cost and long treatment time. UV irradiation typically has insufficient light scattering ability and is ineffective towards bacterial photoreactivation repair mechanism [6].

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https://doi.org/10.1016/j.ultsonch.2019.104820
Received 5 June 2019; Received in revised form 10 September 2019; Accepted 1 October 2019

Nomenclature

C	Concentration, CFU/ml
C_0	Initial concentration, CFU/ml
k	Disinfection rate constant
k_G	Growth rate constant
n	Number of passes
P	Pressure, bar
ΔP	Pressure drop, bar
Q, q	Flow rate, m^3/s
t	Time, s
V	Volume, Liters
φ	Per-pass disinfection factor
τ	Residence time, s

Membrane technology for water disinfection also have operational difficulties along with fouling problem, many times requiring frequent replacement of membrane thereby increasing the cost of treatment. Chemical treatment methodologies such as chlorination and ozonation, though have been widely used with ease of scale-up, have been considered environmentally not friendly in recent years due to unpleasant smell and by-products of the disinfection process can be mutagenic and carcinogenic in nature [7]. Some of the disadvantages of chlorination methods can be eliminated using adsorption technologies employing newer adsorbents/nanocomposites that are capable of eliminating bacteria [8,9,10]. Chemical methods are also unable to decontaminate bacteria from water because of mass transfer limitations and are unable to remove biocides resistant bacteria, bacteria residing in biofilm or any sediment [7].

Hydrodynamic cavitation is believed to be one of the most suitable physico-chemical process for disinfection and is gaining attention in recent years. It has several advantages such as ease of operation, easy scale-up, cost effectiveness, no production of harmful byproducts, representing greener approach and one that can work without use of harmful chemicals [11]. The principle of cavitation involves formation, growth and collapse of cavities of bubbles which is facilitated by specific cavitating device. The collapse of cavities is such that it generates extreme conditions of pressures (~1000 atm or more) and temperatures (~5000 K or more) at the point of implosion and as a consequence homolytic cleavage of water resulting into generation of hydroxyl radicals takes place and these oxidizing hydroxyl radicals participate into chemical oxidation of organic species [12,13]. There can be *insitu* generation of hydrogen peroxide, another oxidizing agent. The overall process is complex and intimate details of generation of different species (HO•, H•, HOO•, HO_2•, and H_2O_2) and subsequent reaction pathways are less understood. Though, in principle, cavitation is classified into four types on the basis of mode of generation of cavities: acoustic, hydrodynamic, optic and particle; from water treatment point of view, only acoustic and hydrodynamic cavitations are considered to be most promising. In the case of acoustic cavitation, cavities get generated by inducing ultrasound waves in the liquid medium ($>$ 16 kHz), while in hydrodynamic cavitation, it is achieved by realising low pressure regions (using small constrictions, rotational flows or their combinations) in the flowing fluid. Although significant work has been reported in the area of sonochemical reactors, its application in water disinfection for real life is practically invisible due to the reasons of high cost of treatment (capital investment as well as power consumption) and difficulties related to scale – up. The cavitating device can be simple linear flow based venturi or orifice or rotational flow based device such as vortex diode [7,11,13,14,15,16]. Most of the studies were carried out using single and multiple hole orifice plate or venturi for water disinfection [17,18]. However, the study of effect of various parameters such as temperature, pH and inoculum size on hydrodynamic cavitation has been reported largely for organic pollutant degradation using conventional devices. Sun et al. [19] reported rotational hydrodynamic cavitation reactor and disinfection efficiency of reactor towards *E. coli* removal. Cerecedo et al.[20] explored various geometries of the cavitation channels between rotor and stator for disinfection of large numbers of *E. coli* and *E. faecalis* bacteria. Madge and Jenson, [21]used 20-kHz ultrasound unit for disinfection of domestic wastewater and found that the disinfection of fecal bacterial efficiency increased with ultrasound power. A number of hybrid techniques have also been reported for disinfection mainly for hydrodynamic cavitation, acoustic cavitation, hydrogen peroxide, ozone, UV etc. and for different reactor geometries [14,15,22,23]. However, there are several limitations of conventional devices and efficiencies were not very high. Further rotor based devices and methodologies are expensive and impose higher operating/maintenance costs [5,24]. The philosophy of enhancing performance of conventional hydrodynamic cavitation for disinfection relies on either intensification using ozone, hydrogen peroxide etc or by process integration with method such as UV; both approaches depict only incremental benefits at rather increased cost. Natural oils can have antibacterial, antifungal and antiviral and antioxidant properties [25] and find use in various applications such as food preservations, aromatherapy and fragrance industries. The antibacterial properties are largely due to the high contents of oxygenates (Phenolics/alcohols). The antibacterial properties of a large number of essential natural oils such as Eucalyptus, clove oil have been well reported [2,26,27,28]. However, there are no reports showing systematic study on disinfection of pathogenic bacterial from water through addition of natural oil, for real life application or in cavitation. The addition of natural oil in cavitation is expected to enhance and/or alter disinfection process and hence can be suitably used. Further, application of natural additives such as oils can also reduce the cost of operation. Thus, it is instructive to evaluate effect of additives such as oils having disinfection properties in conjunction with cavitation for increased rates of disinfection and for improved efficiency.

In the present study, we explore a newer form of process, for the first time, to provide proof of concept for hydrodynamic cavitation using different natural oils and for different reactor geometries for two model microbial strains- gram negative (*Escherichia coli*) and gram positive (*Staphylococcus aureus*). A newer form of cavitating device, vortex diode and gram-positive *S. aureus* bacteria were investigated in detail and the generality of results was also confirmed using conventional type of cavitation device-orifice and more commonly reported gram-negative bacteria, *E. coli*. Different oils such as clove oil, eucalyptus, cinnamon and castor oil have been studied for their impact on cavitation. A plausible disinfection mechanism was evaluated to confirm the role of cavitation and oil in cell destruction. A cavitation based model using per pass disinfection was successfully applied. The developed newer method is expected to provide practical, low cost and improved operation for complete destruction of bacterial cellular structure/ death of cell. The results of this work would also lead to newer designs of cavitation reactor and easy scale-up.

2. Materials and methods

2.1. Materials

Staphylococcus aureus (ATCC-6538) and *E. coli* (ATCC-8739) were obtained from NCIM-National Collection of Industrial Microorganism at CSIR, National Chemical Laboratory, Pune, India. The different natural oils such as clove oil (Scientific Name: *Syzygium aromaticum* MW 205.642, Boiling point 250 °C, Solubility 2460 mg/L at 25 °C, density 1.0652 g/cc at 20 °C), Nilgiri oil (Scientific Name: *Eucalyptus globulus*, MW 154.23, Boiling point 176.4, solubility 3500 mg/L at 21 °C, density 0.9267 g/cc), Castor oil (Scientific name: *Ricinus communis*, MW

933.45, Boiling point 313 °C, Solubility less < 1 mg/mL at 68° F), Dalchini oil (Scientific Name: *Cinnamon verum*, MW 282.383, solubility 1 vol in 3 volumes of 70% ethanol at 20 °C, density, 1.052–1.070 g/cc) were procured locally and used as it is without any prior treatment.

2.2. Cavitation reactors

A vortex diode (66 mm chamber diameter) of 1 m^3/h nominal capacity of CSIR-NCL design (US9422952B2, 2016) was used as a cavitating device for vortex flow based cavitation. Another cavitating device of conventional type, orifice was also locally made using 3 mm diameter single hole for linear flow based cavitating device. Details of experimental set-up and operation are provided in the experimental section and Fig. 1.

2.3. Bacterial cultures growth

Bacterial cultures were grown on 50 mL Nutrient Broth (Himedia Nutrient HiVeg broth); incubated at 37 °C, 200 rpm in an incubator-shaker for overnight. The incubation was given to the mid-point of bacterial log phase, which was determined by UV–VIS spectrophotometer at 600 nm, to ensure bacterial population is in robust stage of growth and not in saturation or death phase. The known concentration of bacterial culture was added to the 20 L of water to obtain final concentration of $\sim 10^4$ CFU/mL.

The number of viable bacteria present in the system was estimated by plate count method. A sample of 10 mL was withdrawn from the cavitation tank at regular intervals of 15 to 60 min for spreading to sterile petri dish containing N. agar medium. The plates were incubated at 37 °C for 24 h, and the colonies were counted as colony forming unit per milliliter (CFU/ml).

$$CFU/ml = \frac{Number\ of\ colonies\ on\ N.\ agar\ plate}{volume\ plated\,(ml)} \times dilution\ factor$$

2.4. FE-SEM and TEM analysis

The Field Emission Scanning Electron Microscopy (FESEM, FEI-Nova NanoSEM-450) was carried out to observe the morphological changes of bacterial cell after disinfection and to prove efficacy of cavitation treatment. Samples were withdrawn at different time intervals (0 min: before cavitation, with oil treatment and after 60 min of treatment) and were fixed with 4% (v/v) glutaraldehyde in 0.1 M phosphate buffer (pH 7.0) for 1 h, subsequently washed with phosphate buffer (0.1 M) for 10 min. Further, the fixed samples were dehydrated by using graded series of ethanol solutions (30, 50, 70, 90 and 100% ethanol) for 30 min each before the analysis.

TEM (Transmission Electron Microscopy; Tecnai G2 20 STwin; LaB6 filament as the electron source) analysis was carried out for detailed examination of disinfection process and to study effects of combined cavitation with oil treatment with respect to cell destruction and cell death.

2.5. Disinfection using hydrodynamic cavitation

A schematic of the hydrodynamic cavitation using different cavitating devices is shown in the Fig. 1 along with the photograph of experimental set-up housing the different cavitating devices and the present work focuses on two devices namely orifice and vortex diode. The essential components of the experimental set-up include a high pressure multistage centrifugal pump, a 50 L volume water storage tank, cavitating devices, temperature control (JULABO Chilling system, Model FL 1701, 20 L); pressure and flow controls/indicators etc. The details of experimental set-up are described in our earlier publications [12,13,16] therefore have not been repeated here. Typically, 20 L volume of contaminated water was used for each experiment. The water was pumped through desired cavitating device under controlled conditions. The flow rate was controlled using bypass. The inception of cavitation was confirmed in the pressure drop range of ~30 to 50 kPa and 125 to 180 kPa (0.3 to 0.5 bar and 1.25 to 1.8 bar) for vortex diode and orifice respectively from the data of pressure drop vs. flow rate and analyzing the deviation of pressure drop from the usual square law (ΔP proportional to square of flow rate or mean velocity) specific to cavitating device. In view of the obtained cavitation inception, the disinfection experiments were carried out at pressure drop conditions of 0.5, 1.0 and 2.0 for vortex diode and for 2, 5 bar for orifice. For the study of

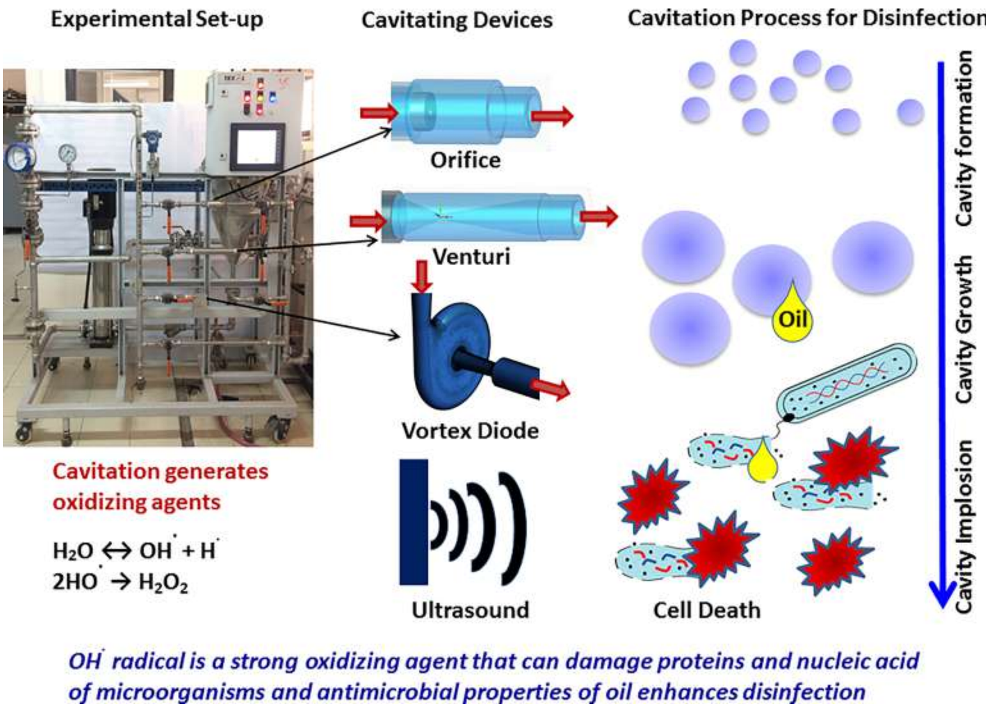


Fig. 1. Experimental set-up and schematic of disinfection using cavitation.

oil effect, a known quantity of natural oil was added in the water tank (0.1% or 20 mL for 20 L volume) at the start of the experiment. Samples (10 mL) were withdrawn at regular intervals and colony forming units (CFU) were determined. The reproducibility of the experiments was checked and was found satisfactory.

2.6. Disinfection using acoustic cavitation

Acoustic cavitation was carried out using ultrasound-40 kHz frequency and 500 W of power (UCP-20 Sonication Unit). A 200 mL of water containing known amount of bacteria was exposed to acoustic cavitation for a period of 15 min. Samples were withdrawn every 5 min and percentage of disinfection estimated. The experiments were performed using both with and without oil addition (Oil addition of 0.1% similar to that in hydrodynamic cavitation).

2.7. Disinfection without cavitation

The contaminated water sample of the same mix of that used for cavitation was separately studied by keeping in incubator shaker at 120 rpm and at 37 °C; with and without oil addition. Samples were withdrawn at regular time intervals and percentage of disinfection estimated.

3. Results and discussion

S. aureus and *E. coli* were selected as model organisms in the present study to provide proof of concept for application of hydrodynamic cavitation using natural oils for disinfection. *Staphylococcus aureus* is a facultative anaerobic or aerobic gram-positive bacteria having cocci shape, formed in singly, pairs, and irregular clusters and causes variety of skin disease, pustules, septicemia and pneumonitis. *E. coli* is a Gram-negative, facultative anaerobic, rod-shaped, coliform bacterium mostly occurred in water and known to cause various diseases, including pneumonia, urinary tract infections, and diarrhea. Effect of different process parameters were studied, in isolation as well as in conjunction with natural oil to bring out differences in the cavitation behavior. Effect of different reactor geometry was also evaluated in this regard. The detailed characteristics of natural oils are shown in Table 1.

3.1. Effect of pressure drop

Pressure drop (ΔP) is one of the most critical parameters in cavitation reactors as it dictates the number density and quality of the cavities based on the cavitation device type. Apart from quantity and quality of the cavities, the implosion of cavities is most critical to the real oxidation mechanism. Further, high shear generated during the cavity collapse may also physically break open the outer shell of microbes and therefore cause disinfection [29].

In our earlier studies, the effect of pressure drop for disinfection was discussed in detail and hence, only the essential and new findings in this regard are discussed below [4]. The optimization of pressure drop is utmost important to achieve complete disinfection of microorganism. The results for vortex diode showed that extent of *S. aureus* removal was enhanced from 75 to 89% with increasing pressure drop from 0.5 to 1 bar respectively. Increasing the pressure drop to 2 bar, the *S. aureus* removal efficiency could be further increased to 97% within one hour, which indicates the consistency and efficacy of vortex diode for disinfection of pathogenic bacteria.

The optimum pressure is typically in between lowest and highest operating pressure corresponding to the low cavity density and cavity cloud respectively [30]. High pressures can also lead to escaping cavities from water without collapse, reducing the production of hydroxyl radicals and therefore reduced disinfection efficiency. Badve et al. [31] also observed increased inlet pressures (orifice, venturi) leading to increased disinfection up to certain pressure followed by decrease. The present study, however, found consistently increasing disinfection in the case of vortex diode up to 2 bar pressure drop.

3.2. Effect of pH on disinfection of S. aureus

The effect of pH for disinfection using cavitation has not been investigated so far which could be important from the point of view of wastewater treatment, recycle and reuse. The effect of pH was studied at three different conditions of pH: 4, 7 and 10. All the experiments were conducted at optimized inlet pressure of 1 bar. Fig. 2 shows the results on disinfection of *S. aureus* at different pH with and without cavitation. While acidic conditions favor disinfection, the cavitation is equally effective at neutral pH which is important from its practical application point of view. The acidic pH tends to make microorganisms sensitive to hydrogen ion and enzymatic proteins are affected leading to loss of enzyme catalytic activity and simultaneous denaturation [32]. At pH 4, little disinfection was observed without cavitation, compared to that with cavitation. It is also possible to exploit increased rate of disinfection due to acidity by reducing the treatment time, as 72.0% disinfection was observed within 15 min, while in the same time 37 and 20% of disinfection observed at pH 7.0 and pH 10 respectively. Thus, cavitation, in conjunction with lower pH can have improved disinfection behavior. The enhancement of disinfection at lower pH can be attributed to the lower rate of recombination of hydroxyl radical, thereby making more hydroxyl radicals available for oxidation. It can be presumed that at acidic pH, bacterial enzymes will denature and higher concentration of hydroxyl radicals is possible at interface compared to bulk liquid when the bacteria is in ionic form leading higher percentage of disinfection. The positive effect of acidic pH in cavitation is however largely studied for organic pollutant degradation [17,30,33].

3.3. Effect of temperature on disinfection of S. aureus

Temperature plays an important role, for both disinfection and cavitation. Heating to a certain temperature is also one form of disinfection method, though not practical for treating large volumes or isolated small volume treatments. Again, the effect of temperature has been reported in the case of hydrodynamic cavitation for the degradation of organic pollutants, but not many systematic studies for disinfection. In the present study, disinfection of *S. aureus* was investigated using three different temperature viz. 28 (ambient), 40 and 50 °C, with and without cavitation. It can be seen from Fig. 3 that in case of without cavitation, disinfection follows the known trend of increasing efficiency with increased temperature and at 50 °C, about 53% disinfection could be seen within 15 min and 80.7% within 60 min as

Table 1
Properties of natural oils used in present study.

Sr. No.	Name of oil	Viscosity (poise)	Surface tension (dyne/cm)	Active ingredient (%)	Reference
1	Clove	0.066 ± 0.006	5.8 ± 0.72	Eugenol (83.13%)	[38]
2	Eucalyptus	0.337 ± 0.033	7.33 ± 1.49	1,8-eucalyptol (72.71)	[38]
3	Cinnamon	0.041 ± 0.001	23.04 ± 0.07	Cinnamaldehyde (82.5%), eugenol (0.5%)	[38]
4	Castor	6–8	39	Ricinoleic acid (85–95%)	https://www.drugfuture.com/chemdata/castor-oil.html

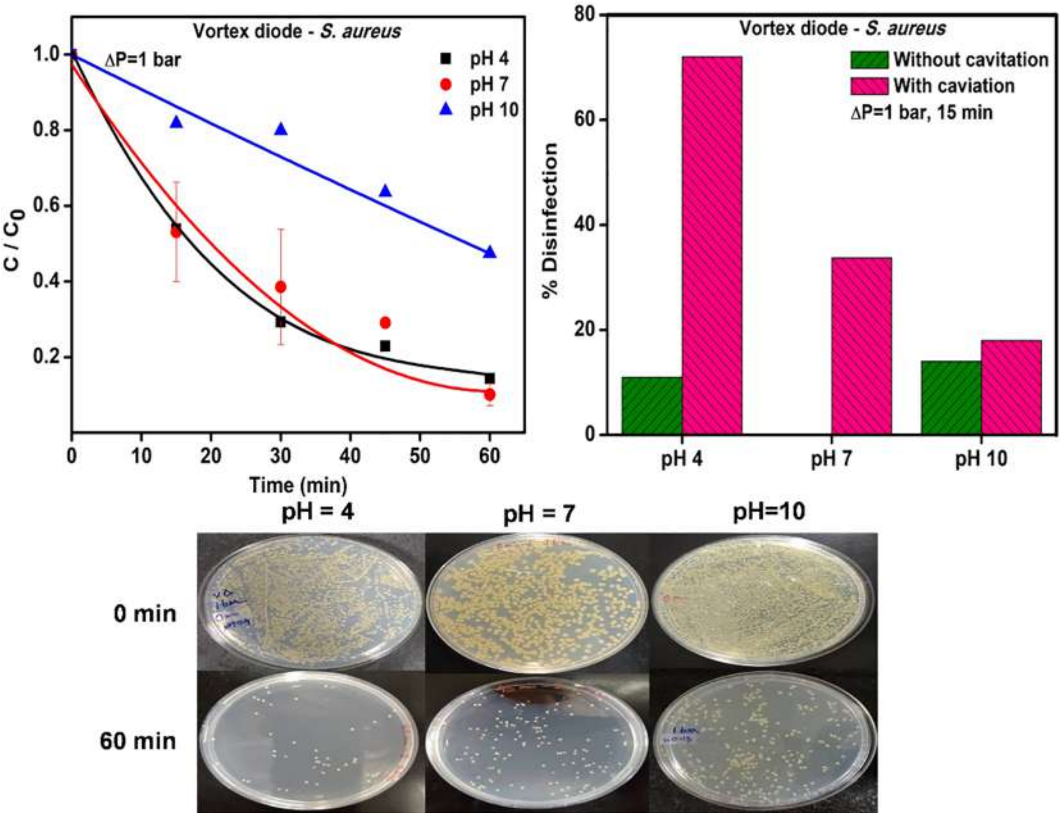


Fig. 2. Effect of pH on water disinfection by hydrodynamic cavitation by vortex diode.

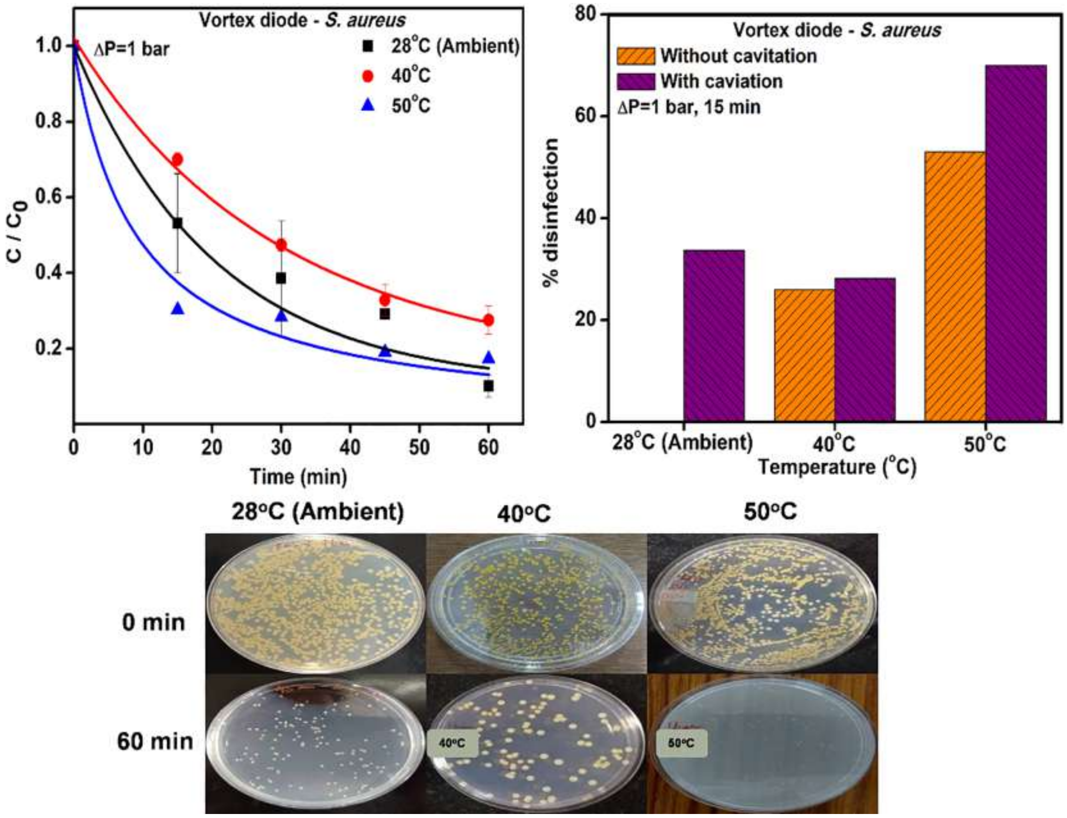


Fig. 3. Effect of temperature on water disinfection.

probability of cell death increases [34]. In the case of cavitation, the effect of temperature is marginal, but importantly, the efficacy of cavitation technique is evident at ambient conditions. It may be noted that with increase in the temperature, viscosity, surface tension and gas solubility reduce, thus cavitation intensity and the number of cavity nuclei also can reduce [33]. There are conflicting reports on degradation of pollutants (dyes) with cavitation at increased temperatures indicating both increase and decrease in the rates beyond certain temperature suggesting uncertainties in the cavitation phenomenon at higher temperatures [35,36].

3.4. Effect of increasing inoculum size

Bacteria concentration in wastewaters can be from insignificant to a very high- $> 10^5$ CFU/mL. The higher concentration of bacteria poses a significant risk to human health and fatal to aquatic life. In the present study, effect of initial bacterial concentration was investigated in the range 20,000 to 2,00,000 CFU/mL. The results of the effect of concentration are shown in Fig. 4. It is evident that the disinfection percentage remains almost constant, largely in the range 70–90% for increasing inoculum size, which shows reliability and efficacy of cavitation reactor, vortex diode in this particular case, for different concentrations of bacteria. Interestingly, for the effectiveness of the cavitation process, microorganisms should be present in cavitation region so that they get killed by collapsing of cavities in their vicinity [37]. However, for the effect of bacterial concentration, a number of situations may arise such as large number of cavities and less number of microorganism; comparable number of cavities and microorganisms or in another extreme, less number of cavities and largely outnumbered microorganisms. The other uncertain elements of process such as number of cavities collapse or fruitful implosion with deactivation of bacteria, that are not measurable, add to unpredictable behavior of the process. Geometry of the cavitating device is also an important aspect in this regard and vortex diode is found to be much more effective as compared to conventional devices [4,11,18].

3.5. Exploring use of natural oils in cavitation for disinfection

Medicinal plants are rich source of antimicrobial active compound. It would be prudent to exploit the presence of active compounds of natural oils for disinfection of water, without adversely affecting the quality of water. For the first time, the effect of such oils/extracts is being reported for large scale disinfection application and with cavitation. While, such oils can be easily separated after the treatment, it may also be possible to use positive ingredients from such natural extracts/oils for improving quality of treated water. The properties of some initial selected oils; clove, eucalyptus, cinnamon and castor oil are given in Table 1. The primary basis of selection of these oils for studies in cavitation is that these oils are not harmful in nature. The effect has been evaluated using different cavitating devices i.e. vortex diode, orifice and also for acoustic cavitation.

The results of disinfection are given in Fig. 5 for the four oils and for vortex diode as a cavitating device; for clove oil and orifice as a cavitating device. The proof of concept is also provided for acoustic cavitation and clove oil in Fig. 5c. Only a fraction of oil, 0.1% of total volume of water was added in all the experiments. There are a number of observations from these results (Fig. 5 and Table 2). First, the oil can have both positive and negative impact in terms of extent of disinfection:

1) Clove oil and eucalyptus oil have best effect in terms of increased efficiency while castor and cinnamon oils have lower disinfection efficiency compared to hydrodynamic cavitation alone for vortex diode as a cavitating device.
2) A very important aspect of the results of Fig. 5a, is that there is an order of magnitude increase in the rates of disinfection, implying significantly reduced time of operation. For example, in the case of clove oil and eucalyptus oil, the increase in the rates in initial period is as high as 2–4 folds in 15–20 min compared to cavitation alone.
3) The results clearly indicate positive impact of clove and eucalyptus oil, both in terms of rate of disinfection as well as for increased disinfection.
4) Similar results are observed in case of orifice using a pressure drop of 2 bar (Fig. 5b). It is to be seen that orifice requires significantly higher pressures, almost double or more, as compared to vortex diode for similar extent of disinfection. In 15 min, ~32% disinfection of *S. aureus* was observed by orifice, which was enhanced to 55% by addition of clove oil.
5) The concept of cavitation using oil for disinfection was validated using acoustic cavitation as well and from the results of Fig. 5c it is evident that acoustic cavitation using oil (0.1%) has hugely increased the disinfection; without oil and with acoustic cavitation alone, there was negligible disinfection. Use of clove oil with acoustic cavitation here gave ~51% disinfection in 15 min.
6) For the case of cinnamon oil and castor oil, the disinfection rates were adversely affected.
7) It is evident that selection of natural oils is crucial for improving the rates and extent of disinfection that could also positively impact in reducing the cost of operation.

It is quite instructive to evaluate the differences in the disinfection behaviour of different oils, especially from the view point of cavitation where bubbles/cavities get formed, grow and finally collapse to yield desired impact. Three factors can directly affect the collapse or implosion of cavities- the surface tension of the bubble, the inertia of the fluid and the pressure of the gas inside the cavities [39]. The pressure difference between the inside and outside of a cavity depends upon the surface tension and the size of the cavity. Thus, the properties of oil can modify the cavitation behaviour according to their physical properties. Apart from the physics of the bubbles and their altered collapse, antibacterial activity of the natural oil is another important aspect. A high antibacterial activity of *eucalyptous* oil was reported by Lu et al. [40] and Bachir and Benali, [26]. The high disinfection ability of *eucalyptous* oil is due to the presence of 1,8-cineole active compound. The active compound of eucalyptus oil can destroy the permeability of bacterial membranes, leading to loss of electrolytes such as K^+, Na^+ and Ca^{+2} [40]. Similarly, clove oil has high bactericidal activity due to high level of eugenol [27]. The eugenol can react with the phospholipids of the cell membrane altering its permeability and as a consequence denature

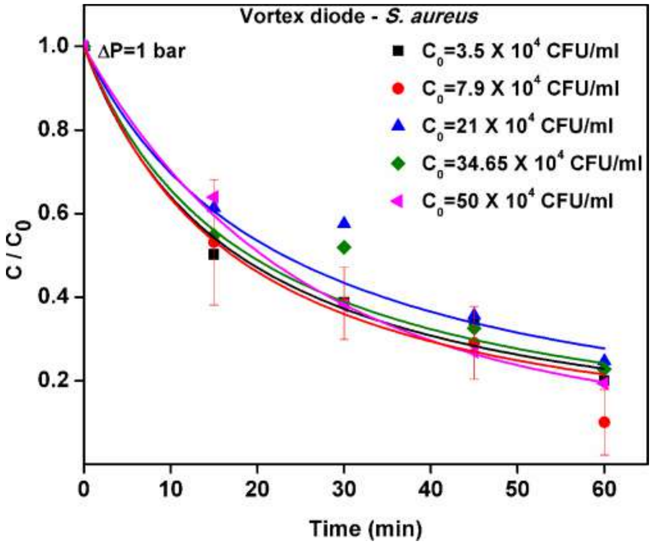


Fig. 4. Effect of inoculum size on water disinfection.

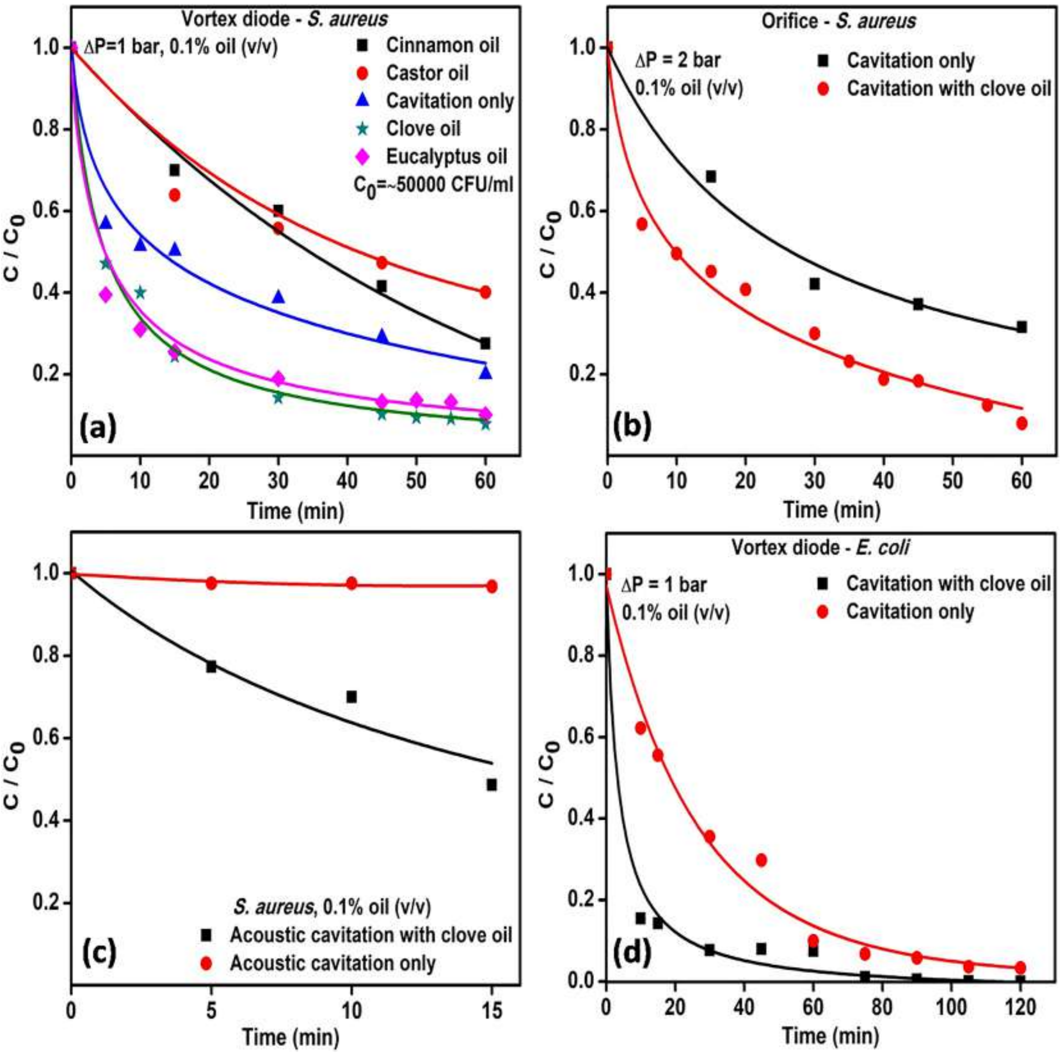


Fig. 5. Effect of oil in cavitation for disinfection. (a) Vortex diode – *S. aureus* (b) Orifice- *S. aureus* (c) Acoustic cavitation- *S. aureus* (d) Vortex diode- *E. coli.*

Table 2
Rate of disinfection for *S. aureus* (15 min).

Study	Parameter	Initial CFU/ml	% Disinfection	Rate of disinfection, CFU/(mL.s) (conventional model)	Rate of disinfection, CFU/(mL.s) (cavitation model)	Rate constant (s^{-1}) × 10^4	Per-pass disinfection (ϕ)
Effect of Pressure Vortex Diode	**ΔP, bar**						
	0.5	50,000	32	18.0	17.8	4.3	0.0598
	1	35,000	43	17.2	16.8	6.3	0.0622
	2	60,000	39	26.4	25.9	5.5	0.0376
Effect of pH Vortex Diode (ΔP = 1 bar)	**pH**						
	4	78,500	71	70.5	62.4	14.0	0.1314
	7	68,000	21	15.6	15.6	2.6	0.0249
	10	55,000	18	11.2	11.1	2.2	0.0211
Effect of Temper-ature, (°C) Vortex Diode (ΔP = 1 bar)	**T, °C**						
	28	68,000	21	15.6	15.6	2.6	0.0249
	40	88,500	30	29.8	29.4	4.0	0.0388
	50	36,300	70	31.4	28.1	13.3	0.1310
Effect of oil 0.1% (v/V) Vortex Diode (ΔP = 1 bar)	**Oil**						
	Clove	35,000	63	26.6	24.6	11.1	0.1106
	Eucalyptus	43,800	74	41.7	36.2	15.2	0.1491
	Cinnamon	58,000	30	19.5	19.3	4.0	0.0400
	Castor	73,500	36	29.9	29.4	5.0	0.0497
Effect of Pressure Orifice (ΔP = 2 bar)	**ΔP, 2 bar**	38,000	32	13.5	13.3	4.2	0.0970
Effect of oil 0.1% (v/V) Orifice (ΔP = 2 bar)	Clove Oil	25,000	55	16.0	15.2	8.8	0.2061
Acoustic (15 min)		66,100	3.18	2.3	NA	0.36	NA
Effect of oil 0.1% (v/V) Acoustic (15 min)	Clove Oil	62,700	51	37.3	NA	8.0	NA

cell protein. The denaturation of cell protein causes death to cell [41]. The lower disinfection using *cinnamon* (62%) and castor oil (60%) may be attributed to adverse effect on number and quality of the cavities, as both the formation and energy release rate depends on surface tension and viscosity of oil. Increasing surface tension reduces size of the cavities and promotes less violent collapse [42]. Thus, in the present case, lower disinfection is observed for oils having high surface tension properties (castor oil 39 dyne/cm, cinnamon 23.04 dyne/cm) compared to oils having low surface tension (eucalyptus oil 7.3 dyne/cm, clove oil 5.8 dyne/cm). Further, microbial inactivation is process in which viability of organisms exposed to oil additive varies with time [40]. The inactivation depends on the type of microorganism, type and concentration of oil additive, and environmental conditions such as temperature and pH. Thus, the effect of oil can be significantly different for different microorganisms. However, these aspects are complex in nature due to interacting physical, chemical and microbial attributes and hence require more detailed investigations.

The methodology was extended for the removal of gram-negative bacteria (*E. coli*) and only the proof of concept is provided by using clove oil and vortex diode as a cavitating device using the optimum pressure drop of 1 bar. The results are shown in Fig. 5d which clearly confirm order of magnitude increase in the initial rates of disinfection compared to cavitation alone and practically complete removal can be obtained in 90–100 min.

3.6. Kinetics of disinfection

A development of model based on per-pass conversion for hydrodynamic cavitation was presented in our earlier work [4] and the same is extended to evaluate kinetic data of the present study under different conditions. The cavitation process can be schematically shown as per Fig. 6.

The kinetics of disinfection can be modelled in two ways: one is by conventional rate model and another is cavitation based model [43]. It was observed that the concentration of bacteria decreased exponentially with time and the kinetic data for disinfection of water can be fitted using Pseudo-first order equation in terms of k_G (growth rate of microorganisms) and k (disinfection rate of microorganisms).

Step	Conventional rate model	Cavitation based model
1	Assuming first order reaction$-\frac{dc}{dt} = \boldsymbol{kC}k$ is a rate constant	Pseudo-first order equation in terms of k_G (growth rate of microorganisms) , k (disinfection rate)$\boldsymbol{V\frac{dc}{dt} = V(k_G - k)C}$
2	Integration of rate gives the pseudo first-order relationship$\mathbf{ln}\frac{C}{C_0} = \boldsymbol{-kt}$ $\boldsymbol{C = C_0e^{-kt}}$	The concentration of microorganisms C can be obtained by assuming the rates to be constant: $\boldsymbol{C = C_0e^{-(k-k_G)t}}$where C_0 is the initial concentration of bacteria (CFU/ml), t is the time for disinfection (min)
3	Not Applicable	The extent of disinfection in terms of per-pass disinfection factor (ϕ) and number of passes (n): $\boldsymbol{V\frac{dC}{dt} = Vk_GC - Q\varnothing C}$; $\boldsymbol{n = \frac{Q}{V}t}$
4	Not Applicable	For the assumption of constant ϕand k_G, the concentration of microorganism at time t is estimated for the residence time of τ (V/Q).$\boldsymbol{C = C_0e^{-(\varnothing-k_G\tau)n}}$
5	$\boldsymbol{C = C_0e^{-kt}}$	Correlating the growth rate constant to doubling time, t_D as $k_G = (\ln 2/t_D)$ $k_G = \frac{\ln 2}{t_D}$ and assuming negligible growth of microorganism during the treatment time, the disinfection of water can be described as: $\boldsymbol{C = C_0e^{-kt} = C_0e^{-\varnothing n}}$
6	The effective disinfection rate constant (k) is: $\boldsymbol{k = \frac{\ln(C_0/C)}{t}}$	The effective disinfection rate constant (k) may be related to residence time (τ) and ϕ as: $\boldsymbol{k = \frac{\varnothing n}{t} = \frac{\varnothing}{\tau}}$
7	The overall cavitation yield, $\boldsymbol{Y = \frac{V(C_0 - C)}{\Delta PQt}CFU/J}$	The overall cavitation yield, can be obtained as: $\boldsymbol{Y = \frac{V(C_0 - C)}{\Delta PQt}CFU/J}$
8	Not Applicable	For small values of ϕ, $\boldsymbol{Y = \frac{\varnothing C}{\Delta P}CFU/J}$
9	Rate of disinfection, R is: $\boldsymbol{R = kC_{avg}CFU/(mls)}$$C_{avg}$ is average concentration; $\boldsymbol{C_{avg} = \frac{C_0 + C}{2}}$	The average disinfection rate over time 't_{op}' is: $\boldsymbol{R_{avg} = \frac{C_0(1-e^{-kt})}{top} = \frac{C_0(1-e^{-\varnothing n})}{top}CFU/(mls)}$

The mathematical model based on the physical description of cavitation process is closer to the real life operation and is also easy to solve using the experimentally obtained parameters such as flow rate (Q), volume (V) and concentration-time data. The value of number of passes is of practical importance since it determines the cost of operation and lower values are desirable. The value of per-pass disinfection factor can be simply obtained using Eq. 6. As discussed in our earlier work, per-pass disinfection factor based cavitation model is more realistic, as nature of geometry of the cavitation device can be reflected into per-pass disinfection. The mathematical treatment clearly indicates dependence of disinfection on residence time and less dependence on initial concentration compared to conventional reaction rate model.

The results of kinetics study for the conventional rate model and those using cavitation model are presented in Table 2, specifically for 15 min of operation, where differences in the initial rates are evident. Similar to our earlier findings [4], the values of rate of disinfection are very high indicating effectiveness of cavitation, in general and vortex

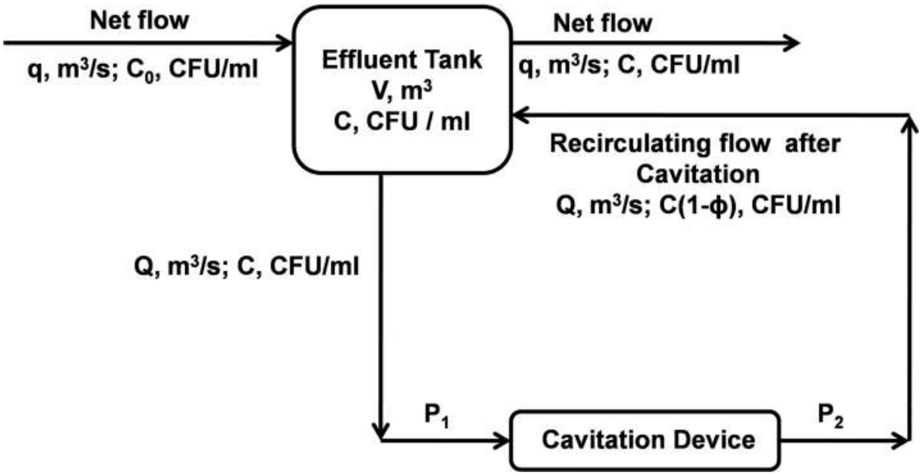


Fig. 6. Schematic diagram for decontamination of water using cavitation.

diode, in particular. Thus, the results clearly establish strong dependence of rate of disinfection upon type of cavitating device. In this work, apart from different cavitating devices, we have also attempted to evaluate the performance under acoustic cavitation (using ultrasonic bath) and the rates of disinfection for the same are also listed in Table 2. Further, oil as an additive was evaluated for the improvement of the process. A number of interesting observations could be made in this regard.

1. The rates of disinfection in hydrodynamic cavitation are significantly/order-of-magnitude higher compared to acoustic cavitation.
2. The rates of disinfection are higher using vortex diode as compared to orifice and orifice requires significantly higher pressures compared to vortex diode.
3. Low pH (4) gives substantially increased rates of disinfection.
4. Higher temperature, naturally and as expected, improves disinfection.
5. There is drastic effect of oil on disinfection behavior. While the two oils, namely clove and eucalyptus oil positively alter the cavitation behavior, the other two oils, cinnamon and castor oils adversely impact the disinfection behavior. This effect is also observed even in the case of acoustic cavitation, where more than 20 times increase in the initial rate of disinfection was observed by addition of clove oil.
6. The reasons for the variations in different oils can be explained on the basis of characteristics of oil and the constituent properties, as explained in the earlier section and also using the proposed mechanism.
7. Vortex diode is found to be superior compared to orifice even in the case of increased rates of disinfection by oil addition.

The differences in the rates for acoustic cavitation and hydrodynamic cavitation are quite understandable on the basis of the intensity of cavitation since large differences have been reported even within acoustic cavitation using ultrasonic bath and ultrasonic horn [14]. The temperatures also aid disinfection process and increased rates can be obtained at higher temperatures [31]. The conventional methodologies typically considered using the combination of different treatment methods. The oil as an additive can be one alternative to many of the hybrid techniques reported in the literature such as hydrogen peroxide treatment, ozone, ultrasonic cavitation coupled hybrid processes; implying uniform and intense cavitation effects in disinfection with possible health benefits for the oil characteristics apart from the conventional attributes of high efficiency and also ease of operation compared to ultrasonic cavitation, conventional hydrodynamic cavitation or hybrid methods.

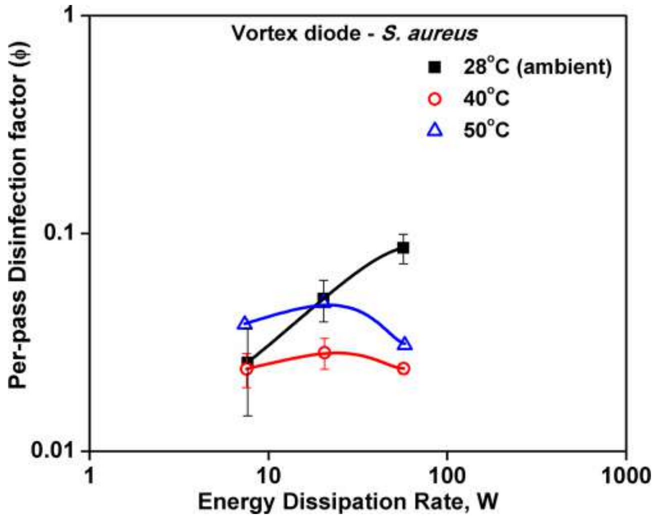


Fig. 7. Effect of Temperature- Per- pass disinfection factors at 60 min.

The effect of temperature on per- pass disinfection factors for *S. aureus* is shown in Fig. 7. For vortex diode and under ambient conditions, as the pressure increases from 0.5 bar to 2 bar, per-pass disinfection factors increase from 0.057 to 0.086 and subsequently energy dissipation rate also increases. However, similar trend is not found at higher temperatures (40 °C and 50 °C), as the pressure increase reduces per-pass disinfection factor partly due to the vapour cloud formation; large number of cavities lead to large vaporous bubbles which get carry-forward without collapsing [44,45].

The impact of addition of natural oils on per-pass disinfection, especially in the initial rates, is shown in Fig. 8 for vortex diode at the optimum pressure drop of 1 bar. The errors were largely below 1.5% for all sets, except for eucalyptus oil. The maximum error for eucalyptus oil was ~8%. It can be seen that per-pass disinfection factors for *S. aureus* are higher for clove and eucalyptus oil with cavitation than other oils. It is evident that in 15 min, cavitation with clove oil and cavitation with eucalyptus oil showed more than 100% increase in the per-pass disinfection as compared to cavitation alone. The benefits diminish with time and hence selection of best suitable oil and time of treatment is crucial. Thus, the results clearly highlight that the increased rates of disinfection and per-pass disinfection in hydrodynamic cavitation can be exploited to reduce the time of operation, consequently to reduce the cost of disinfection.

Although the initial rate of disinfection could be significantly increased using oil as an additive, more rigorous efforts are further required to establish the relationship of oil properties and its synergy with cavitation process so that appropriate guidelines can be developed for the selection of most suitable oil.

3.7. *Disinfection of water using hydrodynamic cavitation: A plausible mechanism*

Oxidation process is known since long time for the destruction of bacteria, however their usage is limited due to major shortfalls. The conventional oxidation is a slow process and sometimes required additional catalyst to improve the removal rate. Also, the treatment is unsatisfactory for the complete killing of bacteria and rather only deactivates the bacteria. As per the EPA manual of water treatment, hydrogen peroxide is considered as a poor disinfectant. Thus, it would be prudent to find alternatives to existing many chemical disinfectants in this regard.

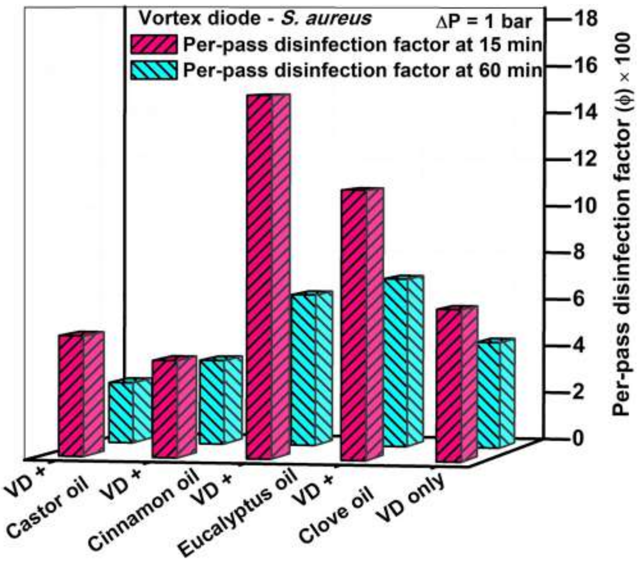


Fig. 8. Effect of oil on per- pass disinfection (VD-Vortex diode).

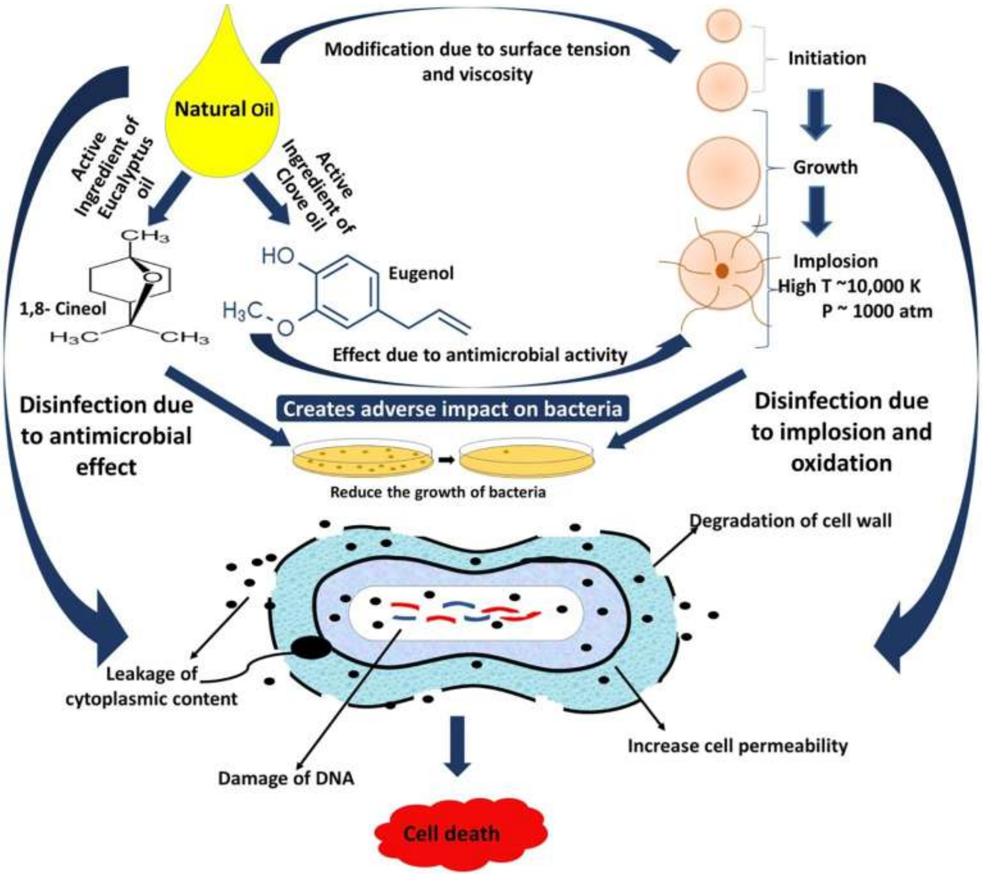


Fig. 9. Plausible mechanism of disinfection using natural oils and cavitation.

In the present study, cavitation with addition of natural oil was shown to achieve complete destruction of bacteria within shorter time period. The selection of natural oils is, however, not straightforward and a number of parameters are to be considered that would directly impact either the disinfection process or the cavitation process. Thus, in order to obtain synergetic effect of both cavitation and anti-microbial properties of natural oils, it is essential to envisage the possible mechanism of disinfection. Based on the results of the present study, a plausible mechanism for cell destruction is proposed and shown in Fig. 9. The destruction of cells can be attributed to hydroxyl radicals generated during the cavitation resulting into oxidative damage of the cells. Localized heat conditions of cavity implosion can also damage the DNA. The main reason for cell death is cell disruption since once cell membrane and/or cell wall is severely damaged, the bacteria become dead without DNA and protein denaturation. It has been well reported that important constituents of microorganisms such as proteins, lipids, DNA and polysaccharides can be affected by oxidation. The reactive species such as ·OH radicals can attack and oxidise double bonds and sulfhydryl groups of protein constituents and produce oxidative stress that creates unalterable consequences for the microorganisms [46,47]. Moreover, the active compound present in the natural oil can react with the phospholipids of the cell membrane thereby altering its permeability and also denature cell protein. The denaturation of cell protein causes cell death [41].

To further support the mechanism, the difference in cell morphology of bacterial cell before and after the cavitation with oil treatment was investigated using SEM and TEM techniques (Fig. 10). The results of FE-SEM clearly highlight the intact nature of the cells of *S. aureus* (0 min), round shaped and in a cluster form before treatment (Fig. 10a) and their mutilated form after the treatment (60 min), where cellular morphology of bacteria is changed in terms of increased cell permeability, distorted cell membrane and creation of holes or wrinkles on bacteria (Fig. 10b). These results were further reinforced by TEM analysis. The results of TEM analysis confirmed that at 0 min, the bacterial cell was intact as well as round shaped with clear cell membranes (Fig. 10c), while after combined cavitation with oil process, the cells were seen unevenly distributed, condensed, loss of cytoplasm and leakage of cytoplasmic content (Fig. 10d). Lu et al. [40] studied on antimicrobial activity of eucalyptus oil towards *Pseudomonas* sp., and stated that the antimicrobial effect of eucalyptus oil may be due to the active ingredient of oil that reacts with surface of bacterial cell and penetrate to plasma membrane leading to distortion of bacterial cell. The morphological changes and alteration of bacteria after oil treatment have been reported by several researchers [20,40].

While, the antibacterial activity of various oils and reasons thereof are well reported in the literature, its synergetic effect in enhancing efficiency in combination with other processes such as cavitation are not well researched so far. The plausible mechanism as depicted in Fig. 9 therefore is an attempt to qualitatively provide causes of cell damages, such as the membrane rupture due to extremely high stress produced during cavitation process, generation of extremely high temperatures during bubble implosion leading to the leakage of cytoplasmic matter apart from possible cell membrane rupture and DNA damage due to generation of active free radicals. The role of cavitation in disinfection in this regard is in accordance with that reported by Cerecedo et al. [20]. Palacios et al. [48] have reported *B. stearothermophilus* elimination by ultrasonic treatment and proposed that high pressures affected the permeability of protoplast membrane due to which dipicolinic acid, calcium and other low molecular weight substances get leaked and cell properties get modified which is in agreement with the present findings.

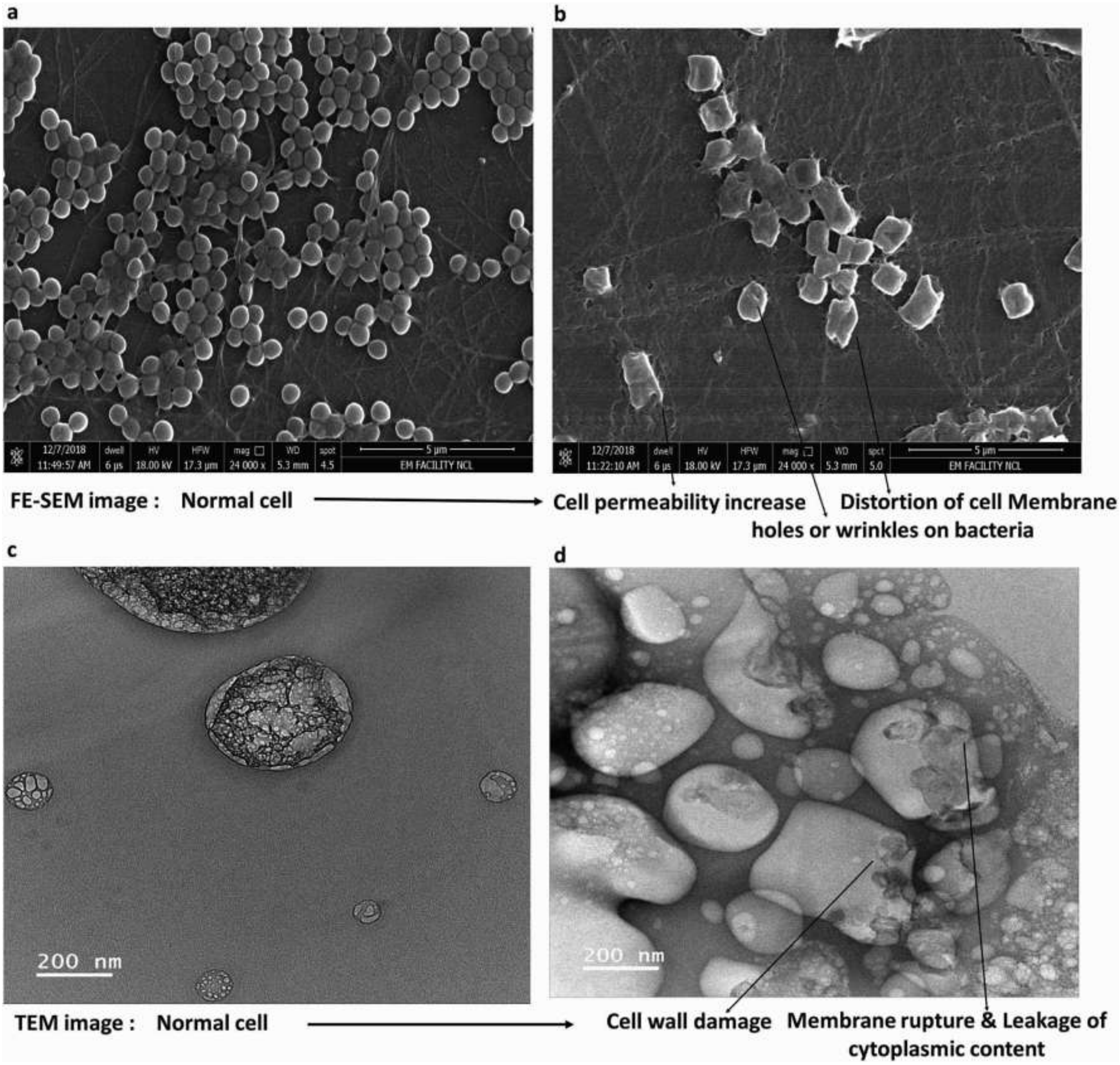


Fig. 10. Effects of cavitation with natural oil on morphology of bacteria. FE-SEM image (24,000 X) (a) 0 min sample (b) 60 min of treatment (c) TEM image, 0 min (d) TEM image, 60 min of treatment.

3.8. *Comments on the practical application of the new method*

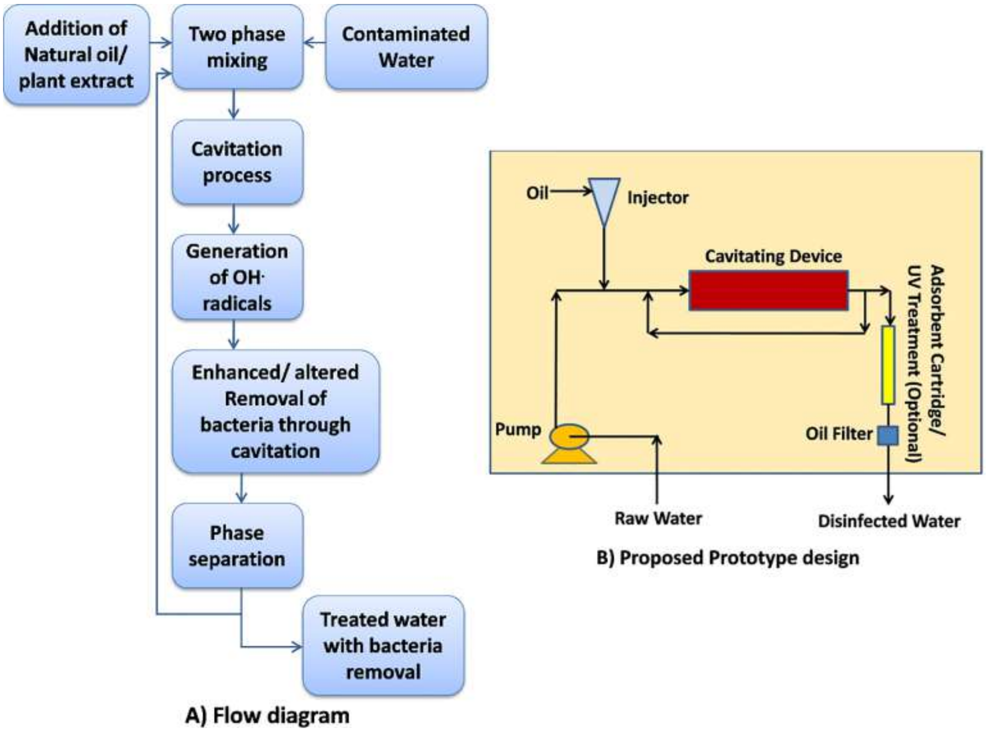
The cavitation process for disinfection of water is known and has been well reported in the literature, especially for acoustic cavitation and for hydrodynamic cavitation using conventional devices such as orifice, with and without process intensifications such as ozone, hydrogen peroxide addition, and so on. The success with these was, however, limited and as a result, practical application of such techniques is not available for either household applications or for large scale water treatment installations.

The results presented in this work are important from two counts. One, the hydrodynamic cavitation can eliminate the bacteria to the extent of 100% as desired by various norms. Secondly, the proof of concept in the form of addition of natural oils can significantly increase the rate of disinfection, thereby reducing the time of operation and consequently reducing the cost of operation. Although, the natural oil can be separated after use using standard methods, it may also be possible to exploit the health benefits of specific oils, with appropriate designs. Further, in such cases, it may also be useful to couple the process with other established methods such as adsorption for complete removal of bacterial contamination for cost optimization. It is necessary to investigate the effect of natural oils in detail to further enhance the performance of the developed process.

A typical flow diagram for the practical operation and conceived prototype design is shown in Fig. 11. The process essentially has the following essential steps:

- Creating a two phase system by contacting of oil phase with water/aqueous phase
- Creating of third vapor phase and conditions of *insitu* cavitation
- Allowing cavities to collapse so as to generate *insitu* hydroxyl radicals or hydrogen peroxide
- Allowing removal of bacteria from the contaminated water containing bacteria such as *E. coli*, *S. aureus* etc.
- Separating the oil phase and aqueous phase after the process is completed
- Removing bacteria or having bacteria content altered as per desired limits
- Recycling oil for further use.

In the case of partial destruction of bacteria using cavitation, the process can be suitably combined with other established processes such as adsorption, where suitable adsorbents effective for disinfection can be employed, e.g. silver nanocomposites, bio-nanocomposites and so on [8,9]. It is believed that process integration using hydrodynamic cavitation and cavitating device-vortex diode has a potential to provide



A) Flow diagram

B) Proposed Prototype design

Fig. 11. Flow diagram for disinfection using cavitation and proposed prototype.

practical solution to disinfection of water so that the disadvantages of existing chemical disinfection processes can be circumvented.

4. Conclusions

The present study, for the first time, clearly demonstrated the useful application of natural oils having antibacterial properties in combination with cavitation technology to enhance the efficiency of disinfection of water. Both gram-negative (*E. coli*) and gram-positive (*S. aureus*) bacteria can be effectively removed by optimizing the process parameters for hydrodynamic cavitation such as pressure, temperature and by use of suitable oil. It was shown that a very small percentage of oil (0.1%) can be sufficient to enhance initial rates of disinfection to the extent of 2 times for *S. aureus*, 5 times for removal of *E. coli* in the case of hydrodynamic cavitation using vortex diode and up to 17 times as compared to that in acoustic cavitation. The nature of oil modifies the cavitation behavior and hence a number of possible combinations can be anticipated in this manner. In the present study, clove oil was found to be the most effective natural oil in combination with cavitation as compared to eucalyptus, cinnamon and castor oil. Further, process is effective even at very high concentrations of bacteria, not reported so far. Practically 100% disinfection can be obtained using the hydrodynamic cavitation technology at very low pressure drop conditions, as low as 1 bar, especially for vortex diode as a cavitating device compared to orifice. A possible mechanism is proposed for the effect of oil and hydrodynamic cavitation in cell destruction through the rupture of cell wall, oxidative damage and possible DNA denaturation. The increased rates of disinfection using oils, where natural oils can be perceived as biocatalysts, along with reduced time and ease of operation, easy scale-up indicate potential to provide significant advantages in practical applications.

Acknowledgement

The authors, Dr. Bhandari, Dr. Balapure would like to acknowledge the financial support of DST-WTI project (GAP 317526) of Department of Science and Technology, India. Ms. Mane would like to acknowledge support from DST-Women Scientist program for providing fellowship.

Conflict of Interest

One of the authors (VVR) is a founder director of Vivira Process Technologies Pvt. Ltd. which commercially offers vortex diode based cavitation devices.

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Ultrasonics - Sonochemistry 69 (2020) 105272

Contents lists available at ScienceDirect

Ultrasonics - Sonochemistry

journal homepage: www.elsevier.com/locate/ultson

Destroying antimicrobial resistant bacteria (AMR) and difficult, opportunistic pathogen using cavitation and natural oils/plant extract

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ARTICLE INFO

Keywords:
Water treatment
Disinfection
Cavitation
Oil
AMR bacteria

ABSTRACT

The present study reports, for the first time, a new and techno-economic strategy for effective removal of antimicrobial resistant bacteria (AMR) and difficult, opportunistic pathogen using cavitation and natural oils/plant extract. A hybrid methodology using natural oils of known health benefits has been discussed in combination with conventional physico-chemical method of hydrodynamic cavitation that not only provides efficient and effective water disinfection, but also eliminates harmful effects of conventional methods such as formation of disinfection by-products apart from reducing cost of treatment. A proof-of concept is demonstrated by achieving exceptionally high rates for practically complete removal of antimicrobial resistant (AMR) and relatively less researched, gram-negative opportunistic pathogen, *Pseudomonas aeruginosa* and gram-positive methicillin resistant, *Staphylococcus aureus* using a natural oil-Peppermint oil and two different cavitating reactors employing vortex flow (vortex diode) and linear flow (orifice) for hydrodynamic cavitation. > 99% disinfection could be obtained, typically in less than 10 min, using vortex diode with operating pressure drop of 1 bar and low dose of 0.1% peppermint oil as an additive, depicting very high rates of disinfection. The rate of disinfection can be further increased by using simple aeration which can result in significant lowering of oil dose. The conventional device, orifice requires relatively higher pressure drop of 2 bar and comparatively more time (~20 min) for disinfection. The cost of the disinfection was also found to be significantly lower compared to most conventional processes indicating techno-economic feasibility in employing the developed hybrid method of disinfection for effectively eliminating bacteria including AMR bacteria from water. The developed approach not only highlights importance of going back to nature for not just conventional water disinfection, but also for eliminating hazardous AMR bacteria and may also find utility in many other applications for the removal of antimicrobial bacteria.

1. Introduction

Access to safe drinking water is one of the greatest challenge of 21st century [1], especially due to increased urbanization, industrialization, pollution, water scarcity/limited availability and changing climatic conditions. Antimicrobial resistance (AMR) is becoming a global crisis, threatening the future of drugs and also millions of lives worldwide [2]. Many resources of water are faecally contaminated, resulting nearly half million diarrhoeal deaths each year, including children below 5-year age. Apart from faecal contaminants (*Enterobacter*, *Klebsiella*, *Citrobacter*), different enteric viruses such as norovirus, calcivirus, cyanobacteria and algae also cause serious health problems [3]. Thus, disinfection of water is most critical issue for healthy life, especially for the developing countries. Disinfection of water also demands complete destruction or removal/inactivation of pathogenic microorganisms from drinking water/raw water/ground water to prevent recontamination of water in distribution system and maintain safest quality of water [4]. The most common bacteria reported for disinfection studies include gram-negative *E. coli* and gram-positive *S. aureus*. *E. coli* is an indicator bacteria that helps to know degree of fecal contamination in water and wastewater and therefore routinely used as a model bacteria for water disinfection. In recent years, bacteria that are resistant to antibiotics are causing concerns worldwide [5]. Presence of antibiotic resistant bacteria has been reported in untreated drinking water sources such as wells [6–8], rivers, and lakes [9] and also in presumably safe water such as in tap/bottled water [10]. According to WHO report, overuse and misuse of antibiotics in human and animal health is considered to be the main cause for accelerating the

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https://doi.org/10.1016/j.ultsonch.2020.105272
Received 5 February 2020; Received in revised form 2 June 2020; Accepted 20 July 2020

Nomenclature

C	Concentration, CFU/mL
C_0	Initial concentration, CFU/mL
k	Disinfection rate constant
k_G	Growth rate constant
n	Number of passes
P	Pressure, bar
ΔP	Pressure drop, bar
P_E	Cost of electricity, Rs/KWh
Q, q	Flow rate, m^3/s
t	Time, s
V	Volume, Liters
φ	Per-pass disinfection factor
τ	Residence time, s

emergence and spread of AMR bacteria [11]. However, disinfection studies pertaining to antimicrobial resistant bacteria such as methicillin resistance *Staphylococcus aureus* and also difficult, opportunistic pathogen such as *Pseudomonas aeruginosa* have been sparsely reported, probably due to difficulty in its removal. *Pseudomonas aeruginosa* is a common nosocomial, opportunistic pathogen, mostly found in water/wastewater and hospitals that causes serious infections with a high mortality rate. It is resistant to various antibiotics and therefore considered as a harmful and dreaded pathogen [12]. It is one of the three critical bacteria species because of its adaptive antibiotic resistance [11,13]. Since late 1980 s, there has been a void in the discovery of new antimicrobial drugs for combating staphylococcal infections, which makes it imperative to develop techniques to destroy present day AMR bacteria [14]. The presence of such AMR bacteria in various water sources clearly indicate the urgent need for techno-economically feasible methodologies for destroying these and for mitigating the proliferation of AMR bacteria in drinking water systems.

Disinfection studies pertaining to gram-negative bacteria, *Pseudomonas aeruginosa* have been sparsely reported, probably due to difficulty in its removal. Armstrong [15] reported use of ionic copper for elimination of *P. aeruginosa* and could achieve up to 4 log reduction in longer duration of about 6 h. Lineback et al. [16] found only limited disinfection using chemical route employing Hydrogen peroxide and sodium hypochlorite. Use of Nano-silica silver nanocomposites was also reported for effective disinfection [17]. Application of acoustic cavitation was not found to be effective [18], though use of hydrodynamic cavitation was reported with limited success even after employing for longer treatment times [19]. Recently, Jain et al. [20] and Mane et al. [21] discussed effective application of hydrodynamic cavitation methodology for the elimination of different bacteria such as *E. coli* and *S. aureus*; Mane and co-workers [21] introducing the concept of using natural oils in conjunction with cavitation techniques for disinfection and for increased rates of disinfection. However, not many disinfection studies on effective disinfection of *P. aeruginosa,* known to have adaptive antibiotic resistance, and also for antimicrobial resistant bacteria methicillin resistant *s. aureus* are reported so far. Kanchanapally et al. [22] suggested nisin peptide conjugated three dimensional (3D) porous graphene oxide membrane for the removal of methicillin-resistant - Staphylococcus aureus (MRSA) pathogens from water. McKinney and Prude, [23] studied disinfection of MRSA, vancomycin-resistant *Enterococcus faecium* (VRE), *E. coli* and *P. aeruginosa* using UV with only limited success.

The disinfection of water for eliminating different types of microorganisms is typically carried out using a large number of different mechanical, chemical and biological/biochemical methods, either in isolation or in combination [21,24,25]. UV irradiation, Chlorination and ozonation are most commonly used methods, but majority of these have many limitations [26]. UV irradiation breaks down the molecular bonds of microbial DNA, leading to formation of thymine dimers that can destroy the bacteria, however, the technique is inefficient when bacteria has its own photo-reactivation repair mechanism [27]. Chemical methods of chlorination and ozonation, though provide ease of operation, can form toxic/harmful by-products of carcinogenic nature and are therefore currently not considered to be a “healthy” practice or environment friendly. It was also observed that disinfection by-products in drinking water distribution systems might play role in increasing bacterial resistance. Moreover, chemical methods are not effective for those bacteria which form hidden flocs in biofilms and have high resistance to biocides [28]. The physical methods such as heating, radiation, microwave, filtration and plasma have many disadvantages in their practical application on large scale due to high cost and long treatment time [29,1]. To overcome the limitations of physical and chemical methods and also to avoid production of harmful by-products, several new techniques have been proposed that include electrochemical, adsorption using newer nanocomposites, photocatalytic and copper-silver ionization, cavitation etc., of which use of novel magnetic nanocomposites for disinfection can certainly be found attractive if operational difficulties and scale-up issues can be appropriately addressed [30,31].

As an alternative to the conventional physical and chemical processes, a physico-chemical method-cavitation, especially hydrodynamic cavitation, appears to be highly promising. Though a large number of studies were discussed on cavitation for disinfection in last two decades or so, not many commercial applications were reported. Cavitation is a physico-chemical technique employing suitable mechanism for formation, growth and collapse of cavities in a liquid that create suitable conditions of extreme temperatures (up to 10000 K) and pressure (up to 5000 atm) at the points of implosion, resulting in generation of oxidising agents and as a result generating environment conducive for disinfection of bacteria [20,21]. Both acoustic and hydrodynamic cavitation are suitable in this regard [32–36]. The performance of cavitation is influenced by different parameters such as pressure drop, temperature, pH, salt content, density, viscosity and surface tension apart from nature of the microorganism [21,37]. Due to serious limitations of employing acoustic cavitation on a large scale, hydrodynamic cavitation appears to be most promising technique in this regard. Several different configurations and designs of hydrodynamic cavitation reactors have been proposed/used. Balasundaram and Harrison, [38] compared effectiveness of multi-hole orifice design and single hole orifice for bacterial destruction. Increasing discharge pressure was shown to have positive effect on bacterial destruction in case of multi-hole orifice, whereas, there was negative effect in case venturi leading to lower inactivation rate. Badve et al. [39] and Pandit et al. [36] investigated effect of inlet pressure on water disinfection, and found that with increase in the pressure, destruction rate increases but only up to a certain point. Jain et al., [20] used newer type of cavitating device employing vortex flow, vortex diode and observed pressure impacting the disinfection performance depending on the nature of bacteria. Moreover, the vortex diode required low pressure drop (1 bar), while orifice required higher pressure drop (2 bar or more) for complete destruction of bacteria. Hybrid approaches were also reported e.g. addition of H_2O_2 or ozone or by process integration with different physical methods such as UV [40]. However, most of the conventional methods are associated with many drawbacks mainly in terms of inefficient disinfection, slow rates, especially for different kinds of microorganisms and also high cost.

The use of natural oils [21] having antimicrobial property in the cavitation process is envisaged as a unique and also practical strategy that can address issues of high efficiency, increased rates of disinfection apart from also providing green process to eliminate AMR bacteria. A number of natural oils such as clove oil, cinnamon oil, eucalyptus oil, peppermint oil, tea tree oil can be highly useful in this regard. The selection of natural oils needs to be judiciously made to exploit functionalities for effecting disinfection and for additional health benefits.

The present study, for the first time, provides useful method for destroying antimicrobial resistant bacteria (AMR) and difficult, opportunistic pathogen using cavitation and natural oils or plant extract and also for enhancing and altering removal of bacteria by use of natural oils/plant extracts in cavitation with positive implications for possible commercial applications in the form of greener technology, especially for rural use. The study has specific relevance today due to the fact that, recently the World Health Organization (WHO) listed *P. aeruginosa* as one of the three critical bacteria species requiring new antibiotics development because of its adaptive antibiotic resistance [11,41–43]. The developed process does not require use of catalyst, harmful chemicals or does not have disadvantages of conventional chlorination processes and operates at nearly ambient conditions. Intensification of simple type such as aeration (sparging of air) has also been studied to further improve the process performance.

2. Materials and methods

2.1. Cavitating devices

Two different types of devices, one employing rotational flow-Vortex diode and other employing linear flow-Orifice were used. The vortex diode (US9422952B2, 2016) used was similar to that reported in our earlier work having a nominal capacity of 1 m^3/h (fabricated locally; chamber diameter 66 mm, Throat diameter 11 mm, Material of construction- SS 316). The orifice includes a single circular hole, 3 mm diameter and 1 m^3/h capacity. The photograph of the experimental set-up and details with schematic are provided in our earlier publications [20,21,34].

2.2. Microorganisms

Microorganisms can be divided into two groups based on their cell wall composition gram-negative and gram-positive bacteria. Gram-negative bacteria have complex multi-layered structure of the cell wall whereas gram-positive bacteria have cell wall of thick single layer of peptidoglycan. In the present study, one gram-negative (*Pseudomonas aeruginosa* ATCC 15442), one gram-positive bacteria (*Staphylococcus aureus* ATCC-6538*)* and Methicillin resistance bacterium, *S. aureus* ATCC BAA-44 (Himedia), were used as model bacteria contaminants of each type. The first two organisms were obtained from NCIM- National Collection of Industrial Microorganism at CSIR, National Chemical Laboratory, Pune, India. MRSA is a Biosafety Level 2 (BSL 2) bacterium and appropriate guidelines for its use need to be followed [44]. For evaluating the efficacy of disinfection, both the cultures were grown individually in 50 mL Nutrient Broth (Himedia Nutrient HiVeg broth) and incubated at 37 °C, 200 rpm in an incubator-shaker for overnight. The overnight incubation ensures that bacterial population residing in broth medium is in robust stage of growth and not in saturation or death phase, since it is more difficult to kill the cells of robust stage.

2.3. Natural oils as bio-additive

Three different types of natural oil were used - Peppermint oil, Lemongrass oil and Tea tree oil. These were procured locally from Pune, Maharashtra, India. The detailed characteristics of different natural oils are given in Table 1.

2.4. Experimental

The experimental procedure and experimental set-up was discussed in detail in our earlier reports and therefore is only briefly described here to avoid repetition [20,21]. The set-up included water storage tank of 50L capacity, high pressure pump, different cavitation devices and process control for the measurement and control of parameters such as pressure, temperature and flow rate. The hydrodynamic cavitation experiments were performed using two cavitation devices- vortex diode and orifice and by employing specific pressure drop conditions of cavitation, typically 1 bar for vortex diode and 2 bar for the orifice under controlled temperature conditions (~30–35 °C). For model wastewater, a known concentration of bacteria was prepared in 20 L of water to get initial bacterial concentration ~10^4 CFU/mL. On the basis of preliminary work on natural oils, a concentration of just 0.1% by volume was used in each experiment, corresponding to 20 mL for the 20 L of synthetic contaminated water. The performance of cavitation was monitored by using bacterial viability test (Plate count method) – 10 mL of samples withdrawn from cavitation tank at periodic intervals, and 0.1 mL of culture spread on N. agar containing sterile Petri dish. After, 24 h of incubation, number of colonies were counted from each plate and represented as colony forming unit per milliliter (CFU/mL).

$$CFU/mL = \frac{Number\ \ of\ \ colonies\ \ on\ \ \text{N. agar plate}}{\text{volume plated (mL)}} \times dilution\ \ factor$$

Table 1
Characteristics of Natural oils.

Sr.No.	Name of oil	Characteristics
1.	Peppermint oil (*Mentha × piperita*) [45]	**M.F.:** $C_{10}H_{20}O$ **M.W.:** 156.265 g/mol **Composition**: Menthol (29–60%), menthone (15–30%), methyl acetate (2–8.5%), menthofuran (1–7%), isomenthon (2–5.5%), limonene (1–4%), and germacrene D (0.5–3%) **Boiling Point:** 215 °C **Density**: 0.896–0.908 g/cc
2	Lemongrass oil (*Cymbopogon citrates*) [46,47]	**M.F.:** $C_{51}H_{84}O_5$ **M.W.:** 777.2 g/mol **Composition:** Main constituents Citral (70%), Linalool (1.34%), Geraniol (5%), Citronellol, nerol (2.2%), Citronellal (0.37%), Linalylacetat, geranyl acetate (1.95%), α-Pinene (0.24%), Limonene (2.42%), Caryophyllene, β-pinene, β-thujene, myrcene (0.46%), β-Ocimene (0.06%), Terpenolene (0.05%), Methyl heptanone (1.5%) and α-terpineol (0.24%) **Boiling Point:** 224 °C **Density**: 0.887 g/cc at 25 °C
3	Tea tree oil (*Melaleucaalternifolia*) [48]	**M.F.:** $C_{28}H_{60}O_4P_2S_4Zn$ **M.W.:** 777.2 g/mol **Composition:** Terpinen-4-ol (35–48%), γ-Terpinene (14–28%), α-Terpinene (6–12%), 1,8-Cineol (traces-10%), terpinolene (1.5–5%), α-terpineol (2–5%), α-pinene (1–4%), p-Cymene (0.5–8%), Sabinene (traces-3.5%), limonene (0.5–1.5%), aromadendrene (0.2–3%), ledene (0.1–3%), globulol (traces-1%) and viridiflorol (traces-1%) **Boiling Point:** 165 °C **Density:** 0.898 g/cc at 25 °C

For all the experiments, the average error was generally within ± 5% and reproducibility was confirmed for the experiments.

2.5. Evaluating cell destruction by FE-SEM and TEM analysis

To confirm the destruction of bacterial cells, different microscopic techniques such as Field Emission Scanning Electron Microscopy (FESEM, FEI-Nova NanoSEM-450) and TEM (Transmission Electron Microscopy Tecnai G2 20 S Twin; LaB6 filament as the electron source) were used. Morphological changes of bacterial cells before cavitation (0 min) and after cavitation (60 min of treatment) were confirmed by FE-SEM. For the sample preparation, bacterial culture was fixed with 4% (v/V) glutaraldehyde (prepared in 0.1 M phosphate buffer (pH 7.0)) and incubated for 1 h, subsequently washed with phosphate buffer (0.1 M) for 10 min. The fixed samples further dehydrated by using graded series of ethanol solutions (30, 50, 70, 90 and 100% ethanol) for 30 min. TEM analysis of initial and final samples were carried out for examining cell destruction during the process.

3. Results and discussion

It is a common knowledge that for hydrodynamic cavitation, the most important process parameters include pressure drop, initial concentration of the contaminant apart from reactor geometry. In our earlier work [20,21], the comparison of acoustic cavitation, hydrodynamic cavitation and also impact of bacterial concentration for the two bacteria, *E. coli* and *S. aureus* was reported in detail. The present work, demonstrates elimination of difficult and “opportunistic pathogen”, gram-negative *P. aeruginosa,* elimination of antimicrobial resistant bacteria, methicillin resistance *Staphylococcus aureus* and further improvises some of the findings reported earlier in this regard by comparing the results with *S. aureus*, where required to substantiate. Highly useful and important findings in terms of nature of bacteria, natural oils apart from nature of the reactor geometry are also discussed for a range of bacteria, oils and the two cavitating reactors- vortex diode and orifice.

3.1. Effect of pressure drop

Pressure drop (ΔP) is one of the most important parameter in hydrodynamic cavitation, which dictates not only the performance of cavitation process, but also major cost of the process. The flow rate and pressure drop data was reported earlier for the device [34]. Cavitation number is defined based on vapour pressure and throat velocity. However, cavitation number is relevant for cavitation devices using linear flows such as orifice or venturi where it is used to identify possible inception of cavitation. The cavitation numbers for orifice operated at 2 and 5 bar pressure drop are 0.75 and 0.35 respectively. Unlike these conventional devices, vortex based device used in the present work uses tangential velocity for generating low pressure regions. Therefore conventional cavitation number defined above is not relevant for vortex based cavitation devices. We have ensured that both the devices are operated in cavitating regime.

The disinfection was studied for the cavitating device- vortex diode and for the new bacteria, *P. aeruginosa* using three different pressure drop conditions, 0.5, 1 and 2 bar (the inception of cavitation is at ~0.48 bar and hence pressure drop of 0.5 bar represents lowest pressure drop for which cavitation takes place [21]). The results are shown in Fig. 1. The experimental results on removal of *P. aeruginosa* show ~40% disinfection at ΔP of 1 bar. Further, increasing pressure drop to 2.0 bar, has not resulted in significant gains and the disinfection efficiency remained practically similar.

It is evident that the extent of disinfection for the *P. aeruginosa*, using the conventional hydrodynamic cavitation is quite less and not satisfactory from the practical application point of view. The results also clearly indicate the difficulty in the destruction of microorganism *P. aeruginosa.* Young et al., [49] stated that *P. aeruginosa* has a higher degree of cross linking compared to *E. coli* and *S. aureus*. In our previous findings, the results of *S. aureus* indicated substantially higher disinfection efficiency of ~89 which could be further enhanced to 97% by increasing pressure drop from 1 to 2 bar. The disinfection behavior of different microorganisms depends on the cavitation device and degree of cell rupture. The limited destruction also implies need for exploring newer methodologies.

3.2. Effect of bio-additives (natural oils) in hydrodynamic cavitation for elimination of pathogenic bacterial strains from water

It is instructive to develop methodology looking beyond the traditional methods including that of conventional cavitation to effectively circumvent the drawbacks pertaining to low efficiencies, longer time of treatment and high cost apart from possible formation of harmful disinfection by-products. The previous attempts were typically chemical modifications such as hydrodynamic cavitation with ozone and hydrogen peroxide.

The addition of bio-additives such as natural oil in hydrodynamic cavitation can be a newer and promising approach for disinfection [21]. A very small concentration of 0.1% (v/V) of natural oil was sufficient for disinfection. The effect of dose of the natural oil is one of the important parameter which is expected to depend on the nature of the oil. An optimum dose is required to achieve the complete disinfection of bacteria within shorter time period. In the present study, for the first time, highly effective natural oil, in the form of Peppermint oil, was found, that could practically provide > 99% disinfection for various types of bacteria such as *S. aureus* (SA), Methicillin Resistant *S. aureus* (MRSA) and opportunistic/adapting bacteria *P. aeruginosa* typically in less than 10 min. Preliminary experiments using vortex diode as a cavitating device at 1 bar pressure drop for different dosage of peppermint oil (0.1 and 0.05%) confirmed 0.1% v/V dose of oil as optimum since at 0.05% of oil concentration, 94% disinfection was observed within 60 min and nearly complete (> 99%) disinfection within 10 min for 0.1% dose.

3.3. Destroying difficult, opportunistic pathogen P. aeruginosa

The complete elimination of *P. aeruginosa* using hydrodynamic cavitation for vortex diode as a cavitating device is shown in Fig. 2. It is evident that the hybrid method of combining natural oil and hydrodynamic cavitation is highly effective in disinfection of water. The extent of disinfection using cavitation alone is ~40% in 60 min, while

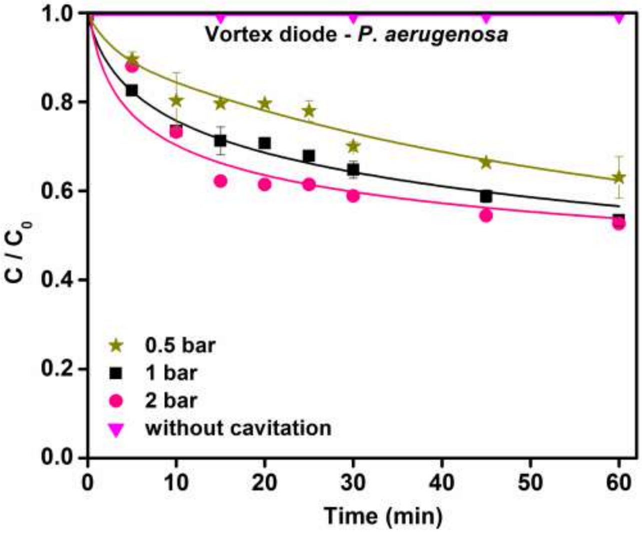

Fig. 1. Effect of pressure drop on disinfection of *Pseudonomas aeruginosa.*

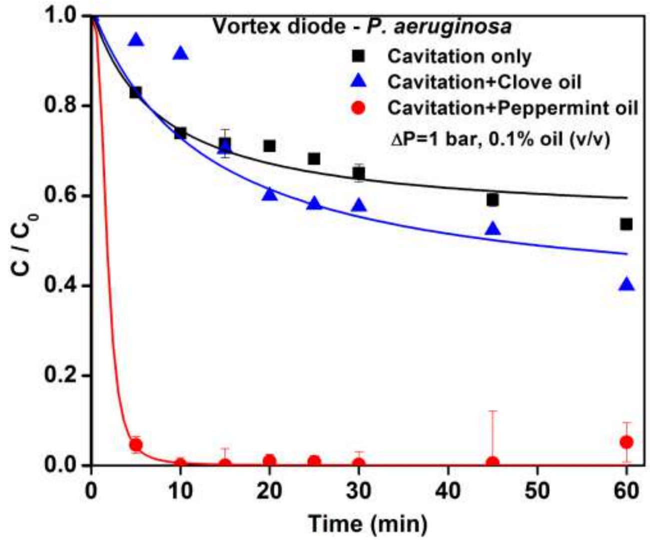

Fig. 2. Effect of natural oil for disinfection of *P. aeruginosa.*

with the hybrid method in combination with 0.1% peppermint oil; practically > 99% disinfection was observed in about 10 min, an order of magnitude enhancement in the disinfection rate. The efficiency seen here is the highest compared to that reported in the literature so far. Mane et al. [21] had previously suggested clove oil as one of the highly effective oil for the elimination of *E. coli* and *S. aureus.* In order to evaluate the comparative efficacy of peppermint oil, the experiments were also carried out by using clove oil (0.1%) for *P. aeruginosa* and the results are also compared in Fig. 2. The clove oil too gave enhancement in the disinfection rate and ~60% disinfection was obtained in 60 min. Comparing the results, it is evident that peppermint oil is far superior and drastically increases the rate of disinfection. The reduced time of operation and close to complete disinfection clearly highlights the efficacy of the hybrid technology in practical/commercial applications, especially using peppermint oil and vortex diode.

The concept of cavitation using oil for disinfection was further validated using orifice as a cavitating device (Fig. 3). The reactor geometry here employs linear flow for cavitation as against vortex flow in vortex diode. The results indicate ~30% disinfection using orifice at ΔP of 2 bar while the hybrid technique with 0.1% peppermint oil gave ~99.9% disinfection within 20 min. The difference in the disinfection behaviour due to change in the reactor geometry are clearly evident. While both the reactor types can achieve close to 100% disinfection by hybrid methodology using peppermint oil, the orifice requires substantially higher pressures compared to vortex diode implying higher cost of disinfection. Also, the time for complete disinfection is longer in orifice compared to vortex diode, again implying higher cost.

A large number of natural oils are known to have antimicrobial properties. Our preliminary investigations indicated cavitation will not adversely alter properties of natural oils, the finding agrees well with recently reported data [50]. The use of natural oil not only alters the collapse of cavities but also helps to destroy the permeability of bacterial membranes by inherent antimicrobial property of active ingredient. Also, Peppermint oil contains menthol which significantly reduces virulence ability of *P. aeruginosa* [51].

It is instructive to evaluate the synergistic effect for the addition of natural oils in cavitation. The synergistic effect can be calculated using the following equation,

$$f = \frac{K_{HC+oil}}{K_{HC} + K_{oil}} \quad (1)$$

Where, HC is the hydrodynamic cavitation and HC + oil is the hydrodynamic cavitation along with oil. For *P. aeruginosa*/peppermint oil, the synergistic index *f was* 6 and 5 for vortex diode and orifice respectively; values well above 1, confirming the synergistic effect.

3.4. Destroying AMR Bacteria: Methicillin resistant S. aureus

After having established the efficacy of the hybrid methodology using peppermint oil for *P. aeruginosa*, it would be prudent to extend it further for the elimination of antibiotic resistant bacteria. Methicillin resistant *S. aureus* (MRSA) strain carries a mec gene, conferring the resistance to multiple antibiotics, which makes it resistance to methicillin, nafcillin, oxacillin, and cephalosporins. MRSA is the evolution of *S. aureus* (SA) into multi-resistant strains that makes is difficult to disinfection [52]. Investigations were carried out on destroying MRSA (shown by continuous lines in Fig. 4 and Fig. 5) and also elucidate comparative efficacy for SA (shown by dotted lines in Fig. 4 and Fig. 5) for the following:

1. Extent of disinfection using cavitation alone for both the bacteria
2. Extent of disinfection using cavitation and 0.1% peppermint oil (hybrid method)
3. A newer form of process intensification by means of simple aeration-again with and without oil, i.e. using conventional disinfection and hybrid disinfection process.

It is evident from Fig. 4 that in the case of vortex diode as a cavitating device, the MRSA required significantly more time to disinfection compared to *S. aureus* in all the cases, viz. with only cavitation, cavitation + aeration and also in hybrid method with natural oil. The slower rates of disinfection in the case of MRSA clearly outline the difficulty compared to SA. The addition of 0.1% peppermint oil drastically improves the disinfection efficiency in both of the bacteria-MRSA and *S. aureus,* an enhancement to the extent of ~200% which is phenomenal and not reported so far. It is also pertinent to note the time of disinfection using the hybrid method which is only 5–10 min for close to complete disinfection for any type of bacteria which obviously has positive commercial implications.

Apart from the effect of nature of bacteria on rates of disinfection, the results of Fig. 4 also clearly outline the differences in the disinfection behaviour because of aeration and because of dose of natural oil. It is essential to note that both aeration and addition of oil improve the disinfection behaviour over that of cavitation alone. A maximum benefit could be obtained, however, with addition of the natural oil and the positive effect of aeration can be exploited to reduce the requirement of natural oil. It can be seen that the requirement of peppermint oil can be

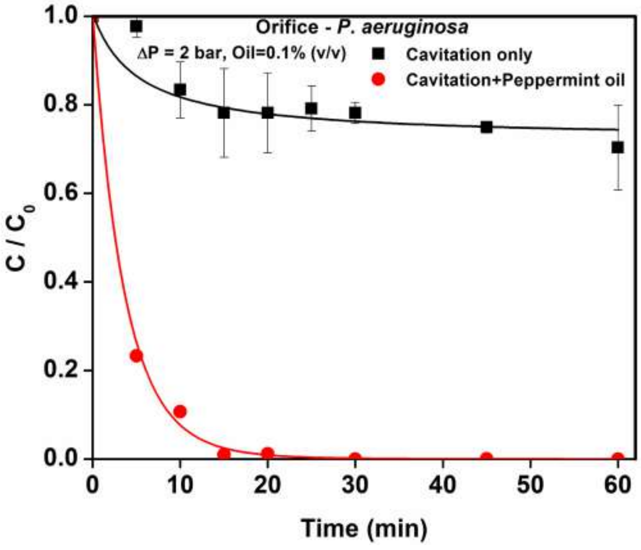

Fig. 3. Effect of Reactor Geometry: Orifice/*P. aeruginosa.*

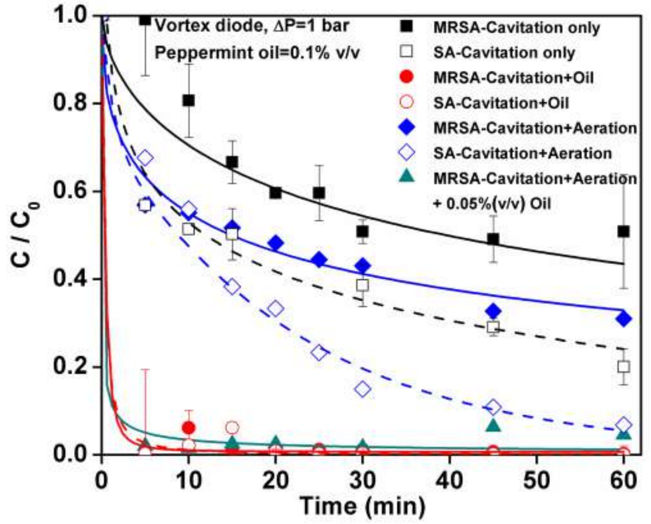

Fig. 4. Destruction of bacteria using vortex diode: Comparison of MRSA and SA.

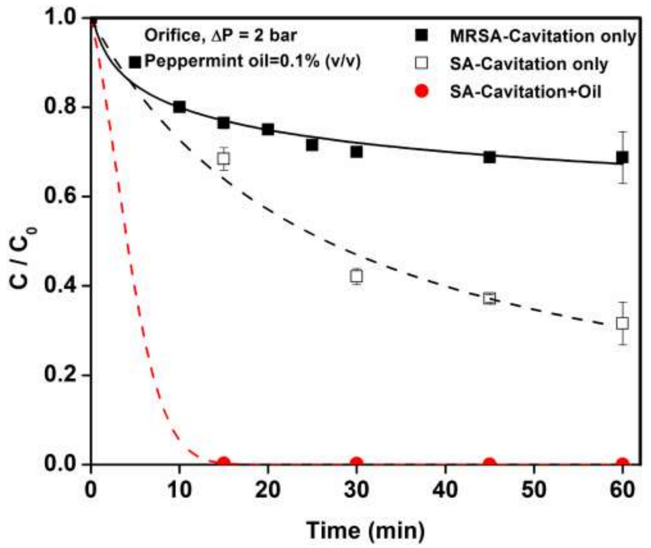

Fig. 5. Destroying Methicillin Resistant *S. aureus* (MRSA) and *S. aureus* (SA) using Orifice.

reduced to nearly half (0.05%), if aeration is employed in the hybrid process of disinfection. The use of aeration in cavitation increases the shock wave impact, number of cavities and implosion inside the cavitation zone [53,54]. Therefore, the aeration shows significant improvements possibly because of (1) enhanced dissolved oxygen - leading to enhanced generation of hydroxyl radicals (2) improved mixing of aqueous phase and oil phase and (3) altering compressibility of the medium. Thus, the increased rates of disinfection and reduction in oil dose can be attributed to the contributions of aeration as well as that due to antimicrobial properties of oil. A trade-off is, however, required for optimization between the operational cost due to aeration and savings due to oil requirement.

3.5. *Effect of reactor geometry- disinfection using orifice*

The reactor geometry is expected to have significant effect on disinfection behaviour, and is crucial for techno-economic considerations. The reactor geometry directly affects the inception of cavitation and cavity implosion behaviour due to differences in the flow pattern [33,34,55,20]. In the present work, a single hole orifice, a cavitating device employing linear flow was compared with vortex diode, a cavitating device employing vortex flow. The disinfection behaviour, to establish the proof of concept in this regard, using orifice are given in Fig. 5, mainly for SA. Two aspects are clear from the results- that the orifice requires significantly higher pressures (ΔP 2 bar) as compared to vortex diode (ΔP 1 bar) and also that the disinfection efficiency is higher in vortex diode compared to orifice. The MRSA destruction using orifice alone is only ~30% compared to that of 45% with only vortex diode; destruction of SA to the extent of ~65% using orifice while corresponding value for vortex diode is ~80% and finally ~99.9% destruction of SA in orifice in ~15 min compared to 5–10 min with vortex diode when hybrid process using natural oil (peppermint oil) is employed.

3.6. *Nature of natural oils and disinfection*

The importance of extract of medicinal plant/natural oil derived from such plants, having antioxidant, antifungal and antibacterial properties, in disinfection has been widely recognised [45–48,56–58]. However, the studies are largely limited to using the zone of inhibition or only estimate antibacterial disk diffusion assay. Natural oils have the ability to kill the bacteria or retard the growth of pathogens because of the presence of natural active ingredients specific to the plant/oil. The antimicrobial activity of peppermint oil is believed to be mainly due to combined presence of compounds such as L-menthol, menthone, menthyl acetate and limonene [59]. The antibacterial activity of peppermint extract towards ten multi-drug pathogenic strains has been reported by [60]. Sujana et al. [61], reported that the leaf extract of peppermint contains effective active compounds which are responsible for disinfection of bacteria. Weak antimicrobial activity of peppermint oil for gram negative pathogens was mentioned in some studies [62–64]. In view of the above, the present hybrid process can be said to exhibit the “resonance effect” of both-antimicrobial activity of natural oils and also disinfection due to hydrodynamic cavitation that is hugely effective in the destruction of both gram-positive as well as gram-negative bacteria.

Table 2
Rate of disinfection for *P. aeruginosa* and Methicillin Resistance *S. aureus*.

Process	% Disinfection	Rate of disinfection CFU/(mL.s)	Rate constant (s^{-1}) × 10^4	Per-pass disinfection (ϕ)
Rate of disinfection for *P. aeruginosa* (15 min)				
Cavitation alone Vortex Diode, ΔP = 1 bar	28	55.56	3.7	0.0371
HC + Peppermint oil Vortex Diode ΔP = 1 bar	99	144.33	79.7	0.7852
Cavitation alone Orifice, ΔP = 2 bar	22	7.44	2.74	0.0647
HC + Peppermint oil Orifice, ΔP = 2 bar	99	46.22	51.71	1.23
Without cavitation-Only Peppermint oil	20	NA	2.5	NA
Rate of disinfection for Methicillin Resistance *S. aureus* (MRSA) (15 min)				
Cavitation alone Vortex Diode, ΔP = 1 bar	33	29.77	7.05	0.0713
HC + Peppermint oil Vortex Diode ΔP = 1 bar	98.7	88.89	48.83	0.4919
HC + aeration Vortex Diode, ΔP = 1 bar	48	155.56	7.32	0.0733
HC + aeration + Peppermint oil, 0.05% Vortex Diode, ΔP = 1 bar	97	106.11	40.76	0.4067

To illustrate the above aspect pertaining to nature of oil, the results using different natural oils are shown in terms of disinfection factor and for vortex diode as a cavitation device; ΔP of 1 bar and for 0.1% v/V for natural oil for the data of this work and also from that reported in the literature [21]. The per-pass disinfection factor, ϕ, in terms of rate constant (k), number of passes (n) and residence time (τ) is defined as:

$$\boldsymbol{k} = \frac{\varnothing \boldsymbol{n}}{\boldsymbol{t}} = \frac{\varnothing}{\tau} \tag{2}$$

Where, k is an apparent first order rate constant of disinfection. The per pass disinfection factor, ϕ, can be obtained by fitting the following equation to experimentally obtained disinfection data.

$$\phi = \frac{-\ln(C_e/C_0)}{n} \tag{3}$$

The parameters (effective rate constant and per pass disinfection factor) of Eq. (2) and (3) for different experiments reported in this work are listed in Table 2. The results clearly indicated that the use of peppermint oil in cavitation process in a very small concentration (0.1%) increases the rate and per-pass disinfection values by almost 20 times. The corresponding values of per pass disinfection factor (ϕ) are 0.7852 and 0.0371 for cavitation with oil and cavitation alone for vortex diode as a cavitating device. Similarly for orifice as cavitating device, ϕ values are 1.23 and 0.0647 for cavitation with oil and cavitation alone respectively. The orifice requires higher pressures to obtain similar extent of disinfection compared to vortex diode. The differences due to the nature/type of bacteria, characteristics of oil/oil constituents are clearly evident. Similarly, drastic effect of peppermint oil on reduction of antimicrobial resistance bacteria MRSA in hydrodynamic cavitation was observed; 3 times higher rates for hybrid process compared to only cavitation. The respective values of ϕ are 0.4919, 0.0713 for hybrid process and cavitation alone respectively. Further, aeration improves the performance of hybrid cavitation process and not only the cavitation behaviour is altered, but also quantity of oil gets reduced by half and ~3 times higher rates compared to the conventional cavitation process. The value of ϕ for advanced hybrid hydrodynamic cavitation process (vortex diode + aeration + 0.05% peppermint oil) is 0.4067 and for only cavitation is 0.0713. It is evident that the hydrodynamic cavitation with 0.1% peppermint oil and cavitation with 0.05% peppermint oil and aeration showed > 100% increase in the per-pass disinfection as compared to cavitation alone.

From Fig. 6, it is evident that the nature of natural oil significantly affects the disinfection behaviour and therefore finding the most suitable natural oil is crucial from commercial application point of view. From the data of different oils, it can be seen that peppermint oil is the most effective natural oil compared to tea tree, clove, eucalyptus and lemongrass oil from the data of removal of *S. aureus*. The value of per-pass disinfection factor ϕ for peppermint oil is 31, significantly higher than tea tree oil (18), clove oil (11), eucalyptus oil (9), and lemongrass oil (5). The per-pass disinfection factor for cavitation alone is only 6. A grading of disinfection efficiency for various natural oils can be useful in the selection of natural oil in the hybrid process.

3.7. Mechanism for disinfection using hydrodynamic cavitation and natural oils

A plausible mechanism of the hybrid process was discussed in our earlier work where it was shown that various physical/mechanical forces along with antibacterial properties of natural oils contribute to bacterial cell destruction [21]. The physical effects of cavitation include implosion of cavities creating hotspots and consequently damaging microorganism cells. The extreme temperatures during cavity implosion process can affect the intact nature of bacterial outer layer and make it more susceptible for further damage with reactive species [27,65]. The chemical effect includes generation of active free radicals that can oxidize the main constituents of bacterial cell such as proteins, lipids and DNA [4]. The biological effects include, antimicrobial activity due to the active ingredients present in natural oil (such as menthol, menthone and menthofuran in peppermint oil) having high antibacterial properties. The menthol is most active ingredient in this regard. Sing et al. reported that menthol has ability to affect the lipid fraction of bacterial plasma membrane, impacting the membrane permeability which induces the leakage of intracellular materials [66,67].

The results of the present study are also in agreement in this regard. Figs. 7 and 8 show SEM and TEM images of the samples before and after the disinfection clearly providing visual inference in terms of cell destruction. The TEM analysis of *P. aeruginosa* indicates the intact and rod shaped bacterium before treatment (0 min), whereas after treatment (60 min) bacterial cell membrane and its intracellular organization has been disrupted. These results were further supported by FE-SEM analysis, which showed that at 0 min, bacterial cell was intact and in chain form and thereafter (60 min) was mutilated in terms of alternation in cell morphology (Fig. 7). The FE-SEM analysis of MRSA shows the initial condition of 0 min, where the bacteria is seen round shaped with intact cell membrane and after the treatment (60 min), the shape of bacterial cell has been distorted as evident from hole formation and cell rupture (Fig. 8). These results are further corroborated using TEM analysis where the initial spherical MRSA cells with smooth cell walls (0 min) get swollen and irregular in size and shape after the treatment. Moreover, discolouration of cytoplasm and leakage of cytoplasmic content was also observed. Swamy et al. [68] reported that the natural oil can destabilize the cellular structure of the cell, leading to breakdown of cell membrane integrity as well as increase cell permeability. Radaelli et al. [69]indicated that a food borne pathogen *Clostridium perfringens* was inhibited by the antibacterial action of peppermint oil. The natural oil may exhibit a different mechanism against different microbes depending on the inherent constituents [68]. Thus, it can be suggested that hydrodynamic cavitation using peppermint oil results in disinfection due to complete bacterial disintegration of *P. aeruginosa* and MRSA and the synergetic effect of oil in hydrodynamic cavitation is important.

Fig. 9 schematically depicts the role of the different constituents and hydrodynamic cavitation in water disinfection. The peppermint oil (Mentha piperita, L.) belongs to the Family Lamiaceae, primarily contains 0.1–1% of volatile oil, composed of menthol (29–48%), menthone (20–31%), menthofuran (6.8%) and menthyl acetate (3–10%). Other pharmacologically active ingredients include bitter substances, caffeic acid, flavonoids (12%), polymerized polyphenols (19%), carotenes,

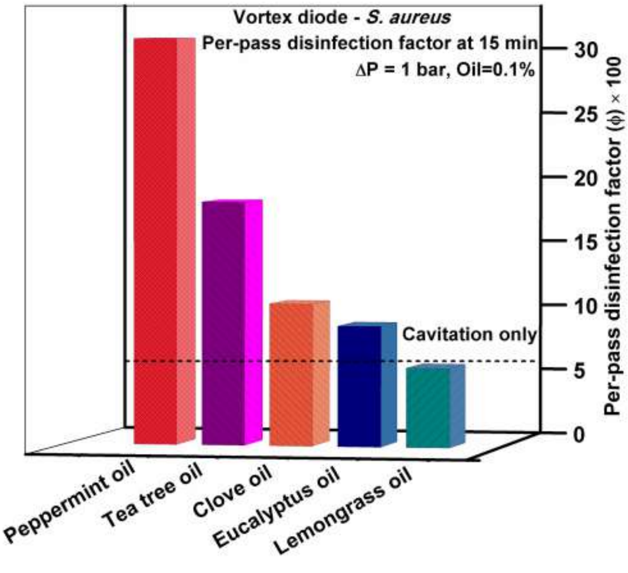

Fig. 6. Comparison of natural oils in disinfection.

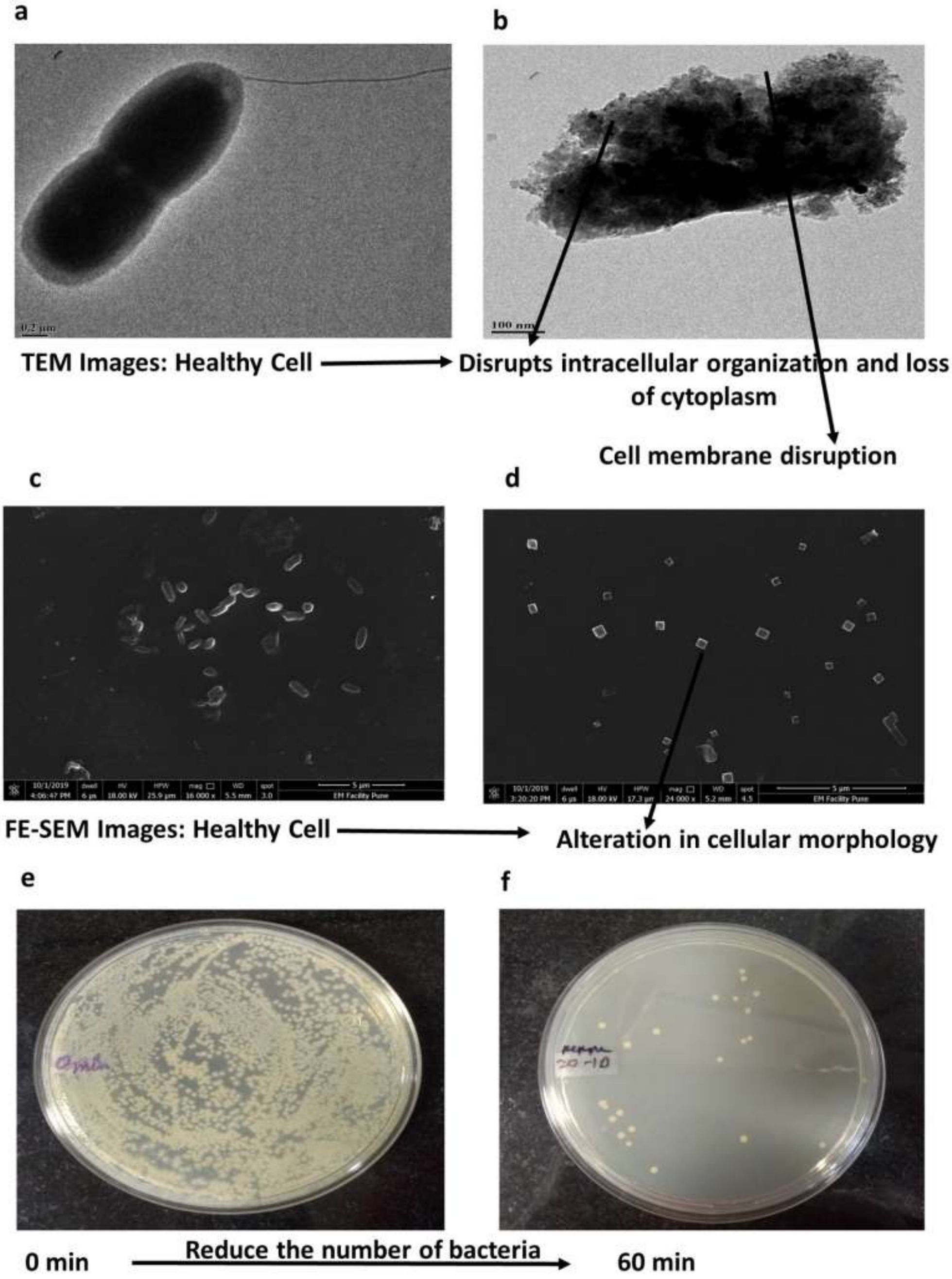

Fig. 7. Elucidating disinfection through SEM and TEM characterization: *P. aeruginosa.*

tocopherols, betaine, choline and tannins. It is widely used in food, pharmaceutical and cosmetics industries. Moreover, menthol as a raw material is used in toothpaste, toothpowder, confectionary, mouth fresheners, analgesic balms, cough drops, perfumes, chewing gums, etc. It is also used for a variety of health conditions and can be taken orally in dietary supplements or topically as a skin cream or ointment. Peppermint oil seems to reduce spasms in the digestive tract. Similarly, clove oil has advantages such as healing properties for toothaches and other tooth pains, improving blood circulation, reducing foul odor etc. It is also used for adding flavouring agent to the cough medicines. Eucalyptus oil is used to treat variety of diseases such as nasal congestion, asthma, arthritis etc. Thus, there could be several possible health benefits of using natural oil.

Most of the earlier work on cavitation focused on conventional devices such as orifice, venturi or on use of ozone, hydrogen peroxide etc., in isolation or in combination [70,39,36]. Further, disinfection efficiency was poor, in general and long treatment time was required. The hybrid process developed in this work not only demonstrates close to 100% disinfection, but also demonstrates significantly shorter time periods and no use of harmful chemicals.

4. Cost considerations and evaluating techno-economic feasibility of the hybrid disinfection process

The cost calculations are presented in detail for the new hybrid process using the following representative data:

Bacteria: *S. aureus*
Volume: 20L
Reactor: Vortex diode,
Flow rate: 721.7 LPH, ΔP: 1 bar
Natural Oil: 0.1% peppermint oil (20 mL)
Initial concentration of bacteria = 312000 CFU/mL and in 5 min,

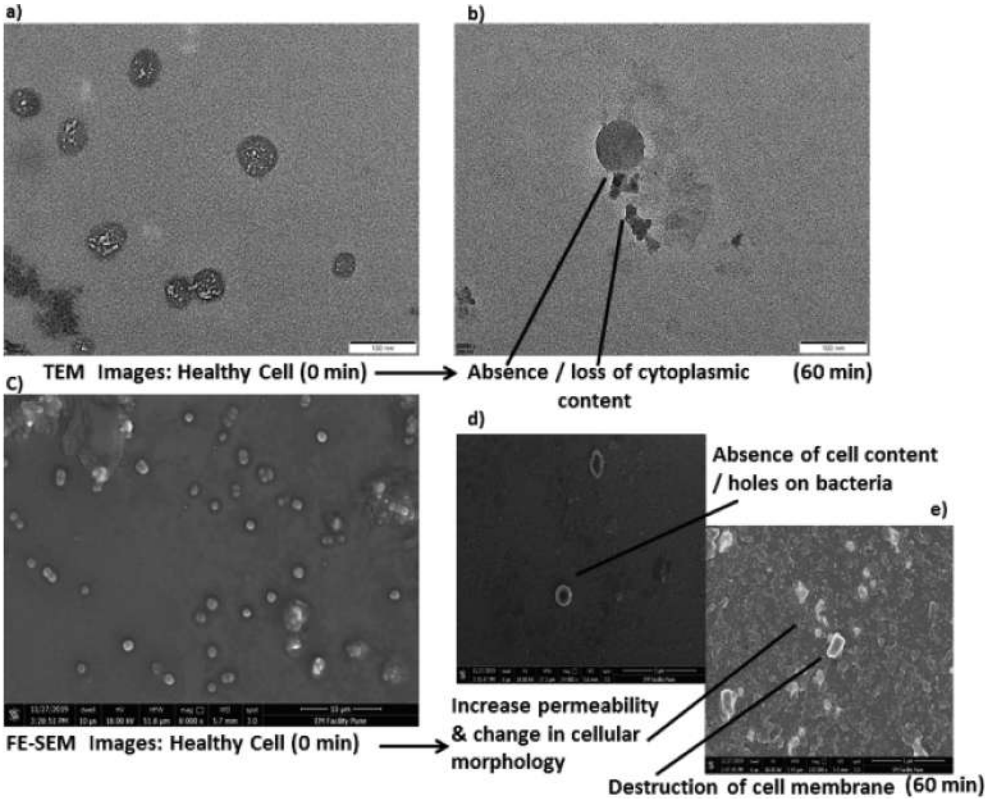

Fig. 8. Elucidating disinfection through SEM and TEM characterization: MRSA.

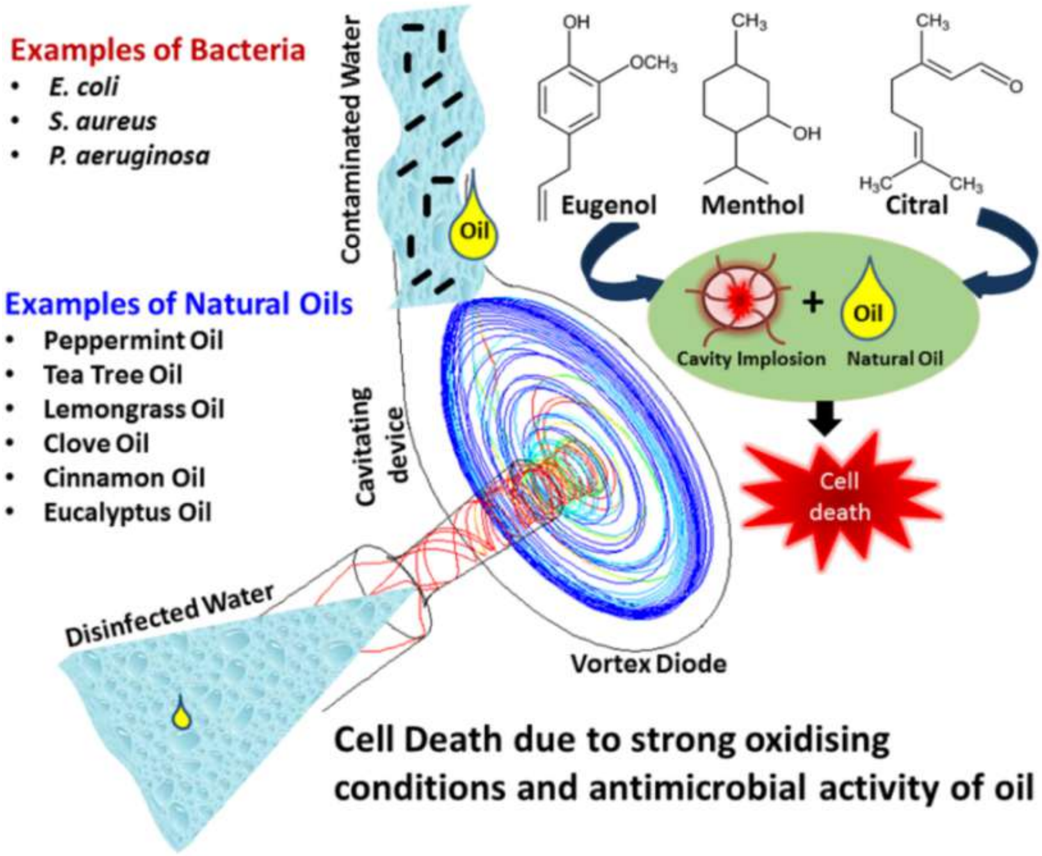

Fig. 9. Schematic illustration of hybrid process and effect of natural oil.

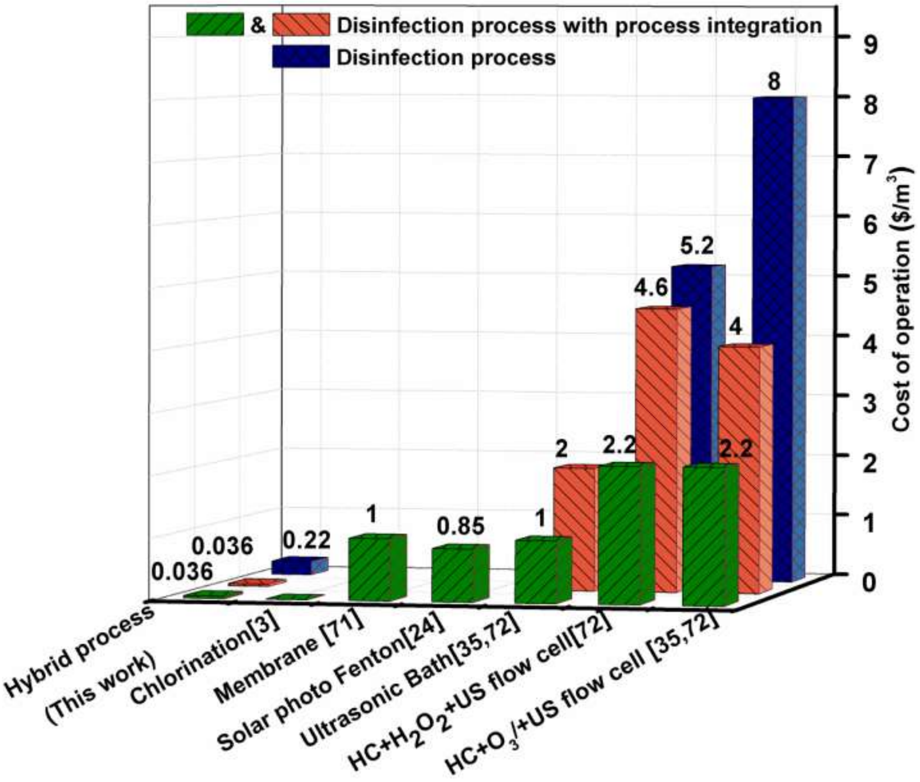

Fig. 10. Cost comparison for various water disinfection processes.

99.7% removal/disinfection

$$\text{Cavitation yield/volume treated (CFU/mL/J)} = \frac{(C_0 - C)}{(\Delta P \times Q \times t)} = 51.05\ \text{CFU/mL/J}$$

The number of passes can be obtained as: $n = \frac{(Q \times t)}{V}$

For 1 bar of pressure drop, corresponding flow rate is 721.7 LPH. The number of passes needed for treatment (n) is 3.01

$$\text{Cost of treatment/m}^3\text{of water} = \frac{n\Delta P P_E}{36\eta}$$

Assuming the cost of electricity as 10 Rs/kWh and efficiency of the multistage pump (η) as 0.66, the cost of treatment per m^3 of water is 1.28 Rs/m^3.

4.1. Techno-economic feasibility and possible real-life application

A tentative cost comparison of some of the useful methods using the data of this work and also from that reported in the literature is presented in Fig. 10. As per the EPA (1996) [71], UV is a cheaper disinfection method as compared to chlorine and ozonation for small scale unit. The cost of UV for 40 and 140 mJ/cm^2 doses are $ 0.05/m^3 and $ 0.07/m^3 respectively, whereas, chlorination and ozonation (1 mg/L dose) require cost of $ 0.75/m^3 and $ 0.92/m^3 respectively. Though, UV is cost effective, it requires high dose for complete destruction of microorganisms and also need regular preventive maintenance to avoid fouling of the tubes. Moreover, UV is ineffective when colloidal and total suspended solids are present in water. According to Environment Canada survey of Municipal Water and Wastewater (2004) [72], chlorination is largely used disinfection technique (93.38%) as compared to Chloramines (3.67%), Chlorine Dioxide (2.2%), UV and Ozone (5.9%). However, in recent years chlorination is not considered as an environment friendly, as it is associated with the formation of trihalomethanes and other halogenated by-products, which are carcinogenic in nature.

More recent disinfection techniques include high pressure homogenizer [3], high speed homogenizer [3], Ultrasonication (Ultrasonic horn, Ultrasonic bath) [3,40], membrane filtration [73] and hydrodynamic cavitation with or without process integration [3,35,36,40,74,20,21]. Jyoti and Pandit, [3] reported operation cost of high pressure homogenizer as 3.9 $/m^3, for high speed homogenizer with speed range of 1000–12,000 rpm as 0.48 $/m^3 and for hydrodynamic cavitation as 0.83 $/m^3. Cavitation with ozone, hydrogen peroxide, oxygen etc. was also reported to improve the treatment efficiency and reduce the cost of operation. For ~50% of disinfection in the case of ultrasonic horn alone, cost was calculated as 160 $/m^3 which is higher than operation cost required for Ultrasonic bath (0.56 $/m^3) with 75% disinfection, whereas hydrodynamic cavitation at 5.17 bar alone requires operating cost of 8 $/m^3 [35,40]. Process intensification was carried out to reduce the cost of operation and the approximate costs are: Ultrasonic horn + 2 mg/L O_3 (10 $/m^3); Ultrasonic bath + 2 mg/L O_3 (1 $/m^3); Hydrodynamic cavitation (Orifice, ΔP, 5.17 bar) + 5 mg/L H_2O_2 (4.6 $/m^3); Hydrodynamic cavitation (Orifice, ΔP, 1.72 bar) + US flow cell, 40 kHz, (2 $/m^3) and using 5 mg/L H_2O_2 (2.2 $/m^3) [3,35,36,40,74]. However, there have been no reports of commercial implementation of many of the processes.

Membrane processes such as “ROAM plus” portable membrane which is made up of Polyethersulfone (0.02 µm pore size) has cost of < 1 $/m^3 and ability to remove > 7 log coliform [73]. The problems such as fouling, biofilm formation and secondary waste generation are associated with membranes.

From Fig. 10, it is evident that the proposed hybrid method for disinfection can provide green alternative and techno-economically feasible solution for disinfection of pathogenic bacteria. The hydrodynamic cavitation using vortex diode as a cavitating device alone has 0.22 $/m^3 as cost of operation, whereas after process integration by addition of peppermint oil (0.1%) or with aeration, the cost can be drastically further reduced to only 0.036 $/m^3 for complete disinfection of water. The hybrid hydrodynamic cavitation process requires lower pressure drop, ambient conditions and is easy to operate. A possible commercialization outline of the proposed hybrid process is schematically shown in Fig. 11. A typical water treatment plant includes screening, coagulation, flocculation followed by filtration and finally

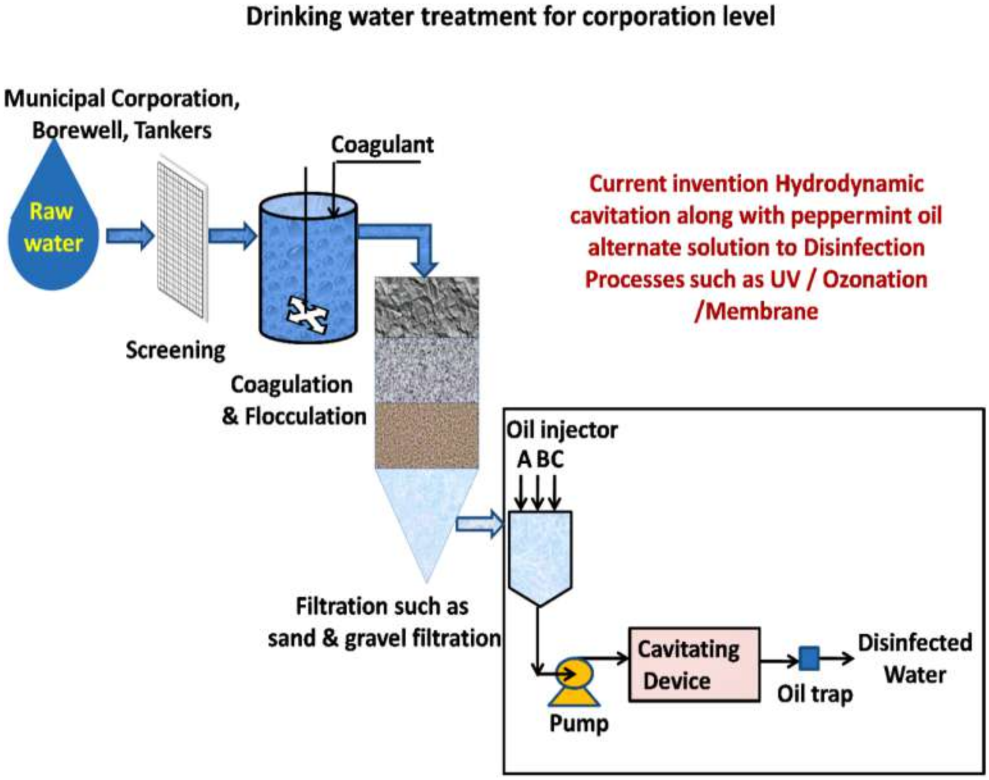

Fig. 11. Flow diagram of hybrid disinfection process using natural oils.

disinfection processes. The hybrid water disinfection process by hydrodynamic cavitation can be integrated with the existing set-up for the supply of bio-contaminant free water.

5. Conclusions

The present report on hybrid methodology employing hydrodynamic cavitation with natural oil-peppermint oil (0.1%) clearly highlights effective destruction of bacteria, antimicrobial resistant bacteria (AMR) and difficult, opportunistic pathogen. The specific findings include:

1. Exceptionally high rates of removal and effective destruction of antimicrobial resistant (AMR)-gram-positive methicillin resistant, *Staphylococcus aureus.*
2. Exceptionally high rates of removal and effective destruction for relatively less researched, gram-negative opportunistic pathogen, *Pseudomonas aeruginosa.*
3. Vortex diode as a cavitating device and natural oil-peppermint oil practically ensures complete removal within 10 min under mild operating conditions.
4. The hybrid process is also shown to be effective with other conventional cavitating devices such as linear flow based orifice.
5. Application of simple form of process intensification such as aeration was shown to further enhance the disinfection efficiency apart from possible lowering of oil dose.
6. The developed green process eliminates the use of harmful chemicals and can provide alternative to existing chemical processes such as chlorination.
7. The techno-economic evaluation indicated cost of the hybrid methodology to be significantly, order of magnitude, lower compared to the most conventional processes.

The above conclusions clearly indicate that the hybrid process can be easily adapted for the elimination of bacteria including AMR bacteria from water, thereby providing alternative water disinfection process for safe drinking water.

Declaration of Competing Interest

One of the author Prof. (Dr.) Vivek V. Ranade is a founder of VIVIRA process Technologies Pvt. Ltd. which commercially offers vortex diode based cavitation device.

Acknowledgment

The authors, Dr. Vinay M. Bhandari, Dr. Balapure would like to acknowledge the financial support of DST-WTI project (GAP 317526) of Department of Science and Technology, India. Ms. Maya B. Mane would like to acknowledge the support from DST-Women Scientist program project (GAP 316926) for providing fellowship.

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Journal of Water Process Engineering 43 (2021) 102280

Contents lists available at ScienceDirect

Journal of Water Process Engineering

journal homepage: www.elsevier.com/locate/jwpe

Safe water and technology initiative for water disinfection: Application of natural plant derived materials

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ARTICLE INFO

Keywords:
Cavitation
Disinfection
Natural oil
Plant extract
Water treatment

ABSTRACT

Safe drinking water is the necessity of life. The present study reveals use of natural resources such as plant extracts and natural oils for water disinfection. Differences between oil and water soluble additives were highlighted for plant extracts and insoluble natural oils. A hybrid hydrodynamic cavitation process was quite effective in both the cases and high rates of disinfection were achieved. Studies were reported using oils (ginger, turmeric, lavender, tulsi) and rhizome derived plant extracts such as ginger, turmeric and mango ginger, as additives in process intensification (0.1% v/V). A vortex based cavitation device (vortex diode, nominal capacity 1 m^3/h) was used with pressure drop of 1 bar. A high disinfection of 96% and 88% was obtained in 15 min for ginger oil and mango ginger extract respectively as compared to 44% using cavitation alone. Acoustic cavitation gave 94% and 30% disinfection with and without additive-mango ginger extract. The FTIR analyses before and after cavitation, with ginger additive, showed no by-products formation and indicated gingerol as active component in disinfection. The per-pass disinfection values were also higher, up to 5 times than cavitation alone. Hybrid hydrodynamic cavitation using natural plant derived materials can offer a promising technology alternative in water disinfection.

1. Introduction

Availability of safe drinking water is an important issue in today's context. Disinfection of water is essential for removing pathogenic microorganisms that are responsible for causing a number of water borne diseases as 88% of diseases in the developing world are largely due to unsafe drinking water; about 842,000 people die every year from diarrhea, especially children, due to unsafe drinking water, improper sanitization and hand hygiene [1]. Water scarcity in various parts of the world also demands preserving drinking water sources by recycle and reuse of water, consequently demanding effective treatment methodologies. According to various norms, total coliform should be absent in drinking water [2]. Over the years, many different physical and chemical treatment methods are being used for disinfection of water and the most common is chlorination. The physical techniques for water disinfection are typically heating, filtration, microwave, UV irradiation, and plasma which generally have long treatment times, limited capacity and high cost. The chemical treatment method involves mainly chlorination and is widely used worldwide as the most preferred method for disinfection of water due to its effectiveness, ease of operation and low cost. However, formation of disinfection by-products (DBP) which are highly carcinogenic make chlorination process as not so environment and human friendly and in recent times is considered negatively, especially in many developed countries. The other possible technological alternatives are mainly adsorption, photocatalysis, membranes — reverse osmosis, etc. Newer types of adsorbents in the form of bio-nanocomposites, especially that using antimicrobial properties of biomaterial and magnetic properties for easy separation can be promising from practical application point of view [3,4]. Similarly, photocatalytic disinfection using catalysts such as TiO_2 coupled with processes such as UV radiation can effect disinfection in short time [5]. Many of these are cost intensive, especially for higher volumes of operation and have fouling problems. It is therefore instructive to further evaluate and develop more techno-economically feasible alternative technologies for disinfection of water that would not have the disadvantages of chlorination and at the same time are cost-effective. Hydrodynamic Cavitation is reported as an effective technology for disinfection that does not generate any secondary disinfection byproducts. Hybrid technologies

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https://doi.org/10.1016/j.jwpe.2021.102280
Received 26 June 2021; Received in revised form 9 August 2021; Accepted 18 August 2021
Available online 26 August 2021

based on hydrodynamic cavitation such as by combining it with natural oils can be highly promising [6,7].

The fundamental aspects of cavitation process are relatively well known [8], though its implementation and different applications are not so straightforward. The process involves formation, growth and collapse of cavities using suitable cavitation devices. The collapse of cavities concentrates energy up to 1–10^{18} kW/m^3 which apart from playing direct role in disinfection, also assist in homolytic cleavage of water with generation of hydroxyl radicals and consequent oxidation damage to microorganisms effecting water disinfection. Thus, disinfection using cavitation typically includes combination of mechanical, thermal and chemical effects; mechanical effects in the form of shock waves, intense shear stress with high pressures (~5000 atm), thermal effects in the form of extreme temperatures (~10,000 K) and chemical effects in the form of oxidation due to in situ generation of hydroxyl radicals ($^{\cdot}$OH) and such oxidizing species. The various forms of cavitation process are therefore exploited in different applications such as cleaning, water disinfection, wastewater treatment specifically for the removal of organic pollutants, removal of ammoniacal nitrogen and also recently in desulfurization of fuels for the removal of refractory sulfur compounds [6,7,9–13].

From practical and technological view point, today, acoustic cavitation (AC) and hydrodynamic cavitation (HC) appear most promising for disinfection of water. The effects of AC or ultrasound on pathogenic bacteria were investigated by many, especially as small-scale operations. Gogate and coworkers found that intensity of cavitation decreased with increased distance from horn; negligible effect above 2–5 cm from tip [14]. In view of high cost, unsatisfactory thermal efficiency and limitations in scale-up, hydrodynamic cavitation is being considered as a more robust technology in this regard. HC offers ease of operation and different reactor designs/variety of devices with/without moving elements. It can provide many a times simple design/construction, easy to scale-up and low cost solutions compared to acoustic cavitation reactor. In hydrodynamic cavitation reactors (HCR) using rotational mechanism, shear, shockwaves and heating are the main causes of disinfection. Milly et al. reported [15,16], a Shockwave Power Reactor converting electrical energy into thermal energy and increased temperature from 20 to 65.6 or 115 °C for complete pasteurization and sterilization of various fluids, foods such as calcium-fortified apple juice, tomato juice and skim milk. Rotor, driven by a simple milling cutter showed decreased ability of division of 75% for *E. coli* cells in 3 min [17]. Other advanced rotational HCR such as rotor and stator type device by Jyoti and Pandit [18], Cerecedo et al. [19], Sun et al. [20] and rotational generator by Sarc et al. [21] were effective for various bacteria with high levels of disinfection. However, super cavitation and high thermal effects in these rotational HCR may lead to serious erosion problems, and coupled with low durability and higher costs, practical applications of these can be limited. Thus, it is imperative that newer forms of process intensifications for disinfection be explored using hydrodynamic cavitation employing cavitating devices without moving elements, simple in design, having ease of operation, mild process/operating conditions and at the same time accomplish equal or improved disinfection efficiencies for real life operations.

In HCR without moving elements, cavitation is induced when static pressure falls below saturated vapor pressure either due to geometrical constriction in linear flow or due to vortex flow. There are different types of cavitating devices that are reported mainly using linear flow based devices (orifice, venturi, etc.) and vortex/rotational flow-based devices (vortex diode). The pressure/energy requirement in linear flow devices is rather high. Loraine et al. reported pump pressure of 345 kPa and 554 passes to achieve 99.999% of disinfection using a venturi reactor of 1.8 L water capacity [22]. Hybrid cavitation approaches using chemical process intensification are reported to enhance the performance of conventional cavitation devices such as venturi by addition of additional oxidizing agents such as H_2O_2 for increasing disinfection efficiency [21,23–27]. The disinfection efficiencies were not satisfactory, in general, ranging from 24% to more than 90% for inactivation of *E. coli*. Satisfactory disinfection of 100% was reported with excessively high operating pressures of the order of 12 MPa in 30 min by using orifice plate with high operational cost [28]. Recently, vortex flow based cavitating device, vortex diode has been reported for water and wastewater treatment/pollution control [10,11], desulfurization [12,13]. Jain et al. reported inactivation of Gram-negative and Gram-positive bacteria, *E. coli* and *S. aureus,* by vortex diode with substantially higher disinfection than conventional cavitation devices such as orifice and requiring lower operating pressure [9]. Mane et al. developed a hybrid hydrodynamic cavitation process using natural oils having antimicrobial properties and could obtain practically complete disinfection within 10 min for different microorganisms [6,7]. The optimized conditions were pressure drop of 1 bar and additive natural oils in 0.1% by volume. The approach was shown to be effective from common to antimicrobial resistant (AMR) bacteria and opportunistic difficult pathogen *P. aeruginosa*; with costs comparable to chlorination.

The use of plant extract coupled with cavitation technology for disinfection of water has not been discussed in the literature so far. The present study extends the philosophy of hybrid hydrodynamic cavitation technology beyond natural oils to other natural plant derived materials such as plant extracts, identify the differences in disinfection when the extract goes in water as a homogeneous mixture compared to heterogeneous oil water system reported earlier and evaluate the disinfection efficiencies for different oils and plant extracts. In view of the earlier reports in this regard, studies were carried out using comparable process conditions (vortex diode, ΔP of 1 bar, 0.1% of plant extract). The objective is to obtain insight into disinfection process to confirm no formation of disinfection by-products or intermediates and finally evaluate possible use of the natural plant materials for not just making water safe for drinking but also for additionally securing possible health benefits — a hybrid cavitation process that can be said to be Safe Water and Sustainable Technology Initiative from Indian Knowledgebase (SWASTIIK).

2. Materials and methods

2.1. Cavitation reactors

The hydrodynamic cavitation experiments were carried out by using vortex diode (VD) as a cavitating device. The design of vortex diode consists of a chamber of diameter 66 mm (throat diameter of 11 mm) with nominal capacity 1 m^3/h. Schematic of experimental set up and experimental details were discussed in our previous publications and only essential details are provided in the Experimental section [6,7]. The experiments were performed with typically 20 L of contaminated water, with known microorganism, *E. coli* and known initial concentration at predetermined operating conditions of ΔP 1 bar, additives 0.1% v/V, unless otherwise specified. Samples were withdrawn at regular time intervals and analyzed for percentage disinfection.

Acoustic cavitation was carried out using UCP-20 Sonication Unit having ultrasound — 40 kHz frequency and 500 W of power.

2.2. Microorganisms

For ease of comparison with literature reports, a commonly used model microorganism, Gram-negative bacteria *Escherichia coli* (ATCC-8739) was used in the present study and was obtained from NCIM — National Collection of Industrial Microorganism at CSIR, National Chemical Laboratory, Pune, India. For disinfection study, bacterial culture was grown in 50 mL of N. broth solution, incubated at 37 °C in orbital shaker with speed of 200 rpm for overnight. After incubation logarithmic (or exponential) phase of bacteria are measured by UV–Vis spectrophotometer at 600 nm wavelength. This robust stage of bacteria of 50 mL added to the 20 L of distilled water to obtain desired concentration (~10^4 CFU/mL).

2.3. Plant extracts and natural oils as bio-additive

Different plant extract such as *Zingiber officinale* (Ginger) extract, *Curcuma longa* (Turmeric) extract and *Curcumin amada* (Mango ginger) extract were prepared in the laboratory using the plant materials procured from local sources, Pune, Maharashtra, India. Extraction was carried out without using any solvent (e.g. acetone, methanol, hexane) in simple home appliance-mixer followed by separation where inherent liquid phase from rhizomes is separated using centrifugation with 1000 rcf speed for 15 min. (ESCO centrifuge, Versati T1000 ESCO model — TCV-1500-B (T1000-MB-B).

The different types of natural oils used include *Zingiber officinale* (Ginger) oil, *Lavandula angustifolia* (Lavender) oil, *Ocimum tenuiflorum* (Tulsi) oil, *Curcuma longa* (Turmeric) oil and *Azadirachta Indica* (Neem) oil. These were procured locally from Pune, Maharashtra, India. The detailed characteristics of different natural oils and extracts are given in Table 1.

Table 1
: Characteristics of natural plant derived materials — oils and extracts.

Sr. no.	Name of oil/ extract	Chemical composition	Physicochemical properties — oil	Reference
1	Neem	Hexadecanoic acid (78.25%), tetradecanoic acid (7.24%), Silane, triethylfluoro (3.96%), oleic acid (3.64%), octadecenoic acid (3.5%), linoleic acid (1.39%), etc.	Density — 0.91 g/cc Viscosity — 58.94 cP Surface tension — 40.69 dyn/cm	[29,30]
2.	Lavender	1,6-Octadien-3-ol,3,7-dimethyl (41.74%), silane, triethyl fluoro (36.71%), bicyclo [1.2.2] heptan-2-one, 1,7,7-tri-methyl (6.91%), eucalyptol (5.99%), methane sulfonyl chloride (5.67%) and 3-cyclohexene-1-methanol, a,a4-trimethyl (2.99%)	Density — 0.883 g/cc Viscosity — 46.6 cP Specific gravity — 0.887	[29,31,32]
3.	Tulsi	Methyl eugenol (82.9%), eugenol (0.9%), β-caryophyllen (4.1%), borneol (2.4%), germacrene D (2.3%), α-copaene (1.9%), δ-cadinene (1.1%), germacrene A (0.7%), linalool (0.5%), α-elemene (0.5%), cubebol (0.3%), α-pinene (0.2%), limonene (0.2%), β-bourbonene (0.2%), α-humulene (0.2%), etc.	Density — 1.552 g/cc Viscosity — 26.75 cP Surface tension — 84.29 N/m	[33,34]
4	Ginger	α-Zingiberene (35–40%), β-sesquiphellandrene (11.5–13.5%), ar-curcumene (6.5–9%), camphene (5–8%), β-bisabolene (2.5–5.5%)	Density — 0.9104–0.9108 g/cc Viscosity — 5 cP Surface tension — 30.9 dyn/cm	[35,36]
5	Turmeric	α-Turmerone (40.8%), zingiberene (16.9%), β-turmerone (14.1%), ar-turmerone (11.0%), and β-sesquiphellandrene (10.0%)		[37]
6	Mango ginger extract	Myrcene (88.6%), ocimene (47.2%), ar-turmerone (29.12%), (*Z*)-β-farnasene (21.9%), guaia-6,9-diene (19.8%), cis-β-ocimene (18.8%), cis-hydroocimene (18.79%), transhydroocimene (15.94%), α-longipinene (14.8%), α-guaiene (14.5%), linalool (13.37%), β-curcumene (11.2%) and turmerone (10.8%)		[38,39]

3. Experimental

The experimental set up of hydrodynamic cavitation and experimental procedure was explained in detail in our earlier work [6,7] and hence only essential details are included here to avoid repetition. The experimental set up comprises a holding tank having 50 L capacity, a multistage vertical centrifugal pump (Model CNP make CDLF2-26, SS316, 1.2 m^3/h at 228 MWC, rating 3 kW (4 hp), 2900 RPM, discharge pressure 0–15 bar), vortex diode as a cavitation device and measurements and controls for flow, pressure and temperature. A 20 L volume of contaminated water with ~10^4 CFU/mL of initial concentration of bacteria was used for disinfection study. Bio-additives (Oil/plant extract) were used with optimized concentration of 0.1% in the hybrid process. The samples were withdrawn from holding tank at periodic intervals of time and were analyzed by plate count method. For analysis, 100 μL of bacterial sample was spread over sterile N. agar petri dish. After incubation for 24-h, viable colonies were counted and measured as a colony forming unit per milliliter (CFU/mL).

$$\mathrm{CFU}\Big/\mathrm{mL} = \frac{\text{Number of colonies on N.agar plate}}{\text{Volume plated (mL)}} \times \text{dilution factor}$$

The confirmation of cell destruction by cavitation was done by FE-SEM (Field Emission Scanning Electron Microscopy, FEI-Nova Nano-SEM-450) and TEM (Transmission Electron Microscopy; Tecnai G2 20 STwin; LaB6 filament as the electron source) analysis. The samples before and after cavitation were analyzed for detailed morphological changes of bacterial cells to prove process efficacy. The functional groups of the natural oils and plant extracts, prior to cavitation and after cavitation, were characterized by Fourier transform infrared spectroscopy (Perkin Elmer's Spectrum One FTIR Spectrometer).

4. Results and discussion

4.1. Cavitation using miscible plant extracts

Plant extracts derived from different parts of natural plants can provide useful alternative to the use of natural oils and can offer similar benefits along with good disinfection efficiency in the hybrid cavitation process described earlier for natural oils. A proof of concept is established here in this regard for the first time using different plants extracts from rhizomes such as turmeric extract, ginger extract and mango-ginger extract. For ease of comparison with similar natural oils, use of similar concentration, 0.1%, was made to evaluate disinfection efficiencies. In selection of the natural plant resources, medicinal properties of rhizomes of ginger, turmeric and mango ginger are well thought-out apart from their wide use in day to day life.

In order to establish the proof of concept, experiments were initially carried out using acoustic cavitation. Fig. 1 shows the results of acoustic cavitation using mango-ginger extract. It was observed that even simple process of acoustic cavitation can yield more than 90% disinfection in 15 min.

Having established the disinfection efficacy of plant extract using acoustic cavitation, further experiments were carried out using hydrodynamic cavitation due to its commercial potential in terms of ease of operation and energy effectiveness. The results are presented in Fig. 2. It can be seen that the disinfection efficiency for the mango-ginger plant extract is high, of the order of 90% in 15 min. For the other two extracts

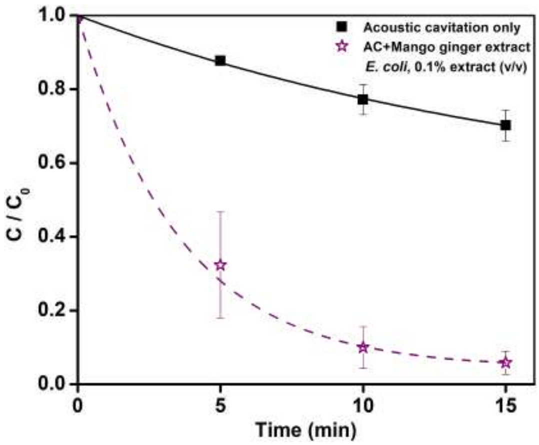

Fig. 1. Disinfection efficiency using acoustic cavitation for mango-ginger plant extract.

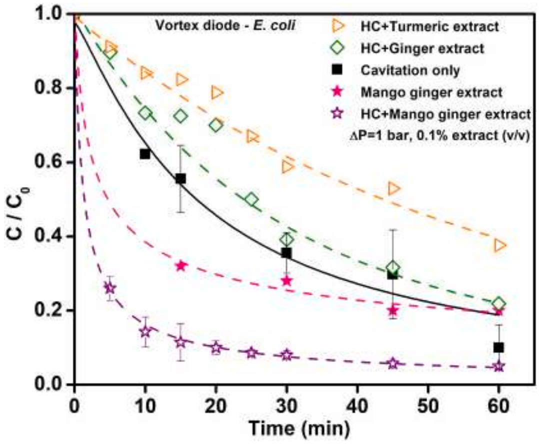

Fig. 2. Disinfection efficiency for various plant extracts using hydrodynamic cavitation.

namely turmeric and ginger extract, the extent of disinfection was lower than that using cavitation alone similar to that observed with many natural oils. It is possible that the extraction efficiency for turmeric and ginger could be lower reflecting lowered content of the active ingredients as compared to mango-ginger. The roots of ginger, turmeric and mango ginger contain essential oils and other active ingredients such as curcuminoids. Hanif et al. [40] reported the essential oil yield of different plant extract by CO_2 supercritical fluid extraction and their antimicrobial properties, indicating % oil yield for rhizomes of *Curcuma amada* as 6.38, roots of ginger as 5.59 and for *Curcuma longa* as 3.56. It reveals higher antimicrobial activity for mango ginger than ginger and turmeric extract. The aqueous plant extract with cavitation gives higher disinfection for mango ginger — up to 95% disinfection in 60 min. This can be attributed to presence of higher curcuminoids and higher % of oil in mango ginger, than for ginger extract and for turmeric extract. The curcuminoids are lipophilic in nature and can reacts with phospholipids of the cell membrane and easily destroy the permeability of microorganisms.

Policegoudra et al. reported previously ignored component-difurocumenonol as active ingredient responsible for antimicrobial activity and nonpolar extracts of mango ginger by chloroform demonstrated higher inhibition zone for different Gram-negative bacteria such as *M. luteus*, *S. aureus*, *B. cereus*, *B. subtilis*, *L. monocytogenes* as compared to extraction obtained using hexane, ethyl acetate, acetone and methanol where negligible disinfection was obtained for *E. coli* [41]. The higher disinfection efficiency with mango-ginger extract may also be attributed to the presence of oil content in the extract and lipophilic curcuminoids and difurocumenonol.

The results with the plant extracts of this study in cavitation clearly demonstrate their potential application in water disinfection.

4.2. *Synergistic effect*

When working with hybrid methodology of cavitation, it would be prudent to evaluate synergistic effect of plant extract in hybrid cavitation method. Extraction of active ingredients from mango ginger rhizomes without addition of any solvent gave good disinfection efficiency of 80% without cavitation. The experiments using hybrid cavitation methodology with mango ginger extract exhibited higher rates of disinfection than cavitation and mango ginger individual effect (Fig. 2). Proof of concept is established by carrying out experiments using acoustic cavitation with same small quantity of mango ginger extract, 0.1%. It was observed that acoustic cavitation with mango ginger exhibited ~95% disinfection which is higher than acoustic cavitation alone, of 30%.

The synergistic effect for plant extract is evaluated using the following Eq. (1).

$$f = \frac{K_{HC+oil/extract}}{K_{HC} + K_{oil/extract}} \tag{1}$$

where, K is for rate constant in s^{-1}, HC and HC + oil/extract indicated for hydrodynamic cavitation and hydrodynamic cavitation along with natural essential oil/extract.

The value of ***f*** for mango ginger extract are 1.85 and 1.22, clearly indicating synergistic effect in hybrid process due to hydrodynamic cavitation along with mango ginger extract and acoustic cavitation along with mango ginger extract respectively. Similarly, for other extract such as ginger extract synergistic index is found less than 1 and therefore no synergistic effect found.

4.3. *Cavitation using immiscible oils*

The use of immiscible natural oils as bio-additives in cavitation represents a complex heterogeneous system where oil phase is in addition to the conventional aqueous phase subsequently getting transformed into two phase — gas (e.g. water vapor/ air)–liquid (water) system during cavitation. The cavitation processes are known to generate emulsion and the type of cavitation, nature of cavitation device and such parameters dictate the extent of emulsion or micro-mixing, in general. Volatile organic compounds are the main components of essential oil that are expected to contribute in the process of disinfection and enhance the rates of disinfection as well. The present work describes the effect of various immiscible oils namely ginger oil, tulsi oil, turmeric oil, lavender oil and neem oil, not reported so far in this regard. Fig. 3 shows the disinfection efficiency using these natural oils in the hybrid cavitation process using vortex diode as a cavitating device and using the same process parameters as discussed in previous section for plant extracts. It is seen that Ginger oil and Lavendor oil show significant increased efficiency of disinfection while the remaining oils perform negatively, with decreased efficiency.

Ginger is typically considered as a safe natural product to treat respiratory and gastrointestinal disease for many decades. It belongs to *Zingiberaceae* family, perennial herb and because of its characteristic spicy aroma and taste, it is traditionally used as a spice in foods and beverages. In addition, it is an excellent source of many bioactive phenols such as gingerols, shogaols, and zingerones. It is reported that the antimicrobial activity of ginger essential oil (GEO) has higher inhibition zone for various bacteria, *Staphylococcus aureus* and *Listeria monocytogenes*, followed by *Pseudomonas aeruginosa* while some bacteria such as *Salmonella typhimurium*, *Shigella flexneri* and *Escherichia coli* were reported to be resistant to ginger essential oil [42]. Also, *S. aureus* has higher sensitivity for GEO than *E. coli*, as these bacteria commonly used

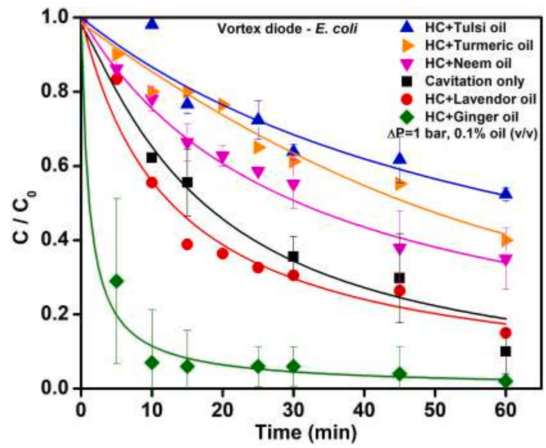

Fig. 3. Disinfection efficiency for various natural oils using hydrodynamic cavitation.

for disinfection study [43]. Minimum inhibitory concentration of GEO for *S. aureus*, *B. subtilis*, *E. coli* and *Penicillium* spp. exhibited the value of 8.69, 86.92, 173.84 and 869.2 mg/mL respectively [44]. *E. coli* required much higher inhibitory concentration of GEO compared with other microorganisms. In the light of the reported literature, it is evident from the present work that a small quantity of ginger oil along hydrodynamic cavitation exhibited excellent disinfection efficiency for *E. coli* (Fig. 3).

A more scrutiny to elucidate the disinfection effects reveals the role of bio-active components of ginger oil which include hydrophobic gingerol and hydrophilic polysaccharides. The Lipophilic gingerols have many pharmacological activities such as anti-oxidant, anti-inflammatory, antimicrobial, anticancer, anti-emetic, anti-metabolic syndrome, and neuroprotection [45]. Owing to lipophilic nature they are easily penetrable through cell membranes of microorganisms which may affect both the inner cellular components of cytoplasm and the external cell envelope. Consequently, these contribute to enhanced bacterial cell membrane permeability subsequently leading to loss of ions and leakage of cellular components. In some cases, presence of active ingredient of natural oils such as thymol, menthol, and linalyl acetate leads to higher antimicrobial activity [46]. The results of this work are also consistent with the reports of Kumari et al. [47] on antioxidant activity of essential oil and aqueous extract of ginger where essential oil was shown to exhibit higher antioxidant property due to the presence of high phenolic content (or major contents of monoterpenoids) than the aqueous extract of ginger (contains lower content of sesquiterpenoids). Also, similar to the findings of Baris et al. [48], hydrodynamic cavitation with ginger extract showed lower disinfection due to the presence of polar phenolics — components with low activity. It does not easily penetrate through cell membrane of microorganisms and may require higher dosage to obtain similar disinfection efficiency as that for cavitation with ginger oil. A high disinfection of 98% in 60 min with oil (0.1%) can be obtained using hybrid cavitation methodology.

It is possible that higher viscosity and surface tension of oils have adverse impact on cavitation. The hybrid process using neem oil and tulsi oil showed lower rates of disinfection, probably due to higher viscosity of these oils. The neem oil has viscosity of 37 cP [49], tulsi oil has viscosity 26.75 cP and surface tension 84.29 N/m [34], the ginger oil has low viscosity of 5 cP and surface tension of 30.9 dyn/cm. Higher values of viscosity and surface tension adversely affect the growth stage of bubbles, and increased the time of collapse [50]. There could be reduced collapse of bubbles, delay in collapse of bubble, or implosions of low intensity, producing less energy; all contributing to reduced disinfection efficiency in the hybrid process.

The antimicrobial activity of ginger oil is mainly due to the high percentage of eugenol (50.94%) as an active ingredient [36]. Considering easy availability of these medicinal plants and inherent health benefits associated with different plants, applying this traditional knowledge mainly from Ayurveda and advance oxidation technologies such as hydrodynamic cavitation can offer practical alternative to disinfection of water with possible health benefits of plant extracts.

Followings revealing observations can be made from Figs. 2 and 3 corresponding to hybrid cavitation technology operation of 15 min:

1. The rate of disinfection with ginger oil are higher, an order of magnitude, 2 times than cavitation alone and 3 times than cavitation with ginger extract.
2. Ginger oil showed higher degree of disinfection than ginger extract for the reasons explained above.
3. The lavender oil exhibited higher rate of disinfection, of the order of 1.5 times higher than cavitation alone.
4. The turmeric oil and turmeric extract both showed nearly similar and lower extent of disinfection performance than cavitation alone.
5. The neem oil and tulsi oil showed lower efficiency similar to turmeric oil.
6. The rate of disinfection for mango ginger extract for both hybrid hydrodynamic cavitation and acoustic cavitation were significantly higher than cavitation alone. For hydrodynamic cavitation, the rates were 2 times higher and for acoustic cavitation, 3 times higher rate of disinfection could be obtained.

The synergistic coefficient for ginger oil is greater than 1, again confirming superiority of combined effects of natural oil along with cavitation. The results also indicate natural oils are more effective compared to plant extract in disinfection of water.

4.4. Kinetics of disinfection — per-pass disinfection model of hydrodynamic cavitation

The kinetics of disinfection based on per pass disinfection factor is useful in understanding the disinfection behaviour [6,7]. The rate equations in this regard are elaborated below:

For the conventional model, the effective disinfection rate constant ($\boldsymbol{k}$), s^{-1} is defined as:

$$\boldsymbol{k} = \frac{ln(\boldsymbol{C_0}/\boldsymbol{C})}{\boldsymbol{t}} \tag{2}$$

where, C_0 and C are bacteria concentrations, initial and at any time $\boldsymbol{t}$ respectively, CFU/mL.

For per-pass disinfection model of hydrodynamic cavitation, the effective rate constant is defined as below ($\boldsymbol{k}$), s^{-1} and is related to residence time, τ

$$\boldsymbol{k} = \frac{\boldsymbol{\varphi}\,\boldsymbol{n}}{\boldsymbol{t}} = \frac{\boldsymbol{\varphi}}{\boldsymbol{\tau}} \tag{3}$$

where, φ is per-pass disinfection factor and n is number of passes.

Per-pass disinfection model is more realistic and requires parameters like flow rate (Q), volume treated (V) operating pressure drop across cavitating device (P) and concentration-time data. The per-pass disinfection factor (φ) represents the significance of cavitating device.

$$\varphi = \frac{-ln(C/C_0)}{n} \tag{4}$$

Also, number of passes (n) is an important parameter used in cost calculations — lower the value of n, lower is the cost of disinfection process. The number of passes can be obtained as:

$$n = \frac{Q \times t}{V} \tag{5}$$

Using the model, effective rate constant and per-pass disinfection factor can be calculated and these values are listed in Table 2. The per-pass disinfection factor (φ) for ginger oil in cavitation process is 5 times higher than cavitation alone and also 10 times higher than ginger extract

Table 2
Rates of disinfection for *E. coli.*

Hydrodynamic cavitation (HC), vortex diode, $\Delta P = 1$ bar				
Process oil/extract = 0.1%	% disinfection	Rate of disinfection CFU/(mL·s)	Rate constant (s^{-1}) × 10^4	Per-pass disinfection (φ) × 100
Cavitation alone	44	99	7.05	7
HC + ginger oil	96	254.5	36	36
HC + tulsi oil	23	12.3	3	3
HC + neem oil	34	22	4.55	4.4
HC + lavender oil	61	52.5	10.5	10.5
HC + turmeric oil	20	22.3	2.5	2.45
HC + mango ginger extract	88	94	24.1	24.3
HC + ginger extract	27	18	3.6	3.6
HC + turmeric extract	18	17	2.16	2.13
Without cavitation—only mango ginger extract	68	21	13	NA
Acoustic cavitation (AC)				
Cavitation only	30	9	4	NA
AC + mango ginger extract	94	108	31.5	NA

as shown in Fig. 4. The values of (φ) are 0.36, 0.07 and 0.036 for cavitation with oil, cavitation alone and cavitation with extract for vortex diode as a cavitating device. The per-pass disinfection factor (φ) for cavitation with mango ginger extract is 3.5 times higher than cavitation alone by using vortex diode as cavitation device. The value of (φ) for HC + Mango ginger extract is 0.243. The results for acoustic cavitation, cavitation with mango ginger extract also show consistent results. The variations in the values of (φ) because of the type of extract/oil, active components of extract/oil are clearly evident.

It can be seen that per-pass disinfection factors (φ) for *E. coli* are higher for ginger oil and mango ginger (MG) extract with cavitation than other oils and extract. It is also evident that in 15 min, increase in per-pass disinfection for cavitation with ginger oil is of the order of 500% and for mango ginger extract it is ~300% more as compared to cavitation alone. However, since 100% disinfection is desired, selection of oil and process integration is crucial. It is also to be noted that 0.1% extract represents substantially low dose as compared to corresponding oil dose of 0.1% and therefore, for higher disinfection efficiency, more than 0.1% of extract is desirable. The results clearly highlight utility of natural oil and plant extracts in enhancing the rates of disinfection.

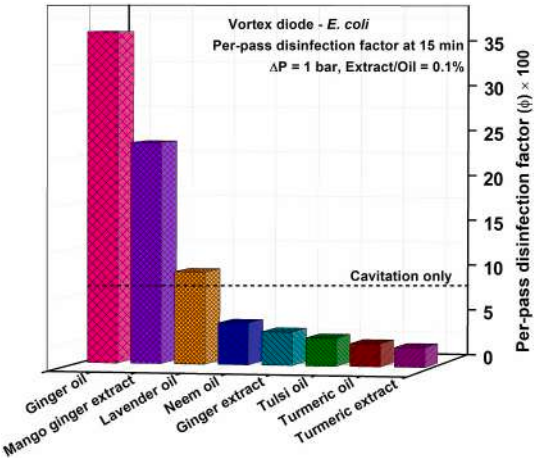

Fig. 4. Comparison of per-pass disinfection factors.

A comprehensive comparison of performance of different hydrodynamic cavitation reactors is presented in Table 3. Many reactors such as high pressure homogenizer, high speed homogenizer/mixer blender and hydrodynamic cavitation with orifice plate utilized for cell disruption [51–54]. Majority studies exhibited lower disinfection efficiency and required more time for disinfection, though the performance of can be enhanced by process intensification such as ozone (O_3), hydrogen peroxide (H_2O_2) or ultrasonic probe (US) or use of chlorine oxides. For example, orifice alone gave only ~40% disinfection and maximum of 75% using process intensification. Chlorination of some form, as part of process intensification, assists in reaching high levels of disinfection, however, disinfection by-products formation in such scenario is not well reported. The problems with rotor type devices are already well highlighted in earlier text. The present approach, showed a higher efficacy of hybrid cavitation with possible health benefits without forming any disinfection by-products, time saving, with less energy requirement.

4.5. Mechanistic understanding of the process

4.5.1. Philosophy behind selecting plant extract as an additive for hybrid cavitation

Curcuma amada, which is also known as a mango ginger or ambe haldi or aam haldi is traditionally used for medicinal purposes as a herbal medicine in Ayurveda, Unani medicine from centuries and in several food preparations. It is well reported that rhizome is rich source of essential oils, and containing more than 130 active ingredients with biomedical importance. It has antibacterial, insecticidal, antifungal and antioxidant properties [38]. The major chemical components with their biological activity include starch, phenolic acids, volatile oils, curcuminoids and terpenoids like difurocumenonol, amadannulen and amadaldehyde that are important from pharmacological point of view. Ramachandran et al. [59] reported mango ginger's anticancer potential and its action for Glioblastoma cells was reported where *Curcuma amada* extract induces apoptosis in glioblastoma cells. Difurocumenonol, one of active component from mango ginger, is important for antimicrobial activity against Gram-positive and Gram-negative bacteria [41]. De et al. [60] reported presence of non-polar terpenes in Indian curcuma species e.g. *C. amada*, *C. aromatica*, *C. caesia*, *C. longa*, and *C. zedoaria*. Also, the lipophilic curcuminoid helps in killing microorganisms by inhibiting its cellular functioning. *C. amada* has a strong anti-microbial and other biological activity. The other active components may also enhance the disinfection or bactericidal activity by different mechanisms such as inhibition of cell wall synthesis, interference with the permeability of cell membrane, cause membrane disruption, modifying cellular constituents, and cell damage or cell mutation. Chandarana et al. [61] showed the antimicrobial activity of aqueous extract of *C. amada* against *E. coli*, *B. subtilis*, *S. aureus*. Many such plant extracts can prove to be useful from health benefits point of view, if appropriately used in the water treatment process and therefore the present study could provide starting point for elucidating use of plant extracts in hybrid cavitation process for water disinfection.

4.5.2. Functionality changes

The FTIR spectra of disinfection of water before and after cavitation with natural additives are presented in Fig. 5(a) (b) and (c). The different functional groups of natural additives with vibrational frequencies are clearly evident. The FTIR spectra of the oil phase of ginger oil, before and after hybrid cavitation, indicates similarity in wavenumber but difference in intensity of transmittance. The FTIR spectra for the aqueous phase indicated no change in the functional groups before and after hybrid cavitation. The IR band for O—H vibration of alcohol and carboxylic acid group represented in the range of 2500–3300 cm^{-1}, 1700–1750 cm^{-1} interval is for ketone group, the characteristic peak at 1430–1510 cm^{-1} wavenumber for C═C vibration ascribed to benzene group, 1375 cm^{-1} for C—O group, 987 cm^{-1} wavenumber indicated for ═CH—H group and 883 cm^{-1} for para benzene functional group. All

Table 3
Comparison of different hydrodynamic cavitation methods used for disinfection.

Cavitating device	Operating conditions	% Disinfection	Ref.
Multiple hole orifice	P = 5.17 bar ~100 *Faecal coliforms*/100 mL	5 mg/l H_2O_2 **9** (15 min), **21** (60 min) HC **38** (15 min), **92** (60 min) HC + 5 mg/l H_2O_2 **60** (15 min), **96** (60 min) HC (1.72 bar) + US (40 kHz) **60** (15 min), **80** (60 min) HC (1.72 bar) + US (40 kHz) **75** (15 min), **90** (60 min) + 5 mg/l H_2O_2	[23]
Ball type valve	P = 5.17 bar ~100 *Faecal coliforms*/100 mL	2 mg/l O_3 **78** (15 min), **100** (60 min) HC **57** (15 min), **76** (60 min) HC + 2 mg/l O_3 **88** (15 min), **100** (60 min)	[55]
Liquid whistle reactor	P = 500 psi *E. coli* 10^8–10^9 CFU/mL	HC **22** (180 min) HC + O_3 **75** (180 min)	[26]
Orifice	P = 2.5 bar *E. coli* 10^7 CFU/mL	**32.7** (120 min)	[25]
Orifice	ΔP = 1–12 bar *E. coli* 10^7 CFU/mL	0.25–0.3 mg/l ClO_2 **>99** (3–6 min) HC + ClO_2 **99.99** (6 min)	[56]
Multiple hole orifice	0.45 MPa 2500–3000 CFU/mL	HC **67.3** (60 min) 0.5 mg/L ClO_2 **78.2** (60 min) 1.0 mg/L ClO_2 ~**80** (60 min) 2 mg/L NaClO ~**50** (60 min) HC + 0.5 mg/L ClO_2 ~**99** (60 min) HC + 1.0 mg/L ClO_2 **100** (60 min) HC + 2 mg/L NaClO ~**79** (60 min)	[57]
Rotor-stator	*E. coli*	HC (4.3 L/min) **100** (14 min)	[20]
Vortex diode	ΔP = 10 bar for Orifice, ΔP = 2 bar for VD *E. coli*, 10^4 CFU/mL	Orifice **99** (60 min) Vortex diode **98** (60 min)	[9]
Venturi + plasma discharge	P = 6 MPa *E. coli* 10^7 CFU/mL	Silver wire **46** (1 treatment) HC + Silver electrode **98** (1 treatment)	[58]
Vortex diode	ΔP = 1 bar for VD *E. coli*, *S. aureus*, 10^4 CFU/mL	AC **3.18** (15 min) AC + 0.1% clove oil **51** (15 min) Orifice **32** (15 min), **70** (60 min) Orifice + 0.1% clove oil **55** (15 min), **92** (60 min) Vortex diode ~**21–44** (15 min), ~**84–90** (60 min) VD + 0.1% clove oil ~**63–86** (15 min), **92** (60 min)	[6]
Vortex diode	ΔP = 1 bar for VD *S. aureus*, *Methicillin resistant S. aureus*, *P. aeruginosa*, 10^4 CFU/mL	HC ~**21–33** (15 min), ~**49–84** (60 min) HC + 0.1% peppermint oil ~**98–99** (5–10 min) HC + 0.05% peppermint oil + aeration ~**95–98** (5–10 min)	[7]
Vortex diode + 0.1% natural oil	ΔP = 1 bar *E. coli* 10^4 CFU/mL	*E. coli* HC **44** (15 min), **90** (60 min) HC + 0.1% MG extract **88** (15 min), **95** (60 min) HC + 0.1% ginger oil **96** (15 min), **98** (60 min)	Present study

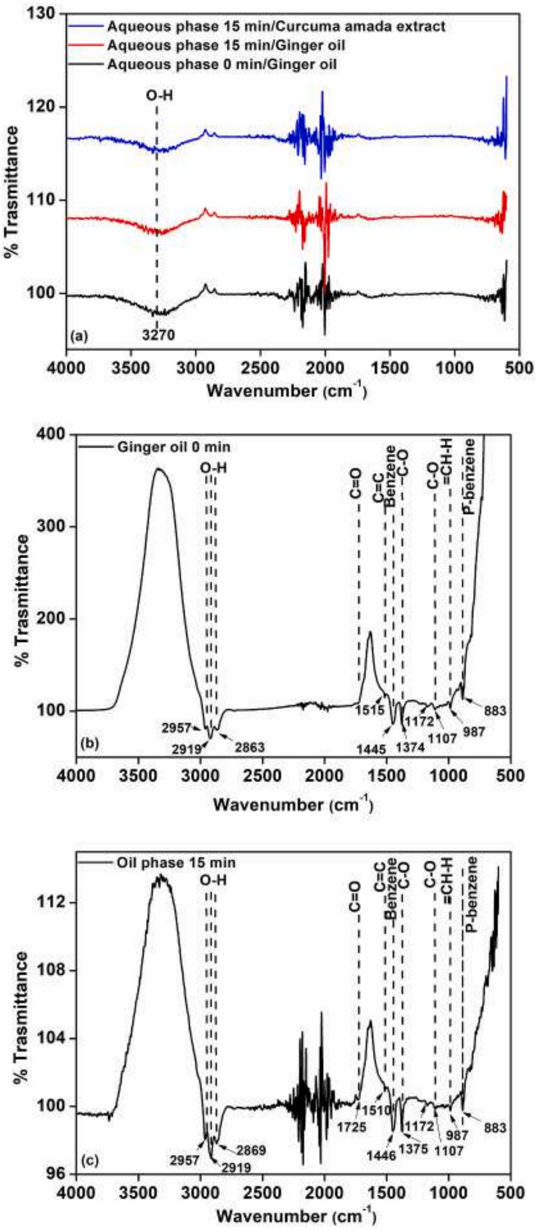

Fig. 5. FTIR analysis before and after cavitation for the hybrid operation.

these functional groups are representing α-gingerol active component of ginger oil. The results of FTIR analysis before and after cavitation showed no indicative change suggesting no formation of byproducts or intermediates.

4.5.3. Structural changes

A morphological analysis of bacteria before and after treatment was studied by TEM (Fig. 6a, b) and FE-SEM (Fig. 6c and d). TEM results indicate intact healthy *E. coli* cells with rod shape, homogenous, smooth

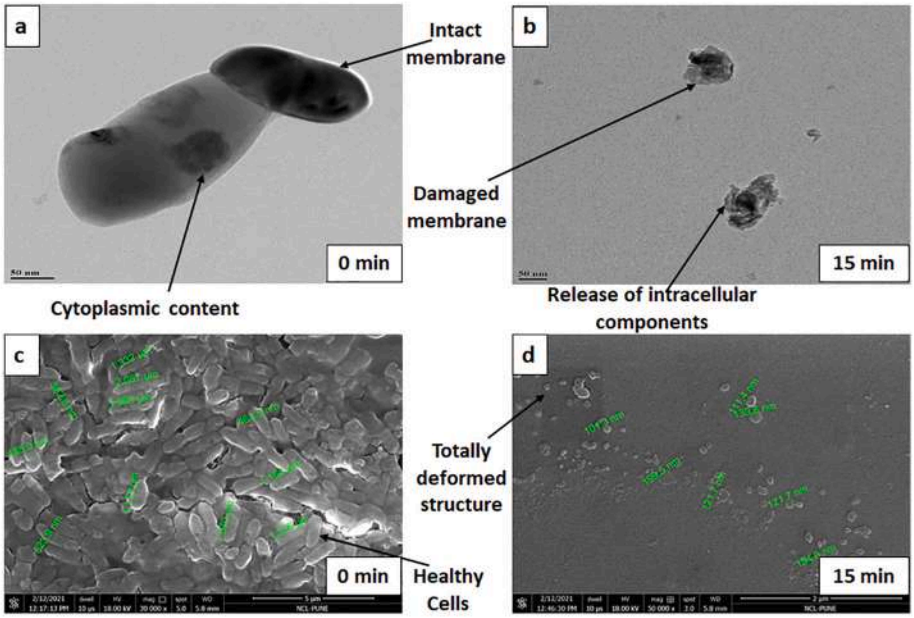

Fig. 6. TEM analysis for establishing cell destruction

surface and visible cytoplasmic contents that get damaged after 15 min of hybrid cavitation treatment. Significant change in shape, size and morphology was observed and damage in the form of cell membrane rupture and leakage of cytoplasmic content due to hybrid cavitation is clearly visible.

4.6. Possible mechanism of disinfection

From the literature studies, it can be deduced that the conventional cavitating devices such as orifice and venturi can impart severe surface damage to the microorganisms but considerably limited cell breakage/cleavage, thereby limiting the overall efficiency. The rotational devices largely effect cell cleavage, rough surface though size reduction and leakage of cytoplasm is not significant [24]. In the present work, hybrid cavitation led to loss of cytoplasm, reduction in size or totally deformed structure, size reduced from 1 to 2 μm to 100–200 nm as seen from Fig. 6 (b) and (d). The combined effect of antimicrobial property of natural additives and hydrodynamic cavitation is evident in the form of increased efficiency. Fig. 7 depicts this plausible mechanism of hybrid cavitation by highlighting contribution of different factors. The results are also consistent with those reported earlier with hybrid method [6,7]. Thus, the extreme conditions of temperature, pressure at the point of cavity implosion, high shear, oxidation or oxidative damage (action of highly reactive hydroxyl radicals) of sulfhydryl group and double bonds of protein components, etc. fragment the cellular content and cell membrane, damage DNA and protein and resulting into cell death. The active components of plant extract and essential oil both have lipophilic properties and permeate the cell wall as well as the cytoplasmic membrane, inducing a loss of membrane integrity in microorganisms [45]. The active component such as gingerol from ginger oil and curcuminoids and difurocumenonol from mango ginger extract can react with phospholipids of outer cell membrane thus altering the cell permeability and denature its protein thereby causes cell death.

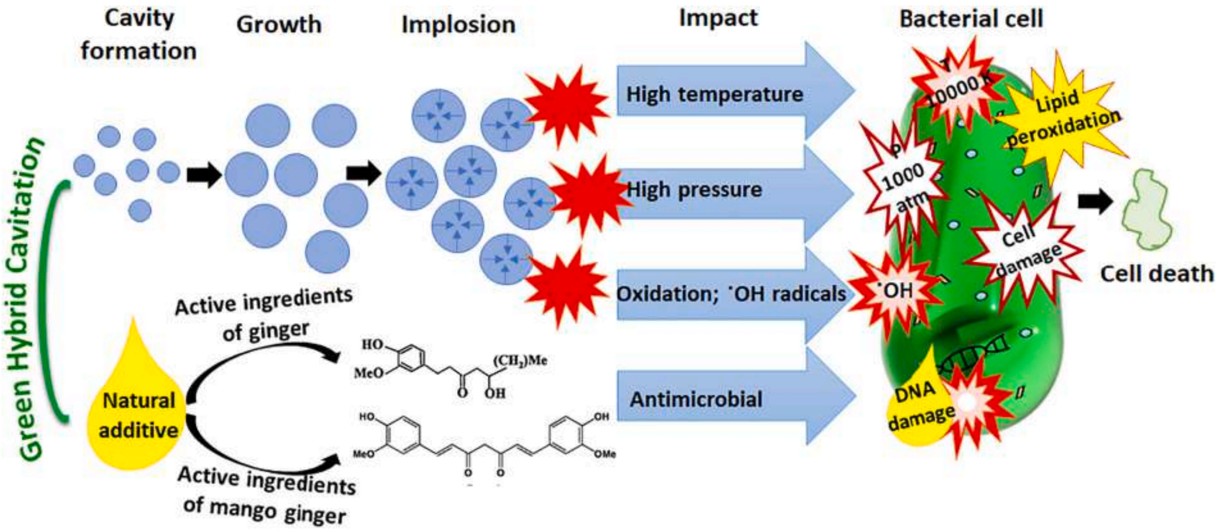

Fig. 7. Plausible mechanism for destruction of *E. coli* by green hybrid cavitation process. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

4.7. Energy and cost considerations

The energy requirement is evaluated for different reactor configurations and is compared in Fig. 8. Filho et al. [28] reported 99.97% of disinfection in 30 min with orifice as a cavitation device and copper coil in cooling system at a pressure of 10 MPa, requiring 12.28 kWh energy. Its disinfection performance is higher than that reported earlier by Chand et al. [26], Arrojo et al. [25] and Jancula et al. [62]. Chand et al. [26] reported disinfection efficiency of 75% using liquid whistle reactor with ozone and required energy of 15.3kWh, pressure of 500 psi and 3 h of time of operation. Arrojo et al. [25] reported % disinfection of 91.1 for venturi and 32.7 for orifice in 2 h under 18 kWh energy, and Jancula et al. [62] reported 99% of disinfection with venturi with 350 kPa discharge pressure, 18 min of time with 18 kWh energy. In recent reports on rotor-stator type of devices reported by Sun et al. [63,64] obtained higher or similar disinfection efficiency of 100% of disinfection in 4–14 min of operation with rotational speed of 4200 rpm, 1.4 m^3/h flow rate and required low energy (0.748–3.48 kWh) compared with other rotational based hydrodynamic cavitation reactor reported by [19,65] and conventional laminar flow based cavitation reactor. Sarc et al. [21] and Cerecedo et al. [19] reported 99.95% (9025 rpm, 150 min) required energy 0.7 kWh and 100% (2400 rpm, 7.8 min) required energy 0.65 kWh respectively. The drawback of the use of rotor and stator type of device is that with increase in the flow rate above 1.4 m^3/h and high rotational speed of 4200 rpm, the disinfection performance decreases; flow rate of 2.6 m^3/h showed no disinfection. Further, very high temperatures above 90 °C essentially indicate disinfection by way of boiling.

On the other hand, Jain et al. [9], utilizing rotational flow-based reactor, vortex diode reported more than 98% of disinfection with only 2 bar of pressure drop within 60 min of time of operation corresponding to only 0.0872 kWh energy requirement. Mane et al. [7] developed hybrid cavitation using natural oils that resulted in drastic reduction in time for disinfection with high disinfection efficiency and more than 99% of disinfection using 1 bar pressure drop for a very low 0.0025–0.005 kWh of energy requirement was obtained. In the present study, the disinfection efficiency for cavitation with ginger oil is 98% in 60 min of time with 0.03 kWh and first time reported the energy required for cavitation with mango ginger is 0.03 kWh with 95% (60 min) disinfection. However, since 100% disinfection is desired, more investigations on plant extracts are essential.

The hybrid cavitation methodology using vortex diode appears to provide substantial advantages and low cost. In addition, the vortex-based cavitation reactors are commercially available and have easy scale up [66]. Therefore, in view of the techno-economic feasibility, no harmful by-products and possible health benefits of plant extracts, the hybrid cavitation process can provide alternative solution to conventional disinfection methods.

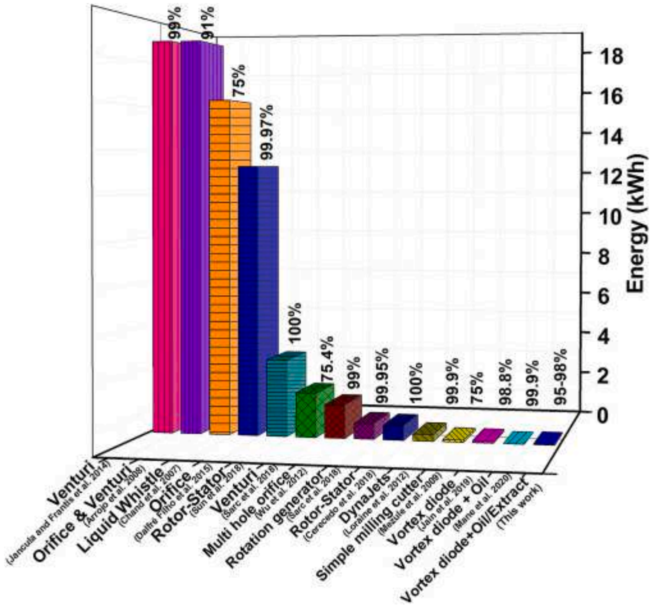

Fig. 8. Comparison between energy required for different processes.

The cavitation yield per volume treated (CFU/mL/J) can be obtained as:

$$\text{Cavitation yield}\Big/\text{volume treated} = \frac{(C_0 - C)}{(\Delta P \times Q \times t)}$$

The cavitation yield per volume treated for hydrodynamic cavitation along with ginger oil and hydrodynamic cavitation along with mango ginger extract at time 15 min is 7.2 and 3.42 CFU/mL/J.

Further, the cost of treatment can be obtained using the following equation:

$$\text{Cost of treatment}\Big/\text{m}^3 \text{ of water} = \frac{n\Delta P P_E}{36\eta}$$

where, n is number of passes can be obtained as $n = \frac{(Q\times t)}{V.}$.

For vortex diode, the flow rate (Q) measured at $\Delta P = 1$ bar is 720 LPH and volume treated is 20 L.

At 15 min of time of operation (t), the number of passes (n) obtained is 9. Assuming the cost of electricity P_E as 10 Rs/kWh and pump efficiency (η) as 0.66, the cost of treatment per m^3 of water is 3.8 Rs/m^3 (0.052$/$m^3$).

In view of disinfection efficiency less than 100% using plant extract (0.1%), it is required that either the process can be evaluated at higher dose of plant extract or be combined with natural oils so that 100% disinfection can be realized. It may be noted that the cost of disinfection would get slightly modified, increased, in such eventuality. Since, this work only provides the proof of concept for the use of plant extracts with limited examples, many other plant extracts/extraction methods/different plant parts need to be investigated where possibly high disinfection can be obtained.

5. Conclusions

The present study, for the first time, reports useful application of plant extracts in the hybrid cavitation process for disinfection of water and for providing possible health benefits. Followings are the main findings of the proposed green hybrid cavitation technology.

1. The process effectively eliminates Gram-negative *E. coli* at significantly higher rates.
2. Ginger oil was found to be effective natural oil and in case of plant extract, mango ginger extract was found to be most effective than other plant extracts.
3. A very small concentration of 0.1% of natural additive (both ginger oil and mango ginger extract) can effect disinfection, though increased amount of plant extract may be required for obtaining high disinfection efficiency.
4. The rate constant values can be improved to the extent of ~3 times for hydrodynamic cavitation with mango ginger extract, ~5 times for hydrodynamic cavitation with ginger oil and ~8 times for acoustic cavitation with mango ginger extract.
5. The lipophilic nature of antimicrobial active ingredient of natural additive is responsible for increased cell permeability and cell denaturation.
6. A plausible mechanism suggests synergistic effect of both natural additive and hydrodynamic cavitation and the rupture of cell wall/cell death can be due to various factors such as oxidation effect, high shear, localized heat/thermal effect and antimicrobial property of active constituents.

7. The energy requirement is significantly low indicating techno-economic feasibility.

The hybrid cavitation technology with plant extract or natural oils can be useful alternative to existing conventional processes for disinfection of water and more investigations into application of different plant extracts are required.

Nomenclature

C	concentration, CFU/mL
C_0	initial concentration, CFU/mL
k	disinfection rate constant
$\mathrm{k_G}$	growth rate constant
n	number of passes
P	pressure, bar
$\Delta\mathrm{P}$	pressure drop, bar
Q, q	flow rate, m^3/s
t	time, s
V	volume, liters
φ	per-pass disinfection factor
τ	residence time, s

CRediT authorship contribution statement

Maya B. Mane: Conceptualization, Methodology, Formal analysis, Investigation, Writing – original draft. **Vinay M. Bhandari:** Conceptualization, Methodology, Formal analysis, Writing – original draft. **Vivek V. Ranade:** Writing – review & editing.

Declaration of competing interest

One of the authors (VVR) is a founder director of Vivira Process Technologies Pvt. Ltd. which commercially offers vortex diode based cavitation devices.

Acknowledgement

The author-VMB wishes to acknowledge the financial support from Water Innovation Center-Technology, Research and Education (WIC-TRE) (DST/TM/WTI/WIC/2K17/100(G)), (GAP-326626) of Department of Science and Technology, The Ministry of Science and Technology India. Ms. Mane would like to acknowledge support from DST-Women Scientist Program for providing fellowship (SR/WOS-A/ET-7/2016(G)).

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International Journal of Environmental Science and Technology
https://doi.org/10.1007/s13762-021-03684-6

ORIGINAL PAPER

Developing spherical activated carbons from polymeric resins for removal of contaminants from aqueous and organic streams

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Received: 12 December 2020 / Revised: 21 May 2021 / Accepted: 20 September 2021

Abstract

Spherical activated carbons from polymer resin were developed with metal modifications, before/after carbonization using copper and nickel, for gradation of zeta potential (−5.01 to 8.64 mV) and high metal loading (up to 12.3%). The materials provide improved removal of various contaminants from aqueous and organic streams—removal of bacteria from water and sulfur removal from fuel. The metal-modified spherical activated carbons were highly effective for removal of both gram-negative *E. coli* and gram-positive *S. aureus* bacteria. The copper-modified spherical activated carbon could eliminate 99.9–100%, both bacterial content proving efficacy in water disinfection with a very high rate ~ 1.33×10^5 (CFU/ml.s). The zeta potential has significant impact with higher disinfection for high values; ~ 10–15% disinfection can be improved up to 100% for zeta potential changes from −5 to 8.6 mV. Kinetics of disinfection was studied by accounting for zeta potential in the conventional rate model, and the efficacy of both the models was compared. The fit of revised model was excellent. The spherical activated carbons can be useful for removal of slightly polar contaminants from organic streams and a high capacity of 12.8, 20 and 28 mgS/g for thiophene, benzothiophene and dibenzothiophene, respectively. The developed materials can provide useful applications in the area of environmental pollution control.

Responsibility editor: Maryam Shabani.

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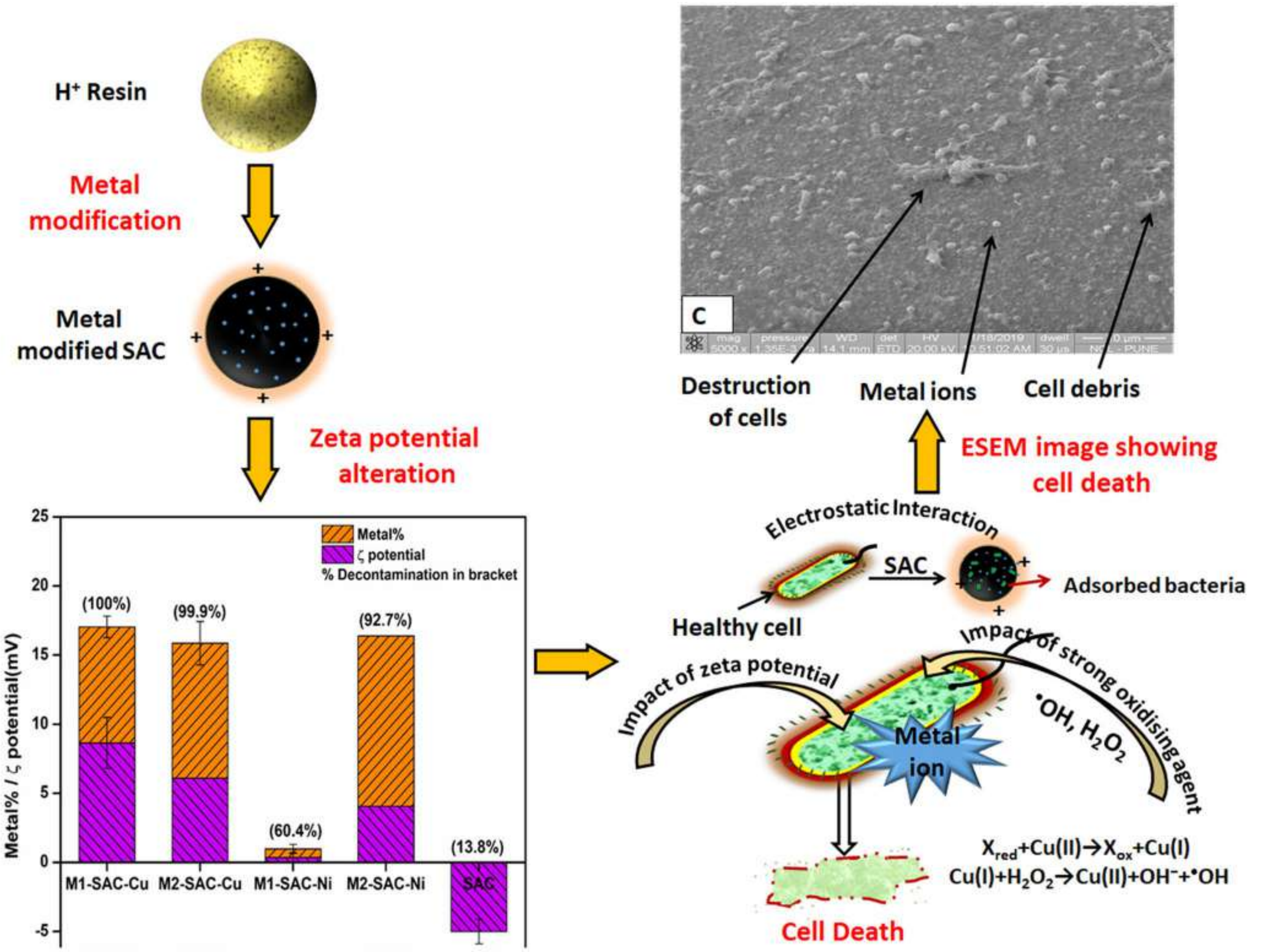
Graphic abstract



Keywords Adsorption · Material · Pollution · Sulfur removal · Water disinfection

List of symbols

C_0	Initial concentrations of sulfur, mg/l
C_e	Equilibrium concentrations of sulfur, mg/l
V	Volume of solution, L
m	Weight of adsorbent, g
A	Initial bacterial count, CFU/ml
B	Bacterial count after 2 h of incubation, CFU/ml
ζ	Zeta potential, mV
k	Rate constant, s^{-1}

Introduction

Activated carbons are probably the most widely used adsorbents worldwide for a variety of applications—ranging from color removal to removal of specific chemicals/metals/pollutants and so on. In view of huge variations in terms of requirements and usage, most commercial adsorbents are available in various forms, such as powder, granules, spherical, fibers (including nanofibers), etc., and largely in modified form—either physical or chemical modification or both, to suit specific applications. The cost variation in most modified materials is also large, ranging from very cheap material to highly expensive advanced materials. The nature of activated carbon and its application mainly depends on its surface area, pore size/pore size distribution and surface properties. Further, the nature of carbons is strongly dependent on the origin/source apart from the activation methodology or surface modification. For common applications, carbons with high surface area are generally suitable and can be used based on the commercial data available with the supplier. However, for specific applications pertaining to separations—process or effluent treatment, usually a tailor-made adsorbent is required to meet the challenge. This has, therefore, directed research and development for variety of activated carbons with surface modification/impregnation of metals/morphology changes to accomplish not just the desired separation, but also for developing techno-economically feasible alternatives to meet precise separation needs. While the conventional practice for making activated carbons employs natural sources, including naturally available waste, studies on spherical activated carbons, hybrid forms derived from polymers, are less researched compared to conventional carbons and also polymeric adsorbents.

Spherical activated carbon (SAC) can be prepared from synthetic source such as polymeric resins, e.g., ion exchange resin. The SAC is expected to have high surface area, high micropore volume and desirable pore size distribution apart from inherent or add-on, functionalities to meet specific adsorption needs, high mechanical strength, wear resistance, providing low pressure drop and high bulk density(Amorós-Pérez et al. 2018). The activated carbons can be derived from a large number of varied sources, can have excellent characteristics and can be modified in a number of ways for surface modifications or for addition of functionalities to meet adsorbent applications in aqueous or organic medium—extensively recognized as versatile materials due to high surface area; wide range of porosity, tunable surface functionalities, stability in acidic medium and low cost. Ion exchange resins are most commonly used for water softening and water deionization. The polymeric resins have excellent surface area and pore structure which can be tailor-made. The ionized forms of polymeric resins have affinity toward ionic species, while non-ionic polymeric adsorbents have preference to non-polar species. In the similar way, spherical activated carbons derived from polymeric resins can be useful tailor-made materials to meet demands of specific applications for the ionic or non-ionic application templates by suitable modification prior to carbonization or post-carbonization.

Activated carbons are hydrophobic in nature, and metal modifications can suitably alter their applications for the removal of contaminants from both aqueous and organic streams. The framework can be used for housing various metals such as silver that provides disinfecting properties and biomass-derived nanocomposite is an emerging research in this regard. Providing safe drinking water at an affordable cost is one of the most critical challenges, especially in developing countries. According to WHO report, four out of every 10 people get affected by water-borne diseases and United Nation suggests improving water quality as one of the Millennium Development Goals (Pandey et al. 2014). Water contaminated with fecal material harbors pathogens like *E. coli,* commonly accepted as biological indicator of fecal contamination of water. Apart from *E. coli,* there are many other bacterial strains both gram-positive and gram-negative reported as causative agent of various water born disease outbreaks (Pandey et al. 2014). Chlorination is one of the most common practices used worldwide for drinking water decontamination. Chlorination, though cost-effective, has a major drawback in the form of generating disinfection by-products, many of these likely to be carcinogenic. Thus, chlorination is considered today as not environment friendly and is being discontinued in some countries. Physical methods like electrochemical disinfection and ozone treatment are also reported to generate chlorine species and other DBP (Kerwick M. I. 2005). Advanced physicochemical method such as hydrodynamic cavitation is gaining more attention for complete removal of gram-negative and gram-positive bacteria, and hybrid cavitation technology by using natural oils having antimicrobial properties as a destructive process by killing the bacteria was recently reported (Mane et al. 2020a, 2020b).

Decontamination by adsorption is significantly safer option in comparison to other chemical and physical treatment process (Simeonidis et al. 2016), (Dias et al. 2007), where many a times, physical removal than destructive killing of the bacteria takes place. Yamamoto et al. reported that activated carbons have good affinity toward microorganisms and adsorbed large amount of bacteria (Yamamoto et al. 2002). Metals such as silver and copper have the disinfection capacity by killing the microorganisms. Silver nanoparticles, carbon nanotubes and sophisticated graphene are being studied extensively for disinfection of water (Simeonidis et al. 2016), (Das et al. 2012). Biomass-derived nanocomposites, especially using specific source such as *Cassia fistula* for the carbon and metal modifications using specialized techniques, are recently reported for improved effectiveness and reduced cost due to low loading of the nanomaterials (Kirti et al. 2018b), (Kirti et al. 2018a). These advanced methodologies have been proved largely in laboratory-scale studies (Sethi et al. 2015); however, the large-scale application of these material can increase the processing and operational cost many fold.

In order to understand the role of positive interfacial potential (zeta potential) in disinfection, we have attempted evaluating the antimicrobial impact of copper and nickel by employing copper- and nickel-modified spherical activated carbons against gram-positive and gram-negative bacteria and found significant disinfection efficiency against pathogenic bacteria in comparison to unmodified SAC with negative zeta potential. The study therefore highlights simple alteration of surface potential leading to significant changes in microbial viability through either physical rupture of cell membrane by depolarization or by enhanced reactive oxygen species (ROS) production. To the best of our knowledge, the kinetics of adsorptive disinfection based on surface potential or zeta potential has not been reported till date. It is also instructive to modify the conventional rate model by accommodating the effect of zeta potential for better fit compared to the conventional rate model.

Contaminant removal from organic streams such as removal of slightly polar sulfur from fuels for ultra-low sulfur fuel is now necessary requirement for petroleum refineries in most countries due to stringent restrictions on the emission of SO_x from combustion of liquid fuels like diesel and petrol. Near-zero levels of sulfur are also essential to avoid poisoning of the catalyst in the fuel cell applications (Patil et al. 2014). Adsorptive desulfurization can be an useful cost-effective alternative in deep desulfurization application compared to conventional hydrogen based or oxidative operations apart from emerging forms such as biodesulfurization, extractive desulfurization, etc. A wide variety of adsorbents have been used for deep desulfurization starting from activated carbon (Yu et al. 2015), (Patil et al. 2014), alumina, silica-based sorbents (Sentorun-Shalaby et al. 2011), zeolites (Bhandari et al. 2006), metal oxides(Kong et al. 2013), metal–organic frameworks (Khan et al. 2016; Dai et al. 2017; Zhao et al. 2018) and metal-exchanged and metal-impregnated activated carbon, zeolite and mesoporous materials. (Hernandez et al. 2010) showed that the activated carbon with nickel gave high capacity than activated carbon. Similar results were obtained by (Selvavathi et al. 2009), (Kim et al. 2006) and (Li et al. 2009) also indicated high capacity and selectivity for refractory sulfur compounds on nickel-dispersed activated carbon compared to metal-dispersed silica, alumina, zeolite and molecular sieve. The incorporation of transition metals such as Ni, Cu, Ag and Zn has the capability to enhance the adsorption of sulfur species from liquid fuels through π-complexation (Yang et al. 2003; Hernández-Maldonado et al. 2005), (Yang et al. 2001) and metal–sulfur interaction (Ma et al. 2003, 2005; Xiaoliang Ma et al. 2004). It is apparent that Ni and Cu have better affinity for refractory sulfur compounds than many other metals. Though a large number of modified carbons were reported for sulfur removal, the capacities and/or selectivity were not satisfactory, apart from problems with regeneration. The quest for new materials and material modifications is thus imperative to provide improved capacities for sulfur removal at reduced costs (Suryawanshi et al. 2019a).

The objective of the present study is to develop different modified spherical activated carbons derived from polymeric ion exchange resin for applications in contaminant removal from aqueous and organic streams. Two specific forms of material modifications, using transition metals nickel and copper, are studied using different forms of carbonization of polymeric resin—before and after metal modification, and for obtaining substantially high metal loading apart from varying the zeta potential. The developed materials were evaluated for disinfection of water and desulfurization of fuels—in both, the role of metal modification is most critical. In water disinfection, removal of bacteria, gram-negative *E. coli* and gram-positive *S. aureus*, was studied to obtain specific insight into the extent of disinfection based on zeta potential of the modified material, while removal of refractory sulfur compounds such as thiophene (T), benzothiophene (BT) and dibenzothiophene (DBT) in n-octane was investigated. The results are expected to provide further directions in material developments/modifications, especially for newer applications in sulfur removal and in water and wastewater treatment. The research has been carried out at CSIR-National Chemical Laboratory, Pune, India, during 2016–2019.

Materials and Methods

Materials

For disinfection studies, a reference strain of *Staphylococcus aureus* (ATCC-6538) and *E. coli* (ATCC-8739) was collected from National Collection of Industrial Microorganism (NCIM), CSIR-National Chemical Laboratory (CSIR-NCL), Pune.

All the chemicals were AR grade and were obtained from companies of repute: n-octane (99%, Loba), thiophene (≥ 99%, Aldrich), 1-benzothiophene (≥ 95%, Fluka), dibenzothiophene (98%, Aldrich), nickel (II) chloride hexahydrate (≥ 98%, Sigma-Aldrich) and $Cu(NO_3)_2.3H_2O$ (≥ 99%, Sigma-Aldrich). A strong acid cation exchange resin, T42H (Thermax Ltd., India), was used as a precursor. Metal modifications were carried out using nickel and copper salts.

Preparation of spherical activated carbon (SAC)

Table 1 shows physical properties of cation exchange resin T42H as obtained from the manufacturer. The different types of spherical activated carbons were prepared using two different methods of material modification on the basis of process for incorporation of the metal.

Table 1 Physical properties of cation exchange resin T42H

Parameter	Tulsion T42H
Manufacture	Thermax Ltd., India
Ionic group	H^+ strong acid cation exchange resin
Particle size distribution	0.3 to 1.2 mm
Physical form	Amber color spherical beads
Dry weight exchange capacity	4.7 meq/g
Moisture content	45%
Stability maximum temperature	140 °C
pH range	1–14
Matrix structure	Polystyrene copolymer

Method 1: SAC—Material modification prior to carbonization

The resin was pretreated, prior to carbonization or metal modification, using the standard procedures of washing with distilled water, and two cycles of cation/anion exchange (Helfferich and Dranoff 1963). The dry weight capacity of the resin was found to be 4.7 meq/g. Metal modification of the resin was done by exchanging H^+ ion of resin with Ni^{2+} ion of 0.5 M nickel chloride hexahydrate solution and Cu^{2+} ion of 0.5 M cupric chloride nitrate solution, respectively, using column technique. Complete conversion to Ni^{2+} form or Cu^{2+} form was ensured. The metal-modified resins are referred as Ni-T42H and Cu-T42H.

The spherical activated carbons using this method were produced by carbonizing the metal-modified resins in an inert atmosphere of nitrogen in a temperature-programmed horizontally aligned electrical tube furnace (Nabertherm, Germany). On the basis of preliminary studies on different temperatures, all the modified carbons were made using the carbonization temperature of 600 °C and carbonization time of 3 h (ramping to 600 °C at the rate of 5 °C/min and constant temperature for 3 h in the presence of nitrogen at the flow rate of 100 L/hr). The different types of activated carbons are referred to as SAC, M1-SAC-Ni and M1-SAC-Cu, where M1 refers to method 1 or material modification 1 of SAC before carbonization.

Method 2: SAC—Material modification after the carbonization

In method 2, the metal modification was carried out after the production of spherical activated carbon using the process as described above—by carbonizing the polymeric resin in an inert atmosphere of nitrogen in a temperature-programmed horizontally aligned electrical tube furnace (Nabertherm, Germany) at 600 °C for 3 h. A known quantity of spherical activated carbon (5 g/100 ml) was dispersed in 1 M nickel chloride hexahydrate. The mixture was stirred well, pH-adjusted to alkaline pH of 9 by dropwise addition of 1 M NaOH. The solution was then heated under reflux at 150 °C for 4 h under nitrogen atmosphere. The modified SAC was washed with distilled water and centrifuged to remove excess metal salt. The product was dried and then reduced under a nitrogen flow at 600 °C for 3 h in the tube furnace to complete metal modification process. For copper modification, the same procedure was followed using 1 M cupric nitrate solution. The two types of metal-impregnated spherical activated carbon are referred as M2-SAC-Ni and M2-SAC-Cu, where M2 refers to method 2 or material modification 2 of SAC preparation and modification after the carbonization.

Material characterization

The morphologies of the carbon samples and elemental analysis were studied by environmental scanning electron microscope (ESEM) (FEI Quanta 200 3D dual beam having a resolution of 3 nm at 30 kV with tungsten filament (W) as the electron source under vacuum mode) and transmission electron microscope (TEM) (FEI, Tecnai G2 20 S-Twin having LaB6 filament as the electron source) equipped with an energy-dispersive X-ray spectrometer (EDS) (EDAX, AMETEK) used for finding the elemental composition as well as selected area electron diffraction (SAED) pattern and detailed morphological study. The BET surface area, pore diameter and pore volume are determined by Autosorb-1 (Thermo Scientific) using nitrogen adsorption. Barrett–Joyner–Halenda (BJH) method was used to determine the cumulative pore volume and average pore diameter. The pyrolysis process was investigated by thermogravimetric analysis (TGA) and differential scanning calorimeter (DSC) analysis (Mettler-Toledo TGA/SDTA851e model). Powder X-ray diffraction patterns of carbon samples were recorded using X'Pert Pro PANalytical XRD with Cu Kα radiation ($\lambda = 1.542$ Å) in 2θ range of 10–80°. The functional groups of the activated carbon were characterized by Fourier transform infrared spectroscopy (FTIR-2000, PerkinElmer). The nickel and copper concentrations were measured by means of an atomic absorption spectrophotometer (Thermo Fisher Scientific iCE 3300). The zeta potential was measured by 90 Plus nanoparticle size and zeta potential analyzer (Brookhaven Instruments, USA).

Experimental

Water disinfection studies

In the present study, the five different SACs (SAC, M1-SAC-Ni, M1-SAC-Cu, M2-SAC-Ni and M2-SAC-Cu) were tested for antimicrobial property against *E. coli* and *S. aureus* using 0.5% of adsorbent loading and 20 ml of bacterial solution.

For the experiment, a loop of bacterial colony was inoculated in the 50 ml of nutrient broth solution. The flask was incubated at 37 °C with constant shaking at 120 rpm (Spectralab Orbital Shaker Incubator). The optical density of culture reached 2.5 at 600 nm (1 O.D = 1×10^9 cells/mL). The known concentration of bacteria was diluted, and 20 ml of bacterial suspension having cellular concentration of ~ 10^7 was used for further experiments. Spherical activated carbon adsorbent was kept suspended in a flask containing nutrient medium inoculated with bacteria. 100 µl of sample from the reaction flask was drawn after 2 h to spread on nutrient agar plate. After a period of 24 h of incubation and 37 °C of temperature, the number of colonies on the plates was counted. The colony forming unit (CFU) was calculated by using following equation,

$$\mathrm{CFU} = \frac{\text{Number of colonies} \times \text{Dilution factor}}{\text{Volume incubated}}$$

where the dilution factor is the reciprocal of the dilution in which the plate count was taken and volume incubated was 100 µl.

Antibacterial efficiency of the materials was represented as percentage of decontamination of bacteria which was calculated using the initial bacterial count (CFU/ml) at the time of incubation and the final bacterial count after 2 h of incubation with materials.

Adsorptive desulfurization studies

Adsorption equilibrium studies were carried out using model fuels of thiophene, benzothiophene and dibenzothiophene in n-octane solvent having known predetermined initial sulfur concentration and adding known amount of adsorbents, equilibrating for a period of 16 h, at ambient conditions (28 ± 1 °C). The activation of the adsorbent was carried out at a temperature of 200 °C for 4 h prior to use. The analysis of the initial and residual sulfur concentration after adsorption was done by using total sulfur analyzer TN-TS 3000 (Thermo Electron Corporation, Netherlands) and gas chromatograph (Agilent 7890A) equipped with CPSil 5CB for sulfur as column (30 m × 320 µm × 4 µm) in conjunction with flame photometric detector (FPD) with helium as a carrier gas, flow rate of 2 ml/min, split ratio of 10:1, injector temperature of 250 °C, injection volume of 0.2µL and total analysis time of 25 min. The oven temperature was ramped at 20 °C/min from 40 to 100 °C and at 60 °C/min from 100 to 230 °C. Reproducibility of the experimental results was checked and was found satisfactory.

Adsorption equilibrium studies were typically carried out using adsorbent dose of 0.1 g and 20 ml model fuel containing known concentration of sulfur in n-octane (sulfur from Thiophene, Benzothiophene and Dibenzothiophene) in the concentration range of 50–500 ppm. Samples were equilibrated using Spectralab HM8T orbital shaker with a shaking speed of 120 rpm at ambient conditions for minimum 8 h to 24 h. The sulfur content was analyzed before and after the equilibrium. The amount adsorbed per gram of adsorbent at equilibrium (q_e, mg/g) was calculated by using the following equation:

$$q_e = \frac{(C_0 - C_e) \times V}{m}$$

where C_0 and C_e (mg/L) are the initial and equilibrium concentrations of sulfur, respectively; V (L) is the volume of solution and m (g) is the weight of adsorbent.

Results and discussion

The results on the characterization of the materials are discussed first along with the implications for the two applications—water disinfection and sulfur removal from fuels.

In order to make proper spherical activated carbons by carbonization of polymer resins, it is essential to know the thermal behavior of the polymer and degradation. Figure 1 depicts TGA curves of the strong acid cation exchange resin T42H (Fig. 1a), its nickel-exchanged form (Fig. 1b)

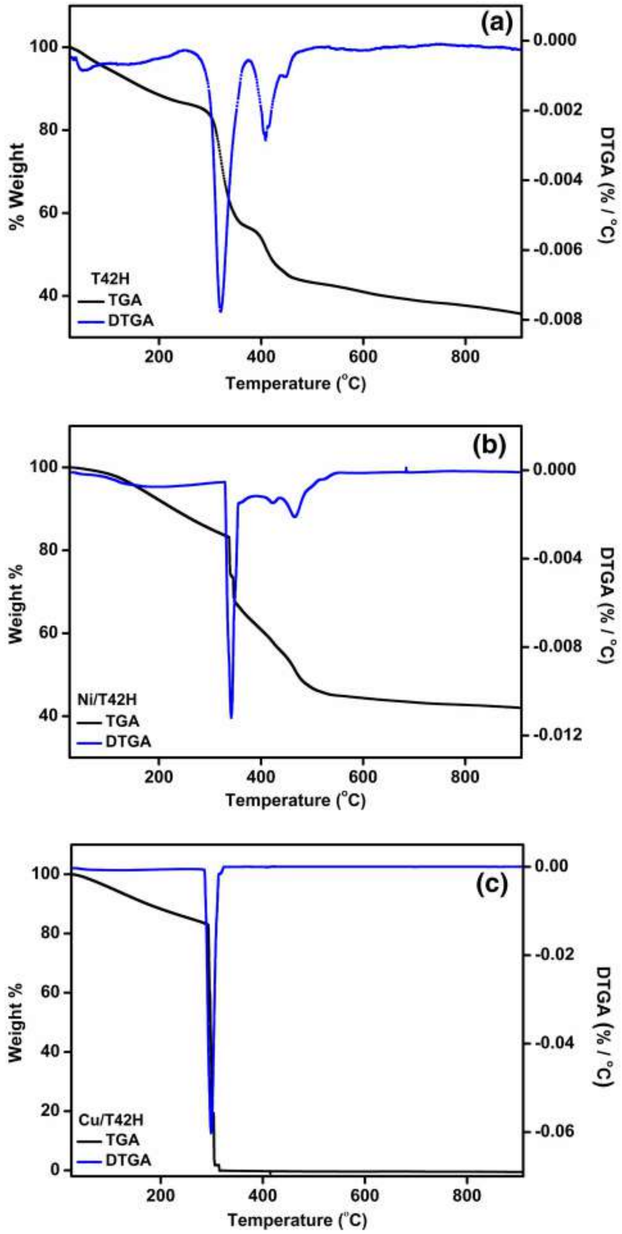


Fig. 1 TGA analysis: **a** Resin T42H, **b** nickel-exchanged resin Ni-T42H, **c** copper-exchanged resin Cu-T42H

and copper-exchanged resin (Fig. 1c), in the temperature range from room temperature to 900 °C in the presence of nitrogen. The polystyrene ion exchange resin gets thermally decomposed in two stages as seen from the major weight loss behavior. A low-temperature thermal decomposition up to 300 °C includes water loss at ~ 100 °C and loss of ion exchange group with the lowest bond energy, i.e., sulfonic acid group (~ 260 kJ/mol) having decomposition temperature 200–300 °C. The stable line indicates stabilization in new structure after initial decomposition until high temperature where complete polymer structure collapses. The second stage of decomposition incorporates high-temperature thermal decomposition above 300 °C wherein straight chain moiety of the polymer matrix (~ 330–370 kJ/mol) having decomposition temperature 350–400 °C gets decomposed and finally the benzene ring moiety (~ 480 kJ/mol) having decomposition temperature 380–480 °C is decomposed(Lin et al. 2007),(Křístková et al. 2004). The thermal behavior of resin in Fig. 1(a) and (b) is quite similar; however, Fig. 1(c) indicates significant difference due to the influence of copper on thermal degradation process of the resin, largely through its catalytic action which enhances the thermal degradation of resin also making more porous structure.

The surface morphology has important role in developing the newer materials. The metal incorporation is confirmed by the ESEM and FESEM images which clearly indicated the presence of copper and nickel metal ions (Fig. 2). The spherical activated carbon without any modification showed simple morphology with few cavities on the surface revealing the large amount of mesoporosity (Fig. 2a). Figure 2(b) is a digital photograph of spherical activated carbon (SAC), showing good spherical shape with smooth surface. The

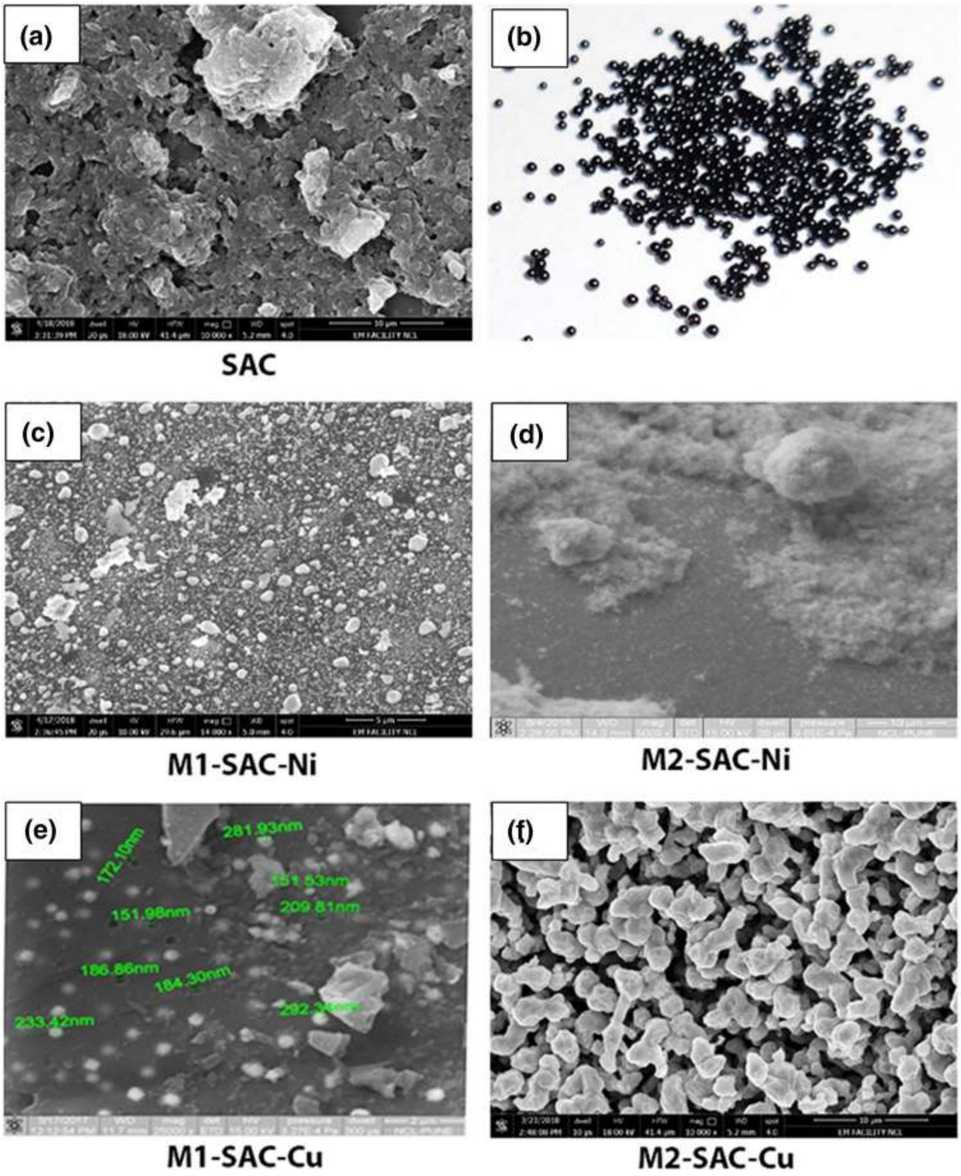


Fig. 2 Material characterization: **a** ESEM: SAC, **b** photograph of SAC, **c** ESEM: M1-SAC-Ni, **d** ESEM: M2-SAC-Ni, **e** ESEM: M1-SAC-Cu and **f** ESEM: M2-SAC-Cu

Table 2 Surface characteristic and porosity of developed adsorbents

Adsorbent	Surface area (m^2/g)	Average pore diameter (nm)	Total pore volume (cc/g)
SAC	64.983	4.016	0.0652
M1-SAC-Cu	393.262	1.473	0.145
M1-SAC-Ni	6.209	3.2	0.008
M2-SAC-Cu	150.167	5.014	0.188
M2-SAC-Ni	117.177	5.008	0.146

modified adsorbents have heterogeneous surface with rough texture and wide range of porosity due to presence of metal and thermal/physicochemical treatment. The presence of elements such as C, O, Ni or Cu in SACs from EDX analysis indicated small to large variations in different types of spherical activated carbons. The atomic absorption spectrophotometer results on the metal content indicated the presence of nickel to the extent of 0.63 and 12.3% in M1-SAC-Ni and M2-SAC-Ni, respectively, as compared to initial nickel-modified resin containing 5.11% Ni. Similarly, the modified SACs were found to have copper content of 8.4 and 9.8% in M1-SAC-Cu and M2-SAC-Cu, respectively, as compared to copper-modified resin containing 8.8% Cu. It is evident that the M1 modification methodology (ion exchange prior to carbonization) for nickel indicated significantly lower metal content in the modified form whereas, for copper loading, both M1 and M2 methods gave somewhat similar metal loading, though, again here ion exchange prior to carbonization failed to provide more metal incorporation into the matrix compared to post-carbonization metal modification of the resin.

The results of ESEM EDX for different spherical activated carbons confirmed the differences due to the two methods of metal incorporation as seen from the morphology of the surface and different inherent metal content. The high temperature of carbonization is important in surface modification for the reasons of pore volume changes. The morphology of M1-SAC-Cu (Fig. 2e) shows white dots of copper in the nanometer (nm) range evenly distributed in spherical activated carbon matrix although this type of metal incorporation was not observed in the case of M1-SAC-Ni (Fig. 2c). Therefore, the selection of metals is important for modification through ion exchange process. For metal modification after carbonization of the resin, formation of heterogeneous surface in place of plain surface of SAC was observed which implies more favorable metal bonding on the rough surface as shown in Fig. 2(d) and 2(f). The extent of metal loading has important bearing in adsorption process and in disinfection of water.

For the adsorbents, the surface area and pore characteristics are crucial from the point of view of both equilibrium capacity and for rates. It was observed (Table 2) that copper-modified spherical activated carbons M1-SAC-Cu and M2-SAC-Cu have higher BET surface area (393.3 m^2/g and 150.2 m^2/g, respectively) in comparison with the surface area of nickel-modified spherical activated carbons M1-SAC-Ni and M2-SAC-Ni (6.2 m^2/g, 117.2 m^2/g respectively) and unmodified spherical activated carbon SAC (65.0 m^2/g). All spherical activated carbons have an average pore diameter, more or less uniform ~ 1.5 to 5 nm, on the lower side in the range of 2 to 50 nm, corresponding to mesoporous structure. The high metal content in the modified materials apart from surface characteristics is important for removal of pollutants.

The N_2 adsorption–desorption isotherms along with Barret–Joyner—Halenda (BJH) pore size distribution plots are shown in Fig. 3. The isotherm of SAC displays type I pattern with absence of hysteresis loop according to IUPAC classification and is a highly microporous. All other modified spherical activated carbons show typical IUPAC type IV pattern with the presence of a H4 type of hysteresis loop and are associated with narrow slit like pores in the sample with a significant amount of mesopores (Passe-Coutrin et al. 2008; Prajapati and Verma 2017).

The Fourier transform IR spectroscopy (FTIR) analysis of different materials is presented in Fig. 4. The results provide identification of functional groups in the materials before and after modification process.

As seen from Fig. 4, the peaks from 675 to 1000 cm^{-1} indicate C–C stretching vibration. The peak at 525 cm^{-1} indicates Cu–O stretch of strong bonding between the metal ions and the oxygen-containing functional groups (Elango et al. 2018). High intense bands between 1000 and 1260 cm^{-1} indicate C–O stretching of alcoholic, ether and

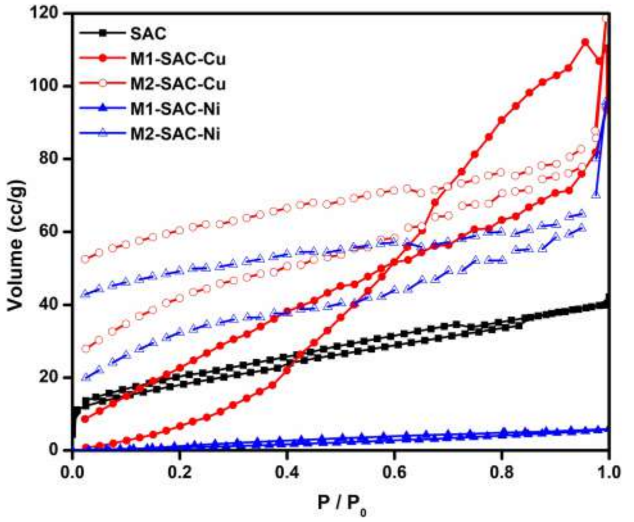


Fig. 3 Nitrogen adsorption–desorption isotherms of spherical activated carbons

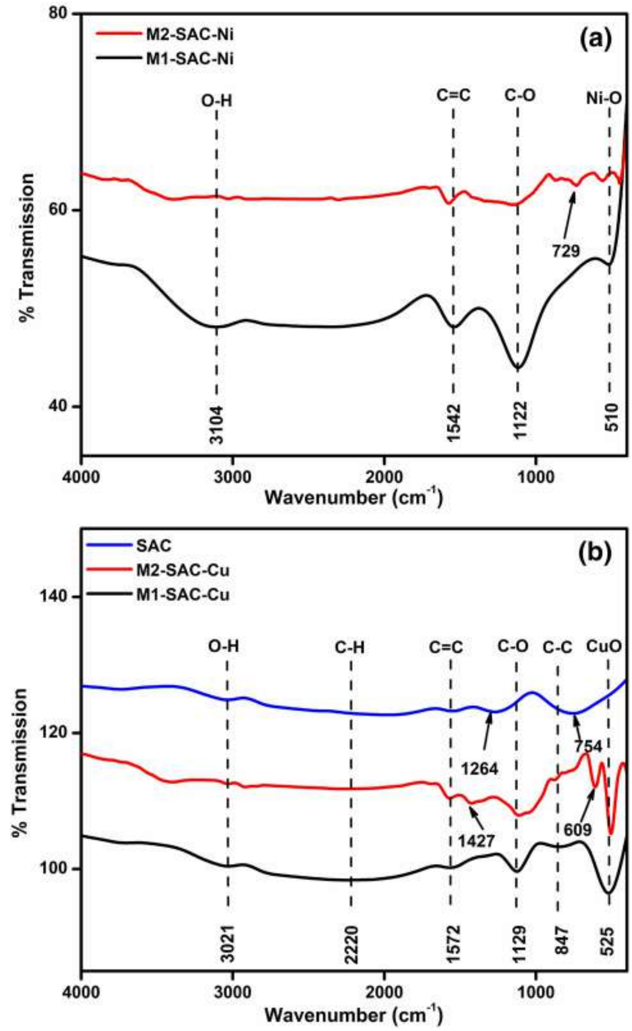


Fig. 4 Fourier transform infrared (FTIR) analysis: **a** M1-SAC-Ni and M2-SAC-Ni **b** SAC, M2-SAC-Cu and M1-SAC-cu

carboxylic groups. The peaks at 2220 cm^{-1} and 3021 cm^{-1} can be attributed to C–H and O–H groups stretching vibration. The broad absorption band at around 3104 cm^{-1} corresponds to O–H stretching vibration of the surface hydroxyl groups. The stretching band of C = C at 1542 cm^{-1} indicates the presence of aromatic ring. The peak at 1122 cm^{-1} indicates C–O stretching of COOH and O–H stretching of alcoholic, phenolic and carboxylic groups. The absorption peaks at ~ 400–870 cm^{-1} indicate Ni–O and Ni–O-H stretching of strong bonding between the metal ions and the oxygen-containing functional groups (Pradeep and Chandrasekaran 2006).

FTIR spectra showed that copper- and nickel-modified spherical activated carbons have the presence of oxygen containing functional groups (OH, COOH, C–O, Ni–O, Cu–O, etc.) which can play an important role in water disinfection and sulfur removal.

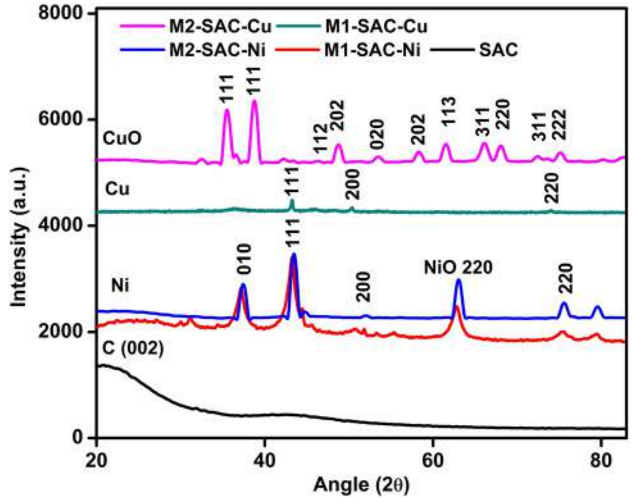


Fig. 5 XRD analysis of spherical activated carbons

XRD result of SAC (Fig. 5) showed a combination of amorphous and crystalline surface of two broad peaks of carbon at C (002) and C (101) planes (JCPDS Card No. 75–1621) at 21.9^0. There is presence of nickel oxide and nickel ions in nickel-doped spherical activated carbon samples which is confirmed by intense and prominent peak of Ni at 010, 111, 200 and 220 planes (JCPDS card no. 88–2326) for M1-SAC-Ni and M2-SAC-Ni and small intensity peak of NiO at 220 (JCPDS card no. 44–1159) indicated Ni partly converted into NiO during activation/carbonization. The intense peak of Cu in SAC-Cu 3/600 sample at 111, 200 and 220 planes (JCPDS card no. 85–1326) and CuO peaks of M2-SAC-Cu predominately indicated at 111, 111, 112, 202, 020, 202, 113, 311, 220, 311 and 222 planes (JCPDS card no. 80–1916).

Evaluating spherical activated carbons for disinfection of water

Metals such as copper and silver are known to assist in disinfection of water. Based on the knowledge, many metal nanomaterials, nanocomposites or metal-modified adsorbents have been reported, many of which have limitations in terms of efficiency, ease of operation, handling and therefore not suitable for large-scale operation. Spherical activated carbons, using metal modifications, can be used similar to that of ion exchange resins for water treatment and hence are suitable for commercial applications provided issues with respect to efficiency of disinfection are addressed. The objective is to remove pathogenic bacteria not by way of only adsorption but by eventually destroying them to make water safe for drinking—the desired limit of total coliforms organisms in the drinking water is zero.

The metal-modified SACs act in different ways in disinfecting water. There is inhibition to microbial multiplication by nickel and copper ions present in metal-modified SACs through charge neutralization of –SH groups present in the cell wall. The studies on antimicrobial activity of different metal-modified SACs revealed effective removal of *E. coli* and *S. aureus*.

The extent of decontamination for the two microbial contaminants, *E. coli* and *S. aureus*, in terms of reduction of bacterial colonies of CFU/ml after 2 h of adsorption treatment using SACs is shown in Fig. 6. It was observed that copper-modified SACs were most effective with close to 100% decontamination for both *E. coli* and for *S. aureus* (100% and 99.93% for M1-SAC-Cu and M2-SAC-Cu, respectively, for *E. coli* and 99.8% for *S. aureus*). The excellent performance of the developed materials is attributed to copper and its high loading on the surface that provides effective interactions. Further, an interesting factor in terms of high positive zeta potential (~ 8.64 mV) is believed to be responsible for the significantly increased efficiency in disinfection. The copper-modified SACs inhibit the metabolism and/or damage the protective membrane of the cell wall consequently resulting in cell death. The nickel-modified adsorbents have comparatively lower efficiencies and M2-SAC-Ni demonstrated disinfection efficiency of ~ 93% for *E. coli* and ~ 76% for *S. aureus*, whereas M1-SAC-Ni had only ~ 60% disinfection with *E. Coli* and ~ 65% disinfection for *S. aureus* possibly due to low Ni content apart from lower values of zeta potential (0.35 mV). The SAC without any modification showed a very little disinfection to the extent of ~ 14% for *S. aureus* and ~ 10% for *E. coli* and had negative zeta potential (− 5.01 mV).

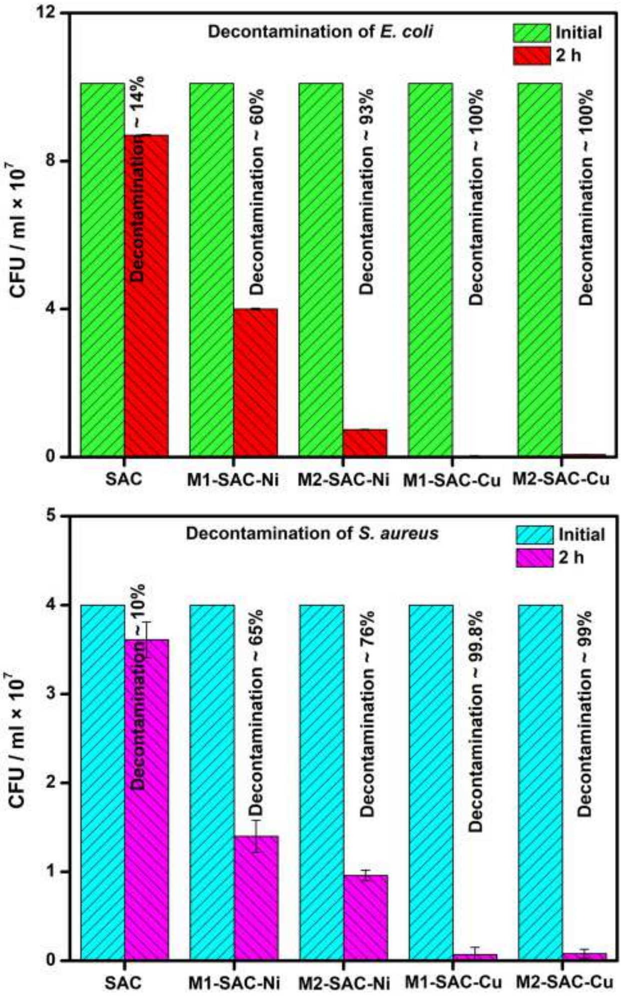


Fig. 6 Disinfection performance of different adsorbents

The role of zeta potential in disinfection

The surface charge of the bacteria and viruses has often been interpreted by the zeta potential measurements. Zeta potential (ζ), here, can be expressed as an electrochemical property of the surface of bacterial cells or particle/nanoparticles which represents the surface charge or potential at the shear plane of the electrical double layer on all sides of a cell or particle/nanoparticles in solution and is measured in millivolts (Tokumasu et al. 2012). The electrostatic interaction between the surface charge of cells and ions of opposite charge is an important aspect of disinfection (Tokumasu et al. 2012). In general, the net surface charge for most bacteria is negative and is balanced by oppositely charged counter ions present in the surrounding media. The interaction between the bacterial surface and various disinfecting agents of the type metal or specific functionality on the adsorbent matrix begins due to electrostatic interactions, impacting zeta potential and may subsequently alter cell surface permeability leading to cell death. Arakha et al. (2015) reported the average zeta potential values for the untreated *E. coli* and *S. aureus* as − 23.6 and − 18 mV, respectively, and evaluated effect of both positive and negative zeta potential ZnO nanoparticles on bacterial cell suspension. The positively charged ZnO nanoparticles (ζ 12.9 mV) were found to interact effectively with the negative bacterial membrane, and the effect was dependent on the concentration of ZnO nanoparticles (250–500 µg/mL) and time (8–9 h for 250 µg/mL and 4–5 h for 500 µg/mL) for the destabilization of the membrane(Arakha et al. 2015). Similarly, it was reported that ZnO nanofluids (0.25 g/L) with 9.4 mV zeta potential can affect 86% disinfection in 10 h (Zhang et al. 2007). A large number of such nanoparticles were researched for disinfection of water (Pal et al. 2006), (Du et al. 2009), (Arakha et al. 2015). Weak antimicrobial activity of the negative value of zeta potential of AC is enhanced by treatment with silver bromide in silver nitrate solution and higher antimicrobial activity for Ag-AC also noted (Pal et al. 2006). The zeta potential values are higher for nanoparticles alone than nanoparticle-modified adsorbent. The antibacterial activity can be correlated to the zeta potential. Apart from disinfection application, the effect of zeta potential on removal of different pollutants such as dyes and pesticides was reported in the literature (Arica et al. 2018; Bayramoglu and Arica 2021),(Garg et al. 2021). Garg et al.(Garg et al. 2021) suggested enhanced imidacloprid degradation due to positive zeta potential in neutral pH compared to other pH conditions.

In the present study, a small dose of 0.5% of adsorbent was found sufficient to alter the zeta potential in both *E. coli* and *S. aureus*, and 100% decontamination was obtained within 2 h. In view of the literature reports as above, the present study has exhibited significant enhancement in values of zeta potential of SAC after metal modification, consequently, in the antimicrobial activity of metals such as copper and nickel. As a result, complete disinfection could be obtained due to higher values of zeta potential for both gram-negative as well as gram-positive bacteria. The zeta potential measurement for all adsorbents was carried out in neutral pH 7. From Fig. 7, it is evident that the nature of metal modification significantly impacts the decontamination behavior and therefore finding the most suitable metal modification is crucial from commercial application point of view. From the data on different metal-modified SACs, it can be seen that copper-modified SAC is the most effective adsorbent compared to nickel-modified adsorbents or unmodified SAC. The value of zeta potential ζ in mV for M1-SAC-Cu is 8.64, significantly higher than M2-SAC-Cu (6), M1-SAC-Ni (0.35), M2-SAC-Ni (4.06) and unmodified SAC (−5.01). Thus, higher value of zeta potential/surface tension implies increased disinfection efficiency.

The results of modified spherical activated carbons in this work have potential to provide techno-economic alternative, especially compared to various nanomaterials and nanocomposites reported for disinfection of water. Carbon nanostructures such as SWCNT and MWCNT have strong inhibitory action in short exposure time on soil microbial activity, and to enhance the effectiveness of CNT, the CNTs are modified by different metals or metal oxides (Chung et al. 2011). It was also reported that the TiO_2/MWNTs/Si surface (annealed at 400 °C) displayed great photo-catalyst activities and killed virtually all *E. coli* cells upon contact (in 60 min) (Akhavan et al. 2009). Further, the functionalized CNT–ZnO inactivated 100% of *E. coli* cells within 10 min of UV–visible light illumination, while the un-functionalized CNT–ZnO could inactivate only 63% of the microorganisms under the same conditions under the visible light illumination (Akhavan et al. 2011). A number of different transition metal-modified adsorbents such as Fe, Al, Ag, Mg, etc., have been studied for disinfection of bacteria. Though silver is a promising metal in this regard and is widely reported since it can eliminate microbes in less time, according to WHO (WHO 2018), silver is not recommended as a primary disinfectant in drinking water supplies. Compared to many metals, the present work showed effective and complete elimination in 2 h and with only 0.5% adsorbent loading (Table 3).

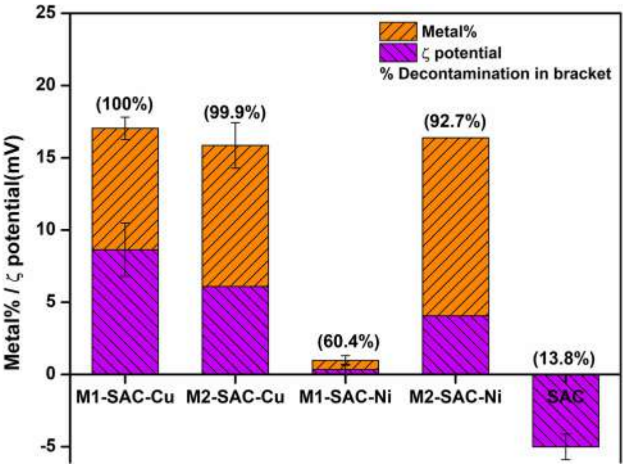


Fig. 7 Zeta potential corresponding to metal % for different adsorbents and *E. coli* removal

It is evident that there are no systematic studies on the evaluation of progression in the zeta potential values for materials, spherical activated carbons or for its application in the water disinfection. Some of the comparable work in this regard is listed in Table 3 for different materials which clearly highlights the consistent and important results of this work pertaining to material development, systematic evaluation of the effect of zeta potential and possible application potential in the real life, in terms of starting material (polymeric resin waste), material development (spherical activated carbons), modification methodology apart from recommendations for most suitable material for disinfection.

Kinetics of disinfection

A revision of model based on zeta potential (ζ) for adsorption is attempted in this work, and the same is applied for evaluating representative kinetic data of the present study.

The kinetics of disinfection using the conventional rate model requires:

Pseudo-first order equation

$$\frac{\mathrm{d}C}{\mathrm{d}t} = -\mathrm{k}\mathrm{C} \tag{1}$$

where $\boldsymbol{k}$ is disinfection rate constant.

The concentration of microorganisms C can be obtained by assuming $\zeta = \zeta_0$,

Table 3 Comparison of % disinfection for various adsorbents

Bacteria/initial Concentration	Adsorbent	% Disinfection	Reference
E. coli; 10^7 CFU/mL	AC: Modification using aluminum hydroxyl chloride; nanoAgBr—AC	99.99% > 6 log reduction	(Pal et al. 2006)
E. coli 10^3 CFU/mL	Plasma-treated AC impregnated with silver nanoparticles	~100% in 10 min for plasma-treated AC-Ag in 60 min for untreated AC-Ag	(Srinivasan et al. 2013)
E. coli and *S. aureus* 100 CFU/mL	Spherical activated carbon coated with zinc oxide	100% in 24 h	(Yamamoto et al. 2002)
E. coli 10^4 CFU/ml	Ag/AC by wet impregnation	~100% in 25 min	(Biswas and Bandyopadhyaya 2016)
E. coli and *S. aureus* 10^6–10^7 CFU/mL	Mg/SAC at 1000 °C	~70% in 6 h for *E. coli* ~25% for *S. aureus*	(Yamamoto et al. 2001)
E. coli 2×10^7 CFU/mL	Ag/zeolite	~99–100% in 40 min	(Matsumura et al. 2003)
E. coli 10^7 CFU/mL	Fe nanoparticles (NP) nanocomposite NC-450; (SPION + CF) NCm1; NCm_1(SPION + CF + clarified butter)	NC-450 59% NCm_1 82% NP 91% in 1 h	(Kirti et al. 2018a)
E. coli 10^7 CFU/mL	Fe nanoparticles (NP), nanocomposite NC-ALV-450 and NC-OCT-450 10 mg/mL	NP 91% NC-ALV-450 90% NC-OCT-450 96% in 1 h	(Kirti et al. 2018b)
E. coli and *S. aureus* 10^7 CFU/mL	SAC, M1 and M2-SAC-Ni, M1 and M2-SAC-Cu 5 mg/mL	SAC 14% M1-SAC-Ni60% M2-SAC-Ni 93% M1-SAC-Cu100% M2-SAC-Cu 100% in 2 h for *E. coli* SAC 10% M1-SAC-Ni 65% M2-SAC-Ni 76% M1-SAC-Cu100% M2-SAC-Cu 100% in 2 h for *S. aureus*	This Work

$$\ln\left(\frac{C}{C_0}\right) = -\mathrm{kt} \tag{2}$$

Modified Model

Since zeta potential changes with respect to time, the modified rate model requires:

$$\frac{\mathrm{d}(C\zeta)}{\mathrm{d}t} = -\mathrm{k}C\zeta \tag{3}$$

and,

$$\ln\left(\frac{\zeta}{\zeta_0}\right) + \ln\left(\frac{C}{C_0}\right) = -\mathrm{kt} \tag{4}$$

where $\boldsymbol{C_0}$ is the initial concentration of bacteria (**CFU/ml**), t is the time for disinfection (**min**), $\boldsymbol{\zeta_0}$ is zeta potential at time $\mathbf{t = 0}$ and $\boldsymbol{\zeta}$ is zeta potential at any time **t**.

The values of the rate constants and rates of disinfection using the conventional model and modified rate model are provided in Table 4 (initial CFU/ml, 10.1×10^7) for the initial solution zeta potential value of −17.01 mV and after disinfection with modified activated carbons M1-SAC-Ni and M1-SAC-Cu, and zeta potential values of solution are −15.36 mV and −8.81 mV respectively.

The fit of the rate models is shown in Fig. 8. The conventional rate model showed a large deviation from the experimental data, and the deviation is predominant for M1-SAC-Cu. In contrast to conventional rate model, the zeta potential rate model fits well. It was observed that the values of zeta potential impact the prediction of the rates by about 11% in the case of M1-SAC-Ni and 3.6% in the case of M1-SAC-Cu. The revised kinetic model incorporating zeta potential clearly highlights the importance of its application as against conventional model. Arakha et al. 2015 reported that there is decrease in zeta potential value of bacterial solution corresponding to decrease in percentage bacterial cell viability in their study on effect of bacterial cell viability and surface zeta potential of *B. subtilis* and *E. coli* cells, observing decrease from ~ −19 to −9 mV for *B. subtilis* and for *E. coli* from

Table 4 Rates of disinfection using conventional and revised model

Adsorbent	% Disinfection	Rate constant, k $(s^{-1}) \times 10^4$	Rate of disinfection CFU/(ml.s) (conventional model)	Rate constant, k' $(s^{-1}) \times 10^4$	Rate of disinfection CFU/(ml.s) (zeta potential model)
SAC	13.9	0.2	1948		
M1-SAC-Ni	60.4	1.29	9069	1.43	10,068
M2-SAC-Ni	92.7	3.63	19,674		
M1-SAC-Cu	100.0	25.6	129,270	26.54	133,884
M2-SAC-Cu	99.9	10.06	50,860		

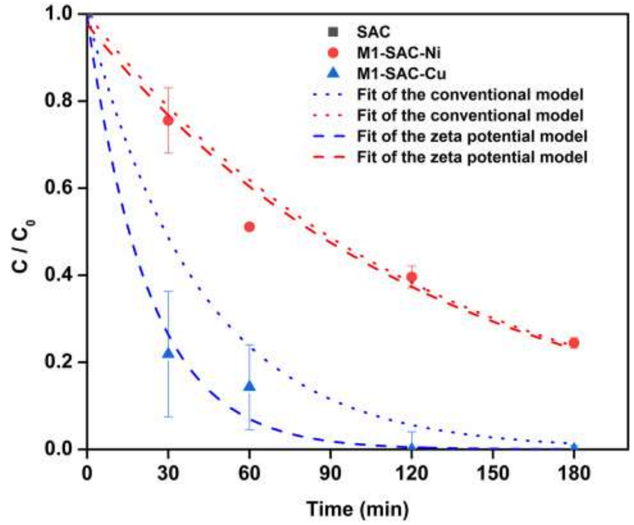


Fig. 8 Effect of adsorbent and conventional rate model vs zeta potential rate model

−24 to ~ −8.5 mV. Thus, the kinetics need to incorporate effect of zeta potential, in general, for accurately predicting rates of disinfection, especially where significant difference exists in zeta potential values.

Mechanism of disinfection

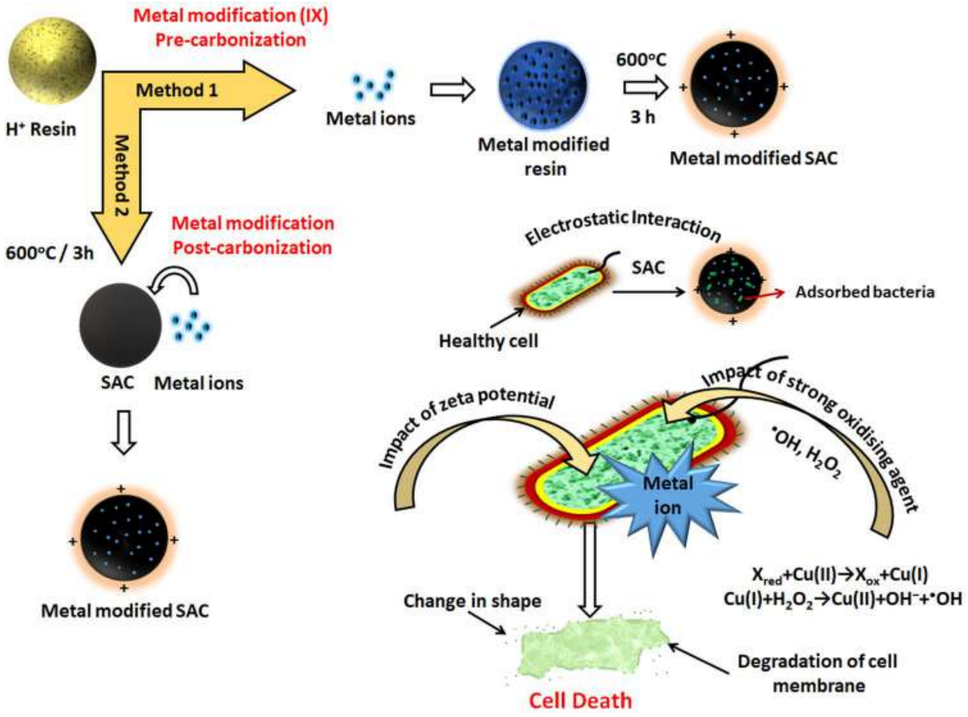
In order to completely destroy the bacteria, the following factors are believed to contribute in the disinfection process:

1. Zeta potential effect: disruption of membrane integrity by powerful electrostatic forces between microbial outer surface and adsorbent, leading to oxidation of the membrane.
2. Generation of the reactive oxygen species due to interaction of metal ions and oxygen functional group present on the adsorbent which may directly harm bacteria and/or indirectly prompt DNA destruction.
3. Presence of metallic particles that are introduced into adsorbent which can contribute through their antibacterial activities.

A possible disinfection mechanism for the modified spherical activated carbons prepared from two different pathways is shown in Fig. 9. The interface in adsorption needs to develop a potential that will result in physical rupture of membrane (membrane depolarization). The chemical effects include enhanced reactive oxygen species (ROS) production (at the interface or inside the bacteria). These ROS are $^{\cdot}$OH radicals or strong oxidizing agent such as H_2O_2/active free radicals that enable oxidation of main constitutes of cell membrane such as proteins, nucleic acid, lipid or DNA. Fernandes et al. reported that alteration of zeta potential by increased dielectric constant or by changing the composition of the medium by supplying maximum amount of oxygen, hydrogen peroxide may often lead to agglutination of bacterial cells (Fernandes et al. 2011). The other effects include antimicrobial activity of the metals such as copper or silver. Copper-modified adsorbents/nanoparticles/surfaces provide cationic surface with strong bactericidal activity and are widely used as disinfectants (WHO 2018), (Yasuyuki et al. 2010). The antibacterial properties and mechanism of the antibacterial action of such metal-modified adsorbents have been widely discussed in the literature for nanoparticles, but not for spherical activated carbons. SAC modifications may provide pathways for preparing adsorbents with enhanced antimicrobial, antiviral properties. As most bacteria, viruses have a negative charge in neutral solutions (Halder et al. 2015); the negatively charged surfaces of SACs are required to be functionalized with various metals or other modification to render them positive for enhanced disinfection efficiency.

The above mechanism is partly substantiated from the results of surface morphology of different SACs and modified SACs before and after the decontamination (Fig. 10). It can be seen that there is adhesion/adsorption of bacteria on SACs. The *E. coli* and *S. aureus* bacteria before adsorption are seen with intact cell morphology (Fig. 10a and d) and subsequent to adsorption by nickel-modified SACs (Fig. 10b

Fig. 9 Possible mechanism of disinfection



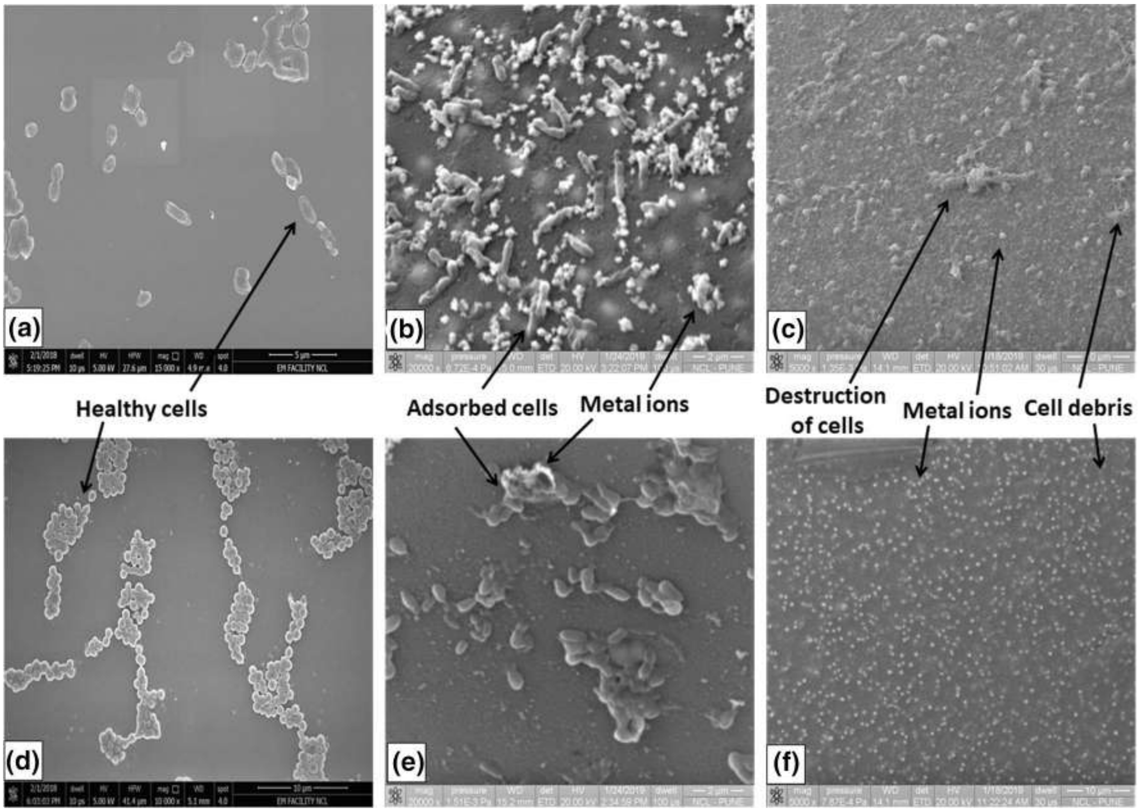


Fig. 10 Surface morphology before and after disinfection, **a** *E. coli* (0 min); **b** M2-SAC-Ni/ *E. coli*; **c** M1-SAC-Cu/ *E. coli,* **d** *S. aureus* (0 min); **e** M1-SAC-Ni/ *S. aureus*; **f** M1-SAC-Cu/*S. aureus*

and e) reveal change in shape due to increase in cell permeability. Further, the destruction of the cell membrane in copper-modified SACs is clearly evident from Fig. 10(c) and (f), due to the strong antimicrobial property of copper apart from interaction of strong oxidizing agents. The active sites/active metal ions of SACs promote electrostatic adsorption of the bacteria on the surface of SACs which promotes active interactions/reaction with bacteria through different actions leading to destruction of cells. The overall mechanism therefore predominantly includes oxidative damage of cells through reaction—e.g., Cu(II) to Cu(I) of M1 and M2-SAC-Cu with generation of strong oxidizing agents such as $^{\cdot}$OH radicals and H_2O_2, initiating oxidation process with cell content. The oxidation of the nucleic acids, lipids and proteins results in further damage to the cell, leading to cell death. Figure 10(f) verifies presence of cell debris due to the cell damage after adsorption of bacteria over M1-SAC-Cu. Figure 10(c) and (f) confirms the absence of bacteria cell and complete decontamination of bacteria by M1 and M2-SAC-Cu. Thus, the copper-modified adsorbents are seen as more effective in the process of complete elimination of bacteria.

Evaluating spherical activated carbons for adsorptive deep desulfurization

There have been numerous reports on various forms of activated carbons and metal-modified carbons for the removal of different sulfur compounds from fuels. In general, ordinary activated carbons have poor capacity for the refractory sulfur compounds, while there has been substantial increase in the adsorption capacity for modified carbons, especially for metal-modified carbons—specific metals such as copper and nickel. In order to evaluate the efficacy of the developed spherical activated carbons and also to differentiate the two methods of metal modification for the ion exchange polymers, the developed materials were studied for the removal of three refractory sulfur compounds—thiophene (T), benzothiophene (BT) and dibenzothiophene (DBT). The equilibrium plots for the adsorption of T, BT and DBT on various SACs are shown in Fig. 11. The following observations clearly identify the differences in not only these materials, but also for the difference in the method of metal modification in the case of polymeric ion exchange resins.

1. All the spherical activated carbons have reasonably good capacity for the sulfur removal, and the adsorption capacity is somewhat higher than many of the materials reported in the literature for commercial/synthesized modified carbons.
2. The copper-modified spherical activated carbons (both M1 and M2-SAC-Cu) were found to be more effective, and the selectivity was of the order: DBT > BT > T.

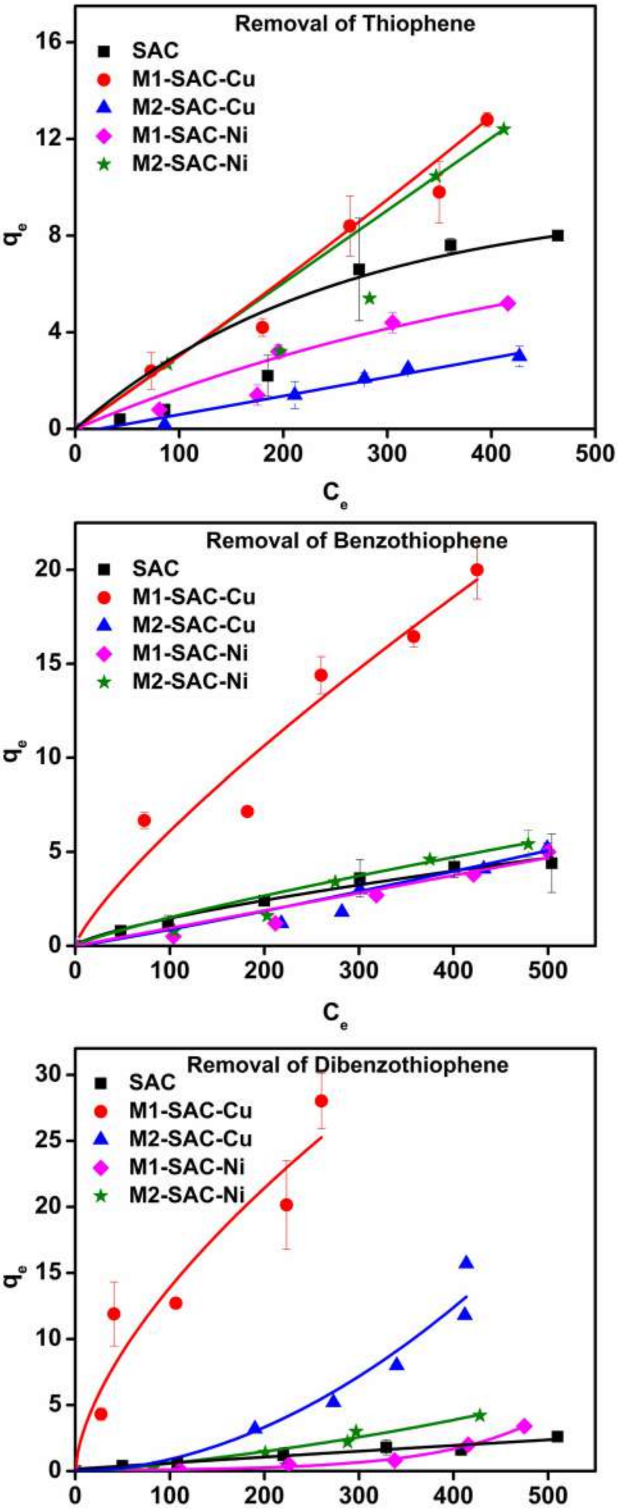


Fig. 11 Adsorption isotherm for removal of refractory sulfur compounds

3. It was observed that the copper-modified spherical activated carbon using ion exchange modification method (M1-SAC-Cu) was highly effective for all sulfur com-

pounds (T, BT and DBT) and a high capacity of 28 mgS/g for DBT, 20 mgS/g for BT and 12 mgS/g for T could be achieved.

4. The nickel modification is comparatively less effective though capacity for thiophene, is reasonably high, ~ 5–12 mgS/g adsorbent. Although the capacity is not commensurate with high Ni loading, it is higher compared to many commercial sulfur specific adsorbents and other adsorbents (Saleh et al. 2017), (Patil et al. 2014).

The high capacity and selectivity for sulfur can be attributed mainly to the nature of metal species, higher surface area and electrostatic attraction for the sulfur moiety. For thiophene, where the capacity is comparatively less, the impact of metal appears to be insignificant. The increased effectiveness using ion exchange prior to carbonization is in contrast with the conventional methods of metal impregnation on the surface of activated carbon. It is also evident that mere high metal content in the adsorbent is not the only important contributions in the sulfur removal since both M1-SAC-Cu and M2-SAC-Cu have similar copper content and only M1-SAC-Cu has higher capacities for different sulfur compounds. The order of magnitude difference here could be attributed to Cu form in M1 modification compared to stabilized CuO form in M2 modification.

It is also to be noted that the spherical activated carbons reported in the literature had much lower capacity than that reported in the present study. The surface area, nature of metal, metal content and oxygen-containing functional groups are thought to have combined effect through interactions such as π–π or π–H interaction of π electrons of thiophenic aromatic sulfur compounds with the carbon surface (Shi et al. 2015), (Nuntang et al. 2008). Table 5 provides comparison of the adsorptive desulfurization capacity for the materials of this work with some of the reported data on similar studies in the literature. It is evident that modification of the materials is essential for obtaining reasonably good capacity, especially for refractory sulfur compounds. Further, metal modification is particularly attractive in all the types of the materials. However, it is also seen that not very high capacities could be obtained for all types of sulfur moieties and typically the highest capacity for the sulfur is up to 25–30 mg/g for single metal modification which can be further increased up to 40 mgS/g using double metal modification approach or metal and chemical modification strategy (Suryawanshi et al. 2019b). By and large, for reportedly cost-effective materials such as conventional activated carbons and biomass derived adsorbents, the capacity is typically much less than 10 mg/g, far from being satisfactory (Sorokhaibam et al. 2015). Thus, the spherical activated carbons of this study derived from used polymeric resin can offer the benefit of cost as well as good sulfur removal capacity.

Conclusion

The present research identifies two different methodologies of preparation of spherical activated carbons using polymeric ion exchange resin (waste) as a starting

Table 5 Comparison of sulfur adsorption capacity of various carbons from liquid fuels

Adsorbent	Sulfur compound	Capacity mgS/g	Reference
MnO-10%/AC	T, BT, DBT	T 4.5, BT 5.7 and DBT 11.4	(Saleh et al. 2017)
Biomass-derived AC	T, BT, DBT	T 4.5, BT 3, DBT 7.5	(Sorokhaibam et al. 2015)
Resin-derived AC and KOH activation	DBT	~ 180	(Pei et al. 2014)
Activated carbon	BT, DBT	~ 0.5–1	(Herna et al. 2004)
Carbon nanofiber Ni-CNF/ACB	T, DBT	DBT 8.2, T 88.2	(Prajapati and Verma 2017)
Ni/ACB	T, DBT	DBT 27.3, T 85	(Prajapati and Verma 2017)
Zn/GAC	DBT	14	(Kumar et al. 2016)
AC	T, BT, DBT	T 4.16, BT 11.52, DBT 16.32	(Wang et al. 2012)
AC, acid-modified AC, Ni/AC	DBT, MDBT, DMDBT	0.5–1.5	(Selvavathi et al. 2009)
AC	T	0.96	(Wang and Yang 2013)
Double metal modifications TAC-Ni-Cu acoustic cavitation TAC-Ni-Cu CFP-Ni-Cu	T, BT, DBT	4.3, 31.6, 38 ~ 2, 12, ~ 33 ~ 4, ~ 13	(Suryawanshi et al. 2019b)
SAC M1-SAC-Ni M2-SAC-Ni M1-SAC-Cu M2-SAC-Cu	T, BT, DBT	8.0, 4.4, 2.6 5.2, 5.0, 3.4 12.4, 5.4, 4.2 12.8, 20.0, 28.0 3.0, 5.2, 15.7	This work

material—one through exchanging of metal ions on resin matrix and other metal impregnation on carbonized form of spherical activated carbon. The spherical activated carbons, especially using metal modifications, were highly effective in disinfection of water and in sulfur removal from organic fuels. The important findings include:

1. A significantly high metal loading in general was obtained in most SACs.
2. The metal-modified spherical activated carbons were highly effective in the removal of both gram-negative, *E. coli* and gram-positive *S. aureus* bacteria.
3. The copper-modified spherical activated carbons completely destroy (100%) both bacterial content proving efficacy of the developed materials.
4. The excellent disinfection behavior can be attributed to metal modification and associated surface charge destroying the cell membrane of bacteria and to the high values of zeta potential.
5. The graded variation in zeta potential clearly highlights implications of materials having high zeta potential—the higher the potential, higher is the disinfection; ~10–15% disinfection can be improved up to 100% for zeta potential from -5 to 8.6 mV.
6. Kinetics of disinfection can be better represented by accounting for zeta potential effect in the conventional mathematical model. The fit of revised model was excellent, and a very high rate of disinfection 1.33×10^5 (CFU/ml.s) was obtained using copper-modified spherical activated carbon.
7. The spherical activated carbons after metal modifications largely improve the sulfur removal capacity apart from altering the selectivity for thiophene, benzothiophene and dibenzothiophene. A high capacity of 12.8, 20 and 28 mgS/g was obtained in copper-modified SAC for thiophene, benzothiophene and dibenzothiophene, respectively.
8. The metal modification of polymeric resins can be useful in utilization of resin waste, starkly different from conventional carbon sources, providing more degrees of freedom in material modifications.

The spherical activated carbons and metal modifications apart from possible cost-effectiveness compared to similar conventional adsorbents or nanoadsorbents can provide suitable methodologies for developing tailor made adsorbents to meet specific demands and for useful applications in the area of environmental pollution control.

Acknowledgements The authors would like to acknowledge the financial support of DST-WTI project, DST/TM/WTI/2K16/144(C) (GAP 317526) of Department of Science and technology, India. Ms. Maya B. Mane would like to acknowledge the support from DST-Women Scientist Program Project, SR/WOS-A/ET-7/2016(G) (GAP 316926), for providing fellowship.

Declarations

Conflict of interest The authors have no relevant financial or non-financial interests to disclose. The authors have no conflicts of interest to declare that are relevant to the content of this article.

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