Studies in Degradation/Removal of Pollutants/Organics Using Cavitation

by

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Under the supervision of
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Synopsis

	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
Name of the Candidate	**PATIL PRAVIN BHIKAJI**
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1. Introduction

Water is precious to the life on earth and in recent years its availability is getting reduced day by day due to the hugely increased use for human consumption, agricultural consumption and for industrial purpose. A large number of chemical and allied industries generate huge amounts of wastewaters which require effluent treatment prior to discharge for meeting stringent norms on Chemical Oxygen Demand (COD), Biological oxygen demand (BOD) and Ammoniacal Nitrogen (NH_4-N). Due to the scarcity of water, it is imperative that methodologies for wastewater treatment, recycle and reuse be developed for effective removal/ degradation of various pollutants and intensified hydrodynamic cavitation process is one such promising alternative to existing methods in this regard. Industrial wastewater treatment is a complex subject and huge research is required in this area to establish, improve and develop technologies. This is especially important in view of the fact that no generalized solutions are available, in general, in view of the unique character of each wastewater and the application to real industrial wastewaters is not straightforward.

The present research mainly focuses on the newer studies that would provide new impetus for the application of hydrodynamic cavitation, in general, and using vortex diode as a cavitation device, in particular for various less explored application of industrial wastewater treatment, specifically for the removal of ammoniacal nitrogen, removal of solvents and removal of API pollutants. Several process intensification approaches in the form of aeration, addition of oxidizing agents such as hydrogen peroxide etc. are also explored and evaluated in detail with cost analysis to prove efficacy of the process and application in real wastewater treatment. A new process, solvent-assisted cavitation for the increased removal of organic pollutants is also developed for the first time and a proof of concept is established and validated using experimental data.

2. Statement of Problem

2.1 Removal of Ammoniacal Nitrogen

The nitrogen content, measured in the form of ammoniacal nitrogen, is a serious problem in many industrial wastewaters due to limitations of both biological and conventional physico-chemical methods. Ammoniacal nitrogen is a measure for the nitrogenous organic matter as ammonia, a toxic pollutant that can directly poison humans and upset the ecosystem. There are many industries such as dyes and pigment, nitrogenous fertilizers, specialty chemicals that that generate wastewaters having high ammoniacal nitrogen (1500 to 3000 mg/L) and demand specific solutions for wastewater treatment. The ammoniacal nitrogen from effluent is conventionally removed using biological, physical, chemical methods or combination of these methods. Adsorption, chemical precipitation, membrane filtration, reverse osmosis, ion exchange, air stripping, breakpoint chlorination and biological nitrification/ denitrification are commonly employed in this regard [1]. It is essential to evaluate newer methods and devices that have potential to offer techno-economically feasible option, specifically for ammoniacal nitrogen reduction. While the use of vortex diode and hydrodynamic cavitation is reported in the literature for wastewater treatment, systematic studies to evaluate effects of various process parameters along with cost consideration are essential from practical point of view and for implementation in real life applications pertaining to the effluent treatment, which is one of the main problem statement of this study.

2.2 Degradation of Solvents using Hydrodynamic Cavitation

Industrial wastewater treatment for removal of small concentrations of harmful solvents is pertinent issue in many chemical and pharmaceutical industries. Solvent waste is recognised as a hazardous waste [2] and conventional methodologies have severe limitations in the removal/degradation due to various reasons apart from poor biodegradability. Cavitation, as an advanced oxidation processes, is a destructive method of treatment which provides in situ generation hydroxyl radicals for the oxidation of the pollutants. It can be regarded as a greener process due to complete mineralization of contaminants. In view of large number of solvents being commercially used and limited information in the literature on degradation, differences due to nature of solvents, number of processes/ reactor configurations and so on, it is instructive to evaluate degradation of various solvents to arrive at practical strategy for their removal.

2.3 Degradation of API Pollutants using Hydrodynamic Cavitation

In recent years, new emerging pollutants such as pharmaceuticals, in the form of active pharmaceutical ingredients (API), have been in the spotlight of the scientific community as they may cause significant human health and environmental side effects, even at low concentrations (ng/L to µg/L) [3,4]. A majority of these compounds are recalcitrant or bio-refractory, in that they cannot be degraded using most of the conventional treatment methodologies [5]. Hydrodynamic cavitation, especially Intensified Hydrodynamic cavitation, can provide useful alternative to the existing methodologies. In view of the stringent norms of zero liquid discharge for many of the pharmaceutical industries, it is imperative that suitable methodologies be evaluated for the treatment for wastewater streams containing low/high concentrations of API pollutants e.g. antibiotics (Ciprofloxacin) and class of antihyperglycemic drug (Metformin).

2.4 Newer Process development using Hydrodynamic Cavitation

In view of the constraints of most of the existing methodologies, high costs of treatment apart from limitations on the extent of pollutants removal with ease of operation, it is instructive to develop newer methodologies for removal of organic pollutants, specifically for ammoniacal nitrogen removal. A new approach of solvent-assisted cavitation for the enhanced degradation of organic pollutants, using suitable solvent as an additive (1-5%v/V) for the degradation of 4-aminophenol as a model nitrogen compound was evaluated.

3. Objectives

- Development of newer cavitation methodologies for removal of organic pollutants, ammoniacal nitrogen, solvents and API pollutants using mainly hydrodynamic cavitation and also process intensifications.
- Study on effect of reactor geometry, nature of organic pollutants, nature of intensification, kinetics of degradation, mathematical modeling, and optimization of process.
- Techno-economic feasibility studies.
- Newer process development for industrial wastewater treatment.

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 wastewater treatment using cavitation, process intensifications and for newer process development of solvent-assisted hydrodynamic cavitation process.

Studies on degradation of various organic pollutants were carried out on model compounds such as p-amino phenol (ammoniacal nitrogen removal), solvents such as octanol, dimethyl formamide and cyclohexanol (solvent degradation) and Ciprofloxacin and Metformin (API pollutant removal). Different analytical techniques such as COD, TOC, HPLC, FTIR etc. were employed for the measurement of appropriate parameters. 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 intensified cavitation methodology, different strategies such as aeration, hydrogen peroxide addition, pH modification etc. were used to evaluate performance behavior and to enhance efficiencies. Kinetics of degradation and cost evaluation for techno-economic feasibility analysis was also studied. Per-pass degradation factor model was applied to evaluate degradation behaviour and cavitational yield. The proof of concept was also validated by treating real industrial wastewaters.

5. Results/ Summary/ Conclusions

I. Improving Efficiency for Removal of Ammoniacal Nitrogen from Wastewaters using Hydrodynamic Cavitation

The present study reports significant improvements in the removal of ammoniacal nitrogen from wastewater which is an important problem for many industries such as dyes and pigment, distilleries and fisheries. Pilot plant studies (capacity, 1 m^3/h) on synthetic wastewater using 4-amino phenol as model nitrogen containing organic compound and two real industrial effluents of high ammoniacal nitrogen content were carried out using hydrodynamic cavitation. Two reactor geometries were evaluated for increased efficiency in removal-orifice and vortex diode. Effect of initial concentration (100 - 500 mg/L), effect of pressure drop (0.5 - 5 bar) and nature of cavitating device (linear and vortex flow for cavitation) were evaluated along with effect of salt content, effect of hydrogen peroxide addition and aeration. Initial concentration was found to have significant impact on the extent of removal: ~ 5 g/m^3 removal for initial concentration of 100 mg/L and up to 12 g/m^3 removal at high concentration of 500 mg/L. Interestingly, significant improvement of the order of magnitude (up to 8 times) in removal of ammoniacal nitrogen could be obtained by sparging air or oxygen in hydrodynamic cavitation and a very high removal of above 80% could be achieved. The removal of ammoniacal nitrogen by vortex diode was also found to be effective in the industrial wastewaters and results on two different effluent samples of distillery industry indicated up to 75% removal, though with longer time of treatment compared to that of synthetic wastewater. The developed methodology of hydrodynamic cavitation technology with aeration and vortex diode as a cavitating device was found to be highly effective for improving the efficiency of the conventional cavitation methods and hence can be highly useful in industrial wastewater treatment, specifically for the removal of ammoniacal nitrogen.

II. Wastewater Treatment and Process Intensification for Degradation of Solvents using Hydrodynamic Cavitation

Industrial wastewater treatment for removal of small concentrations of harmful solvents is pertinent issue in many chemical and pharmaceutical industries. The present work evaluates removal of three common solvents by hydrodynamic cavitation (nominal capacity, 1m^3/h). Solvent degradation of three solvents viz. octanol, dimethyl formamide and cyclohexanol was studied in the concentration range of 50-200 mg/L and for the pressure drop range of 0.5-5 bar. The vortex based cavitation device (vortex diode) was compared with that of linear flow based device (orifice). Process intensification in the form of aeration and addition oxidizing agent- hydrogen peroxide was also evaluated for synergistic effect. The vortex diode required lower pressure drop and is superior to orifice and process intensification using aeration is most effective. A reduction in TOC to the extent of 74% could be achieved for octanol (200 ppm) using aeration with cavitational yield of 1202×10^{-4} mg/J for vortex diode, yield ~10 times of orifice. The degradation depends on the nature of solvent and it was revealed that low values of dielectric constant ($\varepsilon<10$) favour degradation. The kinetics was evaluated using rate model based on per-pass degradation factor. The process techno-economic feasibility is useful in industrial wastewater treatment.

III. Intensified Hydrodynamic Cavitation Using Vortex Flow Based Cavitating Device for Degradation of Ciprofloxacin

The present work, for the first time, establishes degradation behavior of ciprofloxacin (CIP), a widely used fluoroquinolone group of antibiotics, using vortex flow based hydrodynamic cavitation (HC) for low to high concentrations of CIP (10 and 100 mg/L). Effect of pressure on the degradation of CIP and TOC reduction was investigated on pilot plant scale (capacity 1m3/h). Process intensifications using aeration as well as hydrogen peroxide (H_2O_2) were also investigated. While aeration did not yield any significant enhancement, process intensification using H_2O_2 resulted in ~ 200% enhancement in the CIP degradation as compared to HC alone. Excellent degradations, to an extent of 79 & 95%, were achieved corresponding to high cavitational yields of 7.2×10^{-4} mg/J and 86.8×10^{-4} mg/J for CIP concentrations of 10 and 100 mg/L respectively using the process intensified approach of HC and H_2O_2, not reported so far for cavitating devices without moving elements. The developed methodology demonstrated 4-7 times improvement in per-pass degradation and reasonably low cost with high efficiency compared to the conventional cavitation. The results clearly highlight utility of the process intensified approach using H_2O_2 for the degradation of CIP even at high concentrations, specifically important for pharmaceutical industries requiring zero liquid discharge norms.

IV. Studies in Degradation of Metformin

The present work reports degradation of metformin (MTF), a widely used antidiabetic drug, using vortex flow based hydrodynamic cavitation (HC) at two different initial concentrations such as 10 and 20 mg/L. The effect of pressure on the degradation of MTF and TOC reduction was investigated on a pilot plant scale (capacity $1m^3/h$). Process intensifications using aeration, pH modifications as well as hydrogen peroxide (H_2O_2) were also investigated. The process intensification using aeration resulted in marginal improvement whereas, process intensification using H_2O_2 resulted in 10% and 32% MTF degradation at 10 and 20 mg/L MTF concentrations respectively. The pH has significant effect and up to 100% degradation could be achieved by manipulating pH.

V. Development of New Process- Solvent-Assisted Cavitation for Enhanced Removal of Organic Pollutants - Degradation of 4-Aminophenol

A new approach of solvent-assisted cavitation process was proposed for degradation of organic pollutants. The process envisages the use of suitable solvent as an additive, (1-5% v/V), in the conventional cavitation process to enhance the pollutant removal efficiency. A proof of concept was provided for the removal of ammoniacal nitrogen with significantly improved efficiency using solvent-assisted hydrodynamic cavitation (HC) compared to conventional HC. The efficacy of the process was studied on a pilot plant scale ($1m^3/h$) and using vortex flow based vortex diode as a cavitating device. Degradation studies were carried out using a model pollutant, 4-aminophenol and four different solvents as additives, 1-octanol, cyclohexanol, 1-octane and toluene. Relatively polar solvents were found to increase the efficiency of the pollutant removal (>65%) and also increase the rates to an extent of more than 200%, compared to only HC. A very high removal of ammoniacal nitrogen, more than 90%, was obtained for solvents 1-octanol and cyclohexanol, indicating the importance of the selection of solvent. Per-pass degradation model showed 3 to 4 times increase in the per pass degradation for polar solvents compared to cavitation alone. The results confirm no role of conventional solvent extraction and no specific contamination of wastewater due to the use of solvent as an additive in the process. Further, the cost was 2 to 3 times lower as compared to the conventional HC. The interesting observations in the proposed process can fuel further research to provide possible improvements in existing methodologies of wastewater treatment, in general, and for removal of ammoniacal nitrogen, in particular.

6. Future directions

- Studies in different configurations of cavitating devices, process intensifications and process integration with the conventional treatment technologies.
- Extensive studies are required on degradation/ removal of different organic pollutants, in isolation, and in combination along with effects of parameters such as TDS, TSS, and other pollutants in the wastewaters.
- It is necessary to devise guidelines for selection and optimization of process parameters for efficient degradation of pollutants from different classes such as solvents, nitrogen containing compounds, pesticides, dyes of different types such as cationic, anionic, reactive, azo dyes etc., API pollutants of different types such as antibiotics etc.
- Development of newer processes/ process modifications such as solvent assisted cavitation process; optimization of these processes for the removal of different organic pollutants and for the reactor configurations.
- Computational Fluid Dynamics studies (CFD) for theoretically evaluating the flow patterns and establishing the cavitation regimes. Developing criteria for the selection of process/ process parameters and for prediction of the process performance.

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8. Publications and Patents

1. Pravin B. Patil, Vinay M. Bhandari, Vivek V. Ranade. "Improving Efficiency for Removal of Ammoniacal Nitrogen from Wastewaters using Hydrodynamic Cavitation". *Ultrasonics - Sonochemistry* 70 (2021) 105306. https://doi.org/10.1016/j.ultsonch.2020.105306

2. Pravin B. Patil, Vinay M. Bhandari, Vivek V. Ranade. "Wastewater Treatment and Process Intensification for Degradation of Solvents using Hydrodynamic Cavitation", *Chemical Engineering and Processing - Process Intensification* 166 (2021) 108485. https://doi.org/10.1016/j.cep.2021.108485

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Patents

1. Bhandari V. M. and Patil P. B., Solvent Assisted Cavitation for Wastewater Treatment, 2019-INV-0055; Appl. No. 201911050122, (2019).
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3. Bhandari V. M.; Pooja D. Thanekar; Pravin B. Patil; Divya Dixit; Vortex Flow Based Cavitation for Degradation of Antibiotics and Antibacterial Agents, 2021-INV-0051, Appl. No. 202211019277, (2022)

Acronyms

AC	Acoustic cavitation
AFM-IR	Atomic force microscopy based infrared
AMR	Antimicrobial resistant
ANAMMOX	Anaerobic ammonium oxidation
AOPs	Advanced oxidation processes
API	Active Pharmaceutical Ingredient
ASP	Activated sludge process
ATR-FTIR	Attenuated total reflectance fourier transform infrared
BG	Brilliant green
BMP	Biomethane potential
BOD	Biological oxygen demand
BTEX	Benzene, toluene, ethylbenzene and xylene
CANON	Completely autotrophic nitrogen removal over nitrite
CFD	Computational fluid dynamics
CIP	Ciprofloxacin
CNT	Carbon nano tube
COD	Chemical oxygen demand
DC	Diclofenac
DI	Deionized water
DM	Dimethoate
DMA	Dimethylamine
DMF	Dimethylformamide
DNA	Deoxyribonucleic acid
DOC	Dissolved organic carbon
DW	Distilled water
EA	Ethyl acetate
EAOPs	Electrochemical advanced oxidation processes

EH2	Exogenous hydrogen
ELM	Emulsion liquid membranes
FTIR	Fourier transform infrared spectroscopy
ETP	Effluent treatment plant
GAC	Granular activated carbon
GC	Gas chromatography
GO	Graphene oxide
HC	Hydrodynamic cavitation
HPLC	High performance liquid chromatography
HRMS	High-resolution mass spectrometry
HyVAB	Hybrid vertical anaerobic biofilm-reactor
IBU	Ibuprofen
IPA	Isopropyl alcohol
IR	Infrared
KI	Potassium iodide
LC-MS	Liquid chromatography mass spectrometry
LWHCR	Liquid whistle hydrodynamic cavitation reactor
MA	Methylamine
MB	Methylene blue
MBRs	Membrane bioreactors
MEK	Methyl Ethyl Ketone
MIEX	Magnetic ion exchange resin
MIRS	Mid-IR spectroscopy
MOC	Material of construction
MPN	Most probable number
MTF	Metformin
MW	Molecular weight
MWC	Meter water column
NDIR	Non-dispersive infrared
NH_4-N	Ammoniacal nitrogen

NIRS	Near-IR spectroscopy
OA-II	Orange acid-II
PAP	*para*-aminophenol
poly-DADMAC	poly diallyldimethylammonium chloride
PVA	Polyvinyl alcohol
RB13	Reactive blue 13
RHC	Rotating hydrodynamic cavitation reactor
Rh6G	Rhodamine 6G
RO	Reverse osmosis
RO4	Reactive orange 4
RR120	Reactive red 120
RR180	Reactive red 180
RSW	Raw surface water
RTD	Resistance temperature detector
SBR	Sequencing batch reactor
SDZ	Sulfadiazine
SS 316	Stainless steel 316
TDI	Textile dyeing industry
TDS	Total dissolved solids
THMs	Trihalomethanes
TOC	Total organic carbon
USEPA	United states environmental protection agency
UV	Ultraviolet
UV-C	Ultraviolet-chlorine
WHO	World health organization
WWT	Wastewater treatment

Nomenclature

C_0	Initial concentration, (mg/L or ppm)
C	Final concentration, (mg/L or ppm)
g	Gravitational acceleration, m/s^2
k	Rate constant, min^{-1}
Nc	Number of passes required for treatment
P	Pressure, bar
P_E	Cost of electricity per kWh, Rs.
Q	Flow Rate, liter/h
t	Time, min
V	Volume, Liter
V_G	Superficial gas velocity, m/s
W	Energy dissipation rate, W
Y	Cavitational yield, mg/J
ϕ	Per-pass degradation factor
Δ	Pressure drop, bar
η	Efficiency of the pump
ε	Dielectric constant

Chapter – 1

Introduction

Chapter 1

Introduction

1.1 Removal/ Degradation of pollutants- Industrial wastewater treatment

Water is precious to the life and in recent years its availability is getting reduced day by day due to the hugely increased use for human consumption, agricultural consumption and for industrial purpose. Due to the scarcity of water, it is imperative that methodologies for wastewater treatment, recycle and reuse be developed for effective removal/ degradation of various pollutants and intensified hydrodynamic cavitation process is one such promising alternative to existing methods in this regard.

Water plays a vital role in day-to-day life. India possesses 18% of the world's population but accounts only 4% of the world's water sources. In India, the agricultural sector is the water intensive sector which requires more than ~80% of the water from useful available water sources. Domestic water consumption is ~10% and industrial and other sectors consume ~10% of water. In India, industrial sector consumption is using surface water (~41%), ground water (~35%) and municipal water (~24%) [1]. Approximately 44 million m^3/day wastewater gets generated from which industrial wastewater generation contributes about ~6.2 million m^3/day [1]. Only ~25% and ~60% domestic and industrial wastewater is believed to be treated in India and there is a huge gap between wastewater generated and treated. Some of the important industry sectors that are considered water intensive are listed in Table 1.1. The wastewater treatment scenario worldwide and India, in particular, demands for cost effective and sustainable methodologies to reduce the aforementioned gap.

Wastewater, in general, can be classified as domestic (Sewage) and industrial. The domestic wastewater is mostly well characterised and has a relatively known pattern for the pollutants with more BOD component. Thus, sewage wastewater treatment is a well-developed methodology across the globe and biological treatment such as Activated Sludge Process is a common practice. Though, cavitation can have important application in the sewage treatment, especially for high strength wastewaters, the scope of the present investigation largely covers industrial wastewater treatment and for the efficient removal of organic pollutants.

Industrial wastewater treatment is a challenging problem in recent times due to the occurrence of many non-biodegradable/ refractory pollutants and also for the high cost of treatment required to meet the pollution control norms of different states. A single effluent treatment method is hardly useful in effecting efficient wastewater treatment and in meeting the prescribed norms for BOD, COD, and specific pollutants, apart from colour. This, therefore, demands process integration apart from process intensification methodologies for techno-economical real life applications.

A large number of methods/ technologies are available for treatment of different types of wastewaters for the removal of different types of pollutants. The treatment methodologies are broadly classified as physical, chemical, physico-chemical and biological methods of treatment. Further, many of these methods are employed in the primary, secondary and tertiary treatments in Effluent Treatment Plants (ETP). Biological methods are classified as aerobic and anaerobic treatments and are largely suitable for effluents having biodegradable pollutants and for industries such as dairy industry, fisheries, and distilleries etc. Primary treatment of ETP typically employs methods of physical separations such as sedimentation, clarification, coagulation-flocculation, membranes etc. The secondary treatment step in ETP is most crucial where up to 95% of the pollutant load is removed by using a variety of physico-chemical methods of treatment such as oxidation, adsorption, membrane separations and modified forms of these and such methods e.g. photo-oxidation, cavitation, electro-oxidation, emulsion liquid membranes etc. The tertiary treatment is required typically to meet the desired pollution control norms for the release of treated waters or for recycle and reuse of the treated water. Here, methods such as Adsorption, Reverse osmosis (RO), Ion exchange etc. are used as a polishing step.

Advanced oxidation processes (AOPs) are gaining attention in recent years for the development of newer technologies, especially for the degradation of organic pollutants, refractory compounds, to reduce/ eliminate secondary waste generation with complete mineralization. Advanced oxidation processes are defined as the processes that utilize oxidising agents to degrade/ oxidise complex molecules present in wastewater leading to complete mineralization with final degradation products as carbon dioxide and water [1–6]. Advanced oxidation processes such as cavitation, photocatalytic oxidation, Fenton's chemistry and chemical oxidation using ozone, hydrogen peroxide are reported widely for the degradation of complex compounds in wastewater, alone or in combination. There are other hydrothermal oxidation processes such as wet air oxidation, subcritical, critical and supercritical water oxidation which are also used for the degradation of complex compounds in wastewaters which are in recalcitrant form. However, these hydrothermal oxidation processes largely require pressure in the range of ~180-300 bar which makes them more energy intensive and techno-economically unviable for degradation of pollutants. On the other hand, cavitation, photocatalytic oxidation, Fenton's chemistry and chemical oxidations using ozone, hydrogen peroxide can be largely carried out at ambient conditions/ mild conditions and hence, are preferred over hydrothermal oxidation processes.

As an advanced oxidation process, cavitation (baring optic and particle, which are not common and are not considered in this work) produces hydroxyl radicals by means of ultrasonic irradiation or using constrictions such as orifice, venturi or vortex diode in the path of the fluid. A photocatalytic oxidation uses UV light/near UV/ sun light in the presence of a semiconductor catalyst for a generation of hydroxyl radicals while Fenton reagent produces hydroxyl radicals by reaction between Fe ions and hydrogen peroxide. Compared to cavitation, photocatalytic oxidation and Fenton reagent have limitations in terms of narrow pH range, sludge formation, catalyst deactivation and scalability issues. In the case of cavitation, hydrodynamic cavitation is more energy efficient than acoustic cavitation at a larger scale of operation. Hydroxyl radicals are powerful oxidizing agents having a high oxidation potential of 2.33 V compared to other oxidizing agents such as ozone (2.1 V) and hydrogen peroxide (1.8 V). It can degrade organic moieties in wastewater with faster degradation rates compared to conventional oxidizing agents [7–9]. In view of limitations of other AOPs, hydrodynamic cavitation with linear flow or vortex flow-based device alone or in combination with oxidizing agents looks promising alternative for degradation of a variety class of pollutants in wastewater treatment.

Table 1. 1: Water consumption and discharge by different industrial sectors of India

Industrial sector	Annual wastewater discharge (MCM)	Annual water consumption (MCM)	Proportion of water consumption in industry
Thermal power plants	270009	351574	87.87
Engineering	15913	20199	5.05
Paper and pulp	6957	9058	2.26
Textile	6373	8298	2.07
steel	3968	5166	1.29
sugar	1497	1949	0.49
Fertilizer	564	735	0.18
Others	2413	3142	0.78
Total	**307292**	**400120**	**100**

Source: CSE, 2004, New Delhi

1.2 Cavitation - Historical Advances

The word cavitation was derived from the Latin word *cavitas* (void space or cavity). The phenomenon was first reported by Euler in 1756 [10] while studying machines that are in motion by reaction against water. Later in 1859, Besant [11] studied the dynamics of the collapse of a spherical cavity in a fluid. In 1894, Reynolds [12] evaluated the formation and collapse of vapour bubbles in boiling liquids and constricted tubes. During the First World War, in an attempt to develop high speed ships using a rotating marine propeller, a number of problems were faced such as problem of cavitation in which tiny bubbles grew in size and then collapsed as a result of pressure variations in the turbulent water around ships propellers adversely affecting the speed of ships. In this context, British physicist Lord Rayleigh [13] studied a mathematical model of cavitation in an incompressible fluid, that was extended Besant's work, and published the report in 1917 that provided an elaborate analysis of cavitation phenomena on the basis of formation, growth, and collapse of spherical bubbles near rotating impeller leading to noise, vibrations, and erosion of the surface of impeller, ultimately altering the performance of hydraulic devices. Subsequently, extensive studies were reported on single bubble dynamics by many researchers [14–17].The experimental evidence of cavitation was reported in 1952 by mark Harrison [18]. Since then, scientists have been extensively investigating cavitation phenomena in hydraulics such as impellers, pump, valves, turbines etc.

The studies prior to 1990s were largely focusing on the negative consequences of cavitation such as damage in the form of erosion of surfaces of hydraulics caused by cavitation. The research group of Lohse carried out extensive studies on the theoretical and experimental aspects of bubble dynamics in cavitation[19–21]. Versluis et al. [22] reported cavitation phenomena in the nature by conducting a study on snapping shrimp (Alpheus heterochaelis) which produces a very large sound during rapid closure of its snapping claws resulting in high velocity water jet which is used for attacking its prey. Experimental quantification by means of hydrophone measurements in conjunction with time controlled high-speed imaging of the claw closure demonstrate that the sound is emitted at the cavitation bubble collapse and not on claw closure. Lohse [21] carried out the experimental quantification of temperature effects in single and multi-bubble sonoluminescence and found temperatures of the order of >15000 k inside single bubble sonoluminescence and 5000 k inside multi-bubbles sonoluminescence. The features of cavitation in the form of extreme pressure, temperature conditions at the point of collapse of cavities and generation of reactive oxidizing species have attracted various research groups across the globe to harness the horizon of cavitation in physico-chemical transformations.

1.3 Cavitation- What, How and Why

In general, cavitation is a physico-chemical process where the physical aspect of the process deals with the formation, growth and collapse of cavitites/microbubbles in a liquid while the chemical part deals with the homolytic splitting of the water molecules generating hydroxyl radicals- highly oxidising species which participate in the oxidation of organics. The process is schematically shown in Figure 1.1

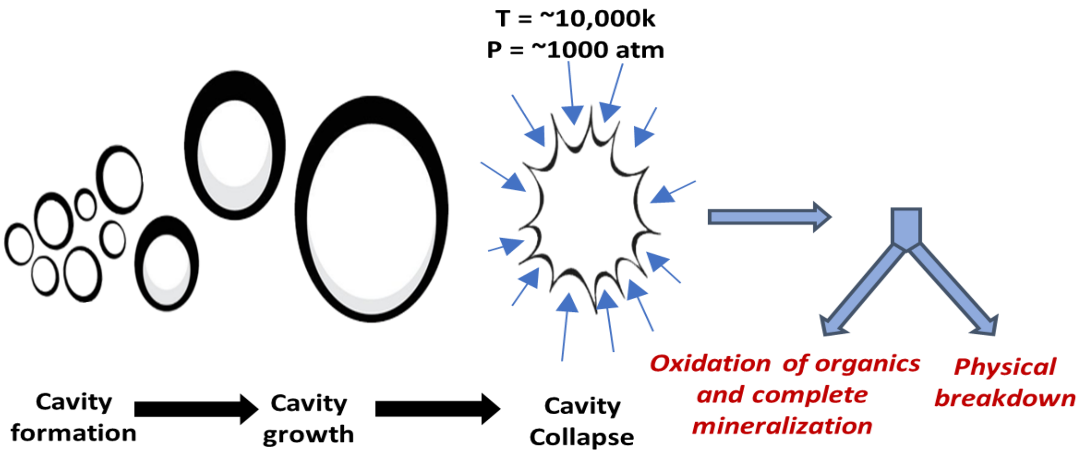

Figure 1. 1: Schematic of cavitation

Cavitation begins with nucleation followed by isothermal expansion of bubbles and after achieving maximum radius, bubbles collapse adiabatically. As the bubble collapses, it results in hot spots with temperatures about 10000 k and pressure about 1000 atm at the point of implosion [23,24]. The microbubbles are typically of the size of 100 nm – 3 mm. During nucleation, vapour filled or partially with fractions of non-condensable gas bubble get formed. The formation of completely vapour filled bubble will takes place in pure liquids while dissolved gas content or impurities contribute in the formation of non-condensable gases. Collapse of bubble plays important role during cavitation. Symmetrical collapse will lead to formation of radicals and that oxidize chemical species within the fluid and favours chemical transformation. While when bubble comes in contact with solid boundary, it will give asymmetric collapse and causes physical transformation in the fluid. The domain of cavitation research is broadly classified into three categories [25]. The first domain covers the spherical bubble dynamics of single or number of bubbles to predict the cavitation phenomena at microscale. This approach is based on Rayleigh's theory of spherical bubble dynamics which includes bubble radius response to oscillatory pressure field. However, the theory ignores surface tension and viscosity effects in modelling of spherical bubble dynamics. The approach was modified by incorporating effects of surface tension and principal effects of viscosity in the Gilmore's equation. Later, accurate bubble radius response to large pressure oscillations was given by Keller-Miksis equation.

The second domain covers reducing negative effects such as vibrations, noise or surface erosion due to cavitation in hydraulics such as pump, valves, impellers, turbine etc. The third domain focuses on harnessing cavitation by means of high pressure, temperature and oxidizing radicals to drive physico-chemical transformations.

Thus, the answers of "Know What, how and why" in cavitation can lead to a number of developments in different research fields apart from evaluating or modifying existing operations. The current study mainly focuses on the third domain of cavitation, more particularly for its utilization in the area of wastewater treatment for the degradation of organics.

1.4 Types of Cavitation

There are four principal types of cavitation based on the mode of generation of cavities (Figure 1.2):

1.4.1 Hydrodynamic cavitation

It is produced by pressure variations in the liquid by using constrictions such as orifice, venturi, vortex diode, etc. in the path of liquid.

1.4.2 Acoustic cavitation

It is produced by pressure variations in fluid by using ultrasound waves of frequency in the range of 16KHz to 100 MHz.

1.4.3 Optic cavitation

It is produced via photons of high intensity light (Laser) by rupturing the liquid continuum.

1.4.4 Particle cavitation

It is produced by a beam of an elementary particle (Protons) by rupturing liquid medium.

Among these principal types of cavitation, the hydrodynamic and acoustic cavitation are produced due to influence of tension in liquid medium while optic and particle cavitation are produced due to localized dissipation of energy [26]. The application of the optic and particle cavitation are mainly found in the biomedical field and also in study of single bubble dynamics while hydrodynamic and acoustic cavitation have the potential to provide useful solutions for household or industrial scale operations.

The present study mainly focuses on the hydrodynamic cavitation. Hence, most of the literature and discussion will be limited to only hydrodynamic cavitation.

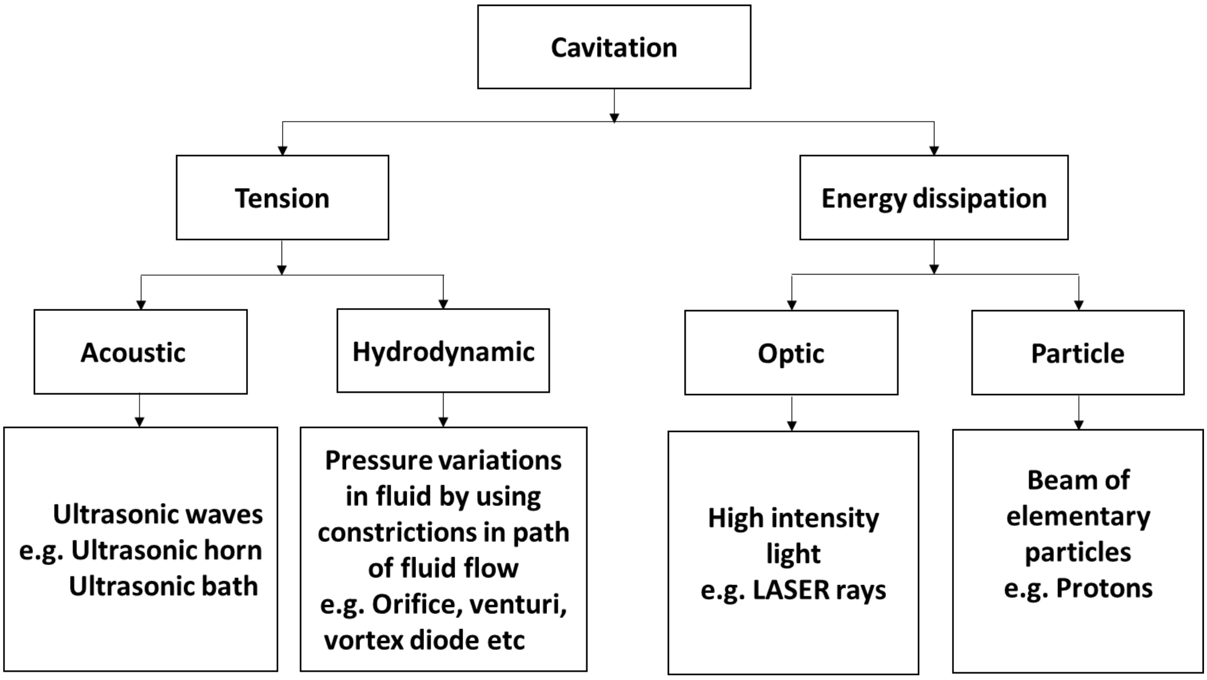

Figure 1. 2: Types of cavitation

1.5 Hydrodynamic cavitation

Hydrodynamic cavitation can be generated by providing constrictions in the path of liquid flow and the common cavitating devices include orifice plate, venturi, throttling valve, vortex diode etc. The liquid is passed at high pressures and due to the constriction, there is sudden drop in the pressure. If the pressure drops near or below vapor pressure of the liquid, some of the liquid flashes into vapor, generating cavities. The design of the cavitating system should be such that the cavities get generated, allowed to grow and collapse. When the cavities collapse, it results in generation of extreme temperature and pressure (10,000K and 1000 atm) conditions at the localized points of implosion, subsequently generating hydroxyl radicals through homolytic cleavage of water molecule [23,27–29]. The studies prior to 1990s mainly focused on the damage caused in hydraulics due to cavitation, and cavitation was not harnessed for physicochemical transformations. 1990+ period saw newer developments and the early reports included hydrolysis of fatty acids and microbial cell disruption using throttle valve respectively [30,31]. A sharp increase in a number of articles on physicochemical transformations driven by hydrodynamic cavitation was observed in last ~25 years. This increase can be attributed to the increased interest for exploiting hydrodynamic cavitation for various useful applications. The studies mostly reported hydrodynamic cavitation using simple cavitating devices such as orifice, venturi or some complex types such as rotor-stator assembly. Some of the reported designs of cavitating reactors are shown in Figure 1.3 The devices such as orifice and venturi employ linear flow of fluids while devices such as vortex diode employ vortex flow in the cavitation. The different devices can also be classified as with and without moving elements. A majority of the cavitating devices are found prone to clogging and erosion thereby restricting their use at large scale of operation. Vortex diodes that employ vortex flow in effecting cavitation have larger chambers for the flow of liquid and hence are relatively less prone for the clogging, thereby increasing their ability in handling dirty fluids in wastewater treatment. The devices that employ moving elements such as rotor-stator assembly, have comparatively higher cost of operation and maintenance, lowering their potential for commercial applications. In the area of wastewater treatment, techno-economic feasibility is a major concern and a number of devices or designs of cavitating device, though can be considered from an academic study point of view, can have little or no relevance from the practical application point of view. The exact theoretical prediction of cavitation behaviour in different devices is also rather not possible even today and hence the empirical approach is largely required using experimental evaluation for each application and for each devices.

There is a need and scope for the development of newer forms of devices that overcome uncertainties in existing conventional forms of cavitating devices and for optimizing process parameters for various applications. It is also required that appropriate computational fluid dynamics (CFD) studies be carried out for theoretically establishing/ predicting the process performance. It is also required that the different forms of cavitating devices be evaluated on different systems for evaluating their efficacy in the degradation of pollutants and for techno-economic feasibility. In the present study, the later aspect is largely covered.

1.5.1 Key geometrical configurations in hydrodynamic cavitation

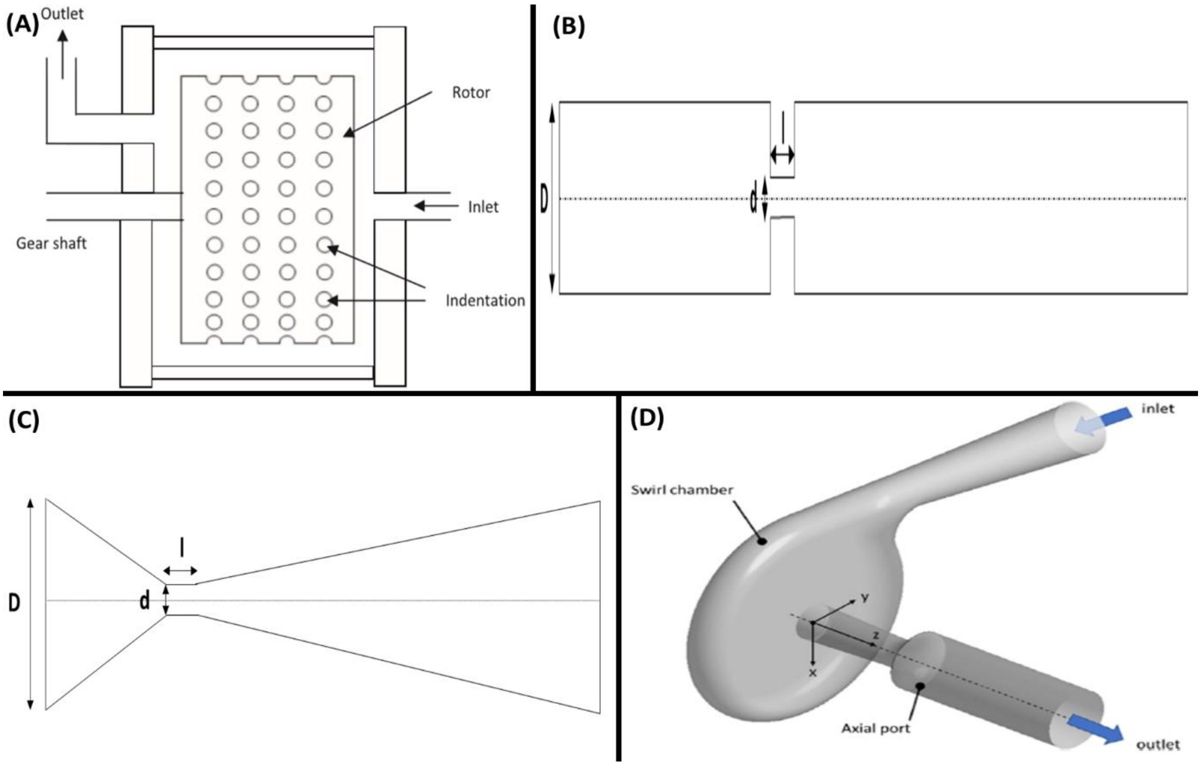

Figure 1. 3: Different geometrical configurations in hydrodynamic cavitation (A) High speed rotor stator assembly [32](B) Circular hole orifice (C) Circular throat venturi (D) Vortex diode [33]

The primary objective to design any hydrodynamic cavitation is to create pressure variations in flowing liquid by constrictions due to which local static pressure falls below vapor pressure leading to the formation of vapor/gas filled cavities. This phenomenon can be achieved by devices with or without moving parts. The hydrodynamic cavitation device with moving parts includes high speed rotor stator assembly which operates at speed of ~4000-20000 RPM [34]. High speed of operation makes rotor stator assembly energy intensive and hence, preferably not first choice of hydrodynamic cavitation device over other devices [35]. The other forms of hydrodynamic cavitation devices without moving parts includes high pressure devices which uses throttle valve and operates at very high pressure of ~30-300 bar and low-pressure devices such as orifice, venturi which are operated in the range of ~1-20 bar and hence, most of the literature is reported widely on orifice and venturi as a conventional form of hydrodynamic cavitation devices. Further, the low-pressure cavitation devices without moving parts are subdivided into two parts as linear flow (Figure 1.3 B and C) and rotational flow (Figure 1.3 D) based hydrodynamic cavitation devices. In rotational flow cavitation device, vortex diode, the flow enters in chamber through tangential inlet, set up vortex and exits through axial port. Due to the strong swirling flow, low pressure region gets formed at the center of the vortex leading to formation of vapour filled cavities which escape from the axial port. The escaped vapor/gas filled cavities realize surrounding high pressure and implosion takes place at the downstream region leading to the formation of hot spots. These generated hot spots, high shear leads to various physicochemical transformations.

The performance of hydrodynamic cavitation is mainly characterized by intensity of cavities produced by constrictions. Conventionally, dimensionless parameter cavitation number (C_v) [36] is used to characterize this event and it is given by,

$$C_v = \frac{P_2 - P_v}{0.5\rho v^2}$$

Where,

P_2 = downstream pressure, P_v = Vapours pressure of liquid at given temperature

ρ = density of liquid, v = velocity of liquid

The above definition is largely applicable for the linear flow-based devices such as orifice or venturi where maximum velocity is occurs at or near throat while in case of newer device like vortex diode which works on rotational flow, the usual definition of cavitation number is not applicable. The cavitation number at which the inception of cavitation occurs is known as cavitation inception number (C_{Vi}) and ideally it occurs at $C_{vi} = 1$ [35]. Yan and Thorpe [37], shown that cavitation inception is function of geometrical configuration and increases with increase in constriction area. However, cavitation number may occur at higher values ($Cv > 1$) due to presence of some dissolved gases and suspended solids in the liquid medium [38]. Due to various physicochemical transformations, hydrodynamic cavitation has the potential to exploit at a larger scale as well as for various applications which led to emerge of various technology initiatives in recent years.

The positive implications of cavitation processes have been useful in a variety of applications, especially in the area of water and wastewater treatment. In water treatment, the cavitation is useful for the destruction of harmful bacteria while in wastewater treatments, a large number of organic pollutants can be effectively degraded. Cavitation, here, is an important operation as it generates no secondary waste and largely proceeds via complete mineralization of the organic pollutants resulting into the final products such as water and carbon dioxide. In cases, where complete mineralization is not possible, the technique can be aptly integrated with other established methodologies of treatment. The cavitation processes have also been found useful in many diverse applications such as desulfurization of fuels [39], biomass valorization [40], microbial disinfection [41–43], droplet emulsions [44], antisolvent crystallization [45] etc.

In view of the possible commercial potential of hydrodynamic cavitation processes and the cavitating devices designs, a number of new start-ups have come up in recent years, some of the examples are given in appendix I. These reveal present and future applications in wide range of chemical/ biological/ water/ wastewater and integrated processing.

1.5.2 Vortex diode

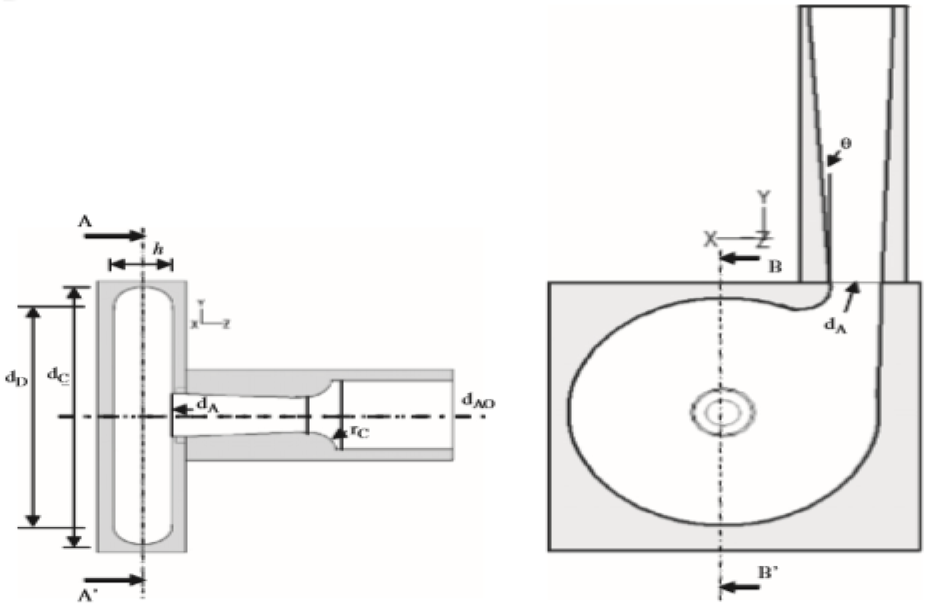

Figure 1. 4: Cross sectional view of vortex diode [46]

Vortex diode [46] is a relatively a recent design that employs vortex flow for generating cavitation as against the conventional linear flow based cavitation devices as shown Figure 1.4 and is a promising alternative to conventional cavitation devices, especially in wastewater treatment. The device has a disc shaped chamber connected with a tangential and axial port.

As discussed earlier, the fluid enters from tangential inlet, sets up vortex and exits from axial outlet. The inception of cavities, cavity growth and cavity implosion occur in the process of cavitation due to the specific design. The effects of cavitation include high pressure, high temperature conditions due to cavity implosions and formation of microjets which leads to various physicochemical transformation. Vortex diodes as cavitating device are now being investigated for various applications. The vortex-based cavitation device has been found superior to many conventional cavitation devices such as orifice, venturi in variety of applications such as dye removal, solvent degradation, microbial disinfection, ammoniacal nitrogen removal, biomass valorization, desulphurization of transportation fuels etc. The present work mainly focuses on the degradation of organics using vortex diode as cavitating device in comparison to conventional linear flow-based device. Table 1.2 lists some of the important investigations pertaining to vortex diode.

Table 1. 2: List of experimental, computational and theoretical studies reported on vortex diode in recent years

Sr.No.	Reference	Remarks
1.	Kulkarni et al., 2008 [47]	1.CFD simulations and experimental validation of data for different sizes of vortex diode
2.	Kulkarni et al., 2009 [48]	1.Flow rate and pressure drop analysis of vortex diode by Reynolds number and Euler number to evaluate performance
3.	Hiremath et al., 2013 [49]	1.Vortex diode for dye degradation at higher concentration 2.Vortex diode promising alternative to conventional HC reactors
4.	Pandare and Ranade, 2015 [50]	1.Flow characteristics of vortex diode were investigated from CFD simulations.
5.	Suryawanshi et al., 2016 [39]	1.Non-catalytic process developed for deep desulphurization of fuels using HC with vortex diode with 100% sulphur removal
6.	Suryawanshi et al., 2017 [51]	1.Cavitation process for desulphurization with very high removal to the extent of 95%
7.	Suryawanshi et al., 2018 [52]	1.Degradation of solvents (acetone, MEK and toluene) by HC 2.Vortex diode found superior over orifice
8.	Sarvothaman et al., 2018 [53]	1.Degradation studies at high concentrations for three solvents acetone; ethyl acetate, EA; and isopropyl alcohol, IPA) using vortex-based cavitation.
9.	Sarvothaman et al., 2019 [54]	1.CFD and cavity dynamics models were coupled with reaction engineering model to evaluate performance of vortex-based cavitation reactor
10.	Jain et al., 2019 [41]	1.Disinfection of water using vortex diode and orifice with complete elimination of bacteria 2.Vortex diode superior over orifice
11.	Nagarajan and Ranade, 2019 [40]	1.Pretreatment of Lignocellulosic biomass using a vortex-based cavitation device was established for the pretreatment of grass silage and sugar cane bagasse

12.	Simpson and Ranade, 2019 [33]	1.Comparison of CFD data with experimental data on pressure drop over a range of flow rates 2.The radial pressure gradient in the cavitating region is shown to dominate over the axial pressure gradient
13.	Simpson and Ranade, 2019 [55]	1.Experimental and numerical investigation of cavitation behavior in linear and swirling flow based devices 2.Inception for vortex diode and swirling Venturi at 50 kPa while for orifice higher than 80 kPa
14.	Sarvothaman et al., 2020 [56]	1.Comparison of linear flow (orifice and venturi) and swirling flow (vortex diode) HC devices for pollutant degradation
15.	Nagarajan and Ranade, 2020 [57]	1.Vortex-based HC used for treatment of distillery spent wash and vinasse resulting with enhancement in BMP (Biomethane potential)
16.	Mane et al., 2020 [42]	1.A hybrid cavitation technology for water disinfection using natural oils having antimicrobial property 2.Vortex diode superior to conventional orifice
17.	Mane et al., 2020 [43]	1.>99% disinfection of bacteria (AMR) in less than 10 min using vortex diode with 0.1% peppermint oil as an additive
18.	Nagarajan and Ranade, 2021 [58]	1.Comprehensive review on biomass valorization with HC-based pretreatment as a promising physicochemical biomass pretreatment method for improving the rate of digestion as well as biomethane yields
19.	Thaker and Ranade, 2021 [44]	1.Experimental and computational studies for an application of vortex-based (HC) device in producing emulsions
20.	Ranade et al., 2021 [59]	1.Inception of cavitation for vortex diode is between 50 and 80 kPa by acoustic analysis
21.	Ranade et al., 2021 [60]	1.Vortex-based HC devices for degradation of 2,4 dichloroaniline with scale-up of nearly 200 times

Cavitation in general, and hydrodynamic cavitation, in particular, is a highly suitable method of treatment for the secondary treatment of ETP where a major portion of organic pollutant can be removed. Further, the advantage is that the cavitation does not generate secondary waste, which is a major concern in the treatments such as coagulation, adsorption and so on. Though, a complete mineralization of organic pollutant is desired in the cavitation, it is rarely achieved and hence process integration for cost optimization and for minimising secondary waste is recommended. Further, intensified cavitation processes such as those using aeration, addition of hydrogen peroxide etc. are extremely relevant from a real life application point of view and need to be explored for the removal of a variety of organic pollutants. In the present work, specific investigations are therefore carried out for evaluating the removal of organic pollutants, solvents, ammoniacal nitrogen, API pollutants that are relevant to most polluting industries of the type, dyes & textiles, pharmaceuticals etc. Apart from the removal of pollutants, specific studies are also carried out to develop newer methodologies using hydrodynamic cavitation for the effective removal of pollutants.

1.6 Scope of the thesis

The scope of the thesis primarily includes,

1. Studies on degradation/removal of different organic pollutants by hydrodynamic cavitation using vortex flow-based cavitation device vortex diode and linear flow-based cavitation device orifice, on a pilot plant scale (1m^3/h)
2. To study the effect of various process parameters such as pollutant concentration, pressure etc. on degradation behaviour of different pollutants.
3. To study process intensification using aeration, addition of oxidizing agents like hydrogen peroxide etc.
4. To evaluate process economics.
5. Evaluation of efficacy of the developed methodologies on real industrial effluents.

1.7 Organization of the thesis

Chapter 1 provides an introduction on wastewater treatment for the removal of pollutants, specifically for industrial wastewater treatment, hydrodynamic cavitation process, origin of cavitation phenomena, cavitation-know what, why and how, types of cavitation and current status of hydrodynamic cavitation for wastewater treatment with specific emphasis on vortex-based cavitation device for degradation pollutants from wastewater.

Chapter 2 provides a systematic literature review on hydrodynamic cavitation and degradation/removal of ammoniacal nitrogen, solvents and pharmaceuticals from wastewater by different methodologies.

Chapter 3 contains details of analytical techniques and experimental set-up used to carry out the work.

Chapter 4 gives detailed account of research on ammoniacal nitrogen removal using hydrodynamic cavitation for vortex diode and orifice as cavitating devices and for 4-aminophenol as model organic compound. A very high ammoniacal nitrogen removal was obtained by process intensification. The efficacy of the developed methodology was successfully evaluated on two real industrial effluents with very high ammoniacal nitrogen content.

Chapter 5 discusses the investigation on degradation solvents such as octanol, cyclohexanol and dimethylformamide from wastewater by hydrodynamic cavitation using vortex diode and orifice as cavitating devices on pilot plant of capacity 1m^3/h. A significant degradation by means of cavitation coupled with aeration was observed. The efficacy of the developed process was also evaluated on real industrial effluent from API manufacturer of having problem of high organics, colour and traces of solvents.

Chapter 6 discusses the degradation of emerging class of organic contaminants, API pollutants, ciprofloxacin from wastewater by hydrodynamic cavitation using vortex flow-based cavitation. Again, significant degradation by using the process intensification strategy-cavitation coupled with the addition of hydrogen peroxide was demonstrated.

Chapter-7 discusses the removal of another API pollutant, Metformin, using hydrodynamic cavitation. The process intensification strategy with acidic pH was found to be most effective for complete MTF degradation with low cost of treatment providing techno economically suitable alternative for existing treatment methodologies in wastewater treatment.

Chapter 8 provides a completely new strategy in the form of development of solvent- assisted cavitation for enhanced removal of organic pollutants in general and ammoniacal nitrogen in particular with significantly higher ammoniacal nitrogen removal efficiency. A WO patent is also published in this regard for the new method/technology.

Chapter 9 lists the overall conclusions of the present work and comments on the future scope.

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Chapter – 2

Literature Review

Chapter 2

Literature Review

This chapter deals with comprehensive literature review of the thesis work. This includes current scenario of wastewater treatment, characteristics, constituents and organic pollutants in wastewater. The conventional methodologies such as adsorption, coagulation-flocculation, biological treatment, ion exchange, membrane separations and fenton process are reviewed briefly with their limitations for removal/degradation of organic pollutants from wastewater. The cavitation as advanced oxidation process for removal/degradation of organic compounds from wastewater is reviewed with its types, influence of operating parameters with specific emphasis on hydrodynamic cavitation. Removal/degradation of organics such as ammoniacal nitrogen removal, solvent degradation and API pollutant degradation by various methodologies has been reviewed systematically. The chapter ends with comments on literature gaps and proposed methodology.

2.1 Wastewater Treatment

Water is a precious natural resource as well as national asset and plays a vital role in the social, economic, and cultural development of any country. In India, the agricultural sector is a major water-consuming sector that requires ~80% of the water from available water resources. Due to rapid urbanization, industrialization, and an increase in population, the future predictions indicate that water consumption of the agricultural sector will come down from 80% to less than 70% while for industrial, domestic, and other sectors the water consumption will increase. The water requirement for the above sectors is met from groundwater, surface water. Huge volumes of wastewaters get generated during its domestic consumption and also in the industrial usage. Due to the scarcity of water, it is imperative that the wastewaters generated in urban areas (sewage wastewater) and industries (industrial wastewaters) be treated effectively, recycled and reused.

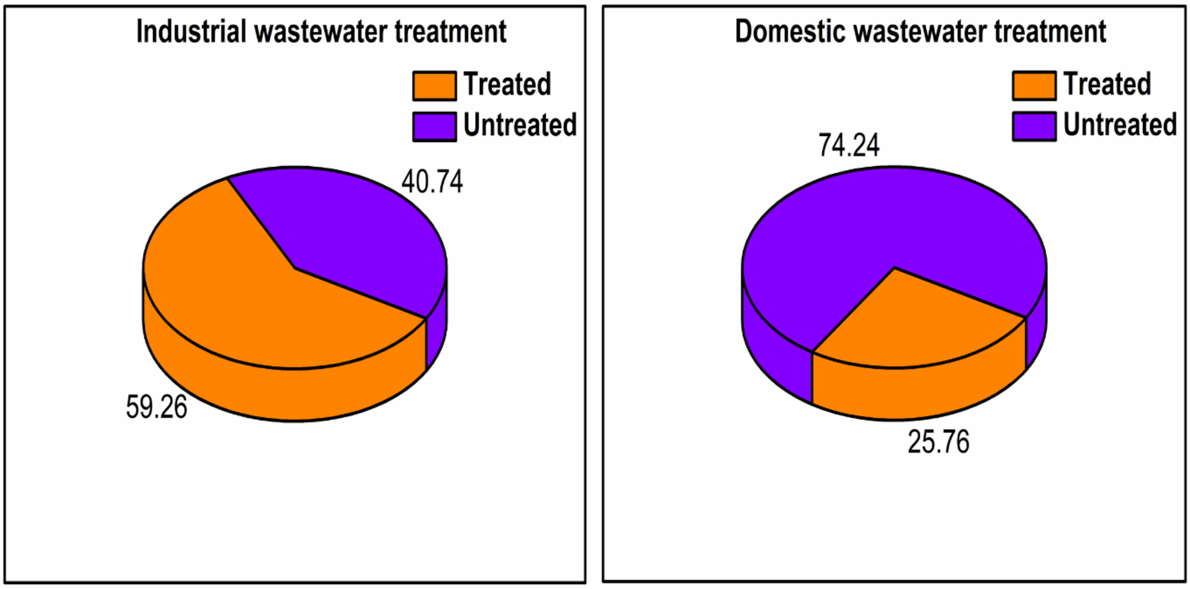

Figure 2. 1: Scenario of treated and untreated industrial and domestic wastewater in India [1].

In India, only 60% and 26% of industrial and domestic wastewater are treated (Figure 2.1) and there is a huge gap between treated and untreated wastewater in both the sectors. The present study mainly focuses on industrial wastewater treatment, though most of the principles of hydrodynamic cavitation and applications such as removal of ammoniacal nitrogen also apply to domestic wastewater treatment.

2.1.1 Industrial wastewater treatment

Water performs several roles and functions in industry e.g. from raw materials to solvents and also is required for washing and in the form of utilities. There are a large number of water intensive industries that are known to require huge quantities of water e.g. dyes and textiles. A major portion of water used in industry ends up with wastewater with different degrees of pollution. The discharge of wastewater from industries into surface aquatic bodies is detrimental to surface water sources and harmful to human living and for the ecosystem. The primary aim of industrial wastewater treatment is to treat waters to such an extent that the discharge effluent meets permissible norms of pollution control and therefore has less adverse impact on the surrounding environment [1].

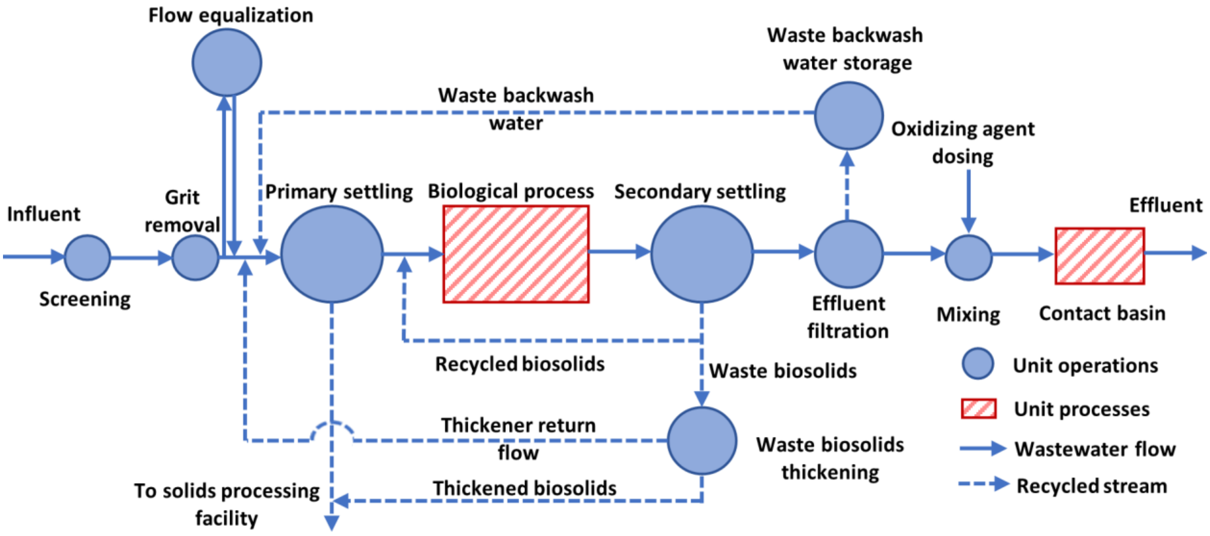

Figure 2. 2: Different stages of industrial wastewater treatment [2]

A large number of physical, chemical, biological processes, or hybrid processes are available for the treatment of industrial wastewater, depending on the nature of pollutants, concentration of the pollutants and volumes to be treated [2]. Figure 2.2 schematically describes various unit operations and processes involved at different stages of operation in an industrial wastewater treatment plant. The physical unit processes used in industrial wastewater treatment are screening, flow equalization, mixing, flocculation, sedimentation, flotation, aeration, and filtration. On the other hand, principal chemical processes used in industrial wastewater treatment are coagulation, chemical precipitation, chemical oxidation, advanced oxidation processes such as cavitation, Fenton reagent, photocatalytic oxidation, ion exchange, chemical neutralization, etc. The selection specific operation and the process depend upon the type and nature of the pollutant. Membrane processes are useful both in the primary treatment (micro or ultra-filtration) or in final polishing step (reverse osmosis). A majority of the treatment processes generate secondary waste that needs further treatment. Coagulation, adsorption and membrane separations processes mainly belong to these types. Treatment processes such as hydrodynamic cavitation do not generate secondary waste and hence are more amenable to wastewater treatment, especially for destroying harmful organic pollutants.

2.2 Characteristics of wastewater

Typically, wastewater is characterized on the basis of physical, chemical and biological composition and each terminology can be interrelated to each other.

2.2.1 Physical characteristics: The physical characterization of wastewater mainly includes determinations of solids in wastewater which are in the form of settleable, floatable or colloidal matter. The solids in wastewater are broadly characterized into total suspended solids and total dissolved solids based on the size of solid particles. The suspended and dissolved solid content gives total solids in wastewater. The significance of measurement of solids in wastewater helps to evaluate selection of suitable methodology for the treatment of wastewater and for the reuse of wastewater. Measurements such as turbidity, colour and transmittance help to evaluate the quality, condition (fresh or septic), and suitability of wastewater for specific type of treatment such as UV. Another physical characteristic is odour which helps to evaluate the intensity and impact of odour on the surrounding environment.

2.2.2 Chemical characteristics: The chemical characteristics of wastewater are further classified into inorganic and organic chemical contents. The inorganic chemical characteristics include pH, alkalinity, nutrients, various salts such as chlorides, sulphates, metals, while organic organics characteristics include measurement of biological oxygen demand, chemical oxygen demand, and total organic carbon apart from identification of specific organic pollutants on the basis of class such as solvents etc.

2.2.3 Biological characteristics: The biological characteristics involves measurement of coliform organisms using MPN (Most probable number) test, specific microorganisms, and toxicity test.

2.3 Organic pollutants in wastewater

Organic pollutants in wastewaters can be simple organics such as biodegradable chemicals and many a times refractory compounds that are difficult to degrade, with structures ranging from simple to complex. The organics in wastewater are analyzed broadly as aggregate organic compounds by measurement of chemical oxygen demand, biological oxygen demand, and total organic carbon of wastewater while individual organic compounds are analyzed by separation methodologies such as HPLC, GC for exact quantification of the individual compound in wastewater.

2.3.1 Priority pollutants

The priority pollutants are a subset of "toxic pollutants" as defined in the Clean Water Act (USA) and categorized based on the carcinogenicity, mutagenicity and high acute toxicity as per USEPA (United States Environmental Protection Agency) guidelines. There are about 129 priority pollutants classified into 65 categories which include organic as well as inorganic pollutants. There are various classes of organic compounds whose members are considered as an individual class of priority pollutant such as volatile organic compounds found in ground and surface water, trihalomethanes (THMs) found in chlorinated water as disinfection by-product, organic solvents discharged from industrial wastewater which are carcinogenic, haloacetic acids formed due to humic substances, aldehydes, acids/bases, phenols, hydrocarbons, pesticides, herbicide and so on. Any organic compound belonging to above-mentioned class if found in wastewater is referred to as a priority pollutant. The above list of priority pollutants covers major classes of organic compounds while the list may be different for a different location as these standards are set by the pollution control boards of the governments.

2.3.2 Emerging organic compounds

Apart from the priority pollutants discussed above, there are some classes of organic compounds which are found in all aquatic domains in lower concentrations in the range of ng/L to ug/L and these compounds are recalcitrant and remain in aquatic bodies event after the treatment of wastewater. These are compounds of emerging concern and there is a need to develop newer, sustainable, and cost-effective methodologies in this regard. The list of some emerging classes of organic compounds is given below in Table 2.1,

Table 2. 1: List of emerging organic compounds found in wastewater [2]

Veterinary and human antibiotics
Carbadox, Tetracycline, Chlortetracycline, Oxytetracycline, Norfloxacin, Ciprofloxacin, Enrofloxacin, Sarafloxacin, Sulfamethazine, Sulfathiazole, Erythromycin, Ivermectin, Lincomycin, Roxarsone, etc
Human prescription and non-prescription drugs
Acetaminophen (antipyretic), Caffeine (stimulant), Cimetidine (antacid), Diltiazem (antihypersensitive), Fluoxetine (antidepressant), Ibuprofen (anti-inflammatory), Metformin (antidiabetic agent), Ranitidine (antacid), Salbutamol (antiasthmatic)
Industrial and household wastewater products
Acetophenone (fragrance), Cholesterol (fecal indicator), Cotinine (nicotine metabolite), para-cresol (wood preservative), Bisphenol (used in polymers), Butylated hydroxytoluene (antioxidant), Diethylpthalate (plasticizer), 1,4 dichlorobenzene (fumigant), Lindane (pesticide), Methyl parathion (pesticide), Naphthalene (PAH), Phenol (disinfectant), Tri (dichlorisopropyl phosphate) (fire retardant)
Sex and steroidal hormones
Cis-androsterone, 3b-coprostanol, Cholesterol, Equilenin, Equilin, 17a-estradiol, 17b-estradiol, Estriol, Estrone, 19-norethisterone, Progesterone, Testosterone

It may be noted that the nature of organic pollutants, their concentration and biodegradability dictate the selection of technology(ies) for the removal/destruction. Also, though some of the organic pollutants found in small concentrations in the wastewaters, the industries associated with these chemicals may produce streams containing these same pollutants in significantly larger concentrations. Therefore, the treatment technologies are required to provide efficient removal of these pollutants in wide range of concentrations. Many of the existing treatment technologies, such as adsorption have applicability in low concentration range. Hence, the selection of wastewater treatment technology(ies), process intensification and also process integration for techno-economical ETP is most desirable.

2.4 Conventional methodologies for removal/degradation of organic pollutants from wastewater

2.4.1 Adsorption

Adsorption is a surface phenomenon used for the removal of organic and inorganic pollutants from wastewater. It is the process in which selective concentration of one or more components of a mixture (Adsorbate) which may be in the form of liquid or gas on the surface of solid material (Adsorbent). Adsorption is used for the removal of variety of organic pollutants from wastewater. The common materials used for removal of pollutants from wastewater include activated carbons [3–6], Zeolites [7,8], ion exchange resins [9], modified biomass or derived adsorbents [10] or biomass derived bio composites [11,12], low-cost adsorbents from waste materials [13,14]. In recent years, there has been increased interests in functional nanomaterials or nanocomposites including biomodification and intensification [15–21]. The surface interactions in adsorption range from weak van der walls interaction to strong bond formation. In the case of industrial wastewater treatment, selection of adsorbent is very important for the selective removal of targeted pollutant species from wastewater. The adsorbent selection criteria include surface area, capacity, pore size and size distribution, selectivity, form of adsorbent, physical, chemical and thermal stability apart from cost of the adsorbent. The adsorption equilibria and adsorption kinetics are helpful in designing and implementation of developed methodology at an industrial scale. The adsorbent surface area for most commercial adsorbents typically ranges from 100-1500 m^2/g [1]. The adsorbent should ideally have high selectivity, high capacity, favourable kinetics, mechanical strength, and low cost for application in wastewater treatment. Generally, adsorption is performed as a column chromatography operation at an industrial scale. Adsorption process is widely used for removal of dyes among conventional methodologies with predominantly activated carbon as adsorbent [22], the textile, paper and pulp industries are common examples of industries discharging dyes into wastewater. Adsorption is also used for removal of many organic pollutants such as phenols, chlorinated compounds, pesticides, pharmaceuticals from wastewater [23]. The significant limitations of adsorption process at larger scale of operation include relatively high capital cost, difficult regeneration, high cost of adsorbent, secondary waste generation and disposal of used adsorbent. Adsorbent progressively deteriorates in capacity as the number of cycles increases. Adsorbent regeneration can be done using chemical or thermal methods of regeneration such as steam or vacuum, Relatively high steam requirements to desorb high-molecular-weight pollutants and spent adsorbent is considered as hazardous waste [24–27]. There is a need for the development of newer materials with high selectivity, high capacity, and ease of regeneration specifically for the removal of recalcitrant emerging organic pollutants from wastewater.

2.4.2 Coagulation-flocculation

Coagulation is defined as the destabilization of colloids by the addition of chemicals called coagulant to form aggregates which get removed by settling the mass. On the other hand, flocculation is a process where neutralized particles come in contact leading to floc formation and agglomeration of flocs takes place for the ease and increased rates of solids removal. Almost 70% of constituents of wastewater are in colloidal form and remain stable in wastewater due to electrical charge. As far as wastewater treatment is concerned majority of colloidal particles are negatively charged. Coagulation is a widely used methodology for the removal of a variety of pollutants from wastewater. Coagulation is typically used in wastewater treatment as a primary. Typically, coagulation is performed by chemical-induced coagulation (conventional) or electrical charge induced coagulation (electro-coagulation) [28]. Bio coagulation is known but not employed widely so far. The prominent biocoagulants include Moringa oleifera, Stryconus potatorum, Cactus species, Phaseolus vulgaris, surjana seed, maize seed, tannin, gum arabic, Prosopis julif lora, and Ipomoea dasysperma seed gum [29]. Generally, coagulation and flocculation in wastewater treatment involve the addition of chemicals to alter the physical state of solid particles that may be in suspended or colloidal form followed by sedimentation. The coagulants are used in industrial wastewater treatment can be classified as organic and inorganic coagulants. The organic coagulants include polymers such as poly-DADMAC (poly diallyldimethylammonium chloride) or polyacrylamide, polyvinyl alcohol, polyvinyl sulfonate etc while inorganic coagulants include aluminum salts (alum), ferric and ferrous salts, lime and polymers such as poly aluminium chloride etc. The selection can be made by carrying out Jar-Test (Figure 2.3) for different coagulants and for optimization of various process parameters such as pH, coagulant dose etc.

Figure 2. 3: Jar test apparatus for coagulation experiments [1]

The coagulation–flocculation process has been successfully employed for colour removal of various dyes [30]. The coagulation–flocculation process is predominantly used for treatment of textile [31], paper and pulp [32] industrial wastewater. Electro-coagulation has gained attention in recent years as an advanced form of coagulation for wastewater treatment, though it has higher treatment costs [33]. The drawbacks of the coagulation and flocculation process include toxicity and health hazard possessed by inorganic coagulants, such as alum and polymeric-coagulants, large sludge production, inability to fully remove heavy metals and emerging contaminants, incomplete removal of effluent colour, etc [28]. The process of coagulation is not very effective for removal recalcitrant complex organic pollutants.

2.4.3 Biological treatment

Biological treatment processes are useful for treatment of wastewaters having high BOD. Biological processes degrade/removes dissolved and particulate carbonaceous organic matter present in wastewater by using a variety of microorganisms principally bacteria. The principal biological processes used in wastewater treatment are categorized into suspended growth and attached growth [2,34]. The metabolic functions of biological processes are categorized as aerobic (in presence of oxygen), anaerobic (in absence of oxygen), and facultative (organisms can function in both an aerobic or anaerobic environment). In suspended growth processes, the microorganisms responsible for treatment are maintained in suspension by proper mixing. On an industrial scale, majorly of the suspended growth processes such as activated sludge process (ASP), are predominantly used for the degradation of organics from wastewater. The biological process in wastewater treatment can remove more than 80% of the organic load of the wastewater. In the case of attached growth microorganisms, fixing on packing material is employed. The most commonly used attached growth process is the trickling filter. For high strength, industrial wastewater, anaerobic process has been shown suitable alternative compared to the aerobic process in terms of energy requirement, nutrient requirement, and reactor volume. The anaerobic process follows hydrolysis, fermentation and methanogenesis to give methane and water as the final product. Grandclement et al. [35] reviewed organic micropollutants removal by biological process using bacteria, white root fungi and enzymes with hybrid approaches. The performance of biological process is strongly influenced by hydraulic retention time, solids retention time, dissolved oxygen, pH and temperature. Pomies et al. [36] reported modelling of biological systems for organic micropollutant removal in activated sludge. The micropollutants investigated were mainly volatile organic compounds, metals, surfactants, pesticides and pharmaceutical compounds. This work provides insight into the main mechanisms leading to the micropollutant removal (volatilisation, sorption, biodegradation, cometabolism). Narayanan et al. [37] reported different types of reactors used in biological treatments such as stirred tanks, packed bed, fluidized bed, moving bed, semifluidized bed, inverse fluidized bed, sludge bed/sludge blanket and downflow stationary fixed film bioreactors with merits and limitations. Machineni et al. [38] reported on resource recovery such as biofuels, biofertilizers, biopolymers, biomethane by biological treatment from wastewater. The major limitations of biological treatments which restrict their use for larger scale operation include high retention time, aerobic digestion- energy intensive, anaerobic digestion of contaminants in wastewater leaves a smaller carbon footprint, temperature sensitivity and poor efficiency against refractory compounds [39].

As far as implementation of biological processes in industrial wastewater treatment for degradation of recalcitrant organic pollutants is concerned, the overall efficiency is not satisfactory.

2.4.4 Ion exchange

Ion exchange process involves stoichiometric exchange of ions between two phases and is used to separate ions/ ionized molecules from aqueous streams. In industrial wastewater treatment, the ion exchange process is used as a polishing technique for the removal of specific refractory pollutants from wastewater. For industrial wastewater treatment ion exchange resin beads are used which are classified on the basis of pore size as microporous (<2nm), mesoporous (2-50 nm) and microporous (>50 nm) shown in the Figure 2.4 below,

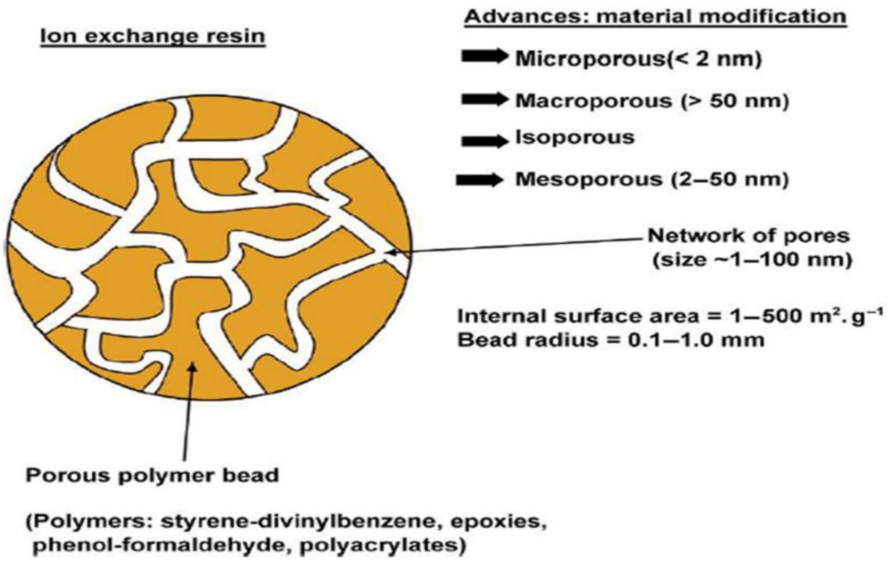

Figure 2. 4: Schematic representation of ion exchange resin bead [1]

The ion exchange resins used for industrial wastewater treatment are typically made using a cross-linked polymer backbone. Although the polymer backbone has a crucial role in the separation of contaminants, the functional groups present on the surface of resins play important role in the removal of specific contaminants. Based on the functional groups, ion exchange resins are further classified as strong acid resins, weak acid resins, strong base resins, and weak base resins. The ion exchange process can be used as a column chromatography operation similar to adsorption in industrial wastewater treatment. Ion exchange has been widely used for removal of various heavy metal ions from wastewater. Qasem et al. [40] provided comprehensive and critical review on removal of heavy metal ions from wastewater with discussion on the operation cost, initial concentration of the metal ions, environmental impact, pH values, chemicals added, removal efficiency, and economic feasibility. Charles et al. [41] reported removal of metal ions and organic load from surface coating industry discharge with three ion-exchange resins (IRA 402Cl, IR 120H and TP 207), and two non-conventional cross-linked polysaccharide-based biosorbents (starch and cyclodextrin). Neale et al. [42] reported removal of micropollutant estrone using magnetic ion exchange resin (MIEX) with 70% removal efficiency. Jiang et al. [43] investigated the removal of three pharmaceuticals, namely, ibuprofen (IBU), diclofenac (DC), and sulfadiazine (SDZ) by using magnetic ion-exchange resins and found interactions were dependent on the specific surface area and functional groups of the resin. The main drawbacks of the ion exchange process include fouling of resins, microbial contamination, thermal stability of the resins, etc [44]. Further, most of the organic pollutants are non-polar in nature and hence conventional ion exchange process is not applicable for the effective removal of organic pollutants.

2.4.5 Membrane separations

Membrane separations are extensively used in industrial wastewater treatment. Membranes are largely employed in primary treatment for the removal of large species using sieving action or as a tertiary treatment for polishing technique in wastewater treatment to produce reusable water by removing all the contaminants. Membrane separation is mainly based on adsorption, sieving and electrostatic phenomena. Conventional membrane separations in wastewater treatment are pressure driven while concentration or electric potential as a driving force in membrane separations is also possible. The membranes are classified on the basis of pore sizes which involves physical separation. The types of membrane are microfiltration (removes particles of size 0.1-0.2 µm, <2 atm pressure), ultrafiltration (removes organics of high molecular weight, size 0.005 µm, pressure up to 10 atm), nanofiltration (removes all types of ions, pressure up to 20 bar) and reverse osmosis (practically removes all types of pollutants, pressure about 50-60 bar) [45]. In the case of industrial wastewater treatment microfiltration, ultrafiltration and reverse osmosis are predominantly used while nanofiltration is still an emerging area. Dharupaneedhi et al. [46] reported membrane-based removal of organic pollutants such pharmaceuticals, pesticides, phthalates, phenols, hormones with nanofiltration and reverse osmosis as viable option for treatment. Couto et al. [47] provided critical review on membrane separation processes applied to remove pharmaceutically active compounds from water and wastewater and suggested membrane distillation process as a promising alternative. Brindle and Stephenson [48] reported membrane bioreactors for treatment of wastewater while there are some limitations for implementation at larger scale such as hydraulic retention time, dissolved oxygen level, pH and temperature adversely affecting the performance of biological process in membrane bioreactors.

The conventional membrane separation is a purely physical separation mechanism while there are some recent developments in this area which overcome limitations of fouling, selectivity and flux. The advancements include membrane bioreactors (MBRs), membrane distillation, dialysis/electrodialysis, emulsion liquid membranes (ELM) and so on. The membrane is a crucial component of membrane separation which dictates separation behaviour. The membranes are used in different formats such as flat sheet, spiral wound or hollow fibre while majorly organic membranes such as cellulose acetate, polypropylene, polyamides, acrylonitrile, and polytetrafluoroethylene are used in industrial wastewater treatment [1]. Apart from this, there are several limitations for membrane separations, especially for the industrial wastewater treatment such as high capital and operating costs, problem of fouling affecting on permeation rate, chemical incompatibilities with process solutions, certain solvents quickly destroy the membranes and the energy cost is higher than chemical treatment [49].

2.4.6 Advanced oxidation – Fenton process

The Fenton process involves a reaction between ferric ions (catalyst) and hydrogen peroxide (oxidant) which produces reactive oxygen species with predominantly hydroxyl radical formation that results in the oxidative degradation of organic pollutants from wastewater. The reaction mechanism of hydroxyl radical formation is given as,

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\bullet}OH \qquad (2.\ 1)$$

$${}^{\bullet}OH + \text{Organics} \rightarrow \text{Products} + CO_2 + H_2O \qquad (2.\ 2)$$

The above reaction 2. 1 represents the Fenton reaction which involves the reaction of ferrous to ferric ions to decompose H_2O_2 into hydroxyl radicals. Further reaction 2.2 represents the reaction of hydroxyl radicals with organics which leads to the formation of products, carbon dioxide and water. Although the Fenton process is used at the larger scale of operations, it still has some limitations and drawbacks. For the oxidation of organic pollutants by Fenton reagent, various parameters need to be considered such as the ratio of hydrogen peroxide to ferrous ions, pH and concentration of the pollutants. The performance of the Fenton reagent is strongly dependent on the pH of the liquid medium (preferred pH 2-3) regardless of the targeted pollutant species [50]. There are various Fenton processes are available such as Fenton, photo-Fenton, electro-Fenton, photo-electro-Fenton, sono-Fenton, sono-photo-Fenton, sono-electro- Fenton, homogeneous and heterogeneous Fenton, photo-Fenton, hybrid Fenton, and Fenton type processes [51]. There are various studies reported on Fenton based processes for degradation of variety of pollutants [52–56]. Lin et al. [57] reported Fenton process for treatment of deseizing wastewater and found hybrid approach of chemical coagulation using polyaluminum chloride and polymer complements the Fenton treatment process in reducing the floc settling time, enhancing color removal and reducing Fe ion concentration. Babuponnusami et al. [58] reported the performance of Fenton, sono-Fenton, and sono-photo- Fenton processes for the oxidation of phenol and found the sono-photo-Fenton technique showed better performance for oxidation of phenol. There are some modified forms of processes obtained by conventional Fenton process which are heterogeneous Fenton process in which catalyst Fe^{2+} of homogeneous Fenton process is replaced by solid catalyst with active sites. Photo Fenton process uses combination light source (UV/visible) in combination with conventional Fenton process and electro Fenton combines electrochemistry with conventional Fenton process which involves *in situ* generation of hydroxyl radicals [50,59]. However, in electro Fenton, current efficiency get reduced due strong acidic pH (2-3) which adversely affects generation of oxidizing species. The efficiency of the electro-Fenton process depends on pH, concentration of catalyst, current density, dissolved oxygen etc [60]. The use of hybrid Fenton processes such as photo-Fenton, electro-Fenton and sono-Fenton are not economically viable options for degradation of pollutants at larger scale of operation due to the high treatment costs and sludge generation during neutralization process.

In general, the conventional methodologies have limitations in terms of cost of treatment, secondary waste generation, scale up issues and inefficient removal of refractory organic pollutants at larger scale of operation. In view of this, there is a need to find viable alternative to overcome these limitations and hydrodynamic cavitation looks suitable alternative which is an advanced oxidation process operating at ambient conditions and is a greener process for removal of refractory pollutants from wastewater.

2.5 Cavitation for wastewater treatment

Cavitation is a specific form of advanced oxidation process, applied effectively for destruction of organic pollutants. In general, cavitation is phenomena of the formation, growth and subsequent collapse of vapor/gas filled microbubbles or cavities occurring in extremely small intervals of time releasing large magnitudes of energy. As cavities collapse it forms hot spots with extreme conditions of pressure (1000 atm- 5000 atm) and temperatures up to 10000k. This violent collapse leads to formation of hydroxyl radicals. There are various studies [61–66] confirming formation of hydroxyl radicals during cavitation phenomena e.g. using model reaction of the oxidation of aqueous KI solution at different operating conditions. Generally, cavitation is classified into four types as acoustic cavitation, hydrodynamic cavitation, optic and particle cavitation. However, only acoustic and hydrodynamic cavitation appear to have potential in terms of applications at industrial scale of operation.

2.5.1 Acoustic cavitation

In acoustic cavitation, the pressure variations in the liquid are effected using sound waves, usually ultrasound in the range of 16 kHz -100 MHz. The chemical changes taking place due to the cavitation induced by the passage of sound waves are commonly known as sonochemistry. There are excellent reviews reported on acoustic cavitation [67–72]. The important parameters affecting the performance of acoustic cavitation are intensity of irradiation, frequency of irradiation and initial radius of the nuclei. Figure 2.5 shows schematic of commonly used different acoustic devices such as ultrasonic horn, ultrasonic bath, dual/triple frequency cell

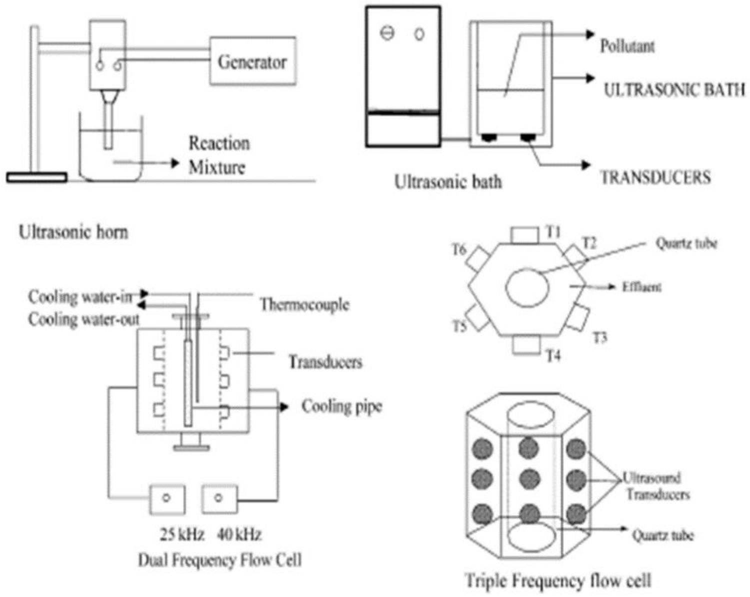

Figure 2. 5: Schematic representation of the equipments based on acoustic cavitations [73]

There are various studies reported on degradation of phenolics such as p-nitrophenol [74], 4,6-Trichlorophenol [75], phenol [76], pesticides such as methyl parathion [77], Alachlor [78], dyes such as brilliant green [79], enzymatic transesterification [80], depolymerization [81] by acoustic cavitation and also in combination with other methodologies to intensify the degradation. The majority of the studies reported by acoustic cavitation for degradation of various class of organic pollutants are mostly conducted on a lab scale with operating volume below ~1000 ml. There are scale up issues for implementing acoustic cavitation at industrial scale due higher frequency requirement which ultimately affects the cost of the treatment. Hence acoustic cavitation is not preferred over hydrodynamic cavitation for industrial wastewater treatment.

2.5.2 Hydrodynamic cavitation

Hydrodynamic cavitation can simply be generated by passage of fluid through constrictions such as orifice/venturi/vortex diode. When liquid passes through constriction, the kinetic energy/velocity of the liquid increases at the expense of pressure. If the throttling is sufficient enough to cause the pressure around the point of vena contracta to fall below the threshold pressure for cavitation, usually vapor pressure of the medium at the operating temperature, millions of cavities get generated [82]. Subsequently as the liquid jet expands, cavities collapse due to surrounding pressure leading to hot spot and extreme conditions of pressure, and temperature. The collapse pressure and temperature generated during cavitation are strong function of operating and geometric parameters [83]. The basic design criteria for any hydrodynamic cavitation reactor is to create pressure difference in the path of fluid by using constrictions [73,82,83]. Principally this can be achieved by devices with moving parts and without moving parts. The device with moving parts includes high-speed rotor stator assembly which is energy-intensive and does not suit for first choice cavitating device for wastewater treatment applications [84]. On other hand, the devices which do not include moving elements are further classified as linear and rotational flow devices which are considered cost-effective and hence preferred over the device with moving parts. The linear flow-based devices include orifice, venturi while rotational flow-based device include vortex diode which are used as cavitating devices for wastewater treatment.

The major advantages of hydrodynamic cavitation are energy efficient method for generation of cavitation resulting into *in situ* generation of oxidising species, no complex equipment required, negligible maintenance, ease of operation and relatively easy scale up. It can be retrofitted easily in existing wastewater treatment plant. These advantages make hydrodynamic cavitation as techno economically viable option for wastewater treatment. The subject and research is gaining attention in recent years for the removal of variety of pollutants apart from process intensification strategies. Some of the typical applications are discussed below.

2.5.2.1 Degradation of Dyes

Hydrodynamic cavitation is reported widely for the degradation of various dyes alone or in combination with other methodologies. Das et al. [85] reviewed dye degradation using hydrodynamic cavitation alone and in combination with other oxidation processes (HC/Ozone, HC/Fenton’s reagent, HC/Photocatalysis, HC/Hydrogen Peroxide) and suggested combined approaches give good synergism for dye degradation. Caliskan et al. [86] studied degradation of high concentrated azo dye RR180 by hybrid process of hydrodynamic cavitation (HC) and photocatalysis in a pilot reactor. Combined approach of HC + photocatalysis together showed better mineralization at 5 bar of inlet pressure with synergetic coefficients for COD and TOC removal as 1.48 and 1.17. Saharan et al. [87] reported effect of geometry of hydrodynamic cavitating devices such as orifice plate, circular venturi and slit venturi on degradation of orange-G. It was found that the slit venturi gives almost 50% higher degradation rate and cavitational yield among all three cavitating devices and geometry of cavitating device (flow cross sectional area, perimeter, shape, etc.) was found to be an important parameter in getting the maximum cavitational effect using hydrodynamic cavitation. In another study, saharan et al. [88] reported effects of various operating parameters such as inlet fluid pressure, cavitation number, solution pH and addition of H_2O_2 as a supplementary oxidizing agent on the degradation rates of Reactive Red 120 dye (RR120) using venturi and found degradation was influenced by acidic pH condition. Rajoriya et al. [89] reported decolorization of reactive blue 13 (RB13) using hydrodynamic cavitation (HC) and effect of geometrical parameters using eight cavitating devices i.e. Circular and slit venturi, and six orifice plates. Approximately 47% decolorization was obtained using slit venturi at pressure drop of 4 bar in acidic condition. In another study, Rajoria et al. [90] reported 100% decolorization of Rhodamine 6G (Rh6G) using hydrodynamic cavitation with circular and slit venturi and the combination of HC with ozone in almost 5–10 min with 84% TOC removal. Gore et al. [91] reported decolourization and mineralization of reactive orange 4 dye (RO4) using hydrodynamic cavitation (HC) in combination with other AOP's and suggested combination of HC with other oxidizing agents is better than the individual processes for the degradation of dye. Bethi et al. [92] reported combined process of hydrodynamic cavitation and packed bed hydro gel for higher removal of the crystal violet dye. S. Kumar et al. [93] reported degradation of methylene blue (MB) dye by using hydrodynamic cavitation combined with H_2O_2 and Bi-doped TiO_2 photocatalyst and found combination of hydrodynamic cavitation and H_2O_2 with high synergetic effect. Hiremath et al. [94] reported vortex flow-based cavitation for degradation of auramine O at (80-1200 ppm) with more than 75% dye degradation at lower concentration and lower pressure drop requirement than conventional cavitation devices. It is clear from most of the reported studies that for dye decolourization and degradation by hydrodynamic cavitation, higher extent of degradation obtained for combined approaches, for lower concentrations and acidic pH condition.

2.5.2.2 Degradation of Pesticides

The treatment of pesticide containing wastewater is subject of concern because of hazardous and carcinogenic nature. The pesticide residue finds way in wastewater via several routes and cavitation has been reported for degradation of various pesticides as advanced oxidation process. Patil et al. [95] reported degradation of imidacloprid by hydrodynamic cavitation using orifice and slit venturi with hybrid approaches. Slit venturi was found to be superior device with optimum operating pressure of 4 bar. Degradation favoured under acidic conditions and hydrodynamic cavitation with H_2O_2 results in complete degradation in 120 min. In another study, Patil et al. [96] reported degradation of methyl parathion using hydrodynamic cavitation with different process intensification approaches and more than 90% degradation of methyl parathion was achieved using combination of hydrodynamic cavitation with H_2O_2 and Fenton's reagent with 76% TOC reduction. Thanekar et al. [97] reported degradation of dimethoate (DM) using different approaches based on hydrodynamic cavitation. About 25% degradation was obtained by only HC while complete degradation of DM within 40 min by HC + Fenton approach was demonstrated. Joshi et al. [98] reported degradation of dichlorvos using hydrodynamic cavitation with different approaches. About 91.5% degradation in 60 min was obtained by HC + Fenton approach and degradation was enhanced in acidic condition. Panda et al. [99] reported degradation of Dicofol by using liquid whistle hydrodynamic cavitation reactor (LWHCR). Highest rate of Dicofol degradation was observed at an inlet pressure of 7 bar with 85% TOC removal in 60 min. Randhavane & Khambete, [100] reported degradation of Chlorpyrifos by hydrodynamic cavitation with hybrid approaches and found maximum degradation at 5 bar in acidic pH condition, while combined approach of HC + ozone resulted in complete removal in 45 min. Bhat and Gogate, [101] reported critical analysis of amines- and nitrogen-based dyes/pesticides degradation by AOPs such as ozonation, Fenton, photocatalysis, cavitation, UV and hybrid processes. It was observed that ozone is a highly reactive to most amines, dyes and pesticides, followed by Fenton processes. From reported studies it is clear that acidic condition favours pesticide degradation while higher pressure drop conditions are required for degradation in conventional devices. Further, hybrid approaches are found more suitable for degradation of pesticides from wastewater.

2.5.2.3 Degradation of Pharmaceuticals/ API Pollutants

Pharmaceuticals being widely used for human and veterinary purposes and in animal husbandry, are an important group of emerging pollutants and have recently been detected in water bodies generating significant concern about adverse impact on the people, living species and environment. Approximately 3000 different constituents are used as pharmaceutical ingredients, including antibiotics, antidiabetics, pain killers, contraceptives, lipid regulators, antidepressants, etc [102]. It is estimated that nearly half of the pharmaceutical wastewaters produced worldwide are released into the environment without any specific treatment [103]. Though the concentration of pharmaceuticals found in wastewater streams is very low, the impact on human health has a potential risk of developing antibiotic resistance. Typically, pharmaceutical ingredients are recalcitrant, and therefore, cannot be degraded in the conventional biological oxidation/ using treatment methodologies. Hence, it is essential to develope efficient technologies for the complete removal of pharma pollutants.

Recently, AOPs have shown considerable promise for the treatment of pharmaceuticals wastewaters. Hydrodynamic cavitation alone and its combination have been found suitable for possible commercial applications in wastewater treatment contaminated with API pollutants. Naddeo et al. [104] investigated the ultrasonic degradation of diclofenac as well as aerobic biodegradability. Ecotoxicity to fresh water and marine microorganisms prior to and after the degradation was evaluated. It was observed that ultrasound irradiation can be employed as a pre-treatment to biological treatment for the treatment of wastewater contaminated with pharmaceutical pollutants. Musmarra et al. [105] investigated the degradation of ibuprofen, an anti-inflammatory drug-using hydrodynamic cavitation, and 60% degradation was reported in 60 min using a convergent-divergent nozzle device. The antibiotic degradation of pollutant, sulfadiazine (SDZ) [106] was investigated using hydrodynamic cavitation and orifice device coupled with hybrid AOP of heterogeneous Fenton/ persulfate system. Bagal and Gogate, [107] reported degradation of Diclofenac sodium by hydrodynamic cavitation with different combined approaches using slit venturi. The maximum extent of degradation was obtained at 3 bar and at pH 4 while further combined approach of HC with UV/TiO_2/H_2O_2 resulted in maximum degradation as 95% with

76% reduction in TOC. Thanekar et al. [108] reported degradation of carbamazepine by hydrodynamic cavitation with different combined approaches using slit venturi. The maximum extent of degradation by HC alone was 39% while combined approach of HC+ H_2O_2+O_3 gives 100% degradation with synergistic coefficient more than 3. In another study, Thanekar et al. [109] reported removal of naproxen by hydrodynamic cavitation using hybrid approach of addition of H_2O_2 and ozone. About 29% naproxen degradation was obtained by only HC in acidic pH of 4 while combined approach of HC+H_2O_2 and HC+ozone resulted in 80% and 100% degradation in 120 min. The degradation of naproxen was also reported by our research group [110] using hydrodynamic cavitation using a vortex diode as a cavitating device and the cavitational yield using a vortex diode was ~5 times greater than that obtained using conventional devices. It is clear from reported studies that cavitation along with other AOPs perform better for degradation of pharmaceuticals. It is also evident that the newer form of cavitating device employing vortex flow appears to be a promising alternative to the existing conventional devices.

2.5.2.4 Degradation of Solvents

Solvents are used extensively in chemical and allied industries at various stages of operation and find their way in wastewater. The conventional methodologies are not able to remove solvents effectively and traces of solvents remain in wastewater even after treatment. Hydrodynamic cavitation, as a destructive method for organic pollutants, appears to be a suitable alternative for destruction of solvents in wastewater. There are very few studies reported for solvent degradation by cavitation, in general, and hydrodynamic cavitation, in particular. Suryawanshi et al. [111] reported degradation of acetone, methyl ethyl ketone, and toluene by HC with vortex diode and orifice. Approximately 80% degradation of toluene was accomplished by HC and there was ~10% improvement in degradation by means of aeration. Sarvothaman et al. [112] reported treatment of commonly used solvents such as acetone, ethyl acetate, and isopropyl alcohol by vortex-based HC. Influence of scale, pressure, concentration, the temperature was studied and per pass degradation factor was used instead of the conventional rate based kinetic model. While, most of the conventional methodologies have limitations of cost, scale up and secondary waste generation, hydrodynamic cavitation looks viable alternative for degradation of solvents from wastewater. In view of limited reported literature in this regard there is a need and scope for degradation studies of various class of solvents by hydrodynamic cavitation.

Hydrodynamic cavitation is also reported for various other applications such as biomass valorization [113,114], desulphurization of transportation fuels [115], microbial disinfection [116–120], food sterilization [121,122], microbial cell disruption [123] and so on.

2.5.3 Operating parameters of Hydrodynamic Cavitation

The performance of a hydrodynamic cavitation device is a function of several parameters such as pressure drop across the cavitation device, initial concentration of pollutant, temperature of liquid medium, pH, and dissolved gases [82,124,125]. A detailed literature review discussing the influence of various operating parameters on hydrodynamic cavitation, especially in wastewater treatment is provided below.

2.5.3.1 Operating pressure drop and inception of cavitation

In hydrodynamic cavitation, cavitation is expected to occur when local static pressure falls below vapour pressure due to constrictions in the path of fluid leading to formation vapour/gas filled cavities that subsequently undergoes implosion due to high surrounding pressure. The analysis of pressure drop and flowrate across cavitating reactor provides information on cavitating and non-cavitating regimes which is very important for finding optimum cavitation condition for the cavitating device and for the system. In general, the selection of operating pressure drop is in between the region of inception and choking cavitation regime which is typically characterized by cavitation number. Generally, in the case of linear flow devices such as venturi or orifice the occurrence of cavitation is analyzed on the basis of cavitation number while on other hand usual definition of cavitation number is not applicable in the case of vortex flow-based cavitation device for finding out inception of cavitation. Suryawanshi et al. [115] used square law to find out inception of cavitation in vortex diode and found inception at ~0.48 bar while Sarvothaman et al. [112] used stethoscope to monitor cavitation and indicated inception below 1 bar. Further Ranade et al. [126] carried out acoustic analysis using mobile phone and found inception in between 0.5-0.8 bar for the vortex diode. The conventional devices such as venturi and orifice report optimum pressure drop studies rather than inception. Saharan et al. [127] and Gore et al. [91] studied effect of pressure drop in the range 3-7 bar for circular venturi, while for orifice the effect of pressure drop was studied above 1 bar [95,98,128]. Though the experimental studies of conventional cavitation devices reported optimised pressure drop, there are no proper experimental guidelines for identification of inception. The determination of inception will help to select initial pressure drop condition operated in the cavitation regime. In general, inception of cavitation for vortex diode occurs at lower pressure drop than conventional orifice and venturi. Table 2.2 compares different reports on inception of cavitation and effect of pressure drop for different type of cavitation devices,

Table 2. 2: Effect of pressure drop and inception of cavitation in hydrodynamic cavitation

Sr.No.	Cavitation device	Pollutant	Inception/Pressure drop	Reference
1.	Vortex diode	10% v/V Octanol-Water	Inception of cavitation at ~0.48 bar	[115]
2.	Vortex diode	Acetone Ethyl acetate and Isopropyl alcohol	Inception < 1 bar	[112]
3.	Vortex diode	Not reported	Inception of cavitation between 0.5 and 0.8 pressure drop	[126]
4.	Venturi	Acid Red 88 Dye	Effect of pressure drop: 3-7 bar	[127]
5.	Venturi	Reactive orange 4 Dye	Effect of pressure drop: 3-7 bar	[91]
6.	Orifice	BTEX	Effect of pressure drop: 1-3 bar	[128]
7.	Orifice	Imidacloprid	Effect of pressure drop: 1-8 bar	[95]
8.	Orifice	Dichlorvos	Effect of pressure drop: 3-6 bar	[98]

2.5.3.2 Initial concentration of pollutant

Most of the literature reported on the effect of initial concentration in hydrodynamic cavitation uses power law for interpretation of kinetics of degradation. It has been observed that the rate of degradation decreases as the initial pollutant concentration increases. This is attributed to insufficient quantity of oxidizing species generated and the number getting increasingly limited as the concentration increases. The effect of concentration was reported to be significant in case of degradation of dyes Auramine O [94], Rhodamine 6G [90] and reactive blue 13 [89] while marginal change was observed in case of degradation of pesticides [95] with 8% degradation at 60 ppm and 13% degradation 20 ppm. It is seen that though the trend follows higher degradation at lower concentration, it also depends upon nature of pollutant and geometrical configuration of cavitating device used for treatment (Table 2.3).

Table 2. 3: Effect of initial concentration of pollutant in hydrodynamic cavitation

Sr.No.	Initial concentration	Cavitation device	Pollutant	Remarks	Reference
1.	10-50 ppm	Venturi	Rhodamine 6G	The rate of decolorization increases from 0.7×10^{-3} min^{-1} to 3×10^{-3} min^{-1} with a decrease in the concentration from 50 ppm to 10 ppm	[90]
2.	10-50 ppm	Swirling jet induced cavitation	Reactive brilliant red K-2BP	The degradation increased from 25 to 94 % with a decrease in the initial concentration from 50 to 10 ppm	[129]
3.	20-60 ppm	Orifice	Imidacloprid	8% degradation at 60 ppm, 13% at 20 ppm	[95]
4.	30-60 ppm	Venturi	Reactive blue 13	% Decolorization - 47% for 30 ppm and 19% for 60 ppm	[89]
5.	80-1200 ppm	Vortex diode	Auramine O	75% degradation at lower concentration and 17% degradation at higher concentration	[94]

2.5.3.3 Temperature

The operating temperature will change the vapour pressure, influencing the degradation behaviour as well as performance of hydrodynamic cavitation. Table 2.4 lists isothermal conditions for degradation of various pollutants. Wang and Zhang [130] reported effect of temperature on degradation of alachlor in the range 30-60 °C and found 40 °C as the optimum temperature and for temperatures >40 °C, degradation gets decreased that was attributed to formation of vapour cloud affecting the cavitational intensity. The degradation behaviour of carbamazepine studied by Braeutigam et al. [131] indicated decrease in the degradation above 25°C degradation. For degradation of 2,4-dinitrophenol, a temperature range of 30-40 °C was studied with optimum temperature of 35 °C [132]. Another study on dye degradation by Gogate and Bhosale [133] found decrease in degradation for Brilliant green dye when temperature was increased from 20 to 40 °C while marginal effect was observed in the case of Orange acid-II dye.

The optimum temperature varies from 20 to 40 °C based on degradation of pollutant. From literature it is observed that temperatures more than 40 °C would be detrimental for degradation performance due to formation vapour cloud affecting the intensity of cavitation while on other hand it will also depend on the physical properties of the pollutant. Sarvothaman et al. [112] reported that an increase in operating temperature enhances degradation rates for all solvents such as ethyl acetate, acetone, and isopropyl alcohol as a pollutant.

Table 2. 4: Effect of temperature on pollutant degradation in hydrodynamic cavitation

Sr.No.	Temperature range	Cavitation device	Pollutant	Remarks	Reference
1.	20-45 °C	Vortex diode	Acetone Ethyl acetate and Isopropyl alcohol	An increase in operating temperature enhancing degradation rates	[112]
2.	30-60 °C	Swirling jet induced cavitation	Alachlor	Cavitation is best performed at 40°C	[130]
3.	20 and >25 °C	Orifice	Carbamazepine	For temperature >25°C reduced degradation performance	[131]
4.	30-40 °C	Orifice	2,4-dinitrophenol	Optimum temperature 35°C	[132]
5.	20-40 °C	Orifice	Orange acid-II (OA-II) and Brilliant green (BG)	Optimum temperature 20°C	[133]

2.5.3.4 pH

The existence of a pollutant whether in molecular or ionic form is dictated by the pH of the liquid medium and the Pka value of the pollutant [124,134]. When pH<pKa, molecular form is predominant allowing molecules to migrate towards the hydrophobic interface. This migration enhances pollutant - radicals interaction produced by cavitation compared to pollutant remaining in bulk solution [135]. In contrast, when pH>pKa, the pollutant is predominantly found in ionic form and will tend to accumulate in bulk liquid. The free radicals are short lived and are not likely to effectively degrade pollutant moiety in the bulk liquid [135] since, only about 10% of the $^{\cdot}OH$ radicals generated in the cavity can diffuse into the bulk solution. The main effect of oxidation in cavitation is majorly contributed by $^{\cdot}OH$ radicals and half-life of $^{\cdot}OH$ radicals is 1×10^{-9} second [136].

Table 2.5 compares different studies on the effect of pH for the degradation of various pollutants in hydrodynamic cavitation. Saharan et al. [127] reported degradation of Acid Red 88 dye in the pH range of 2-11 and found about 92% decolourization at pH 2 while marginal improvement was observed at basic pH condition. For the degradation of dichlorvos, marginal improvement was found by lowering pH form 5.7 to 3 [98]. For degradation of methyl parathion, degradation increased from 19 to 38% when pH was changed to 2 from 8 [96]. Gore et al. [91] studied Reactive orange 4 dye degradation and found increase in decolorisation from 5 to 37% when pH was changed from 10 to 2. Capocelli et al. [134] found three times more degradation for pH<pKa of p-nitrophenol. It should be noted most of the studies report on pollutants containing only one functional group and reveal similar trend. However, API pollutants have complex molecular structure and contain many functional groups in a single compound with more than one pKa value. Therefore, the degradation behaviour in such cases is complex, varies with pH and with the nature of pollutant. Consequently, it is more difficult to predict the behaviour in the degradation.

Table 2. 5: Effect of pH on degradation of pollutants in hydrodynamic cavitation

Sr.No.	Operating pH	Cavitation device	Pollutant	Remarks	Reference
1.	2-11	Venturi	Acid Red 88	Enhancement in degradation at pH of 3	[127]
2.	3 and 5.7	Orifice	Dichlorvos	A marginal enhancement in degradation at pH of 3	[98]
3.	2.2-8.2	Orifice	Methyl parathion	Highest degradation at pH 3	[96]
4.	2-10	Venturi	Reactive orange 4 dye	Highest degradation at pH 2	[91]
5.	3.5, 5.5 and 8	Venturi	p-nitrophenol	Enhancement in degradation at pH of 3.5 and 5.5	[134]

2.5.3.5 Effect of dissolved gases/aeration

Dissolved gases play a crucial role in hydrodynamic cavitation by providing early inception of cavitation and improving the intensity of collapsing cavities. There are various studies reported on the effect of dissolved gases such as argon, helium, oxygen, and air on hydrodynamic cavitation to improve efficiency. For degradation of solvents, Sarvothaman et al. [112] reported doubling in per pass degradation factor for while Suryawanshi et al. [111] reported ~10 enhancement in degradation by combining cavitation with aeration. Thanekar et al. [137] reported ~10-12% enhancement in benzene degradation by aeration. The studies conducted on real effluent also show improvement in degradation by aeration/oxygen along with cavitation. Suslick et al. [65] reported the oxidation reaction of potassium iodide (Weissler reaction) in hydrodynamic cavitation using noble gases such as argon and helium. The study showed five-fold increase in potassium iodide oxidation when argon was used. The introduction of noble gases does not participate in radical generation but is expected to increase the intensity of collapse. There are very few studies reported on introduction of air/oxygen along with cavitation as part of process intensification and this needs to be investigated further for different pollutants. Table 2.6 compares the available data on the effect of gases/ aeration in hydrodynamic cavitation.

Table 2. 6: Effect of dissolved gases/aeration in hydrodynamic cavitation

Sr.No.	Cavitation device	Pollutant	Remarks	Reference
1.	Vortex diode	Acetone Ethyl acetate and Isopropyl alcohol	Doubling in the per pass degradation factor by aeration	[112]
2.	Vortex diode and Orifice	Acetone, methyl ethyl ketone (MEK), and toluene	~10% enhancement in degradation due to aeration	[111]
3.	Orifice	Benzene	~10-12 enhancement in degradation due to aeration	[137]
4.	Orifice	Real industrial effluent	Air and oxygen injections giving 15.5% and 42% COD removal	[138]
5.	Venturi	Textile dyeing industry (TDI) effluent	1. Colour reduction 17-28% 2. HC with oxygen (2 L/min)- 48% TOC, 33% COD, and 62% colour reduction 3. HC with ozone (3 g/h)- 48% TOC, 23% COD, and 88%, colour reduction	[139]
6.	Jet fluidizer	Potassium Iodide	1.The effect of different ratios of argon and helium gas quantified by the oxidation reaction of potassium iodide 2. Five-fold increase in the rate of oxidation of potassium iodide for argon	[65]

The above discussion largely covered the critical evaluation of general literature pertaining to the industrial wastewater treatment and hydrodynamic cavitation for the removal of organic pollutants. In the following sections, specific issues pertaining to the industrial wastewater treatment - removal of ammoniacal nitrogen, solvent degradation and API pollutant removal are further critically analysed for the research subjects of this study.

2.6 Removal of Ammoniacal nitrogen

Water quality and quantity are the major issues impacting human beings as well as the aquatic environment. Ammoniacal nitrogen is defined as the concentration of nitrogen compounds in wastewater that can be converted into ammonia. Conventional wastewater treatment methodologies mainly focus on COD (Chemical oxygen demand)/TOC (Total organic carbon) and BOD (Biological oxygen demand) removal while little attention has been given to ammoniacal nitrogen removal.

Nitrogen-containing compounds are one of the most important class of pollutant in wastewater treatment responsible for eutrophication and strongly affecting on dissolved oxygen content of water bodies leading to depletion of oxygen levels in water bodies. The primary sources of nitrogen in the environment are nitrogenous compounds of plant and animal origin, fertilizers through agricultural runoff, mineral deposits, and atmospheric lighting. The nitrogen in wastewater is found in various forms while ammoniacal nitrogen in wastewater is strongly affected by pH and temperature conditions. In the context of industrial wastewater, nitrogen in wastewater in monitored on the basis of ammoniacal nitrogen. The typical limit for ammoniacal nitrogen in wastewater is below 30-50 mg/lit [1]. There are many industries such as dyes, pigment, speciality chemicals, fertilizer, fishery that release wastewaters with high ammoniacal nitrogen and not meeting the discharge of permissible norms within prescribed limit by using conventional methodologies. Conventional methodologies which are widely practiced at the industrial scale are air or steam stripping and breakpoint chlorination [140]. Stripping causes free dispersion of ammonia into the surrounding environment affecting adversely ground-level air quality. While breakpoint chlorination is used for the removal of ammoniacal nitrogen, especially at a lower concentration as a polishing technique that also generates secondary waste. Both of these conventional methodologies have the drawback of secondary waste generation which affects the cost of the treatment. Apart from these methodologies, there are various physical, chemical, biological, or combinations of these methodologies have been used for the treatment of ammoniacal nitrogen in wastewater. Biological denitrification/nitrification, adsorption, chemical precipitation, ion exchange, biosorption, and reverse osmosis are commonly used methodologies in this regard. No studies have been reported specifically using hydrodynamic cavitation for the removal of ammoniacal nitrogen apart from the study reported by Patil and Bhandari, 2014 [141]. Table 2.7 lists some of the important studies on the removal of ammoniacal nitrogen from wastewater by various methodologies.

Table 2. 7: Removal of ammoniacal nitrogen from wastewater by various methodologies

Sr.No.	Methodology	Remarks	Reference
1.	Biological treatment	1. Discussion on conventional nitrogen removal biological methodologies (nitrification and denitrification), aerobic denitrification and other lithoautotrophic denitrification 2. Conventional biological methodologies requires more carbon source and are energy intensive 3. Methodologies such as partial nitritation, nitrifier denitrification, Anammox, and Canon as an alternative for conventional methodologies 4. Both conventional and newer methodologies are not able to operate effectively at the larger scale of operation	[142]
2.	Adsorption	1. Adsorbents: Shell, limestone, waste paper mixed with refuse concrete, refuse cement, nitrolite, charcoal-bio, and charcoal 2. NH_4-N removal efficiency for various mediums as I) Refuse cement and waste paper 0-13%, II) Shells 6-16%, III) Limestone 7-12%, IV) Nitrolite 65-75% V) Charcoal-bio 31-62% VI) Charcoal 11-32% 3. Nitrolite, charcoal, and charcoal-bio showed better removal efficiency	[143]
3.	Coagulation-flocculation	1. Coagulation–flocculation for slaughterhouse effluent using $Fe_2(SO_4)_3$, $Al_2(SO_4)_3$, and polyaluminium chloride 2. Initial concentration – 24mg/L 3. Aluminium sulphate and polyaluminium chloride shows <10% ammoniacal nitrogen removal	[144]

4.	Adsorption	1. Activated carbon, limestone, and a mixture of both materials for the removal of ammoniacal nitrogen from landfill leachate 2. Initial concentration – 1000 mg/L 3. 40% of ammoniacal nitrogen removal by activated carbon	[145]
5.	Adsorption	1. Fixed and fluidized bed ion exchange column using natural clay minerals, sepiolite and clinoptilolite for removal of ammonia 2. Clinoptilolite superior adsorbent for the removal of ammonia from an aqueous solution 3. For fixed bed study - 95–99 % removal, fluidized bed study- 70–85 % removal	[146]
6.	Ion exchange	2. Initial concentration -10-80 mg/L 3. For fine clinoptilolite column the capacity to 1 mg/l $NH4^+$ breakthrough was reached in 450 BV 4 4. For fine zeolite column the capacity of 1 mg/l $NH4^+$ breakthrough was reached in 350 BV	[147]
7.	Adsorption	1. Adsorbent: zeolite from Dogantepe region in Turkey 2. The highest adsorption capacity (1.08 mg $NH4^+$-N /g) at a pH of 4 3. 100 % removal for initial concentration of 5mg/L	[148]
8.	Adsorption	1. The removal of ammoniacal nitrogen (NH_4-N) using lab-scale downflow reed bed system for artificial landfill leachate 2. Initial NH_4-N of 150±5 mg/L 3. 44% removal in 180 min	[149]
9.	Microwave radiation	1. Initial NH_4-N concentration (500 -12,000 mg/L)	[150]

		2. 96-98% NH_4-N removal, 750 W MW power, pH 11, 3 min radiation time with aeration 2. Study on coke plant wastewater - >90% removal	
10.	Biological treatment	1. The modified zeo-SBR for ammoniacal nitrogen removal 2. Three sets of sequencing batch reactors, control, zeo-SBR, and modified zeo-SBR used 3. Zeolite- floc ammonium adsorption capacity - 6.0–7.4 mg NH_4 -N/g FSS 4. Control reactor - 70% total nitrogen removal 5. Modified zeo-SBR reactor - 82% total nitrogen removal	[151]
11.	Aeration and air stripping	1. Aeration and air stripping for nitrogen removal 2. 90% removal efficiency in 150 hours by aeration at pH 11.2 3. 90% removal efficiency in 7 hours by air stripping at pH 11.5	[152]
12.	Chemical precipitation	1. Chemical precipitation using Mg^{2+}: NH_4^+:PO_4^{3-} mol ratio of 1:1:1 at pH of 8.5-9 2. Initial NH_4-N concentration – 5618 mg/L 3. 98% removal within 15 min	[153]

In view of the limitations of conventional methodologies such as higher treatment cost, secondary waste generation, and high retention time, it is imperative to study viable alternatives and develop cost effective, sustainable newer methodologies for removal of ammoniacal nitrogen from wastewater.

2.7 Solvent degradation

Solvents play a vital role in most chemical and allied industries at various stages of operations such as reaction, separation, purification, drying, extraction, etc. Solvents as pollutants in the wastewater streams can be difficult to remove/degrade especially at a lower concentration by conventional methodologies. Wastewater with solvent having low biodegradability, adversely affects the performance of biological treatment process and even after secondary treatment there is a marginal change in the concentration of solvents in wastewater. Solvent waste is classified as hazardous and may have carcinogenic effects, at higher concentrations in wastewaters. In spite of the importance of the problem, not many reports are available on the removal of solvents, especially using cavitation. Only two studies have been reported on solvent degradation by hydrodynamic cavitation. Suryawanshi et al. [111] reported degradation of acetone, methyl ethyl ketone, and toluene by HC with vortex diode and orifice, and about 80% degradation of toluene was accomplished by HC and there was ~10% improvement in degradation by means of aeration. Sarvothaman et al. [112] reported removal of commonly used solvents such as acetone, ethyl acetate, and isopropyl alcohol by vortex-based HC. Influence of scale, pressure, concentration, the temperature was studied and per pass degradation factor was used instead of the conventional rate kinetic model and it provides a platform for the scale of up of HC device for treatment of effluent. While most of the studies reported on solvent degradation employ biological treatment, it requires high residence time and can be economically unviable. In view of limited studies available on solvent degradation by hydrodynamic cavitation and economically unviable conventional methodologies, it is imperative to study and develop cost-effective and sustainable methodology for solvent degradation. Table 2.8 lists some of the important work on solvent degradation.

Table 2. 8: Industrial wastewater treatment- Solvent degradation

Sr.No.	Methodology	Solvent studied	Remarks	Reference
1.	Hydrodynamic cavitation	Acetone, methyl ethyl ketone (MEK), and toluene	1. 80% degradation for toluene 2. The treatment cost for vortex diode eight times less than orifice 3. ~10% enhancement in degradation by cavitation with aeration	[111]
2.	Hydrodynamic cavitation	Acetone, ethyl acetate, and isopropyl alcohol	1. Effect of pressure drop (150 to 300 kPa), temperature (20 to 45 °C), concentrations (1000 to 50 000 ppm), 2. Per pass degradation model developed 3. Aeration doubled the per-pass degradation factor 4. Ethyl Acetate degrade 4 times faster than acetone and 1.5 times faster than IPA 6. Per-pass degradation factor decrease with the scale of the cavitation device	[112]
3.	Adsorption + Biological treatment	Butanol octanol	1. Granular activated carbon (GAC) and exogenous hydrogen (EH2) 2. Coupling of EH2 and GAC increased methane production and COD removal	[154]
4.	Biological treatment	DMF	1. Mesh-filtration bioreactor for treatment of DMF	[155]

			2. Initial DMF concentration 1000 mg/L, retention time 5-2.5 days 3. More than 98% DOC and 45% nitrogen removal at pH 3	
5.	Adsorption + Biological treatment	DMF	1. Immobilization of microorganisms in spherical PVA hydrogel for DMF degradation 2. Isolation of DMF-decomposing bacteria - Bacillus cereus D-1 3. Efficacy tested at 1 kg/m^3/day	[156]
6.	Biological degradation	DMF	1. DMF degrading bacteria DMF-3 belonging to Paracoccus sp. was enriched and isolated from activated sludge 2. DMF initial concentration -5000-60,000 mg/L 3. Removal of DMF - 98% in 84 h 4. Dimethylamine main degradation product	[157]
7.	Catalytic wet air oxidation	DMF	1. Wet air oxidation of DMF using catalysts (platinum, palladium, and ruthenium) supported on TiO_2 or ZrO_2 2. Intermediates - Dimethylamine (DMA), methylamine (MA), and ammonium, formic acid 3. Initial DMF concentration (5000 mg/L)	[158]

			4. TOC removal 38-89% and total nitrogen removal 13-55% in 6 hours	
8.	Biological treatment	DMF	1. Paracoccus sp. MKU1 and MKU2 for DMF degradation 2. DMF degradation by MKU1 (86.59%) and (80%) by MKU2	[159]
9.	Biological treatment	Cyclohexanone and cyclohexanol	1. Activated sludge collected from caprolactam manufacturing unit 2. Biodegradation of anone and anol, ~90% COD reduction	[160]
10.	Biological treatment	Acetone, cyclohexanol, and N-methyl pyrrolidone	1. Review on genus Alicycliphilus, for xenobiotic biodegradation such as industrial solvents (acetone, cyclohexanol, and N-methyl pyrrolidone), aromatic hydrocarbons 2. A cyclohexanol degradative pathway has been proposed	[161]

From Table 2.8, it is evident that degradation of solvents is mostly reported using biological treatments. In view of the limitations such as high cost, high residence time and adverse impact due to temperature fluctuations, it is imperative to study destructive methodologies for degradation of solvents in wastewater, especially for lower concentrations.

2.8 Degradation of API Pollutants

The pharmaceutical contaminants are found in almost every aquatic domain of environment. There are no proper guidelines and regulations worldwide for pharmaceuticals especially in context of wastewater treatment.

Compounds which are active pharmacologically, resistant to degradation, persistent in aqueous systems, exhibit harmful effects in organisms, and also negatively impact human health were designated “Active Pharmaceutical Ingredients” [162,163]. Pharmaceuticals cannot be classified as group of homogeneous compounds. They are highly polar, having complex chemical structure and multiple ionization sites. Many pharmaceutically active compounds have been detected in water such as anti-inflammatories and analgesics, antibiotics, antiepileptics, antidepressants, lipid lowering agents, antihistamines, β-blockers and other substances (barbiturates, narcotics, antiseptics, and contrast media). The conventional methodologies have severe limitations for the removal of API pollutants from wastewater especially at different levels of concentrations, and there is need to devise a strategy for the removal/degradation of these emerging class of pollutants.

2.8.1 Removal of ciprofloxacin from wastewater

Ciprofloxacin belongs to the class of antibiotics. In recent years, antibiotics in wastewater are considered an emerging class of persistent organic pollutants that are adversely affecting the aquatic environment. The term antibiotic is known as a class of any organic molecule that inhibits or kills the bacterial infection of the targeted source. The consumption of antibiotics is predominantly found in human medicine, veterinary medicine, and agricultural applications which are hot spots of antibiotic sources releasing a major part into water bodies of environment. Fluoroquinolones is a class of antibiotic that contributes about ~7% of consumption in human medicine among all antibiotics [164] and due to their high hydrophilic nature, it is found almost in every domain of the water body. The antibiotic ciprofloxacin belongs to the class of fluoroquinolones which is second-generation broad-spectrum antibiotic effective against both gram-positive and gram-negative bacterial infection. The study reported on the occurrence of antibiotics in wastewater by Bhagat et al. [165] shows that ciprofloxacin has the highest concentration in raw wastewater in India among all antibiotics and is in the range of 28-31 mg/L. Another study reported by Balakrishna et al. [166] found that the concentration of ciprofloxacin along with some antibiotics in Indian wastewater treatment plants is 40 times higher than in other parts of the world. The earlier studies showed the occurrence of antibiotics in the range of ng/L to ug/L, but due to the massive consumption of antibiotics in recent years worldwide, the occurrence range in wastewater is shifted to significantly higher range. There is a need for a sustainable methodology for the removal/degradation of these persistence class of organic pollutants from wastewaters. Conventionally, physical, chemical, and biological methodologies or hybrid approaches are practiced for the degradation of ciprofloxacin from wastewater. Table 2.9 lists important reports on ciprofloxacin degradation by various methodologies. Most of the reported studies for CIP removal/degradation are by adsorption, photocatalysis and hybrid approaches such as fenton, electrochemical, acoustic cavitation, oxidizing agents. The reported literature studies typically employ lower concentration ranges and very few studies report higher concentration of the order of 100 mg/L [167,168]. For hydrodynamic cavitation, only one study has been reported recently by Mukherjee et al. [169] using rotating hydrodynamic cavitation device which is more energy intensive and may not be a suitable option for larger scale of operations.

Table 2. 9: Degradation of ciprofloxacin from wastewater by various methodologies

Sr.No.	Methodology	Initial CIP concentration	Remarks	Reference
1.	Hydrodynamic cavitation	50 µg/L	1. Rotating Hydrodynamic Cavitation (RHC) reactor 2. 44.8% CIP degradation in 60 min 3. RHC with O_3 (0.75 g/h), H_2O_2 (0.3 g/L) and Fenton's reagent (1:3) resulted in 91.4%, 85.6%, and 87.6% degradation in 30 min 4. HC+H_2O_2 (0.3 g/L) suitable combination	[169]
2.	AC + Enzymatic degradation	10 mg/L	1. CIP degradation 51% at 0.02% (w/v) enzyme loading, 60 °C temperature, power input 75 W, 22 kHz frequency, 50% duty cycle, and agitation 200 rpm 2. Ultrasonication with stirring 51% degradation, Ultrasonication without stirring 8% degradation in 5 h, and Conventional stirring method 16% degradation in 20 h	[170]
3.	Acoustic cavitation	1-100 µM	1. Ultrasonic degradation at two frequencies 20 kHz (50 ml) and 620 kHz (125 ml) 2. 1–100-fold faster degradation at 620kHz 3. The difference is less pronounced at 20kHz	[171]

4.	Sono-Fenton process	100 mg/L	60% degradation in 60 min	[167]
5.	Ozonation	15 mg/L	1. 95% CIP degradation in 60-75 min 3. 17 degradation products determined by HRMS 4. Ciprofloxacin degradation shows to occur at least at two functionalities of the molecule (1) at the piperazinyl substituent (2) at the quinolone moiety	[172]
6.	UV-C-H_2O_2	10 mg/L	1. Complete degradation of CIP in 15 min, ($[H_2O_2]$ = 10 mg/L) 2. 40% toxicity reduction towards D. Magna by UV-C process	[173]
7.	Biological treatment	0.5 mg/L	1. Ciprofloxacin and nitrates removal by 3D-BER system 2. More than 90% reduction in 28 hours	[174]
8.	UV/chlorine	10µM	1. 41.2% CIP degradation by UV photolysis and 30.5% by dark chlorination in 30 min 2. 98.5% of CIP degradation by UV/chlorine process in 9 min	[175]
9.	A review on occurrence of CIP	28–31 mg/L	1. Review on occurrence, consumption patterns of different types of antibiotics in wastewater 2. Ciprofloxacin has highest concentration among all the ABs	[165]

			with 28–31 mg/L in the raw wastewater of the Indian subcontinent	
10.	UV/$S_2O_8^{2-}$	10mg/L	98% CIP degradation in 120 min	[176]
11.	Electrochemical	10-100 mg/lit	1. The electrochemical oxidation using a SnO_2-Sb/Ti electrode 2. For CIP (50 mg/L) – 99.5% CIP removal and 86% TOC removal	[168]
12.	Adsorption	5 mg/L	1. Waste palladiums for CIP removal 2. ~30% CIP degradation in 24h @ pH 3.6 3. For biogenic palladium, CIP removal is 87.70% in 24h	[177]
13.	Adsorption and electrochemical	10 mg/L	1. SI-Ti_3C_2Tx MXene nanosheets used 2. 90% CIP removal in 15-20 min at pH 5.5 3. Regeneration by electrochemical approach	[178]
14.	Adsorption	4 mg/L	1. Activated carbon shows best adsorption capacity 1.86 mg/g 2. 90 % CIP removal in 200 min	[179]
15.	Photocatalysis	10 mg/L	1. Catalyst: Fe_3O_4/Bi_2WO_6, light source: λ > 420 nm, adsorbent dose: 30 mg, 100 ml volume 2. 99.7% CIP degradation in 25 min	[180]
16.	Photocatalysis	10 mg/L	1. Catalyst: CDs/$Bi_4O_5Br_2$, light source: λ > 400 nm, 50 ml volume	[181]

			2. 98% CIP degradation in 120 min	
17.	Photocatalysis	10 mg/L	1. Catalyst: g-C_3N_4/$Bi_4O_5Br_2$, light source: λ > 400 nm, adsorbent dose: 50 mg, 100 ml volume 2. 90 %CIP degradation in 75 min	[182]
18.	Acoustic cavitation	0.15 - 15 mg/lit	Favourable frequency - 544 kHz with cavitational yield $1.3\pm0.3 \times10^{-10}$ mol/J	[183]

In view of the limited literature on CIP degradation, it is essential to evolve newer methodologies alone or in combination to provide cost effective viable alternative in wastewater treatment.

2.8.2 Removal of metformin from wastewater

Metformin ($C_4H_{11}N_5$) is an oral antihyperglycemic drug used for the treatment of diabetes. It is a highly polar compound with log P value (-1.4) and a pKa value of 12.4 [184]. The consumption of metformin is very high across the globe, due to increased diabetes. As metformin is not readily biodegradable, most of the conventional biological methodologies are not suitable for degradation of metformin. Due to continuous influx into aquatic bodies despite of treatment by various methodologies, metformin is considered as a pseudo persistent in the aquatic environment. A study reported on occurrence of metformin in various water matrices by Bradly et al. [185] shows more than 80% detecting frequency among various pharmaceuticals in the concentration range 1-10000 ng/L. Janka et al. [186] reported degradation of metformin by hybrid biological treatment employing 4 mg/L initial metformin concentration and found a very high residence time requirement for its degradation. Treatment technologies such as adsorption, photocatalysis, Fenton, UV, and ozone are not effective and/ or are cost intensive approaches. Metformin degradation has not been reported by hydrodynamic cavitation. Table 2.10 compares the degradation/removal by different methodologies.

Table 2. 10: Metformin degradation from wastewater by various methodologies

Sr.No.	Methodology	Initial MTF concentration	Remarks	Reference
1.	Biological treatment	4 mg/L	1. Metformin degradation by combined anaerobic and aerobic biofilm reactor 2. MTF degradation = 84% in anaerobic and 98% in aerobic stage, Guanylurea 98% degradation 3. Without adaptation of culture requires 60 days for 50% metformin degradation while, with culture adaptation 100% metformin degradation in 4 days	[186]
2.	Electro-Fenton process	5 mg/L	1. Boron-doped diamond as anode and carbon felt for the cathode for current generation 2. 99.57 % MTF degradation in 27 min	[187]
3.	Photocatalysis	2-10 mg/L	1. Radiation intensity of 228 µW cm^{-2} 2. MTF removal - 98% for 2 mg/L, 72% for 10 mg/L using modified TiO_2 3. TOC removal - 41% after 60 min	[188]
4.	Adsorption	40 mg/L	1. Adsorbent: Graphene oxide (GO), capacity – 50.47 mg/g 2. 80% MTF removal in 20 min	[189]

5.	Gamma radiolysis	200 µmol/L	1. Hydroxyl free radical-induced oxidation of metformin 2. Four oxidation products identified as MTFOOH, MBG, 4,2, 1-AIMT and 2,4-AMT	[190]
6.	Photocatalysis	1-10 mg/L	1. Photocatalysis using TiO_2 with Calotropis gigantea leaf extract for MTF degradation 2. Catalyst (CG-TiO_2), dosage 0.5–2.0 g/L, pH 3-7 3. 97% metformin degradation in 240 min under visible light	[191]
7.	Adsorption	10 mg/L	1. Adsorbent: Fe-ZSM-5 (Fe-Z) zeolite 2. 95.7 MTF removal at pH 8.33 with 1.1 g/L Fe-Z	[192]
8.	Photolysis, photocatalysis, ozonation, and chlorination	10 mg/L	1. For Chlorination and ozonation 60% MTF degradation 2. For direct photolysis (UV-C) and heterogeneous photocatalysis (TiO_2/UV-C), MTF degradation 9-31%	[193]
9.	Photo-Fenton process	2 µM	24% MTF degradation in 60 min by UV 254/H_2O_2/Fe (II) treatment	[194]
10.	UV/H_2O_2	4-6 ug/L	1. Degradation rate constant of metformin using polychromatic medium-pressure (MP) lamp with MilliQ water matrix is 4×10^4 cm^2/mJ	[195]

			2. For monochromatic LP (LP) lamp with MilliQ water matrix and addition of 10 mg/L H_2O_2 is 37×10^4 cm^2/mJ 3. For polychromatic medium-pressure (MP) lamp with MilliQ water matrix and addition of 10 mg/L H_2O_2 is 55×10^4 cm^2/mJ	
11.	Review on pharmaceuticals occurrence	1-10000 ng/L	1. 38 surface water streams assessment by using 14 target-organic methods (719 compounds). 2. Most frequently detected two pharmaceuticals (caffeine, metformin 25 sites) with detection frequencies ranging 66−84% of all sites	[196]
12.	Review on pharmaceuticals occurrence	1-10000 ng/L	1. Five biweekly water samples from 59 small Piedmont (United States) streams were analyzed for 108 pharmaceuticals and degradates using HPLC-MS 2. MTF was detected in 89% of samples and at 97% of sites	[185]

In view of the limited literature, in general, and no reports on application of cavitation for the degradation of metformin, there is a need for the development of sustainable and cost-effective methodology for complete degradation of metformin.

2.9 Gaps in the literature

The literature on industrial wastewater treatment for the removal of organic pollutants clearly reveals the following gaps in the research:

1. Most of the conventional methodologies have major limitations in terms of efficacy for the removal of organic pollutants, higher cost of treatment and problems of secondary waste generation.
2. Limited research in the area of application of hydrodynamic cavitation in wastewater treatment
3. Little or no comparison of different reactor designs for the removal/ degradation of different organic pollutants and possible industrial applications.
4. Studies on newer type of cavitation reactors employing vortex flow (vortex diode) are lacking.
5. Intensified hydrodynamic cavitation processes need more research, especially for the degradation of organic pollutants.
6. An important industrial wastewater treatment problem of removal of ammoniacal nitrogen has not been discussed in detail using hydrodynamic cavitation.
7. Important class of organic pollutants such as solvents, API pollutants, especially antibiotics, and drugs like metformin are not investigated for their removal using hydrodynamic cavitation. In view of the low concentrations and importance of destroying these harmful pollutants, application of hydrodynamic cavitation can be crucial in such cases and needs to be investigated in detail.
8. Newer alternatives to the existing wastewater treatment processes need to be explored.

In view of the gaps in the research in the existing literature, the present research mainly focuses on the important issues of the removal of ammoniacal nitrogen from industrial wastewaters, removal of solvents from industrial wastewaters and removal of API pollutants-one from the class of antibiotics (Ciprofloxacin) and one from the class of antidiabetic (Metformin). A new alternative, in the form of solvent assisted cavitation is also explored for the removal of organic pollutants. The studies have been carried out on synthetic wastewaters for specific organic pollutants and important results are also validated on real industrial wastewater treatment. A detailed cost analysis is carried out to evaluate the techno-economic feasibility of the process apart from evaluating viability of using newer types of cavitation devices such as vortex diode. The research intends to provide newer insights into the practical aspects of hydrodynamic cavitation, process intensification of cavitation processes and in degradation of refractory organic pollutants.

Based on the above the research gaps the following objectives identified;

Objectives

- Development of newer cavitation methodologies for removal of organic pollutants, ammoniacal nitrogen, solvents and API pollutants using mainly hydrodynamic cavitation and also process intensifications.
- Study on effect of reactor geometry, nature of organic pollutants, nature of intensification, kinetics of degradation, mathematical modeling, and optimization of process.
- Techno-economic feasibility studies.
- Newer process development for industrial wastewater treatment.

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Chapter – 3

Analytical Techniques and Experimental

Chapter 3

Analytical Techniques and Experimental

This chapter provides brief discussion on the various analytical techniques used to carry out the research work. The analysis included mainly Spectrophotometer, Total Organic Carbon Analyzer (TOC), Fourier Transform Infrared Spectroscopy (FT-IR), and High Performance Liquid Chromatography (HPLC). A brief discussion is also provided on the hydrodynamic cavitation experimental set up and scale-up aspects.

3.1 Spectrophotometer

Spectrophotometer is used in chemistry, physics, biochemistry, clinical, and materials testing labs for quantitative measurement of the transmission or reflection properties of materials as a function of wavelength. The spectrophotometer is of two types: single beam or double beam spectrophotometer. Single beam spectrophotometers are cost effective and have greater sensitivity. Single beam spectrophotometer uses a reference standard to measure light intensity for measurement. Double beam spectrophotometers are more stable and easier to use. In this spectrophotometer, the beam is split, one passed through standard and other one is passed through sample solution to compare light intensities. The basic elements of spectrophotometer consists of a light source, a digital display, a monochromator, a wavelength sector to transmit a selected wavelength, a collimator for straight light beam transmission, photoelectric detector and a cuvette to place a sample. The sample is placed between spectrometer and photometer, a beam passes through sample, the photometer measures the intensity/amount of light and delivers a voltage signal to the display response[1].

Photometry: When beam of light is passed through solution, the absorbance is measured at specific wavelength. The monochromators (filter) are used to separate light at specific wavelength from source of light such as tungsten filament lamp, deuterium lamp or xenon lamp [2].

The intensity of absorption is given by,

$T = I/I_0$

Where, I_0 is initial intensity of light and I is intensity of transmitted light

The relation between absorbance, pathlength and concentration of analyte is given by Beer-Lamberts law,

$A = \varepsilon\lambda \cdot c \cdot d$

$\varepsilon\lambda$ = Molar absorptivity, in l/mol x cm

d = Path length of the cell, in cm

c = Concentration of the analyte, in mol/l

Figure 3. 1: Spectrophotometer (Spectroquant® Pharo 100, Merck)

Figure 3.1 shows the picture of spectrophotometer used in the present study. Spectroquant® Pharo 100 (Merck) was used for the measurement of chemical oxygen demand and ammoniacal nitrogen by using photometric test kits of Merck. The spectrophotometer consists of various modes such as concentration, absorbance, transmission, multi wavelengths, scans and kinetics in absorbance or transmission mode. The wavelength range was 320-1100 nm and tungsten halogen lamp as a light source was used.

3.1.1 Chemical oxygen demand (COD)

The chemical oxygen demand is the amount of oxygen required to oxidize organic as well as inorganic matter present in wastewater, expressed in mg/L. The COD value required as per the pollution control norms for the discharge of most of the industrial wastewaters is below 250 mg/L [3]. The COD is often measured using a strong oxidant (e.g. potassium dichromate, potassium iodate, potassium permanganate) under acidic conditions. In the present study, COD was measured by using Spectroquant® COD "solution A", which consist of $HgSO_4$ in combination with Spectroquant® "solution B" which consist of $K_2Cr_2O_7$ with concentrated H_2SO_4 and using reflux apparatus TR 320 Spectroquant® for 120 min at 148°C. The quantity of solution A and B Spectroquant® required is specific for different COD ranges (10-150 mg/L, 100-1500 mg/L and 500-10000 mg/L). After digesting the sample (Solution A+ Solution B + treated sample) for 120 min at 148°C, it was analysed photometrically on Spectroquant® Pharo 100 in concentration mode for COD measurement.

3.1.2 Ammoniacal nitrogen (NH_4-N)

Ammoniacal nitrogen is a measure for the nitrogenous organic matter as ammonia, a toxic pollutant. The typical discharge limit of ammoniacal nitrogen for industrial wastewater is below 30-50 mg/L [3]. Ammoniacal nitrogen was measured photometrically by Spectroquant® Pharo 100 using Spectroquant® NH_4-N solution A and solution B (2-150 mg/L). The procedure involves addition of solution A, solution B and treated sample. After shaking, sample was kept for 15 min at room temperature and NH_4-N was measured photometrically.

3.2 Total Organic Carbon Analyzer (TOC)

TOC analyzer provides measurement of total carbon content in wastewater. In TOC analyzer, complete oxidation of organic molecules from water takes place to produce carbon dioxide which is measured in the form of carbon concentration, by various detection methods such as non-dispersive infrared (NDIR), direct conductometric (Non-selective Conductometric), membrane conductometric detection (Selective Conductometric). NDIR detector measures CO_2 from gaseous phase while conductometric detector is used for liquid phase [4].

Total Organic Carbon Analyzer (TOC) (Figure 3.2) from SHIMADZU CORPORATION, Model: TOC-L (Serial No. H54435301086) with auto sampler, Model: ASI-L (Serial No. H57405300409) was used for measurement of TOC [5].

Figure 3. 2: TOC Analyzer (TOC-L, SHIMADZU)

The total carbon (TC) is collective form of organic (TOC) and inorganic carbon (IC) and relation between them is given as TOC = TC-IC. For measurement of total carbon, sample is introduced in the combustion tube which is heated at 680°C. The carrier gas (flow rate of 150 ml/min) carries combustion products to dehumidifier where gas is cooled and dehydrated followed by passing halogen scrubber to remove halogens. Finally, carrier gas delivers combustion products to non-dispersive infrared gas analyzer where carbon dioxide is detected. The IC is measured by acidifying sample with small amount of hydrochloric acid to obtain pH less than 3 where all carbonates are converted to carbon dioxide. TC-IC method was used for the measurement of TOC for all the samples after the calibration using the standards.

3.3 Fourier transform infrared spectroscopy (FT-IR)

FT-IR is used for the determination of functional groups present in the sample. IR radiation is passed through sample where light gets absorbed and transmitted through the sample. The resulting spectrum represents molecular fingerprint of sample. IR region lies between visible and microwave portion of electromagnetic spectrum. The typical range of IR region is 12800 ~ 10 cm^{-1} which is further divided into three regions: near-infrared region (12800 ~ 4000 cm^{-1}), mid-infrared region (4000 ~ 200 cm^{-1}) and far-infrared region (50 ~ 1000 cm^{-1}). In IR spectroscopy, when sample is exposed to radiation source, the selective absorption of light of specific wavelength leads to changes in dipole moment of molecules. The vibrational energy changes from ground state to excited state. The frequency of absorption peak is determined by the vibrational energy gap. The intensity of peaks gives information about change in energy level of molecule. Various forms of the analysis are, 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. Depending upon the application of FTIR, various sources and detectors are used.

The commonly used IR region is (4000 ~ 400 cm^{-1}) because absorption of most of the organic and inorganic ions takes place in this region. The region between 400 cm^{-1} to 1500 cm^{-1} is called finger print region because it is difficult to identify functional groups in this region due to unique patterns while region between 1450 cm^{-1} to 4000 cm^{-1} is called frequency region where most of functional groups are identified at specific wavelength. FT-IR is used for analysis of gas, solid and liquid samples [6].

In present work, for identification of functional groups, FTIR-2000 (Perkin Elmer, USA) was used, with ATR mode for mid-IR spectra in the range 400 to 4000 cm^{-1}.

3.4 High Performance Liquid Chromatography (HPLC)

HPLC was used for the analysis of various organic pollutants. The detection in HPLC is based on the distribution of analyte between stationary and mobile phase. The intermolecular interactions of analytes with stationary phase defines the elution time of different constituents of the sample. HPLC system has the following components: a solvent reservoir, a pump, an injection valve, a column, a detector unit and a data processing unit. The sample is injected into the column with the help of sample injector, the separation occurs in column, and depending upon elution time, each analyte is detected by detector (e.g. UV detector). Further signals are processed and recorded by data processing unit [7].

HPLC (Agilent, 1260 infinity series) was used for the analysis of organic pollutants for measurement of their concentration and also for the identification by products after the treatment. The details of the instrument are given below:

3.4.1 Column

Two columns, SHIMADZU, C-18 column (Particle size 5µm, Dimensions 250×4.6 mm) and Thermo scientific Hypersil GOLD, C-18 column (Particle size 5µm, Dimensions 250×4.6 mm) were used for the analysis.

3.4.2 Injector

Agilent 1260 infinity manual Injector (G1328C, 1260 Man. Inj.) was used. Sample was loaded into the external 20 µl sample loop through the injection port at the front of the valve which is mounted on a steel mounting pole [8].

3.4.3 Detector

Agilent variable wavelength detector (G1314F, 1260 VWD) with radiation source deuterium-arc discharge lamp for the ultraviolet (UV) wavelength range from 190 to 600 nm was used [9].

3.4.4 Pump

Agilent 1260 infinity quaternary pump (G1311B, 1260 Quart Pump) with flow range 0.2 - 10.0 mL/min and pressure operating range up to 60 MPa (600 bar, 8700 psi) up to 5 mL/min and operating range up to 20 MPa (200 bar, 2950 psi) up to 10 mL/min was used [10].

3.5 Experimental

Figure 3.3 shows the photo of hydrodynamic cavitation pilot plant (capacity 1m^3/h) and a block diagram is provided in Figure 3.4. The experimental set up consists of a 50-liter storage tank with conical bottom. The discharge line of the tank was connected to the suction line of the vertical multistage 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 through Y type strainer and flow is controlled by ¾” NB valves (valve industries ltd) and nominal pipe diameter was ¾”. The Flow transmitter (KROHNE, H250) was used to measure flow in the main line while the pressure transmitter (Honeywell ST 700) was provided at both upstream and downstream section of the cavitation reactor to measure the pressure. Temperature was measured using RTD (EUREKA Eng. Enterprises India; 0–200°C) while temperature was controlled using recirculating chiller (JULABO FL1701). The Horner make HMI display was used for data logging. For aeration, the vertical cylindrical tube was inserted into the tank before sending fluid through the cavitation reactor which was connected to the air pump (SOBO AQUARIUM SB-9905, 2 Nozzle, 4.2W, Max. 5.5 L/min × two output) smoothly by silicone tubing with the provision of air flow rate control by small adjusting valve. Two cavitating devices were used, orifice (3 mm circular hole, MOC – SS316) and vortex diode (Chamber diameter 66 mm, throat diameter 11 mm, MOC – Aluminium/SS316). The entire assembly was mounted on a carbon steel powder-coated skid with wheels. All the experiments were performed in batch mode of operation and samples were withdrawn at periodic intervals for analysis. Figure 3.5 shows photos of lab scale vortex diode of capacity 1m^3/h and scaled up vortex diode (20 and 40 m^3/h capacity.

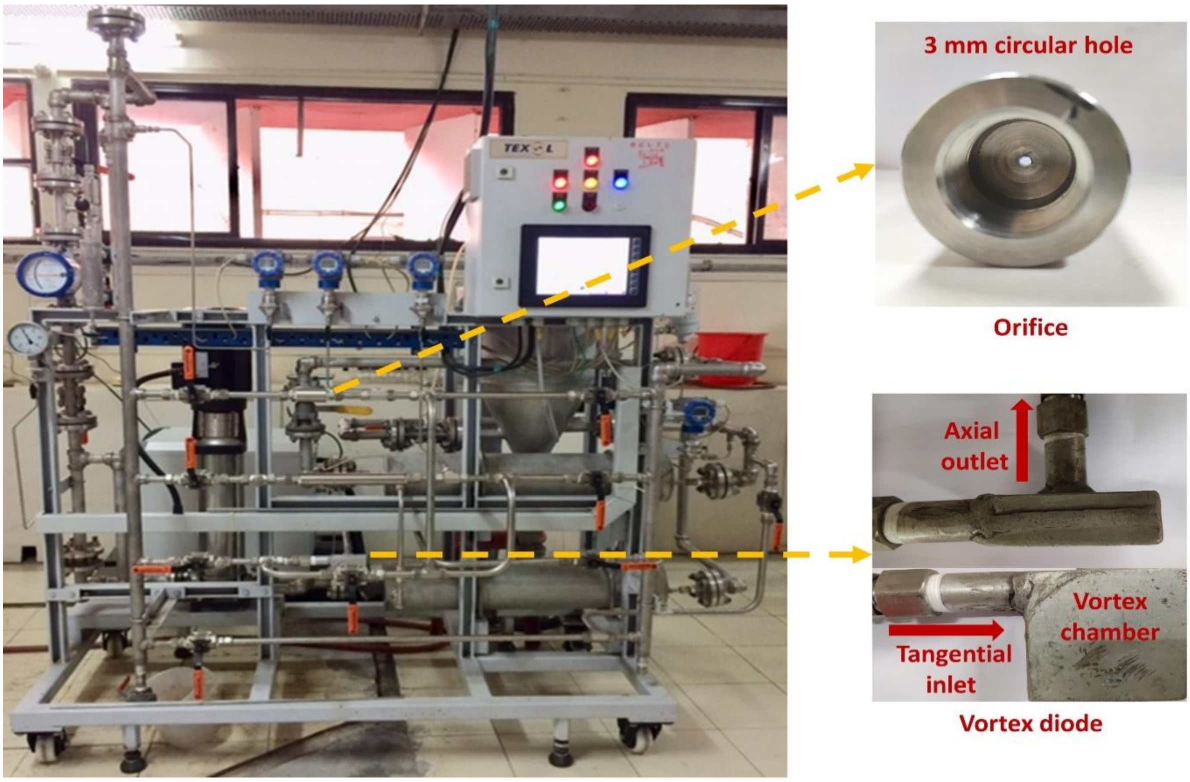

Figure 3. 3: Hydrodynamic cavitation pilot plant (1m^3/h)

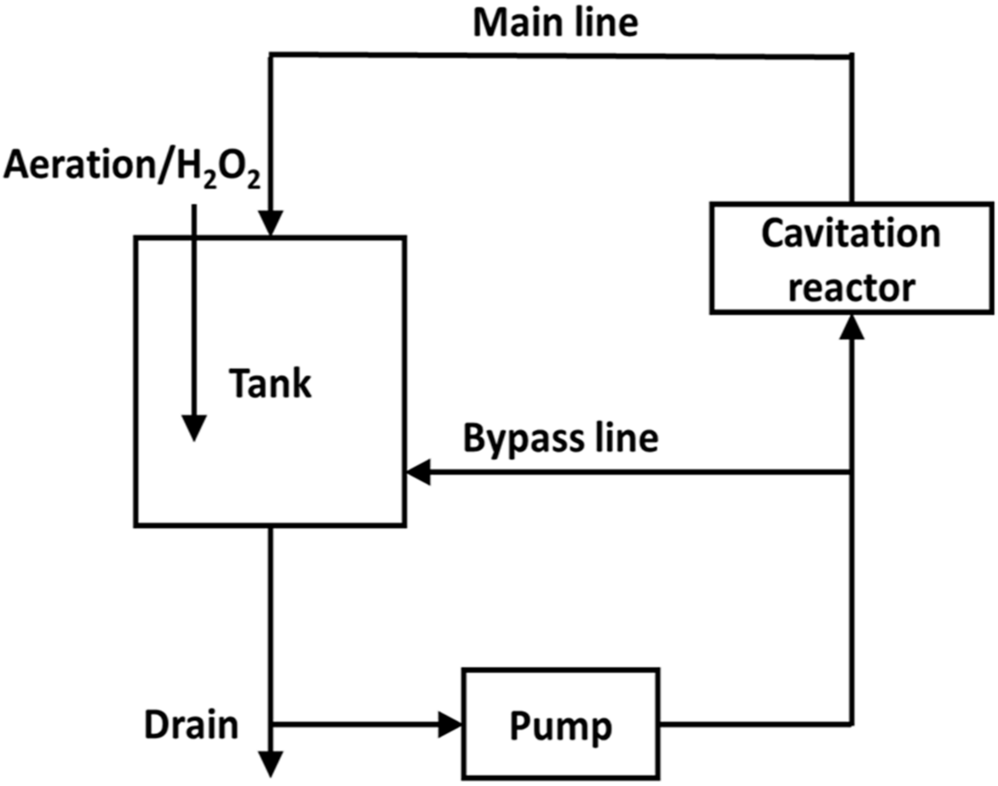

Figure 3. 4: Block diagram of experimental set up

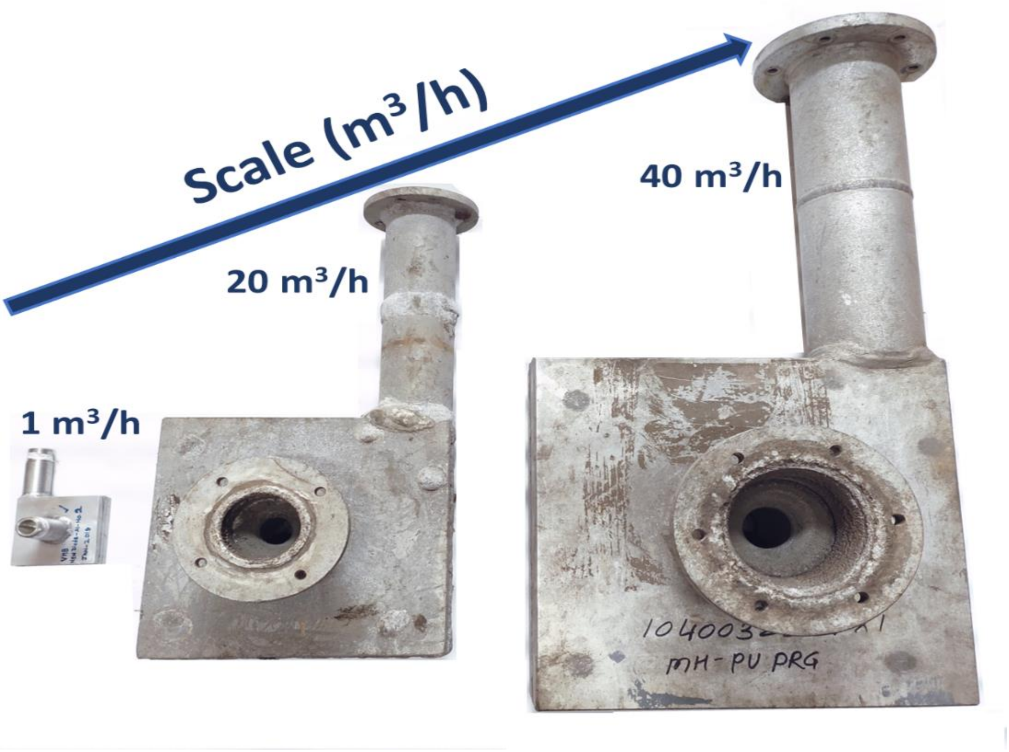

Figure 3. 5: Different scales of vortex diode (m^3/h)

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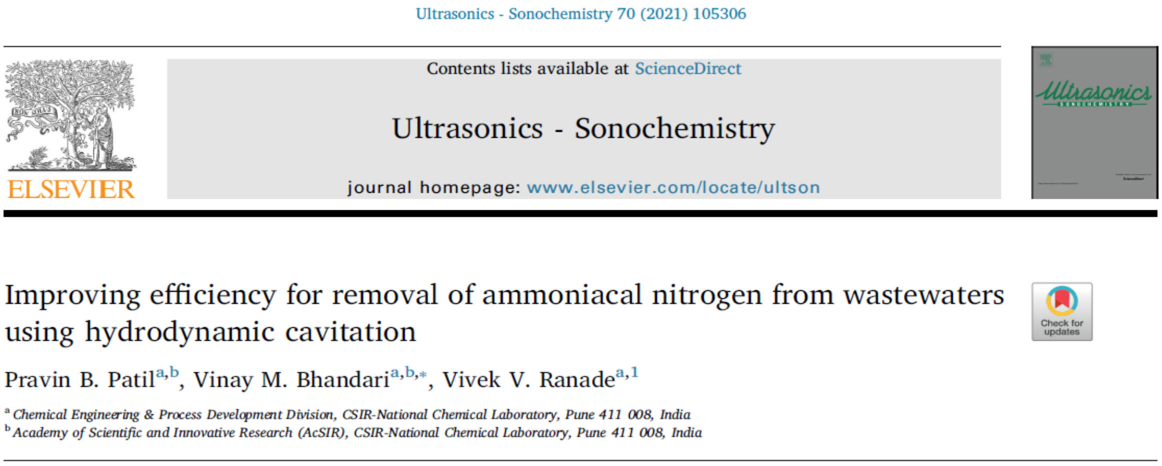

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Improving efficiency for removal of ammoniacal nitrogen from wastewaters using hydrodynamic cavitation

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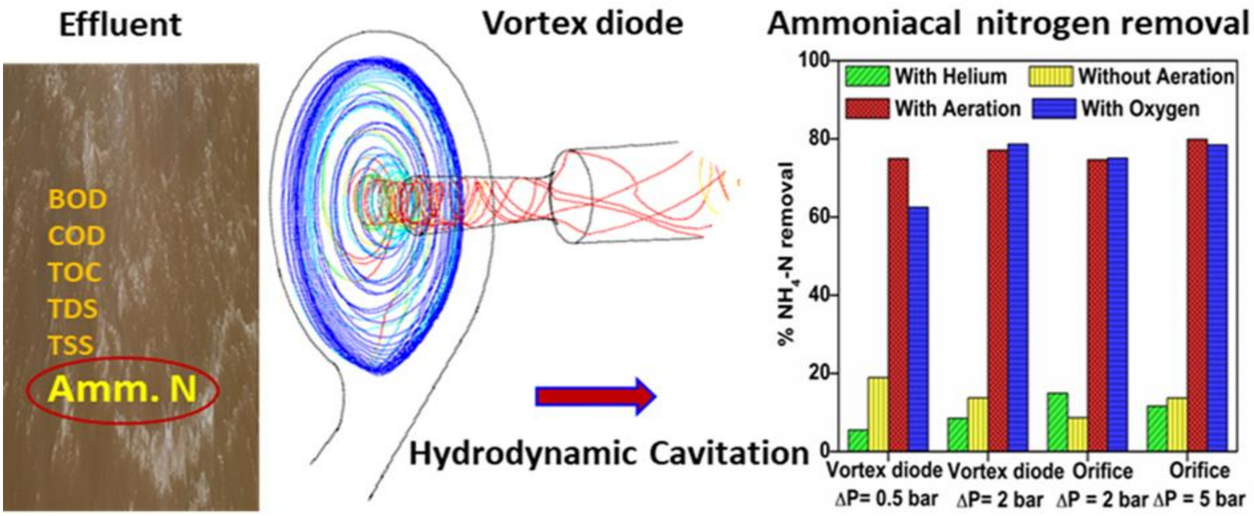
Chapter - 4



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Chapter 4

Improving Efficiency for Removal of Ammoniacal Nitrogen from Wastewaters using Hydrodynamic Cavitation

Abstract

The present study reports significant improvements in the removal of ammoniacal nitrogen from wastewater which is an important problem for many industries such as dyes and pigment, distilleries and fisheries. Pilot plant studies (capacity, 1 m^3/h) on synthetic wastewater using 4-amino phenol as model nitrogen containing organic compound and two real industrial effluents of high ammoniacal nitrogen content were carried out using hydrodynamic cavitation. Two reactor geometries were evaluated for increased efficiency in removal-orifice and vortex diode. Effect of initial concentration (100 - 500 mg/L), effect of pressure drop (0.5 - 5 bar) and nature of cavitating device (linear and vortex flow for cavitation) were evaluated along with effect of salt content, effect of hydrogen peroxide addition and aeration. Initial concentration was found to have significant impact on the extent of removal: ~ 5 g/m^3 removal for initial concentration of 100 mg/L and up to 12 g/m^3 removal at high concentration of 500 mg/L. Interestingly, significant improvement of the order of magnitude (up to 8 times) in removal of ammoniacal nitrogen could be obtained by sparging air or oxygen in hydrodynamic cavitation and a very high removal of above 80% could be achieved. The removal of ammoniacal nitrogen by vortex diode was also found to be effective in the industrial wastewaters and results on two different effluent samples of distillery industry indicated up to 75% removal, though with longer time of treatment compared to that of synthetic wastewater. The developed methodology of hydrodynamic cavitation technology with aeration and vortex diode as a cavitating device was found to be highly effective for improving the efficiency of the conventional cavitation methods and hence can be highly useful in industrial wastewater treatment, specifically for the removal of ammoniacal nitrogen.

4.1 Introduction

A large number of chemical and allied industries generate huge amounts of wastewaters which require effluent treatment prior to discharge for meeting stringent norms on Chemical Oxygen Demand (COD), Biological oxygen demand (BOD) and Ammoniacal Nitrogen (NH_4-N). Industrial wastewater treatment is important for the sustainability of environment and ecology and at times can threaten the very existence of the industry, if the pollution norms are not complied with. The conventional wastewater treatment largely focuses on the managing COD or BOD levels. In comparison, the subject of removal of ammoniacal nitrogen has received sparse attention barring standard biological methods of treatment. The nitrogen content, measured in the form of ammoniacal nitrogen, is a serious problem in many industrial wastewaters due to limitations of both biological and conventional physico-chemical methods. Ammoniacal nitrogen is a measure for the nitrogenous organic matter as ammonia, a toxic pollutant that can directly poison humans and upset the equilibrium of water ecology systems. The ammoniacal nitrogen is required to be below 30-50 mg/L [1], though the limit can vary depending on location. There are many industries such as dyes and pigment, nitrogenous fertilizers, specialty chemicals that that generate wastewaters having high ammoniacal nitrogen (1500 to 3000 mg/L) and demand specific solutions for wastewater treatment. Similarly, industries such as fisheries generate huge volumes of wastewaters, easily treatable using conventional biological treatment methods but end up in “treated wastewater” having high ammoniacal nitrogen of the order of 400-600 mg/L that needs to be again brought down to well below 50 mg/L using cost-effective physico-chemical methods.

The ammoniacal nitrogen from effluent is conventionally removed using biological, physical, chemical methods or combination of these methods. Adsorption, chemical precipitation, membrane filtration, reverse osmosis, ion exchange, air stripping, breakpoint chlorination and biological nitrification/ denitrification are commonly employed in this regard [2]. Physico-chemical treatment or ion exchange/adsorption are widely used for the reasons of being stable, easy to maintain and reliable. Aguilar [3] investigated physico-chemical removal of ammoniacal nitrogen by coagulation-flocculation using activated silica powdered activated carbon and precipitated calcium carbonate. The removal of ammonia was found to be rather low (3-17%). However, the removal of albuminoid nitrogen (nitrogen in the form of proteins) was appreciable (74-89%). Studies are also reported on effectiveness of variety of materials such as clay and zeolite [4–8], limestone [7]; natural and waste materials such as waste paper, refuse cement and concrete [9] for removal of ammoniacal nitrogen. Advanced oxidation processes including photocatalytic processes were also reported for model and industrial wastewater treatment [10,11]. Destructive methods such as catalyst dependent advanced oxidation processes, though can reduce ammoniacal nitrogen, have significantly high cost of operation compared to most other processes. However, for refractory pollutants, due to non-biodegradability and also because of severe limitations of conventional treatment, application of advanced oxidation methods is often required to meet the pollution control norms. The oxidation processes employ oxidizing agents such as hydroxyl radicals, ozone, hydrogen peroxide that react with the pollutant resulting into partial or total degradation through mineralization of species. Persulfates based oxidation processes are also gaining attention in recent years and have been well reviewed recently [12–15]. The severe process conditions in terms of pressure/temperature/catalyst and therefore cost intensive nature of these methods restrict their application due to economic viability. Thus, it is essential to evaluate newer methods and devices that have potential to offer techno-economically feasible option, specifically for ammoniacal nitrogen reduction. Hydrodynamic cavitation can offer one such useful alternative in the existing treatment of industrial wastewaters for reducing the ammoniacal nitrogen [1,16–21]. While the use of vortex diode and hydrodynamic cavitation is reported in the literature, systematic studies to evaluate effects of various process parameters along with cost consideration are essential from practical point of view and for implementation in real life applications pertaining to the effluent treatment, which is the main objective of this study. Further, the methodology can be effectively integrated with other conventional methods of treatment.

In the present work, we report removal of ammoniacal nitrogen using hydrodynamic cavitation with 4-amino phenol as model nitrogen containing organic pollutant. Two different devices were evaluated for their efficacy in the removal of ammoniacal nitrogen- orifice, a conventional cavitating device that employ linear flow, and vortex diode- employing vortex flow for cavitation. Influence of aeration and addition of hydrogen peroxide on intensifying removal of ammoniacal nitrogen was investigated. The efficacy of the developed methodology was also validated for real industrial wastewater treatment. The quantitative data on influence of initial concentration, total dissolved solids, aeration and addition of hydrogen peroxide on removal of ammoniacal nitrogen is presented together for the first time. The data is processed using the per-pass degradation (removal) factor model and dependence of per-pass removal factor on pressure drop across the cavitation device (energy dissipation rates) is presented. The data is also used to calculate cavitation yield and corresponding treatment costs. Two case studies of real life industrial effluents are also included to facilitate application of the presented results to practice. The results presented in this work will be useful for selection of cavitation device and appropriate process parameters for applying hydrodynamic cavitation for treatment of waste water containing ammoniacal nitrogen.

4.2 Applications of fluidic devices without moving parts

Cavitation fluidic devices may be broadly grouped into two types: devices with and without moving parts. The first class of devices is typically comprised of a rotating impeller and stator. These devices are rather expensive and incur a higher maintenance overhead. Cavitation devices without moving parts have significantly lower costs, and are considered to be the most promising route for realizing the full potential of hydrodynamic cavitation. Cavitation devices without moving parts can be further classified into two broad types: those based on linear flow, and those based on rotational flows. In linear flow cavitation devices such as an orifice or Venturi, the working fluid is forced through a restriction, such that low pressure and therefore cavitation is realized. In rotational flow devices, low-pressure cavitating region is generated around axis of rotation. In this second scenario, the cavitating zone can be sufficiently removed from solid surfaces so as to eliminate the risk of associated damage to the device [19].

Hydrodynamic cavitation demands specific designs of cavitating devices for creating low pressure regions in the flow domain, mainly by increasing the linear velocity of liquid by forcing the flow through constrictions such as orifice or venturi (conventional devices) or by increasing the rotational velocity of liquid by forcing it in the form of vortex flow through a device like vortex diode which has an outlet port from the center of vortex. The schematic of hydrodynamic cavitation process using vortex diode is shown in Figure 4.1. The process integration in the form of aeration (optional) is also indicated. In the conventional devices, constrictions are designed such that velocity at the throat (smallest flow area zone) is large enough to generate cavities that subsequently collapse in a region further downstream of constriction resulting in the desired effect. In the latter case, dimensions of the cavitating device- vortex diode, and outlet port are designed such that low-pressure region are generated because of the highly swirling flow in the vortex diode chamber to generate cavities which subsequently escape the chamber via outlet port and then collapse as they enter high pressure region. The performance of cavitation depends on number density and collapse intensity of generated cavities.

4.2.1 Cavitation Process and Hydrodynamic Cavitation

Cavitation is an advanced oxidation process that involves both physical and chemical changes. The physical process mainly involves formation, growth and collapse of micro bubbles (cavities) within a liquid. The cavities subsequently collapse (implosion) and as a consequence, very high pressure (as high as 1000 atm) and temperature (as high as 10000 K or more) get generated locally at the point of collapse. The extreme temperature and pressure conditions at the location of cavity collapse (implosion), generate oxidizing species such as hydroxyl radicals that can chemically oxidize and destroy refractory pollutants. Under ideal conditions, the products of oxidation of organic pollutants are water and carbon dioxide implying complete mineralization. The phenomenon can be exploited for variety of applications, especially in wastewater treatment, disinfection of water and for chemical reactions [18,22–29].

The application of hydrodynamic Cavitation using tangential flow (Vortex Diode) in wastewater treatment and other applications was reported extensively by Ranade and coworkers in recent years [18,21,28,30,31]. The design of Vortex diode is more complicated compared to conventional designs and has three essential components: an inlet tangential port to impart tangential flow, a disc-shaped chamber for generating vortex and cylindrical axial port for the exit of fluid [32]. There are several design variations that are possible which mainly include variations in diameter and height of chamber along with curved surface and providing internals. The vortex establishes a large pressure drop across the device. The flow characterization in vortex diode is well discussed in the literature and will not be repeated here [27,30,33,34]. Recently [1,20,35,36], have discussed degradation of organics such as dyes, solvents and degradation of organics from real industrial wastewater. However, no systematic studies have been reported specifically for removal of ammoniacal nitrogen using hydrodynamic cavitation. In this work, we have used vortex based cavitation device reported in the literature [18, 19, 30, 32] for the removal of ammoniacal nitrogen, evaluated its efficacy under various process conditions and have tried to significantly enhance the removal efficiency using process intensification for overall reduction in the cost of treatment.

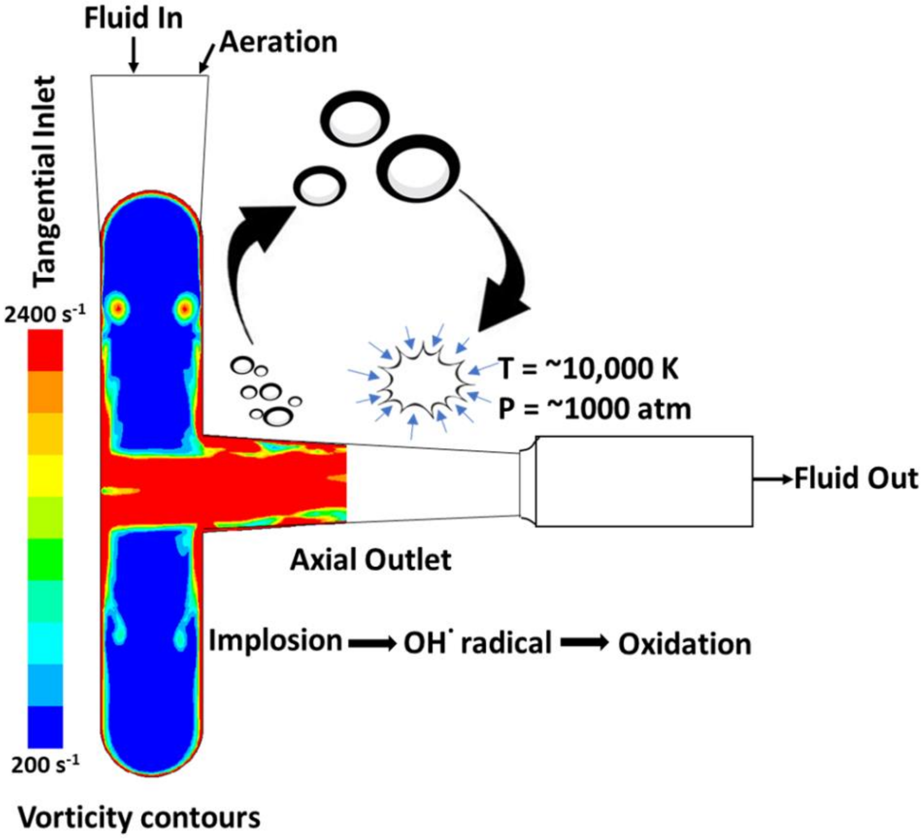

Figure 4. 1: Schematic of hydrodynamic cavitation process using vortex diode

4.3 Experimental

4.3.1 Materials

Reagent grade 4-Aminophenol ($H_2NC_6H_4OH$; 99%) was obtained from Sigma Aldrich. Hydrogen peroxide (30%) was obtained from MERCK India. Sodium chloride (NaCl, > 99%) was obtained from Sigma-Aldrich. Air, Helium and Oxygen (all 99.99% pure) cylinders were procured from M/s Vadilal Gas, India. Single nozzle air pump (SOBO AQUARIUM SB-108, Max. 3L/min) was also used for comparison. A synthetic wastewater solution of 4-Aminophenol was prepared using double distilled water for different known concentrations. Spectroquant® Pharo 100 spectrophotometer (MERCK, India) of wavelength range 320-1100 nm was used for analysis of COD and Ammoniacal nitrogen.

The details of experimental set-up were reported earlier [28,31] and only essential aspects are repeated here for immediate and easy reference and to avoid repetition. The main elements of the hydrodynamic cavitation pilot plant (Figure 4.2) include a 50-liter storage tank with a conical bottom, a vertical multistage 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, control valves and cavitating devices in the main line. A bypass line to main flow is used to control the flow rate. Nominal Pipe diameter was 3/4th inch. Flow transmitters and pressure transmitters are used to record flow and pressure (KROHNE, H250, Honeywell ST 700). The set-up is equipped with temperature measurement (RTD make EUREKA Eng. Enterprises India; 0-200 °C) and control system. Two cavitating devices were used- orifice (single hole, circular with 3 mm diameter) and a vortex diode [30] (fabricated locally; chamber diameter 66 mm, Throat diameter 11 mm, Material of construction- SS 316) operated in reverse flow mode. For the process intensification study, prior to sending the fluid to cavitation device, an arrangement was made for gas bubbling by inserting a tube in the tank and using air pump or air cylinder, oxygen cylinder or helium cylinder (typically air was bubbled using a single nozzle air pump, SOBO AQUARIUM SB-108 with maximum flow rate of 3L/min).

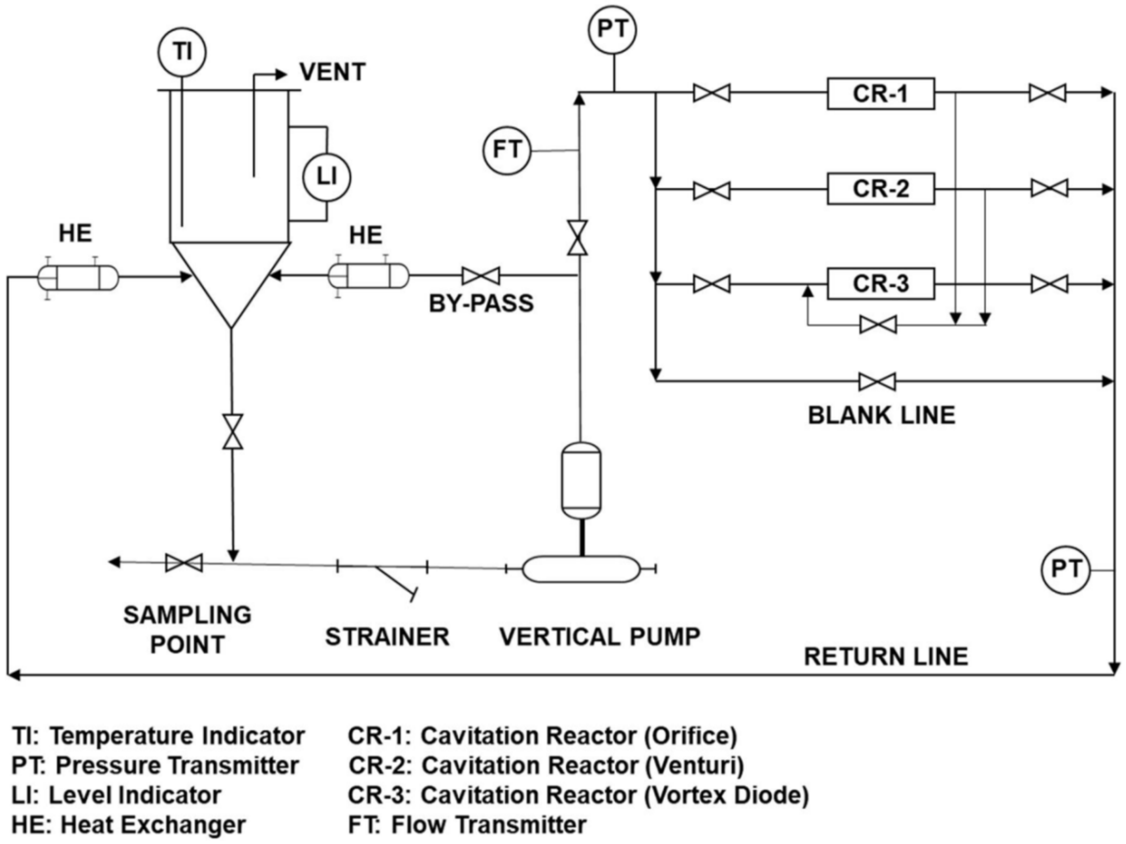

Figure 4. 2: Schematic of hydrodynamic cavitation set-up

The removal of ammoniacal nitrogen was investigated mainly using a synthetic wastewater system with 4-aminophenol as model nitrogen compound and for different concentrations in the range of 100 - 500 mg/L. In view of the inception of cavitation at <0.5 bar for vortex diode and ~1.25 bar for orifice [31], the pressure drop conditions for vortex diode were selected from 0.5 bar and above and for orifice 2 bar and above. Cavitation number for the considered operating range for orifice was less than 1 (Cavitation number of 0.75 corresponding to the flow rate of 0.41 m^3/h and 0.35 corresponding to the flow rate of 0.59 m^3/h, at pressure drop of 2 and 5 bar respectively). The usual definition of Cavitation number is not applicable to the vortex diode. We have ensured that both the devices are operated in cavitating regime. Experiments were conducted for 120 min and samples were withdrawn at periodic intervals and analyzed for ammoniacal nitrogen. The pH of the solution was observed to be in the range of 6.9 to 7.3, indicating no appreciable change.

4.4 Results and discussions

4.4.1 Effect of initial concentration and removal kinetics

The results of initial concentration effect on reduction in ammoniacal nitrogen are presented in Figure 4.3 for two different reactor configurations, vortex diode and orifice. It was observed that initial concentration has significant impact on the removal. While a good removal of ammoniacal nitrogen could be obtained for Vortex diode (up to 45%) at lower concentration of 100 mg/L, it was less than 20% at high concentration of 500 mg/L. The corresponding extent of removal, for orifice was only marginally lower, however, required substantially higher pressures compared to vortex diode.

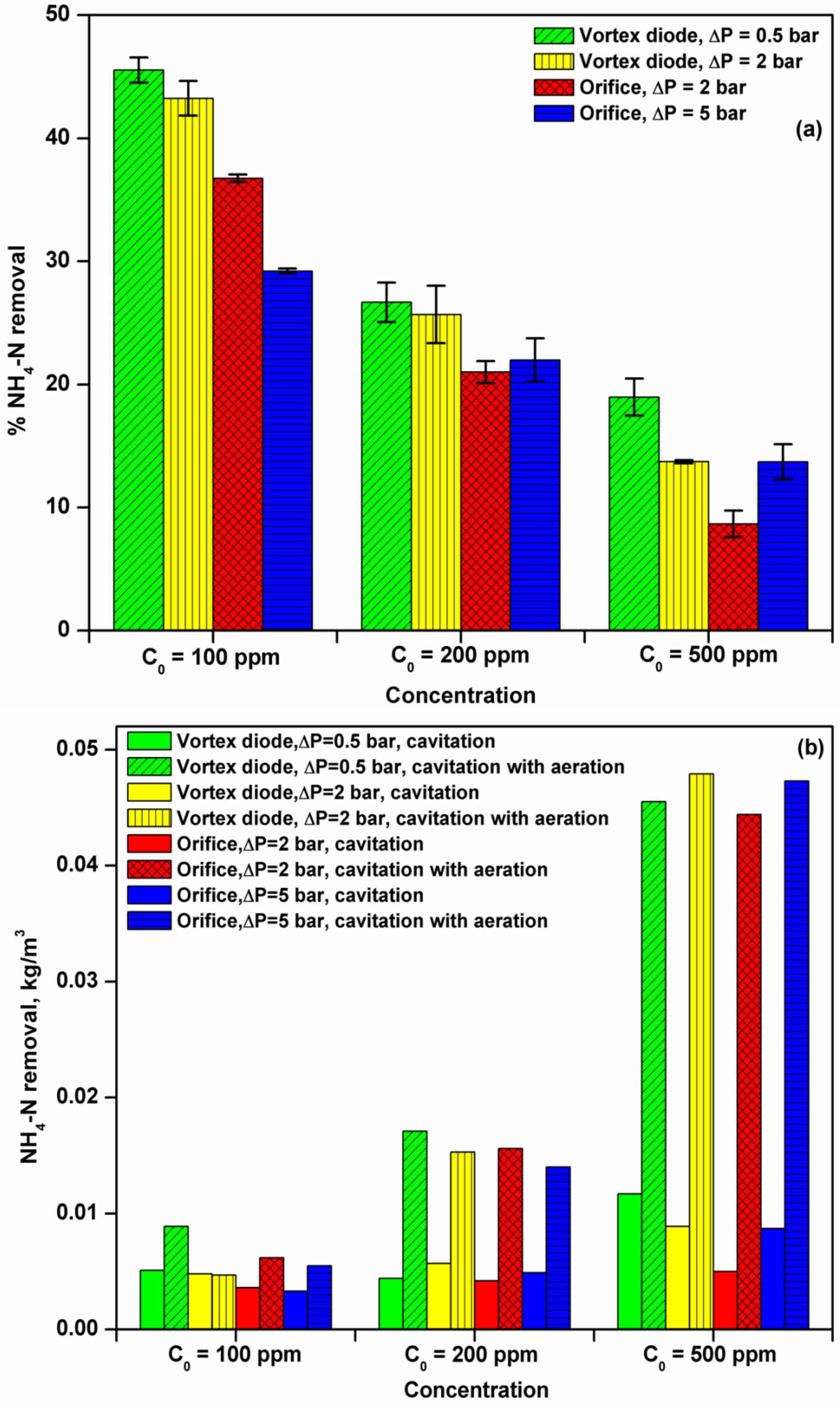

Figure 4. 3: Effect of initial concentration on removal of NH_4-N

The influence of initial concentration on percentage removal of pollutant is similar to that reported in the literature [37–39]. The initial concentration of pollutant influences the vapour and dissolved gas content of the cavity during collapse, similar to that reported [40] and therefore influences overall hydroxyl radical generation rate. The overall extent of degradation depends on concentrations of generated hydroxyl radicals as well as concentration of pollutant. It should be noted that though percentage degradation decreases with increase in initial concentration, the actual amount of pollutant degraded increases with increase in initial pollutant concentration.

In order to study the kinetics of removal, a pseudo-first order kinetics was considered. The reduction in ammoniacal nitrogen could be represented as,

$$C = C_0 e^{-kt} \tag{4. 1}$$

Where C_0 and C indicate ammoniacal nitrogen concentration before and after the treatment, "t" is time (min), and k is an apparent rate constant (min^{-1}) of the reaction. Since removal predominantly occurs in the first 60 minutes, the rate data was fitted accordingly. The values of rate constants are given in Table 4.1. For lower concentration of 100 ppm, k value obtained in case of vortex diode was 7.18×10^{-3} min^{-1} and 6.61×10^{-3} min^{-1} for ΔP of 0.5 and 2 bar respectively. Similarly, in case of orifice, the k value was 5.41×10^{-3} min^{-1} and 5.05×10^{-3} min^{-1} for ΔP of 2 and 5 bar respectively. It is evident that the extent of removal was quite higher in case of vortex diode compared to orifice, especially at lower concentration of 100 ppm. At higher concentration of 200 and 500 ppm, values of apparent rate constant, k, decrease for both vortex diode and orifice as compared to low-100 ppm concentration.

Table 4. 1: Rate constant data for removal of NH_4-N with Vortex diode and Orifice

Reactor	Initial conc. (ppm)	% NH_4-N removal (120 min)	Apparent rate constant $k \times 10^3$ (min^{-1})
Vortex diode			
	100	45.5	7.1
ΔP = 0.5 bar	200	26.7	2.9
	500	18.9	2.1
	100	43.2	6.6
ΔP = 2 bar	200	25.7	2.9
	500	13.7	1.5
Orifice			
	100	36.7	5.4
ΔP = 2 bar	200	21.0	2.3
	500	8.67	1.1
	100	29.2	5.0
ΔP = 5 bar	200	21.9	2.0
	500	13.7	1.6

4.4.2 Effect of Pressure Drop

Pressure drop across the cavitating device is one of the most important parameter that not only determines the efficiency of removal but also decides the cost of operation. The results on the effect of pressure drop are shown in Figure 4.4 for both vortex diode (0.5 and 2 bar) and orifice (2 and 5 bar) and for different initial concentrations. The results clearly reveal significantly higher rates of removal for the vortex diode compared to conventional orifice at all the concentration. Further, low pressure drop is favored in both the reactors, especially at low concentrations and the effect is also dictated by the reactor geometry (corresponding to their point of inception of cavitation). In all the cases, the performance of vortex diode was superior to conventional device- orifice for the removal of ammoniacal nitrogen; both rate as well as in terms of extent of removal. The present results highlight another important aspect concerning the pressure drop; the reduction/removal somewhat insensitive to increase in pressure drop across cavitation device up to a certain level and then decreases at very high pressure drops. This also agrees well with many reports which indicate existence of optimum pressure drop [28,41,42].

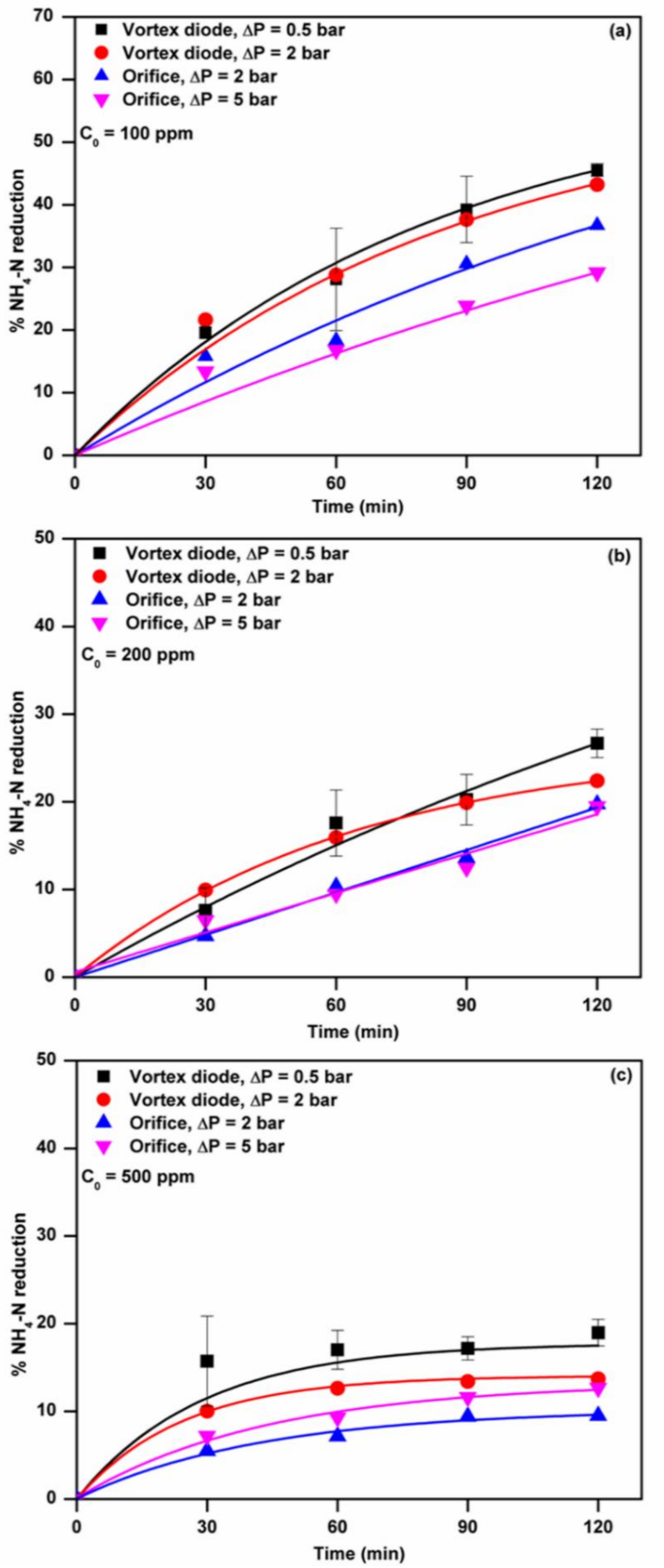

Figure 4. 4: Effect of pressure drop for different initial concentrations

(a) 100 ppm (b) 200 ppm (c) 500 ppm

4.4.3 Effect of Total Dissolved Solids

The hydrodynamic cavitation, by virtue of its dependence on the cavity implosion, is expected to be influenced by presence of dissolved solids; however, no systematic studies have been reported in this regard. In order to evaluate the effect, experiments were carried out using initial concentration of PAP as 100 and 500 ppm and using added initial dissolved salt concentration of 500 ppm and 2000 ppm (NaCl concentration). The results using vortex diode as a cavitating device are shown in Figure 4.5. The results indicate marginal effect of TDS at low salt concentrations while the effect is more pronounced at higher values of TDS. However, within the typical prescribed limits of TDS (< 2100 ppm), effectiveness of the hydrodynamic cavitation for the removal of ammoniacal nitrogen is clearly evident.

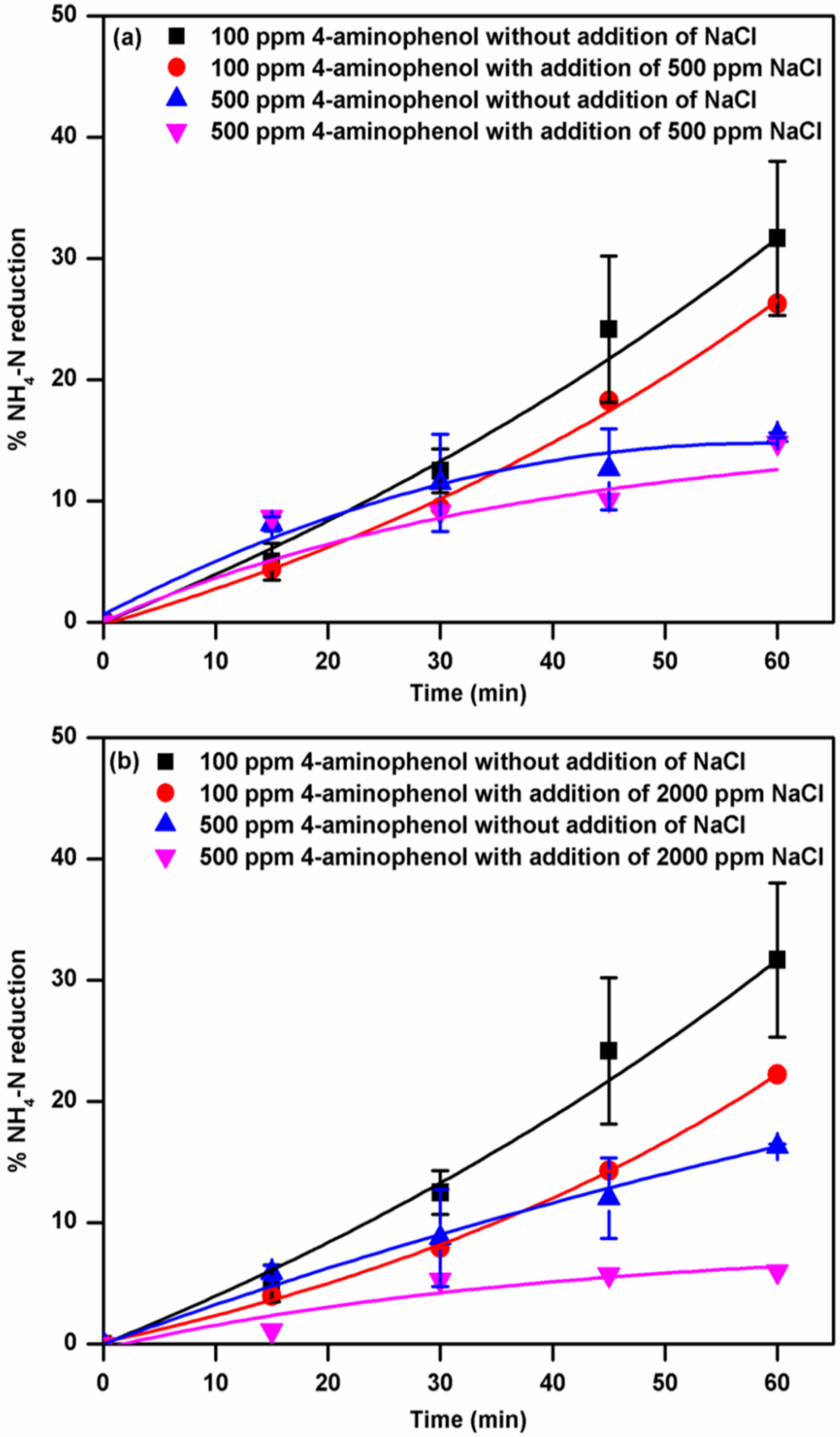

Figure 4. 5: Effect of dissolved solids on hydrodynamic cavitation

(a) Low TDS (b) High TDS

4.4.4 Intensification by addition of H_2O_2

Conventional forms of process intensifications include addition of strong oxidizing agents such as hydrogen peroxide or ozone. Since no studies are available for removal of ammoniacal nitrogen in this regard, representative forms of process intensification have been chosen for studying their impact on removal of ammoniacal nitrogen. Figure 4.6 shows some of the results with the intensification using hydrogen peroxide (30%) as additional or external- to be specific, oxidizing agent on removal of ammoniacal nitrogen (hydrogen peroxide formation is also expected in the normal course of cavitation). In the external addition, the dose of hydrogen peroxide was investigated at the level of five times than concentration of pollutant. It was observed that there is no significant improvement and at low ammoniacal concentration of 100 mg/L, vortex diode and orifice yields about 50% and ~40% ammoniacal nitrogen removal at ΔP of 0.5 and 2 bar respectively, while at higher concentration of 500 mg/L about ~30% removal in ammoniacal nitrogen was obtained. The results indicate that process intensification in the form of hydrogen peroxide does not significantly increase the removal.

The Synergistic coefficient for hydrodynamic cavitation and H_2O_2 was calculated by using formula as given below,[39]

$$\text{Synergistic coefficient} = \frac{k_{(HC+H2O2)}}{k_{HC}+k_{H2O2}} \qquad (4.\ 2)$$

Synergistic coefficient values less than one confirmed the above observation of no synergism for hydrodynamic cavitation with addition of H_2O_2.

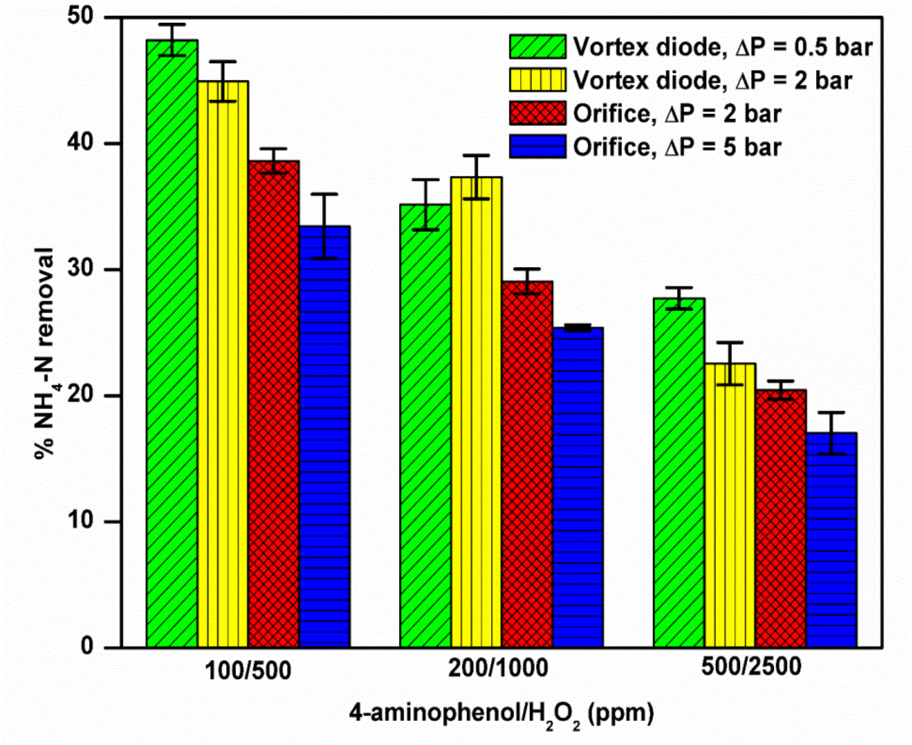

Figure 4. 6: Effect of addition of H_2O_2

4.4.5 Intensification using aeration

Simple form of process intensifications such as aeration can be useful for the reason that cavities constitute vapor, air and other gases which therefore can influence the behavior in term of implosion or oxidation or both. Aeration may cause,

1. Early inception of cavitation
2. Increased number of cavities, thereby increasing probability of reaction
3. Increase number of oxidizing radicals (due to enhanced availability of oxygen)

To evaluate the effect of aeration, experiments were carried out with and without aeration (air was sparged through the effluent storage tank). Independent experiments were also carried out with bubbling of helium and pure oxygen, instead of air. Since, the extent of removal is less at high initial concentrations, a concentration of 500 ppm ammoniacal nitrogen was selected to explore the enhancement. The results of process intensification studies are shown in Figure 4.7. A very high removal of ammoniacal nitrogen was obtained (4 to 10 times), by aeration that was otherwise not possible by normal cavitation. About ~80%

removal was obtained using aeration at 500 mg/L concentration. Suryawanshi et al. [28] reported ~ 10% enhancement in COD reduction due to aeration for the removal of solvents and suggested that the nature of the pollutant species may be important in this regard. Thus, process intensification in the form of aeration was not very effective for the removal of COD from the wastewaters. In view of the present results, a substantially different mechanism may be expected for the removal of ammoniacal nitrogen.

The results of the experiments using oxygen and helium independently are also shown in Figure 4.7. As can be expected, bubbling of oxygen produces more or less similar effect as bubbling of air. In fact, the close similarity of the two clearly indicates role of oxygen in the enhancement rather than any of the physical factors mentioned above. Bubbling of the inert gas such as helium (used only for establishing proof-of-concept and is not required in any form for real application) has not shown any positive impact on cavitation. The observations, therefore, clearly imply chemical form of the process intensification due to increased availability of oxygen as the critical component in the removal of ammoniacal nitrogen. Naturally, it is believed that the removal occurs via formation of NOx and water in the process similar to that of CO_2 and water in COD reduction.

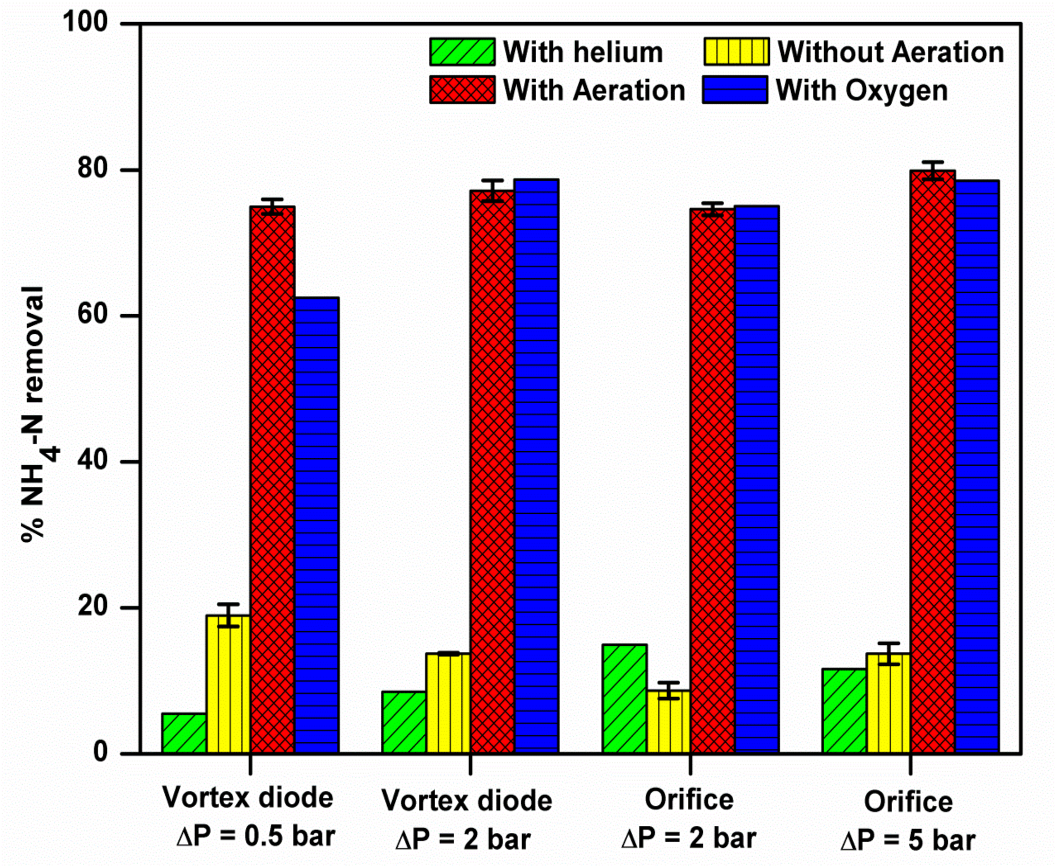

Figure 4. 7: Increased efficiency due to aeration on NH_4-N removal (C_o= 500 ppm) [45]

The removal mechanism is believed to include set of reactions due to collapse of cavities [43], resulting in generation of oxidizing species followed by possible formation of intermediates such as ketone, 4-benzoquinone imine and finally product of oxidation as benzoquinone, water and NOx [44]. This implies no significant reduction in the COD as the carbon number get only partly reduced, as has been confirmed in the present study, where separate COD measurement indicated average COD reduction of only 15%. However, more detailed investigations are required to establish the exact mechanism in this regard.

4.4.6 Per-pass removal

Instead of using an apparent first order kinetic constant to represent removal, it may be useful to use per-pass degradation factor to describe hydrodynamic cavitation experiments presented in this work [21]. The per-pass degradation factor is defined as, Per-pass degradation factor (ϕ) = k τ *(4. 3)*

Where, τ is residence time defined as a ratio of volume of holding tank and flow rate through cavitation device.

The energy dissipation rate,

$$W = \Delta P \times Q \tag{4. 4}$$

The overall cavitational yield (amount of ammoniacal nitrogen degraded per unit energy dissipation) can be written as,

$$Y = \frac{V(C_0 - C)}{\Delta P Q t} \text{ mg/J} \tag{4. 5}$$

Figure 4.8 shows values of per pass degradation factor and energy dissipation rate for the different conditions. At higher pressure drop conditions for vortex diode at 2 bar and orifice at 5 bar, the energy dissipation rate is quite high than low pressure drop conditions. This clearly demonstrates that lower pressure drop conditions are more favorable for both vortex diode and orifice from the cavitational yield perspective. The vortex diode at 0.5 bar shows maximum per-pass degradation compared to all other pressure drop conditions.

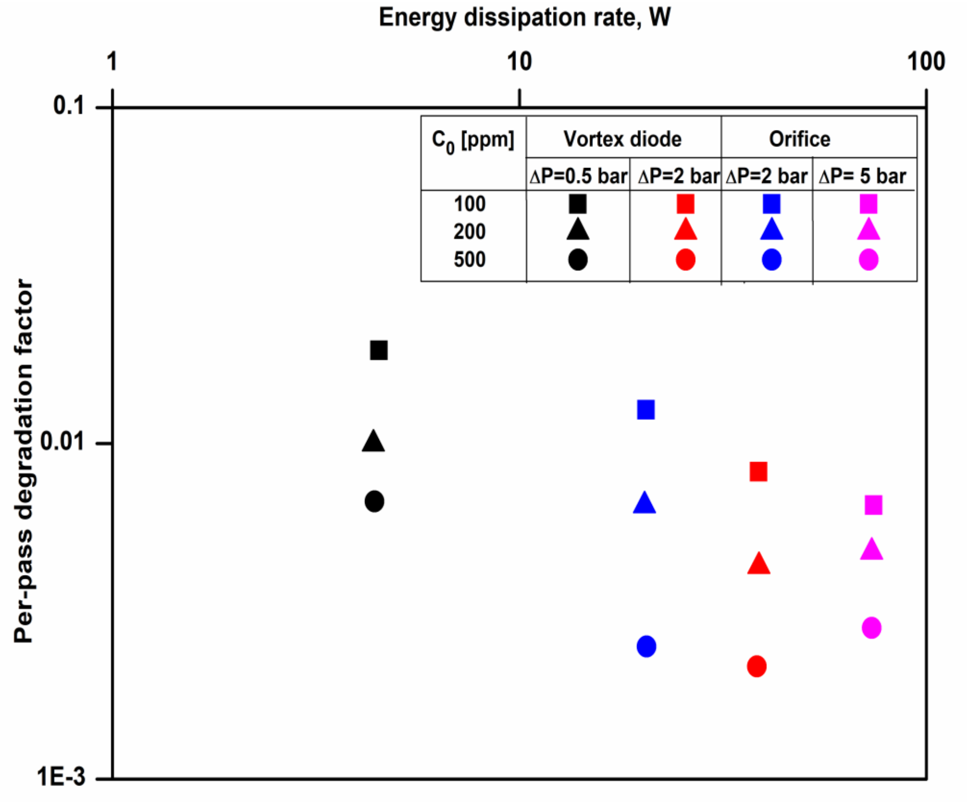

Figure 4. 8: Per pass degradation factor and energy dissipation rate at different concentrations

4.4.7 Comparative analysis of per-pass degradation factor- without aeration and with aeration

It is instructive to quantify the effect on enhancement using per-pass degradation factor for different cases such as removal without aeration and with aeration. The analysis in this regard is shown in Figure 4.9. It is evident from the values of per-pass degradation factor that aeration leads to improvement in hydrodynamic cavitation. With increasing C_0, the improvement by aeration became larger. The analysis also quantitatively reveals effectiveness, especially at low pressure drops and differentiates the impact of reactor geometry.

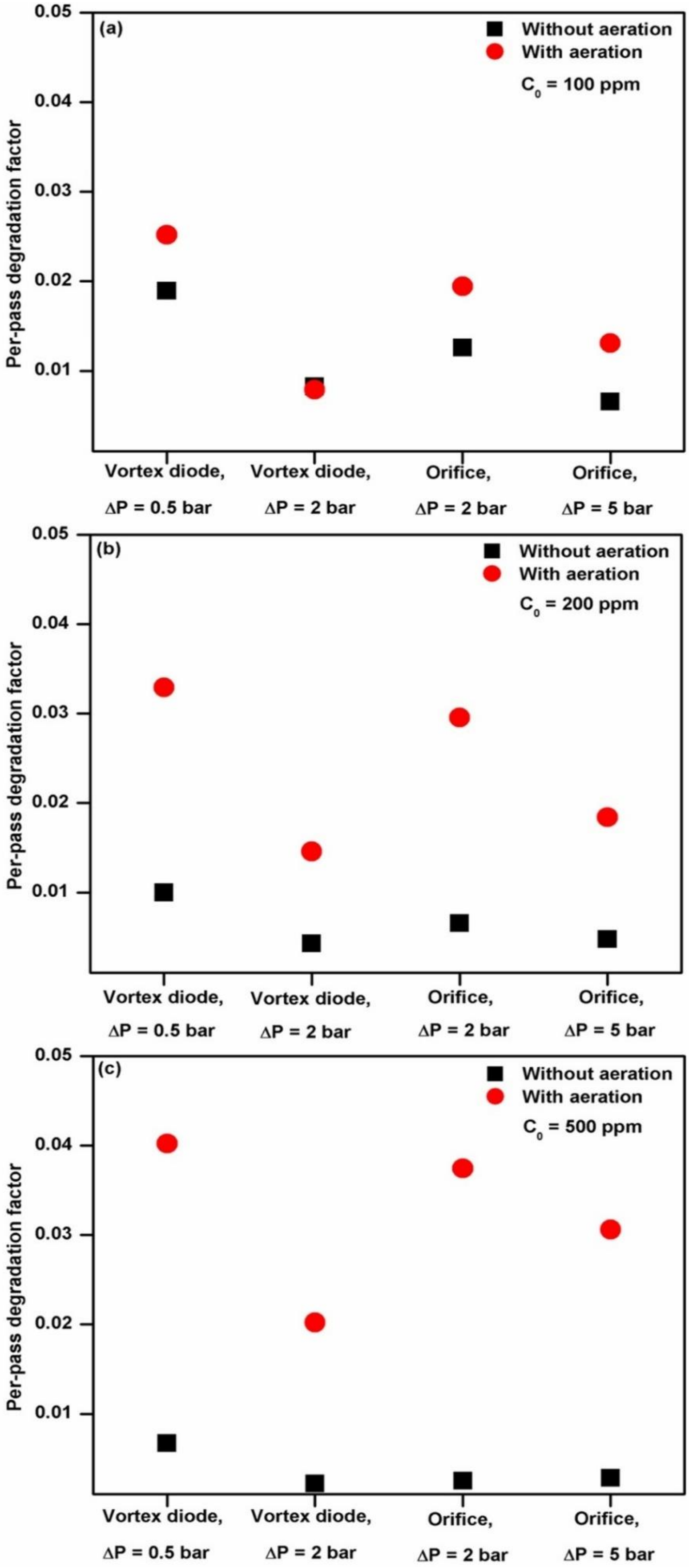

Figure 4. 9: Per pass degradation factors depicting effect of aeration

4.4.8 Reactor geometry and cavitational yield

From the results obtained for ammoniacal nitrogen removal, it is clear that the reactor geometry has a strong influence on the removal behavior. This can be quantified in terms of cavitational yield for different reactors which is the ratio of amount of pollutant degraded and product of pressure drop, flow rate and time. This analysis can be more useful since there is large uncertainty associated with the characterization of the cavitation behavior due to difficulty in obtaining number/quantity of cavities, size of the cavities or size distribution that can imply quality of the cavities and effects of various known and unknown parameters such as presence of organics, dissolved solids, other impurities, liquid viscosity, surface tension, temperature and so on. Thus, the overall performance is largely attributed to the visible and measurable parameters such as pressure drop, reactor configuration. Figure 4.10 provides values of cavitational yield for different reactors- vortex diode and orifice. A comparison is also made for the large enhancement obtained for the process intensification using aeration. The energy dissipated by aeration can be given by $g \times V_G$ (J/kg), where g is gravitational acceleration (9.81 m/s^2) and V_G is superficial gas velocity (m/s). In the present work, under experimental conditions, the energy consumption due to aeration was found to be less than 1% of the total energy consumption and hence, for simplifying and ease of comparison, energy dissipated by aeration is neglected. The values of cavitational yields were 49.2×10^{-4} mg/J and 31.4×10^{-4} mg/J for vortex diode at 0.5 bar pressure drop, 100 ppm initial concentration and for with and without aeration. The corresponding values for orifice were 8.4×10^{-4} mg/J and 4.9×10^{-4} mg/J respectively. For the initial concentration of 500 ppm, the same values for vortex diode and orifice were 261.0×10^{-4} mg/J and 73.8×10^{-4} mg/J and 59.8×10^{-4} mg/J and 6.75×10^{-4} mg/J respectively. It is evident that vortex diode as a cavitation reactor is superior to the conventional device-orifice. It can also be seen that the cavitation yield is higher for higher initial concentration. Also, cavitational yield increases significantly (up to 10 times) using aeration.

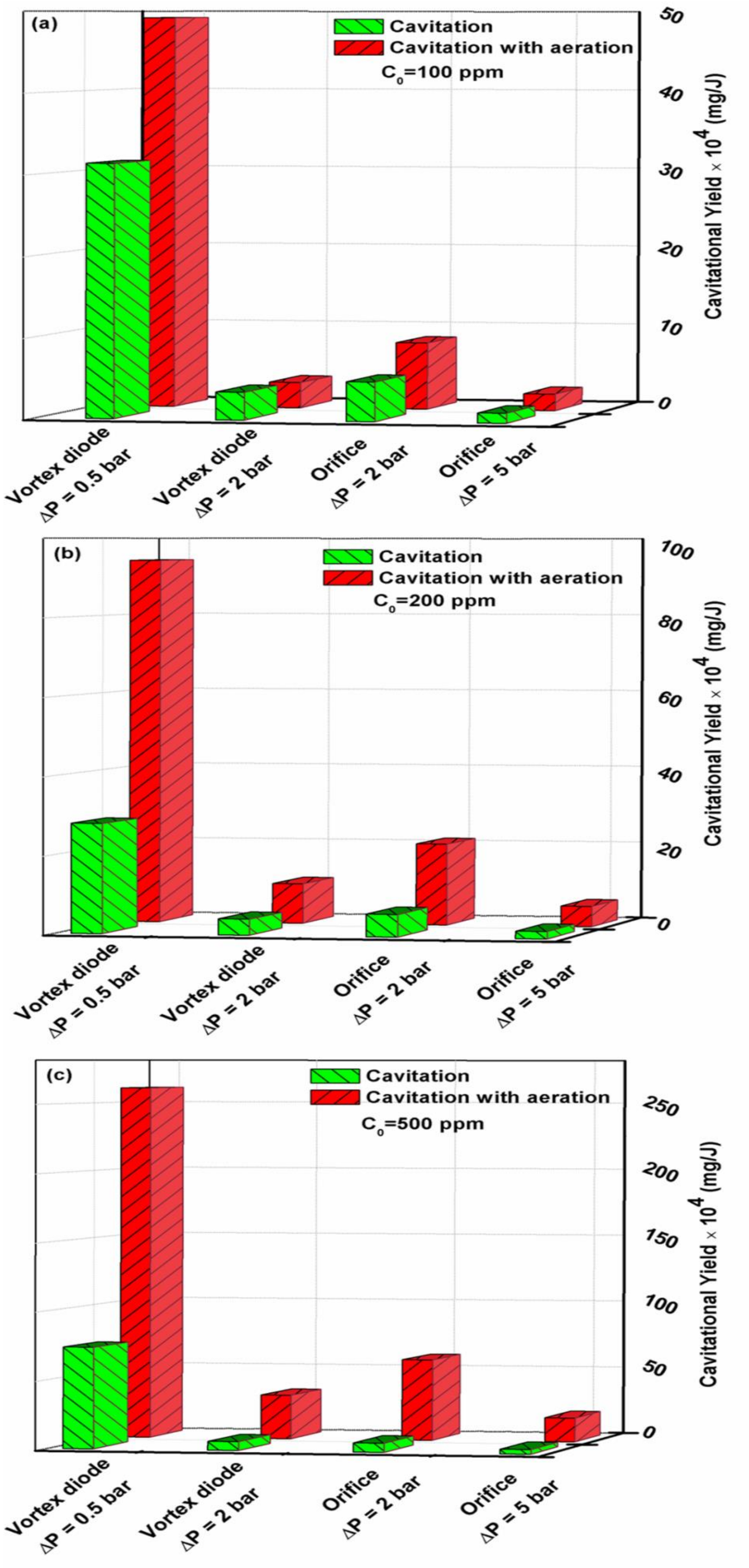

Figure 4. 10: Cavitational yield for vortex diode and orifice; with and without aeration

4.4.9 Cost considerations in removal of ammoniacal nitrogen using hydrodynamic cavitation

In view of the high efficacy of hydrodynamic cavitation technology for the treatment of industrial wastewaters containing high ammoniacal nitrogen, it would be prudent to estimate approximate costs associated with the treatment method. The cost of treatment can be obtained as [1]:

$$\text{Cost of treatment per m}^3\text{ of effluent} = \frac{N_c \times \Delta P \times P_E}{36\eta} \qquad (4.\ 6)$$

For the removal of ammoniacal nitrogen with and without aeration, the cost is estimated for the Indian scenario assuming the cost of electricity as Rs. 10 per kWh (1$ = ~70 Rs). Pump efficiency was assumed as 66%. For the similar levels of removal and for the process conditions found most favorable in the present work, 0.5 bar ΔP and vortex diode, the cost of treatment is 7 Rs/m^3 (~0.1$/m^3), without aeration and 2 Rs/m^3 (~0.02$/m^3) for process intensification with aeration (assuming negligible cost of aeration).

The corresponding costs for the orifice are 30 and 7 Rs/m^3 (approx. 0.42 and 0.1 $/m^3 respectively), at 2 bar ΔP without and with aeration respectively. For a high concentration of 500 ppm, the estimated costs are 7 Rs/m^3 (~0.1$/m^3) and 0.60 Rs/m^3 (~0.008$/m^3) for vortex diode without and with aeration while corresponding values for orifice are 30 and 3 Rs/m^3 (approx. 0.42 and 0.04 $/m^3 respectively). Thus, the treatment cost for vortex diode is significantly lower as compared to the orifice used in this work.

The high effectiveness of vortex diode in the treatment of wastewaters is largely due to the flow pattern- vortex flow in the design of cavitation reactor. The rotational flow in such case is effective in removal at lower pressure drop conditions as compared to the linear flow based conventional cavitation devices.

4.5 Removal of ammoniacal nitrogen from real industrial wastewater- two case studies

Two different industrial wastewater samples mainly having the problem of high ammoniacal nitrogen were procured from a local distillery industry. The first sample was partially treated spent wash with initial COD of 75875 ppm and initial ammoniacal nitrogen content of 2050 ppm. The sample was dark brown in colour with intense odor. pH of the sample was 7. The second sample was of condensate water, after the biological treatment of distillery wastewater and had ammoniacal nitrogen content of 2880 ppm.

Both the samples were specifically evaluated for the removal of ammoniacal nitrogen using vortex diode and employing a pressure drop of 0.5 bar and 2 bar respectively, conditions chosen on the basis of preliminary investigations. The reduction in the ammoniacal nitrogen for the spent wash sample was ~36% in 60 minutes, indicating efficacy of the hydrodynamic cavitation technique in treating real industrial wastewater. The treatment of condensate water however was quite difficult and a high reduction of the order of 75% could be obtained (Figure 4.11) only after prolonged treatment (~10 h), indicating relatively high cost of the treatment of such wastewaters. This difficulty in the treatment can be largely attributed to the nature of highly refractory compounds that remained in the wastewaters even after the biological treatment.

The results on the real industrial wastewater treatment are similar to those reported by [20] for real industrial wastewater treatment of fertilizer industry where ~37 % reduction in the ammoniacal nitrogen was reported for wastewaters of high ammoniacal nitrogen content (530-1330 ppm) and ~87% reduction for the low ammoniacal nitrogen (276 ppm) containing wastewater. The present study on distillery wastewater samples however had significantly higher ammoniacal nitrogen content and hydrodynamic cavitation was found to be effective in treating real industrial wastewaters even at such high levels of concentrations. Essentially, higher removal to desired extent can be achieved using prolonged treatment time or using appropriate process intensification.

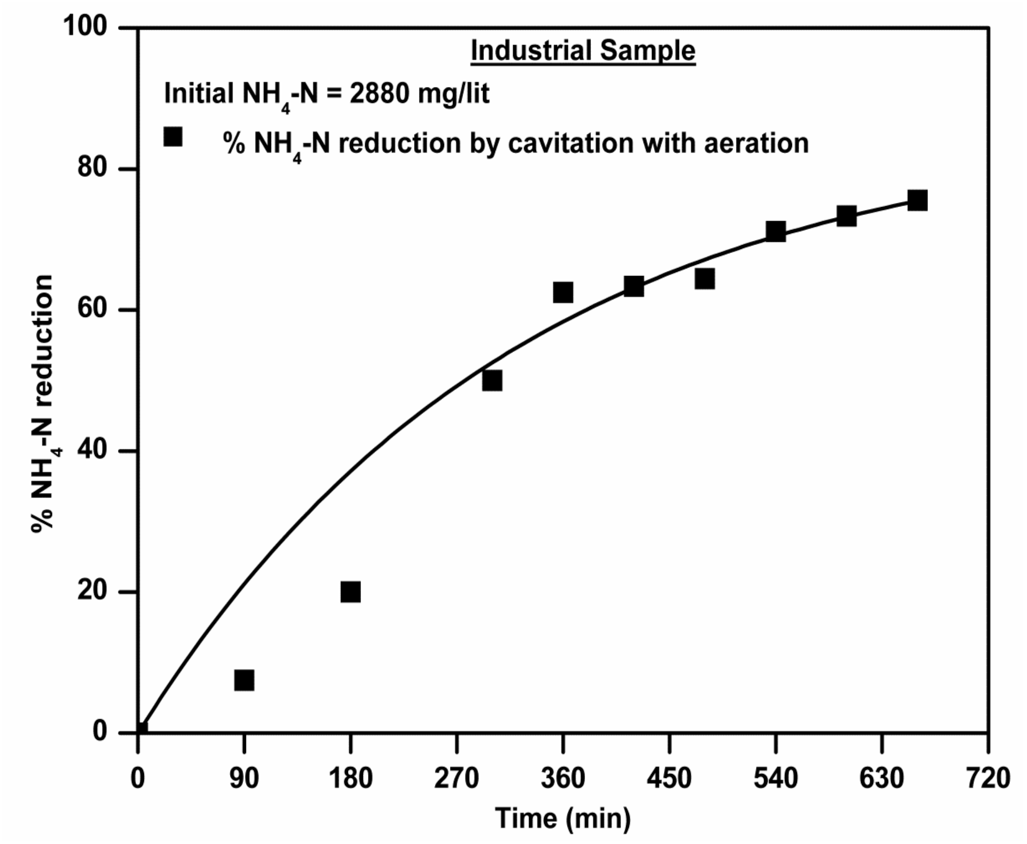

Figure 4. 11: Ammoniacal nitrogen reduction in real life- distillery industrial wastewater

4.6 Conclusion

The present study clearly establishes methodology for improving the effectiveness of hydrodynamic cavitation especially using vortex diode as a cavitating device in wastewater treatment, specifically for the removal of ammoniacal nitrogen. Initial concentration has significant impact on the removal and quantity of ammoniacal nitrogen removed increases with the increase in the concentration for the same pressure drop and reactor conditions. Overall, 9-45% removal could be obtained only using hydrodynamic cavitation depending upon the initial concentration and reactor geometry, high removal using vortex diode for pressure drop of only 0.5 bar. Interestingly, significant improvement, up to 8 times, can be obtained using simple process intensification by sparging air or oxygen and overall extent of removal of over 80% could be accomplished, again high improvement in the case of vortex diode at significantly low pressure drop (0.5 to 2 bar compared to orifice- up to 5 bar). For the initial concentration of 500 ppm, with and without aeration, the values of cavitational yield for vortex diode at pressure drop of 0.5 bar were 261.0×10^{-4} mg/J and 73.8×10^{-4} mg/J and for orifice at pressure drop of 2 bar were 59.8×10^{-4} mg/J and 6.75×10^{-4} mg/J, clearly proving superiority of vortex diode as a cavitation reactor over conventional device-orifice and demonstrating order of magnitude increase in the cavitational yield using aeration. The methodology of improving efficiency gets reflected in significant cost reduction due to process intensification, ranging from 200% to more than 1100%, an crucial and important aspect from industrial application point of view. A plausible mechanism to elucidate effect of aeration clearly highlighted role of oxygen for degradation by cavitation. The application of the technology for the treatment of real industrial wastewaters from distillery industry having high ammoniacal nitrogen content was equally effective in reducing ammoniacal nitrogen proving efficacy of the developed technique. The insight obtained in this study and the results are useful for real life industrial wastewater treatment and hydrodynamic cavitation technology with aeration appears to be a highly promising technology for the removal of ammoniacal nitrogen, in terms of efficiency, ease of operation, easy scale-up and cost effectiveness. The cavitating devices and aeration may be used alone or in combinations with existing established effluent treatment processes to facilitate water recycling and reuse.

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Wastewater treatment and process intensification for degradation of solvents using hydrodynamic cavitation

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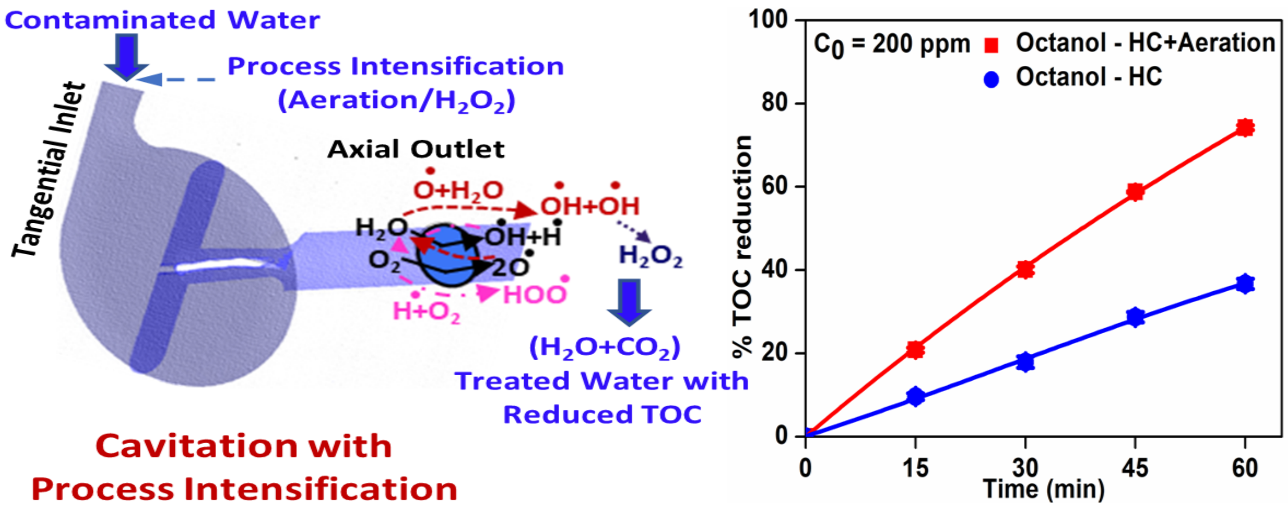
Chapter - 5



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Chapter 5

Wastewater Treatment and Process Intensification for Degradation of Solvents using Hydrodynamic Cavitation

Abstract

Industrial wastewater treatment for removal of small concentrations of harmful solvents is pertinent issue in many chemical and pharmaceutical industries. The present work evaluates bench scale performance of removal of three common solvents by hydrodynamic cavitation (nominal capacity, 1m^3/h) using a vortex flow based cavitation device. Solvent degradation of three solvents viz. octanol, dimethyl formamide and cyclohexanol was studied in the concentration range of 50-200 mg/lit and for the pressure drop range of 0.5-5 bar. The performance of vortex based cavitation device (vortex diode) was compared with that of linear flow based device (orifice). Process intensification in the form of aeration and addition oxidizing agent- hydrogen peroxide was also evaluated for synergistic effect. The vortex diode was found to offer lower pressure drop and superior performance compared to orifice and process intensification in the form of aeration is more effective in improving the removal efficiency. A reduction in TOC to the extent of 74% could be achieved for octanol (200 ppm) using aeration with cavitational yield of 1202×10^{-4} mg/J for vortex diode, yield ~10 times higher than that for orifice. The degradation depends on the nature of solvent and it was revealed that low values of dielectric constant ($\varepsilon<10$) favour degradation. The kinetics of removal was evaluated using rate model based on per-pass degradation factor. The substantially low costs of removal indicated techno-economic feasibility in implementation of the hydrodynamic cavitation in industrial wastewater treatment.

5.1 Introduction

Industrial wastewater treatment is a serious environmental concern due to rapid industrialization in general, and rise of fine chemicals pharmaceutical industries, in particular, posing challenges in treating wastewaters for removal of specific organics such as solvents and specialty molecules. Apart from sustainability of the environment, water scarcity is also important driving force for industrial wastewater treatment, recycle and reuse. In view of its importance, a very large number of studies have been reported in the literature for the removal of chemical oxygen demand (COD) or total organic carbon (TOC) using different techniques, mainly coagulation, adsorption, oxidation, membrane separation, biological degradation and so on typically belonging to the class of physical, chemical and biological methods of treatment [1]. However, specific and detailed investigations on removal of different solvents in effluent water are lacking. Solvents are commonly used in many chemical and pharmaceutical industries at various stages of operations and naturally end up in wastewater in small concentrations, even after recovery. Solvent waste is recognised as a hazardous waste [2] and conventional methodologies have severe limitations in the removal/degradation due to various reasons apart from poor biodegradability. Consequently, even after secondary treatment, solvents traces can remain in wastewater. Suryawanshi et al. [3] reported degradation studies of acetone, methyl ethyl ketone and toluene using cavitation with better removal for only toluene and marginal improvement using aeration. Extended work for higher concentrations, removal of acetone, ethyl acetate and isopropyl alcohol was reported using cavitation [4]; both the studies indicating viability of hydrodynamic cavitation technique for degradation of solvents. In view of large number of solvents being commercially used and limited information in the literature on degradation, differences due to nature of solvents (MW, structure, protic and aprotic nature etc.), number of processes/ reactor configurations and so on, it is instructive to evaluate degradation of various solvents to arrive at practical strategy for their removal.

The technology scenario for wastewater treatment is complex and a large number of methodologies, from simple to highly complex, from low cost to highly cost intensive options add to difficulties in selection of methods. Further, any one method is rarely sufficient in meeting the effluent standards for discharge or for water recycle and reuse and therefore a combination of many methods is practically required resulting into significantly increased cost of treatment. Also, most of the conventional methods generate secondary waste and therefore compared to recovery or physical removal methods, destructive technologies are especially suitable for the wastewater treatment in view of small concentrations of harmful pollutants. Compared to physical and biological methods, chemical methods have a very large variation from concept to application strategy, especially for oxidation processes that employ simple oxidation to complex forms such as catalytic processes with different catalysts, Fenton oxidation, photo-oxidation, UV/H_2O_2, Ozone, cavitation and electro-oxidation. The increased complexity of the advanced oxidation processes (AOPs) and their combination have their own effectiveness and limitations for the removal of difficult pollutants, essentially require higher cost with increased complexity [5-10]. Cavitation, one form of advanced oxidation processes, is a destructive method of treatment which provides in situ generation hydroxyl radicals for the oxidation of the pollutants. It can be regarded as a greener process since complete mineralization of contaminants is possible. Further, hydrodynamic cavitation in this regard can offer ease of operation, multiple reactor geometries, easy scalability and lower cost of treatment.

The principle of cavitation process is well discussed in the literature wherein, flow of liquid through low pressure region resulting into formation, growth and subsequent adiabatic collapse of cavities/microbubbles (~10-100 microns) in liquid. Consequent to cavity implosion, extreme conditions get generated at localized points- hot spots with temperature of ~10000 K and pressures of ~1000 atm. The result is homolytic cleavage of water molecules generating hydroxyl radicals, a strong oxidizing agent that can oxidise organics to the extent of complete mineralization, final product being water and carbon dioxide. Though four principal types of cavitation e.g. acoustic, hydrodynamic, optic and particle cavitation are known, only hydrodynamic cavitation appears practical for wastewater treatment at this point of time, both from chemistry and engineering viewpoint. Different cavitation reactor geometries such as orifice, venturi, high speed rotor-stator assembly are commonly used while vortex diode is a recently discussed and also commercialized reactor configuration. Orifice type devices employ linear flow and generate cavities using small constrictions in the path of liquid, therefore are prone to clogging, erosion consequently not very suitable for wastewater treatment. Unlike conventional HC devices like orifice or venturi, the cavitation realised in vortex diode does not depend on small constrictions. The cavitation is realised by strongly swirling flows. Therefore, for an equivalent capacity of cavitation devices, smallest diameter of vortex diode is significantly larger than smallest diameter in orifice or venturi (without going into details, it is approximately 2.5 times larger). Therefore, vortex diode is much less susceptible to clogging by particles or fibrous materials compared to venturi or orifice. High speed rotor type devices are energy intensive and also pose operational difficulties. In view of these, the recent device based on vortex flow, vortex diode that does not have moving elements and also requires significantly lower energy appears to be most promising alternative to conventional cavitation reactors [1,3,11-13]. The design is simple with tangential entry and axial exit connected to vortex chamber (Figure 5.1). A strong swirling flow causes low pressure region at center of the vortex leading to formation of vapour filled cavities and subsequent collapse after realizing high pressure at downstream region leading to formation of hot spots. The vortex-based cavitation device was evaluated earlier in variety of applications such as dye removal [14], ammoniacal nitrogen removal [12,13,15], microbial disinfection [16-18], biomass valorization [19], and desulphurization of transportation fuels [20].

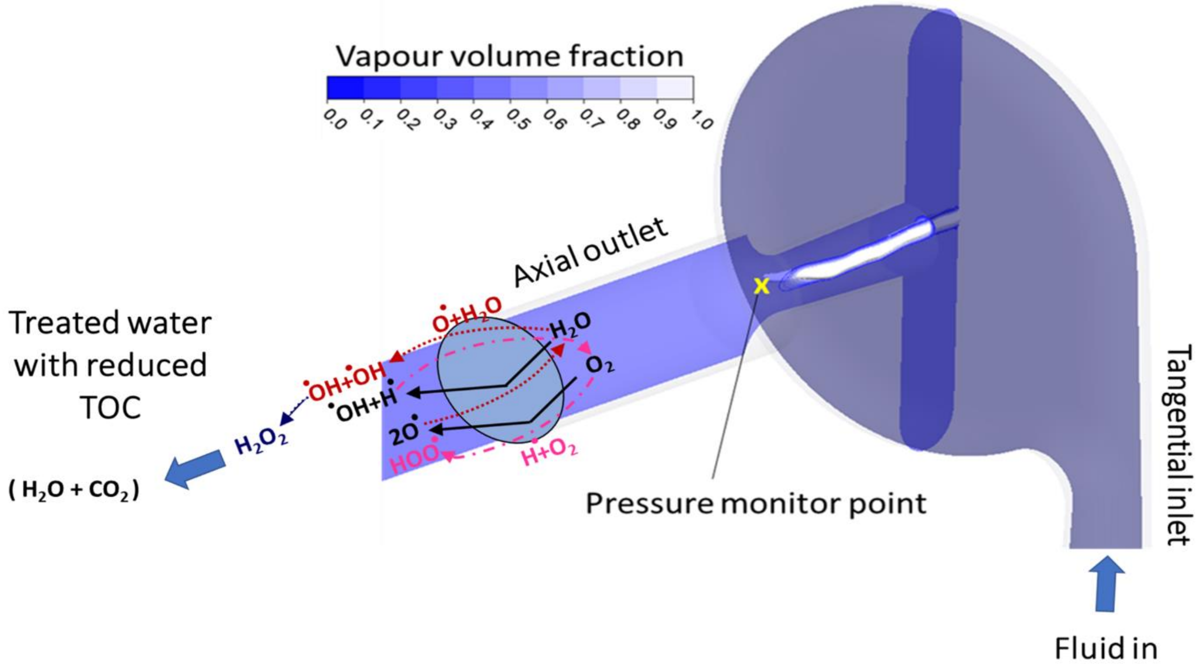

Figure 5. 1: Schematic of vortex diode

In present study, in an attempt to provide a more complete platform for theoretical and practical assessment for solvent degradation, we report degradation of three solvents using hydrodynamic cavitation; two different cavitation reactors- employing vortex flow (vortex diode) and linear flow (orifice); two process intensification strategies using aeration and hydrogen peroxide addition; kinetics of degradation and cost evaluation for techno-economic feasibility analysis. This study, for the first time, has underlined the effect of dielectric constant of the solvent in degradation of the solvent in cavitation processes. Though dielectric constant is related to polarity, we believe that specific data presented in this work will provide a basis for further research on relating key solvent properties to degradation performance and treatment parameters. The solvent, 1-Octanol is widely used in perfume and flavouring industry, solvent dimethyl formamide (DMF) is widely used in pharmaceutical, pesticide, leather and surface coating industry while cyclohexanol is widely used as plasticizer, in soap and detergent industry. A detailed investigation is carried out for all the three solvents at different concentrations and different pressure drop across cavitation reactors. The per-pass degradation factor model [4] was applied to evaluate degradation behaviour and cavitational yield.

5.2 Experimental

The solvents, 1-Octanol, cyclohexanol (HPLC grade from Loba Chemie) and DMF (HPLC grade from Merk) were used for degradation study. Hydrogen peroxide (50%) was obtained from MERCK India. Air pump (SOBO AQUARIUM SB-9905, 2 Nozzle, 4.2W, Max. 5.5 L/min × two output) was used for aeration. SHIMADZU TOC-L series of TOC analyzer was used for analysis of total organic carbon.

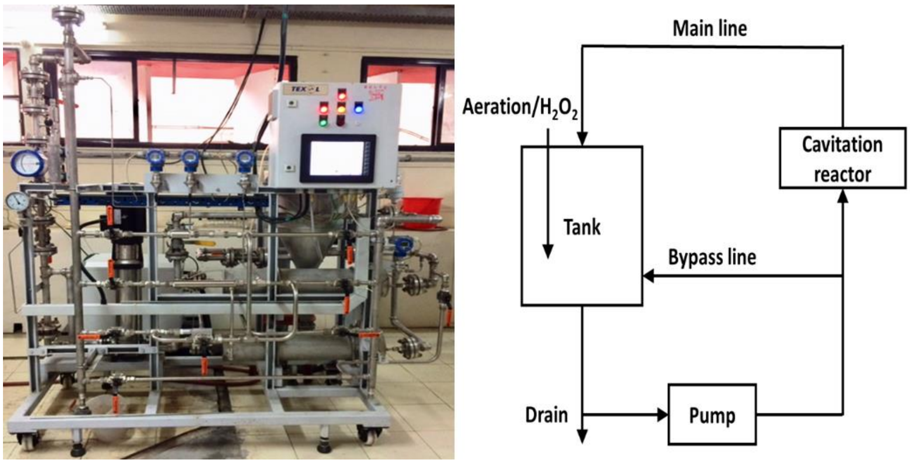

Figure 5. 2: Schematic of hydrodynamic cavitation pilot plant and experimental setup

The degradation studies were carried out using synthetic wastewater containing known predetermined concentration of individual solvent in water. The block diagram and actual experimental setup is shown in Figure 5.2, many details of which are already reported earlier [3,13,20] and hence to avoid repetition only essential components are discussed here. The experiments were carried out using 20 L of wastewater solution in the storage tank (50 L capacity). A vertical multistage 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 is used and flow is controlled by ¾” NB valves (valve industries ltd). Flow transmitter (KROHNE, H250) is used to measure flow in the main line while pressure transmitter (Honeywell ST 700) is provided at both upstream and downstream section of cavitation reactor to measure the pressure. Temperature is measured using RTD (EUREKA Eng. Enterprises India; 0–200° C) while temperature control is carried out by using recirculating chiller (JULABO FL1701) at bypass line. Two cavitation reactors include, orifice (Circular 3mm single hole, SS316) and vortex diode (Chamber diameter 66 mm, Throat diameter 11 mm, SS316). For aeration, vertical cylindrical tube is inserted into the tank before sending fluid through cavitation reactor which is connected to air pump (SOBO AQUARIUM SB-9905, 2 Nozzle, 4.2W, Max. 5.5 L/min × two output) smoothly by silicon tubing with provision of air flow rate control by small adjusting valve. The degradation of solvent was monitored by monitoring reduction in total organic carbon, TOC. In view of cavitation inception for vortex diode at 0.48 bar and for orifice at ~1.25 bar [20], the pressure drop conditions were selected as 0.5 and 2 bar for vortex diode and 2 and 5 bar for orifice respectively to ensure that both the cavitation reactors operate in cavitation regime. Experiments were conducted for 60 min and samples were withdrawn at 15 min interval. The pH of sample was observed to be in the range 6.7-7.4 showing a marginal change during the experiment.

5.3 Results and discussion

5.3.1 Effect of initial concentration

The effect of initial concentration for the three different solvents, octanol, DMF and cyclohexanol, at initial concentration of 50 and 200 ppm is elucidated in Figure 5.3 along with a comparison for the two different reactors-vortex diode and orifice. The effect of initial concentration of solvent is quite significant and amount of solvent degraded increases with solvent concentration. Since the overall extent of degradation is a function of concentrations of hydroxyl radicals and pollutant, though percentage degradation decreases with increase in initial concentration, the solvent amount degraded increases with increase in initial pollutant concentration. Octanol gave ~ 21% TOC reduction at 50 ppm using vortex diode which increased to ~ 37% at 200 ppm initial concentration in 60 min; indicating more than 70% improvement in degradation. The corresponding TOC reduction by using orifice was also quite similar, however, requiring substantially higher pressures compared to vortex diode.

The effect of concentration for DMF and cyclohexanol was quite similar, though the values of degradation were substantially lower as compared to that obtained with octanol at both lower and higher concentrations. DMF shows 12% TOC reduction in 60 min at both 50 and 200 ppm initial concentration while cyclohexanol shows 7% and 2% TOC reduction after 60 min at 50 and 200 ppm respectively.

The concentration of solvent and the nature of the solvent are both important for the viability of hydrodynamic cavitation technique for solvent degradation. Higher values of degradation for lower ranges of concentrations are crucial since effluents typically have low pollutant concentrations. Further, increased degradation with higher concentrations is useful to establish viability of the process in the entire concentration range. The higher initial concentration influences vapour and gas content of cavity during collapse subsequently impacting degradation rate [21]. The results show that the amount of pollutant degraded is more at higher concentration, which is quite important and relevant for real effluent treatment.

The experimental observation reveals that concentration decreases exponentially with time, suggesting use of simple power law model for kinetics of degradation. The reactions in hydrodynamic cavitation can be assumed to be pseudo first order and the kinetics can be evaluated using the following simple mathematical expression.

$$C= C_0e^{-kt} \qquad (5.\ 1)$$

Where, C_0 and C is the pollutant concentration before and after treatment, 't' is time (min) and 'k' is first order rate constant (min^{-1}).

The fit of the model is good (R^2 value >0.98). Table 5.1 lists the k values for different solvents at lower and higher concentration for the two reactor configurations, vortex diode and orifice. For low concentration of 50 ppm and lower pressure drop condition, the k values for octanol, DMF and cyclohexanol were 3.9×10^{-3} (min^{-1}), 2.2×10^{-3} (min^{-1}) and 1.3×10^{-3} (min^{-1}) for vortex diode and 3.9×10^{-3} (min^{-1}), 1.2×10^{-3} (min^{-1}) and 0.2×10^{-3} (min^{-1}) for orifice. While at higher concentration of 200 ppm, the k values for octanol, DMF and cyclohexanol were 7.6×10^{-3} (min^{-1}), 2×10^{-3} (min^{-1}) and 0.3×10^{-3} (min^{-1}) for vortex diode and 7.5×10^{-3} (min^{-1}), 1.8×10^{-3} (min^{-1}) and 0.4×10^{-3} (min^{-1}) for orifice. The rate data clearly highlights the impact of concentration and nature of the solvent in degradation using hydrodynamic cavitation without use of the catalyst or process intensification. Therefore, these results can be construed as primary findings in investigating application of hydrodynamic cavitation for solvent degradation and for evaluating reactor configurations.

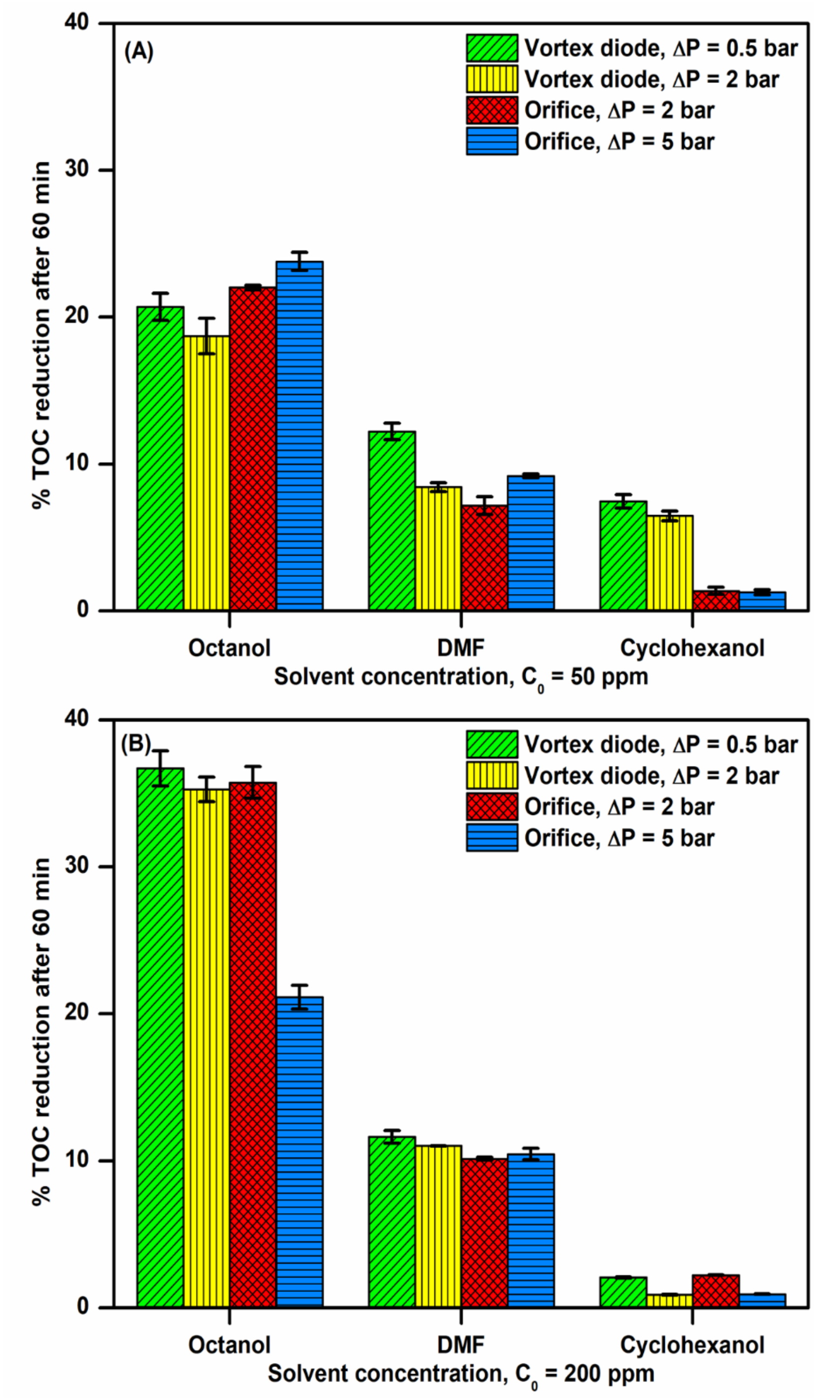

Figure 5. 3: Effect of initial concentration of solvents

(A) C_0 = 50 ppm, (B) C_0 = 200 ppm

Table 5. 1: Rate constant data for different solvents (Octanol, DMF and Cyclohexanol)

Solvent	**Reactor**	**ΔP, Bar**	**% TOC reduction after 60 min**		**1st order rate constant, K × 10^3 (min^{-1})**	
			50 ppm	**200 ppm**	**50 ppm**	**200 ppm**
Octanol	Vortex diode	0.5	21	37	3.9	7.6
	Vortex diode	2	19	35	3.5	7.3
	Orifice	2	22	36	3.9	7.5
	Orifice	5	24	21	4.6	4
DMF	Vortex diode	0.5	12	12	2.2	2
	Vortex diode	2	8	11	1.4	2
	Orifice	2	7	10	1.2	1.8
	Orifice	5	9	11	1.6	1.8
Cyclohexanol	Vortex diode	0.5	7	2	1.3	0.3
	Vortex diode	2	6	1	1.1	0.1
	Orifice	2	1	2	0.2	0.4
	Orifice	5	1	1	0.2	0.2

5.3.2 Effect of pressure

The pressure drop is one of the most important parameter in the application of hydrodynamic cavitation technique dictating energy requirement and consequently cost of the operation. Different reactor configurations require different ranges of pressures in this regard. Our previous work on vortex diode has confirmed low pressure drop requirement for the vortex flow operation using vortex diode compared to linear flow device, orifice [13]. The present study, for ease of comparison with the reported data in the literature and also in view of inception of cavitation at ~0.48 bar for vortex diode and ~1.2 bar for orifice, employed similar conditions of pressure drop, the range of ΔP from 0.5 to 2 bar for vortex diode and ΔP in the range 2 and 5 bar for orifice. The cavitation number for orifice was less than one; 0.75 and 0.35 for 2 bar and 5 bar respectively whereas, in case of vortex diode, the usual definition of cavitation number is not applicable. The selected range of pressures therefore ensures cavitation. The effect of pressure drop for solvent degradation is shown in Figure 5.4 for 50 ppm and 200 ppm initial concentrations. As discussed earlier, octanol gave ~ 21% TOC reduction at 50 ppm using vortex diode which increased to ~ 37% at 200 ppm initial concentration in 60 min; indicating more than 70% improvement in degradation at ΔP of 0.5 bar. For similar/ corresponding TOC reduction, substantially higher pressures were required for orifice, ΔP of 2 bar, compared to vortex diode. The highest values of degradation for the three solvents, octanol, DMF and cyclohexanol, using vortex diode were 37%, 12% and 7% respectively and the corresponding values for the orifice were 36%, 10% and 2%, however at significantly higher pressures compared to vortex diode. The results clearly highlight the increased efficacy of using vortex diode or vortex flow in cavitation, and lower energy consumption. The results also indicate that lower pressure drop condition is more or less equally good in the degradation of solvents especially for vortex diode configuration; orifice requiring substantially higher pressure drop compared to vortex diode to obtain similar extent of degradation in all the cases. Further, the effect of pressure drop is more pronounced in orifice, a linear flow based device for which similar positive impact of increased pressure has been well reported [3]. The degradation behaviour agrees well with that reported in the literature. However, for these solvents and in the range of pressure drop of this study, no identifiable flattening of the trend was observed indicating no choked cavitation as found in previous reports. Therefore, the operation can be performed by further increasing pressures for both the devices. However, increased number of passes would adversely impact the cost of operation. Per-pass degradation is a useful concept in the analysis of hydrodynamic cavitation operations in this regard.

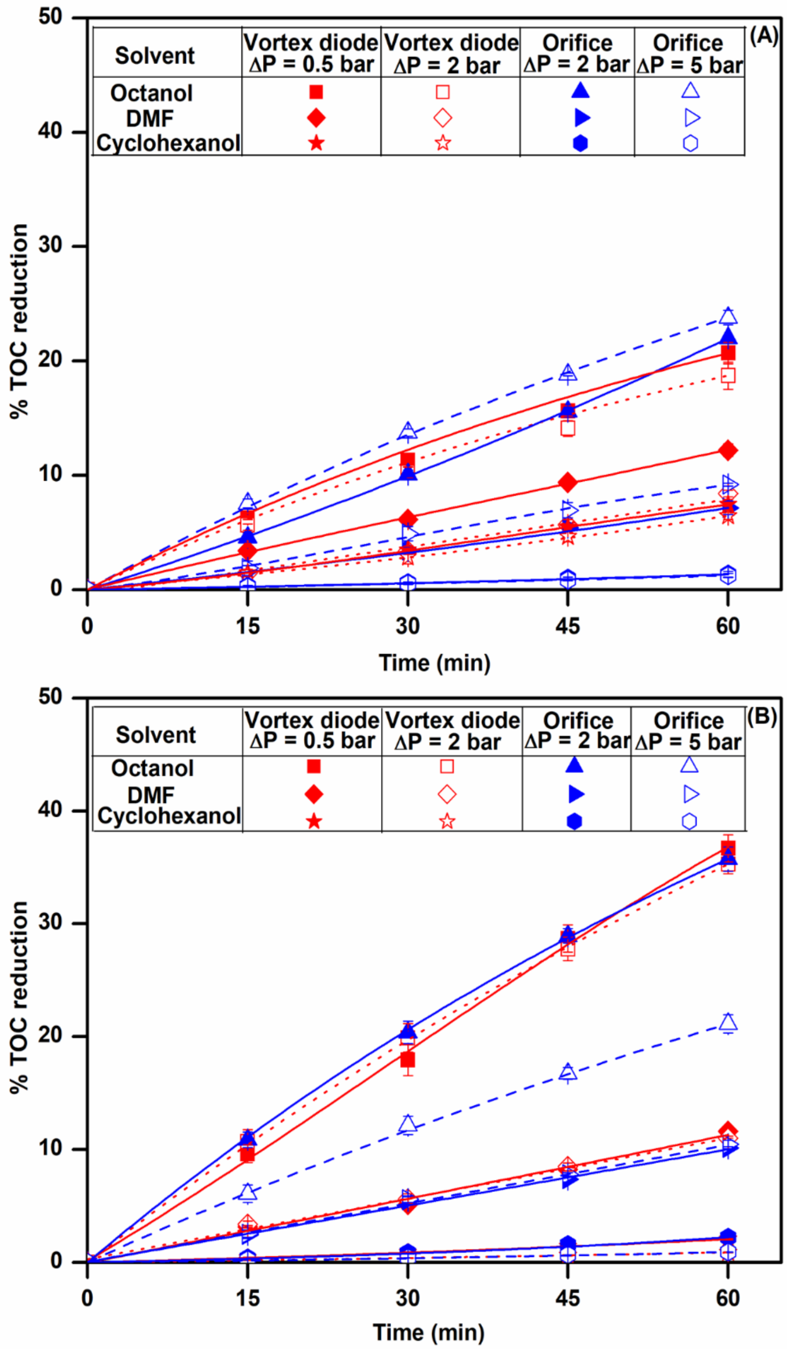

Figure 5. 4: Effect of pressure on solvent degradation

(A) C_0 = 50 ppm, (B) C_0 = 200 ppm

5.3.3 Process intensification using aeration

The process intensification using aeration was earlier reported as highly effective in enhancing the removal of ammoniacal nitrogen [13], though its effect in solvent degradation was not that impressive [3]. Process intensification in the form of aeration is expected to enhance the efficiency of hydrodynamic cavitation due to possible generation of additional nuclei for reaction (number of cavities), for early inception of cavitation apart from improving the quality of the cavities (size/enlargement), consequently contributing to the fruitful collapse (implosion) of cavities and subsequent increased degradation rate and efficiency of hydrodynamic cavitation. In the present study, aeration was effected by bubbling air in the effluent tank prior to liquid passing through cavitation reactor.

The results of degradation of different solvents with and without aeration and for the two reactor configurations are shown in Figures. 5.5 and 5.6. The difference in the rate for vortex diode is highlighted in Figure 5.6 for solvent octanol, where highest impact of process intensification was observed. The values of extent of degradation for the three solvents, octanol, DMF and cyclohexanol using only hydrodynamic cavitation were 21%, 12% and 7% at initial concentration of 50 ppm and at ΔP of 0.5 bar for vortex diode which could be enhanced to the extent of 35%, 19% and 10% using aeration. The same values at 200 ppm initial concentration were 37%, 12% and 2% which could be enhanced to the extent of 74%, 14% and 10% using aeration. A marked difference is evident due to nature of the solvent, octanol showing significant benefits of process intensification. The values for orifice, a cavitation reactor that employs linear flow, for the initial concentration of 50 ppm and at ΔP of 2 bar for the three solvents are 22%, 7% and 1% respectively while the enhancement due to aerations yields the values as 34%, 24% and 5% respectively and for initial concentration of 200 ppm 36%, 10% and 2% which could be improved to the extent of 42%, 14% and 5% respectively. The values for higher pressure drop ΔP of 5 bar and initial concentration of 50 ppm for orifice were 24%, 9% and 1% without aeration and 29%, 15% and 4% with aeration while for 200 ppm, 21%, 11 and 1% without aeration and 39%, 12% and 4% with aeration. Thus, for the solvent octanol, a highest degradation enhancement of 100% could be obtained with useful degradation efficiency of 74%. For other solvents, though order of magnitude enhancement could be obtained due to process intensification, the values of degradation efficiency were not satisfactory, in general.

Suryawanshi et al. [3] reported only ~10% improvement in COD removal by aeration as compared to without intensification. Sarvothaman et al. [4] found close to 100% increase in the per-pass degradation factor by means of aeration in the solvent degradation. Recently, Thanekar and co-workers also reported significant improvement due to aeration in their study on degradation of benzene by hydrodynamic cavitation coupled with aeration using orifice, with 98.9% reduction [22]. From the analysis of the data on different solvents of this study and that reported in the literature, it is evident that the usefulness of the process intensification in the form of aeration largely depends on the nature of the solvent as the physical effect due to aeration in the form of improvement in quantity/quality of the cavities would essentially be similar for all the solvents. Since, *a priori* prediction of the effect of solvent nature in this regard for hydrodynamic cavitation is not possible by any theoretical means at this point of time, it is imperative that experimental investigations on various solvents be carried out to develop empirical guidelines that can help in translating the findings for real life applications apart from forming basis for theoretical framework development.

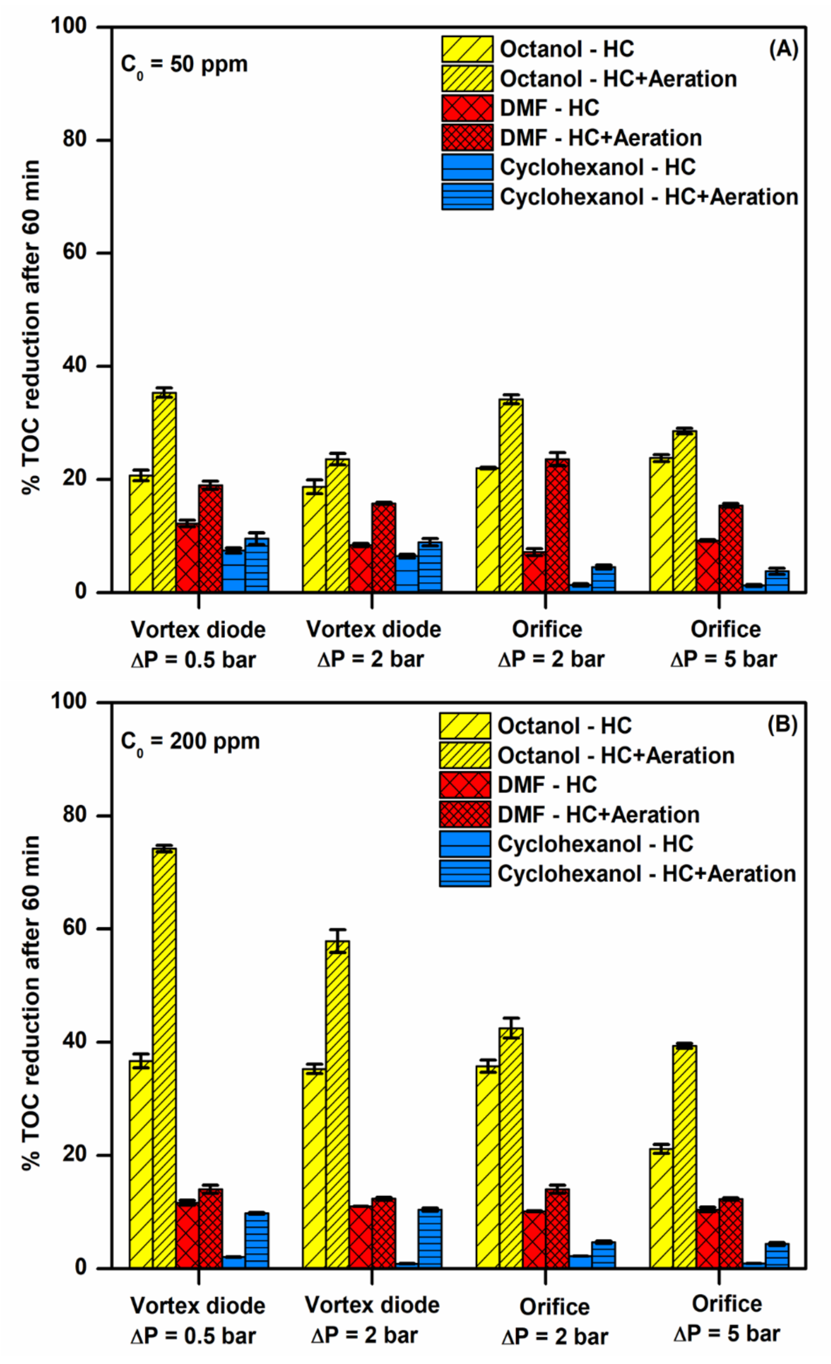

Figure 5. 5: Effect of aeration on solvent degradation,

(A) C_0 = 50 ppm (B) C_0 = 200 ppm

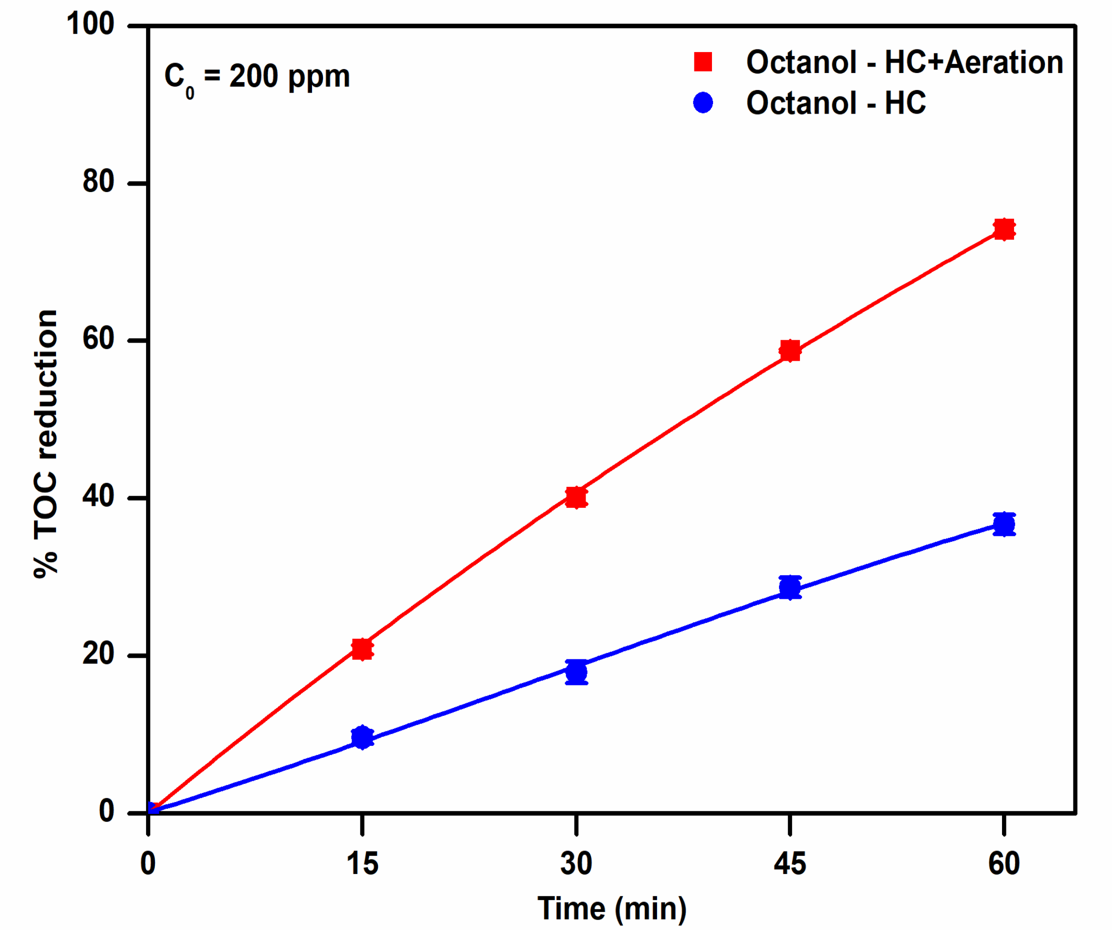

Figure 5. 6: Enhancement in TOC reduction for Octanol Vortex diode, ΔP = 0.5 bar

To evaluate combined effect of hydrodynamic cavitation and aeration, synergistic coefficient was calculated by using formula [23],

$$\text{Synergistic coefficient} = \frac{k_{(HC+Aeration)}}{k_{HC} + k_{Aeration}} \qquad (5.\ 2)$$

The obtained values of synergistic coefficient revealed increased effectiveness of process intensification using the combined approach of hydrodynamic cavitation with aeration thereby in obtaining increased degradation as compared to only hydrodynamic cavitation. For octanol, where highest ~74% TOC reduction was seen, a high value of synergistic coefficient, 2.41, was obtained. For other solvents such as DMF and cyclohexanol, the synergistic coefficient values were expectedly lower though improved degradation was observed using aeration. The values of synergistic coefficient in case of DMF and cyclohexanol were 0.8 and 1.31 respectively.

5.3.4 Process intensification using addition of H_2O_2

Hydrogen Peroxide is one of the most powerful known oxidising agents and is used extensively in not just for oxidation reactions, but also in the form of process intensification in cavitation, especially for effluent treatment [24,25]. The conventional mechanism of hydrodynamic cavitation involves generation, *in situ*, of strong oxidising species such as hydroxyl radicals and also hydrogen peroxide followed by oxidation of organic pollutants and therefore, any further addition of hydrogen peroxide, as process intensification, is believed to generate synergistic effect with the conventional cavitation process, enhancing concentration of oxidising species that contribute to the degradation and increase the efficiency of degradation.

Hydrogen peroxide (50%) was used with external addition of hydrogen peroxide in 1:5 molar ratio (5 moles of H_2O_2 for 1 mole of solvent) for different solvent concentrations. The results of process intensification using hydrogen peroxide are presented in Figure 5.7, for all the three solvents and also for different initial solvent concentrations. It is evident that, though the trend shows increase in the efficiency of degradation, the magnitude of increase in not very high. Interestingly, process intensification in the form of aeration gave huge improvement for solvent-octanol, while process intensification in the form of hydrogen peroxide addition did not have any specific preference for the solvent in this regard. This can be attributed to possible effectiveness of hydrodynamic cavitation technique in generating oxidising agents in sufficient concentration and further increase in the concentration of oxidising species may not be useful. In general, hydrodynamic cavitation will assist H_2O_2 to disassociate and sometimes increased concentration of OH radicals will also lead to self-quenching. Overall effect depends on the relative rate of reaction between OH radicals; in this scenario, reaction between 2 OH radicals, and between OH radical & organic pollutant. If reactivity of organic pollutant is high, addition of hydrogen peroxide is expected to show improvement, else, it may not. The indifference with respect to different solvents also indirectly point to this reasoning.

To evaluate combined effect of hydrodynamic cavitation with addition of hydrogen peroxide, synergistic coefficient was calculated by using formula [23],

$$\text{Synergistic coefficient} = \frac{k_{(HC+H2O2)}}{k_{HC}+k_{H2O2}} \qquad (5.\ 3)$$

It was confirmed that hydrodynamic cavitation with addition of hydrogen peroxide shows only a marginal improvement in TOC reduction and therefore limited synergism with the value of synergistic coefficient close to 1. The present study, in the ranges of the parameters, reactor configurations and for the three solvents, indicates ineffectiveness of process intensification in the form of hydrogen peroxide addition for practical and useful benefits.

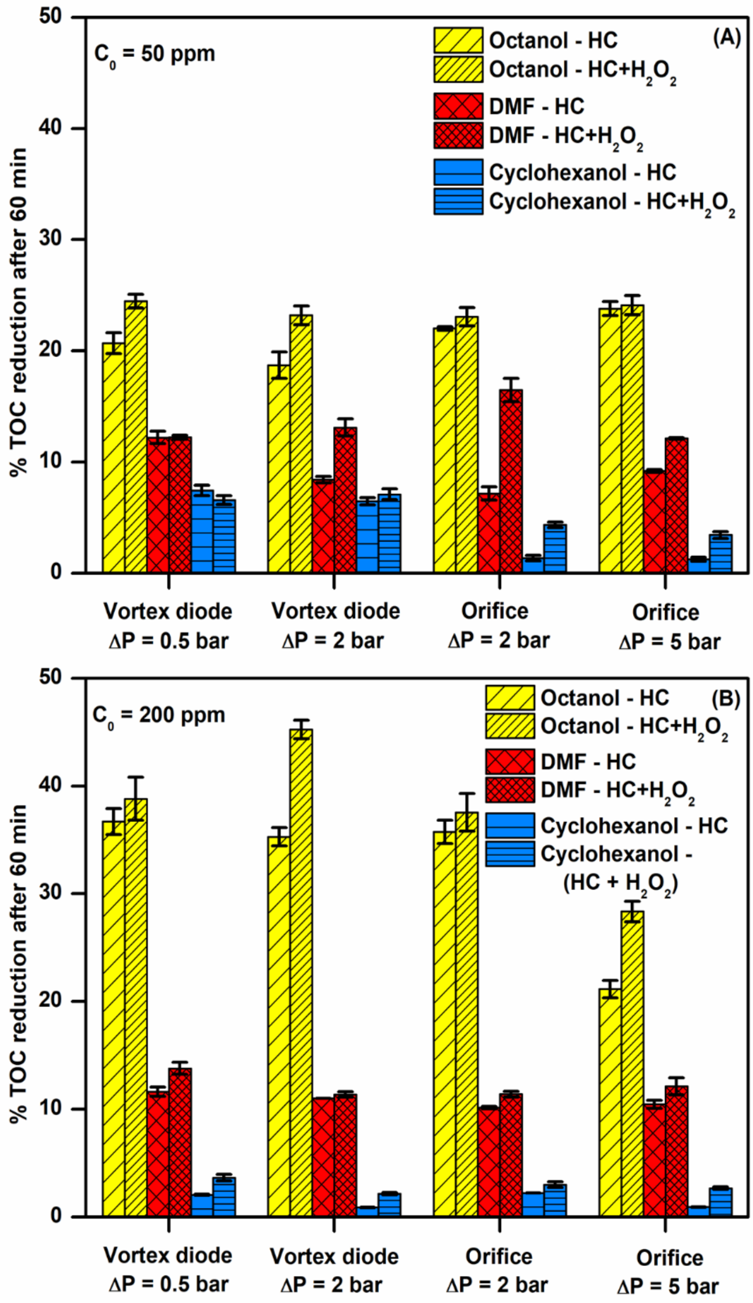

Figure 5. 7: Effect of addition of H_2O_2 addition (A) C_0 = 50 ppm, (B) C_0 = 200 ppm

5.3.5 Effect of reactor geometry, Per-pass degradation factor model and cavitational yield

The conventional approach for degradation kinetics is by using chemical reaction model for kinetics. However, a more rigorous approach would be that using a model that closely resembles the physico-chemical working of the hydrodynamic cavitation process. The use of per-pass degradation factor in hydrodynamic cavitation is therefore more appropriate in description and for implementation at a larger scale [4,16-18]. The per pass degradation can be defined as:

$$\text{Per-pass degradation factor } (\phi) = k\,\tau \tag{5. 4}$$

Where, τ is residence time which is ratio of volume of holding tank and flow rate through cavitation device.

The energy dissipation rate is calculated as,

$$W = \Delta P \times Q \tag{5. 5}$$

Figure 5.8 shows values of per-pass degradation factor and energy dissipation at different conditions. At higher pressure drop conditions of vortex diode and orifice (ΔP = 2 and 5 bar) energy dissipation rate is very high compared to lower pressure drop conditions. The Figure 5.8 clearly shows vortex diode with ΔP of 0.5 bar gives maximum per-pass degradation factor for octanol, cyclohexanol and DMF at both lower and higher concentration.

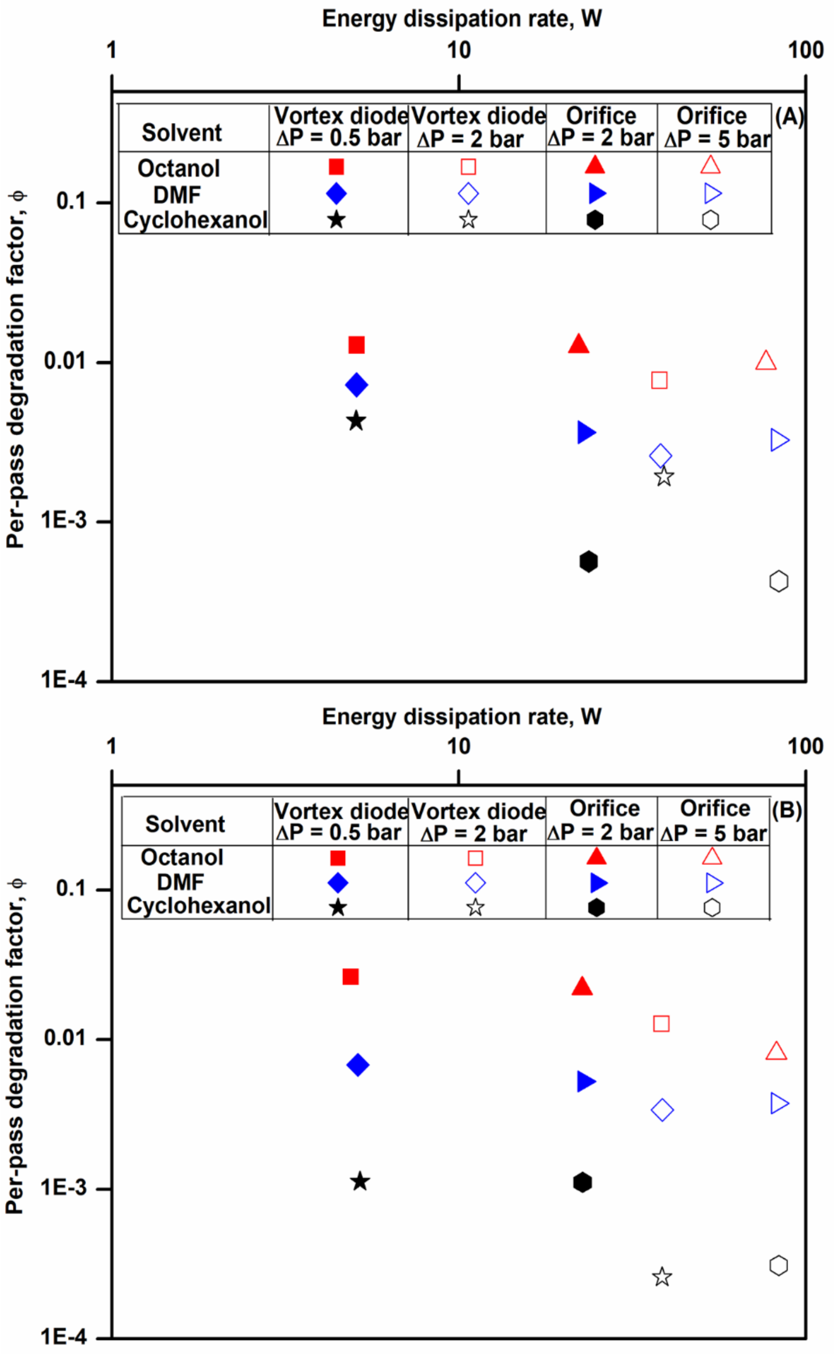

Figure 5. 8: Per-pass degradation factor for solvents

(A) C_0 = 50 ppm, (B) C_0 = 200 ppm

The overall cavitational yield (amount of solvent degraded per unit energy dissipation) can be written as,

$$Y = \frac{V(C_0 - C)}{\Delta PQt} \text{ mg/J} \qquad (5.\ 6)$$

The extent of degradation is different for different geometrical configuration and can be quantified by means of cavitational yield which is ratio of amount of pollutant degraded and product of pressure drop, flow rate and time. Figure 5.9 represents cavitational yield for different rectors – vortex diode and orifice. There was significant improvement by process intensification by means of aeration hence it is instructive to make comparison of the data, with and without aeration, using vortex diode and orifice for octanol, cyclohexanol and DMF at 50 and 200 ppm. Among the three solvents there was significant improvement in case of octanol at both low and high concentrations by aeration especially at lower pressure drop conditions for vortex diode and orifice. The values of cavitational yield for octanol at 50 and 200 ppm were 31.5×10^{-4} mg/J, 503.6×10^{-4} mg/J with cavitation and 58.1×10^{-4} mg/J, 1202.6×10^{-4} mg/J with aeration using vortex diode while for orifice 6×10^{-4} mg/J, 94.9×10^{-4} mg/J with cavitation and 14.2×10^{-4} mg/J, 119.7×10^{-4} mg/J with aeration. It is evident from the analysis of values of cavitational yield that vortex diode is superior to conventional orifice due to high cavitational yield.

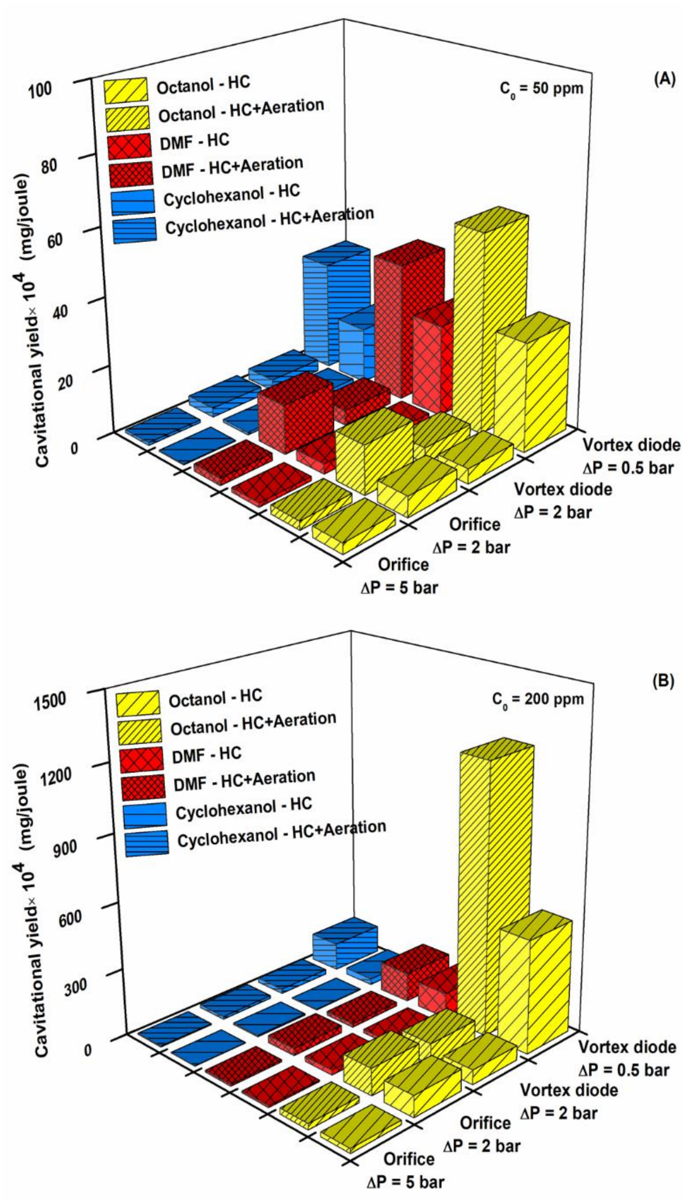

Figure 5. 9: Comparative analysis of cavitational yield with and without aeration

(A) C_0 = 50 ppm, (B) C_0 = 200 ppm

5.3.6 Nature of solvent and effect of dielectric constant

The overall degradation depends on various factors such as molecular weight, molecular structure and size, polarity, pKa, vapour pressure (or boiling point), pH and reactivity (functional groups in the organic molecules) [3]. Since OH radicals are very reactive, their life time is quite small. If organic pollutants have affinity towards vapour bubble, those pollutants will have better contact with OH radicals. Volatile pollutant may also get vaporised in bubble and may thermally degrade (rather than degradation via OH radicals). It is a quite complex mechanism and any simple relationship may not be deciphered at this point of time due to limited availability of data. Chakinala and co-workers could obtain only 58% degradation of phenol using hydrodynamic cavitation in 105 minutes and for the initial concentration of ~237 ppm [26]. Similarly, up to 54% degradation in 90 minutes was reported for degradation of p-nitrophenol [27]. Though the experimental processing and parameters were quite different in these studies, the important suggestion with regard to degradation was that higher degradation in p-nitrophenol could be attributed to its higher mass compared to phenol.

A rather unnoticed parameter so far, the dielectric constant of the solvents, appears to be an important parameter impacting solvent degradation and has not been seriously looked into in any of the previous studies. Higher values of dielectric constant indicate increased polarity. After comparing degradation of various solvents with dielectric constant, ε, values ranging from 2.4 to 40 and degradation using hydrodynamic cavitation, it was apparent that the solvents having low values of dielectric constant are prone to degradation compared to those solvents with higher values of dielectric constant (Figure 5.10). Suryawanshi et al. [3] reported highest degradation to the extent of 78% for toluene (ε 2.38) in comparison with other two solvents MEK (ε 18.85) and acetone (ε 20.07) where degradation was only 29 and 27% respectively in 180 minutes. Similarly, Sarvothaman et al. [4] reported a high degradation efficiency of 80% in 240 minutes for ethyl acetate (ε 6.02) compared to acetone and IPA (ε 19.92). Therefore, solvents such as toluene, ethyl acetate and n-octanol with dielectric constant 10 or much lower can be relatively easily destroyed to an extent of 80%, whereas solvents such as DMF (ε 36.71) tend to yield degradation efficiency of only ~10% under similar conditions. Comparatively low degradation efficiency for cyclohexanol (ε 13.4) can be attributed to its aromatic nature and attached strong hydroxyl group, possibly providing resistance to degradation. The hypothesis suggested here appears to agree well with literature data on different solvent degradation [3,4]. It is to be noted that not many systematic studies on solvent degradation using hydrodynamic cavitation are reported in the literature. Use of limited data on various solvents including that from the present study, it can be stated that high degradation was possible for toluene, ethyl acetate and octanol solvents which have low dielectric constant values among other solvents studied so far. Since the cavitation mechanism is concerned with generation of cavities within the aqueous medium, in water having a high dielectric constant of 80, the nature of solvent species as pollutant moiety can be highly relevant apart from solvent being *protic* or *aprotic*. However, this effect of dielectric constant and that of aromatic structure or linear chain structure has not been systematically investigated and requires detailed study. Therefore, it can be only reaffirmed that the plausible mechanism of physical and chemical degradation may involve contribution of various complex interactions due to mass, structure and functional characteristics of the organic moiety.

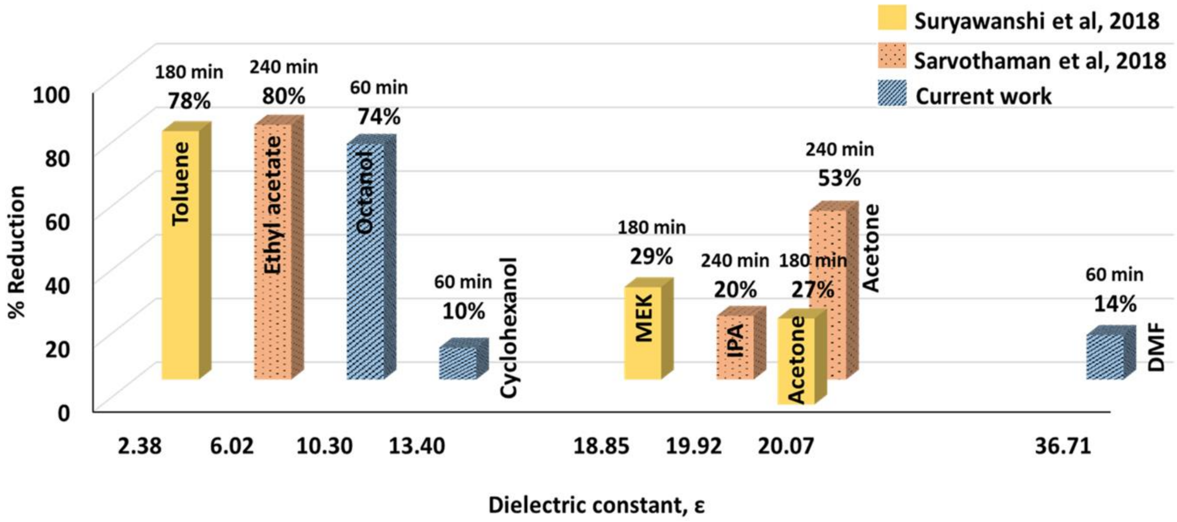

Figure 5. 10: Effect of solvent dielectric constant on degradation efficiency

5.3.7 Cost analysis

Typically, the cost of treatment by hydrodynamic cavitation per unit volume of effluent can be calculated as [1],

$$\text{Cost of treatment per } m^3 \text{ of effluent} = \frac{N_C \times \Delta P \times P_E}{36\eta} \qquad (5.\ 7)$$

Where, Nc is the number of passes, ΔP is pressure drop across cavitation device, P_E is cost of electricity and η is pump efficiency.

A representative cost analysis was carried for the degradation of various solvents to evaluate techno-economic feasibility of the technique. The cost of electricity in India was assumed at Rs. 10 /kWh (1$ = 70 Rs) and pump efficiency at 66%. Using the comparable levels of degradation and process conditions and for the best data of the present work- octanol; 0.5 bar and vortex diode, the cost of treatment is 4 Rs/m^3 (0.0571$/$m^3$), without aeration and 1.68 Rs/m^3 (0.024 $/$m^3$) by process intensification using aeration. The corresponding costs for orifice at ΔP of 2 bar are 17 and 14 Rs/m^3 (0.242 $/$m^3$) and (0.2 $/$m^3$), without and with aeration respectively. It is clear that treatment cost by using vortex diode is significantly lower compared to orifice showing rotational flow cavitation device is superior compared to linear flow device. While technical effectiveness and limitations of solvent degradation are evident from the results under different conditions, it is interesting to note that an order of magnitude, to the extent of 2-3 times reduction in the cost of treatment is possible using simple process intensification in the form of aeration and using suitable form of cavitation reactor.

5.4 Case Study-Real Industrial Effluent from API Intermediate manufacturer

Industrial wastewater from API intermediate manufacturer having problem of high organics and colour in final stream of wastewater was procured from local industry. The initial TOC of sample was 257.8 ppm with light brown colour and total dissolved solids of ~60,000 mg/lit. The pH of sample was 6.72 with small concentration of solvents in wastewater. The sample was specifically tested for organics degradation and colour removal by hydrodynamic cavitation using vortex diode as cavitating device on pilot plant of capacity 1m^3/h and in combination with aeration and addition of hydrogen peroxide.

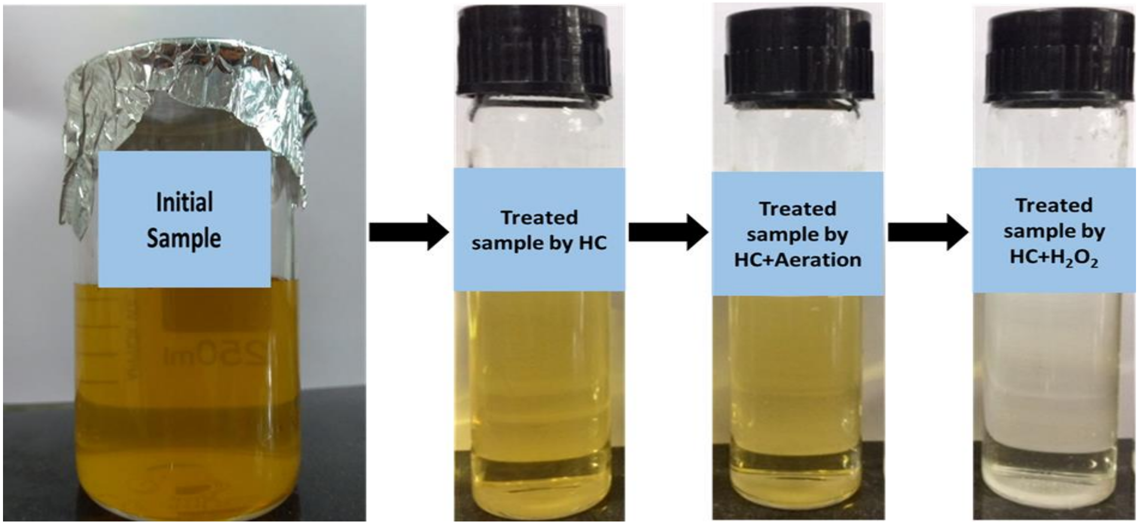

Figure 5. 11: Case study of real industrial wastewater treatment by hydrodynamic cavitation

Initially sample was tested by using vortex diode at different pressure drops such as 0.5, 1 and 2 bar respectively. The combined approach of cavitation with aeration and cavitation with addition of hydrogen peroxide (1:10 ratio) with respect to initial concentration of effluent was investigated and the photographs reflecting treatment results are shown in Figure 5.11. The reduction in TOC was ~45% after prolonged treatment (HC followed by HC +aeration followed by HC+H_2O_2) of ~6 hours. The prolonged treatment required may be due to presence of various other organics-difficult to degrade type, metals such as Ni, Fe, and some inorganics such as sodium sulphate, sodium chloride which are found in final stream of effluent. The colour removal was less using only cavitation or cavitation coupled with aeration as compared to that using hydrogen peroxide where drastic colour removal was obtained. Further, no significant changes were found in pH or in suspended solids. The strategy and the results for the treatment of real industrial effluent clearly demonstrate efficacy of hydrodynamic cavitation with vortex diode as cavitating device along with process intensification- aeration and addition of oxidizing agent such as hydrogen peroxide for possible treatment of industrial effluent contaminated with organics and for colour removal.

5.5 Conclusion

The present study clearly underlined the differences in the degradation behaviour of the three solvents, octanol, DMF and cyclohexanol using hydrodynamic cavitation techniques due to nature of the solvent apart from highlighting differences due to reactor configurations- linear flow based and vortex flow based cavitation. Different forms of process intensifications were also successfully evaluated for increasing the efficiency of degradation. The important findings are:

1. The vortex flow in cavitation was found to offer superior performance (cavitational yield) compared to orifice- Low pressure drop conditions i.e. 0.5 bar for vortex diode and 2 bar for orifice were most effective in solvent degradation.
2. Process intensification in the form of aeration was highly effective in improving the degradation efficiency; only marginal improvement by addition of oxidizing agent such as hydrogen peroxide.
3. A reduction in TOC to the extent of 74% could be achieved for octanol (200 ppm) using aeration with cavitational yield of 1202×10^{-4} mg/J for vortex diode, yield ~10 times higher than that for orifice.
4. The degradation depends on the nature of solvent and it was revealed that low values of dielectric constant ($\varepsilon<10$) favour degradation.
5. The strategy for degradation was also confirmed to be useful for real effluent treatment.

The substantially low cost of solvent degradation indicates techno-economic feasibility in implementation of the hydrodynamic cavitation in industrial wastewater treatment. The presented results and approach will be useful for further investigations on effluent treatment of water contaminated by various solvents.

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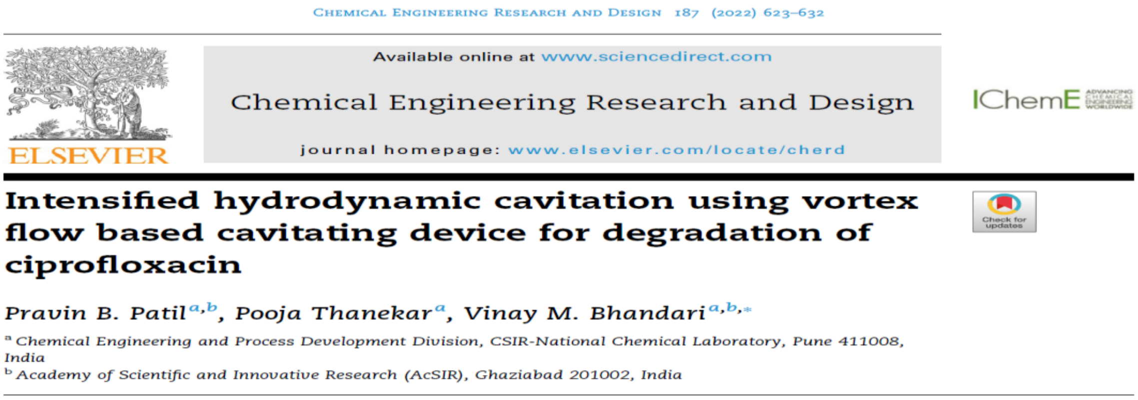

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Intensified hydrodynamic cavitation using vortex flow based cavitating device for degradation of ciprofloxacin

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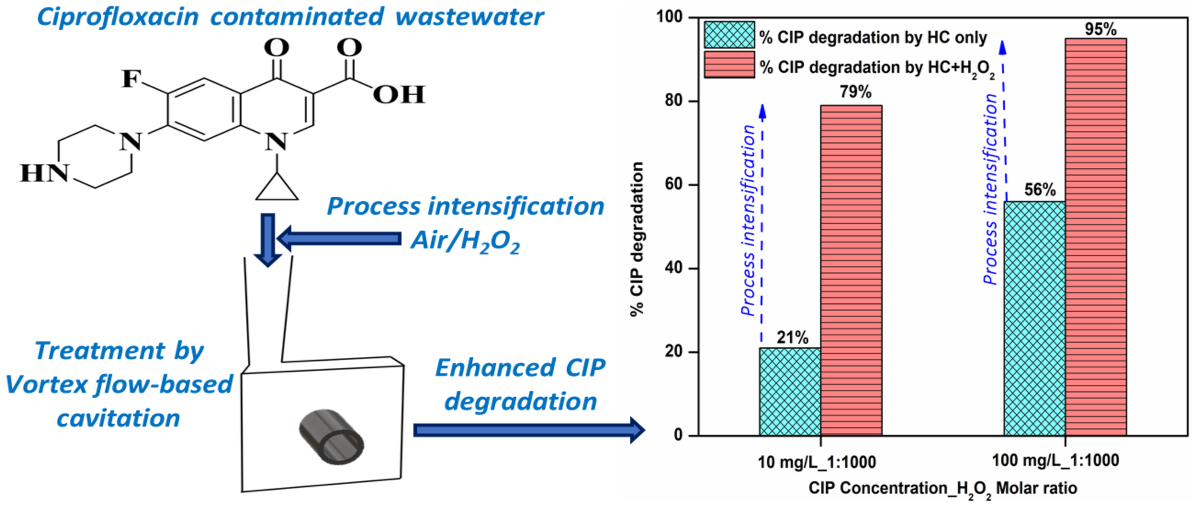
Chapter – 6



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Patent

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Chapter 6

Intensified Hydrodynamic Cavitation Using Vortex Flow Based Cavitating Device for Degradation of Ciprofloxacin

Abstract

The present work, for the first time, establishes degradation behavior of ciprofloxacin (CIP), a widely used fluoroquinolone group of antibiotics, using vortex flow based hydrodynamic cavitation (HC) for low to high concentrations of CIP (10 and 100 mg/L). Effect of pressure on the degradation of CIP and TOC reduction was investigated on pilot plant scale (capacity $1m^3/h$). Process intensifications using aeration as well as hydrogen peroxide (H_2O_2) were also investigated. While aeration did not yield any significant enhancement, process intensification using H_2O_2 resulted in ~ 200% enhancement in the CIP degradation as compared to HC alone. Excellent degradations, to an extent of 79 & 95%, were achieved corresponding to high cavitational yields of 7.2×10^{-4} mg/J and 86.8×10^{-4} mg/J for CIP concentrations of 10 and 100 mg/L respectively using the process intensified approach of HC and H_2O_2, not reported so far for cavitating devices without moving elements. The developed methodology demonstrated 4-7 times improvement in per-pass degradation and low cost with high efficiency compared to the conventional cavitation. The results clearly highlight utility of the process intensified approach using H_2O_2 for the degradation of CIP even at high concentrations, specifically important for pharmaceutical industries requiring zero liquid discharge norms.

6.1 Introduction

In recent years, new emerging pollutants such as pharmaceuticals, in the form of active pharmaceutical ingredients (API), have been in the spotlight of the scientific community as they may cause significant human health and environmental side effects, even at low concentrations (ng/L to µg/L) [1,2]. The usage of antibiotics, among the various pharmaceuticals, has been tremendously increased and as a result, their concentrations in wastewaters becoming a serious emerging environmental issue -either in the form of the parent compound or as metabolites in natural reservoirs including surface water, groundwater, as well as wastewater treatment plant effluent [3,4]. A majority of these compounds are recalcitrant or bio-refractory, in that they cannot be degraded using most of the conventional treatment methodologies [5]. A much serious concern is in the form of wastewaters generated in the manufacturing plants involving significantly high concentrations of API pollutants, order of magnitude higher than those found in the commonly researched surface water streams having very low concentrations in µg/L. In view of the stringent norms of zero liquid discharge for many of the pharmaceutical industries, it is imperative that suitable methodologies be evaluated for the treatment for wastewater streams containing high concentrations of API pollutants.

Ciprofloxacin (CIP) belongs to the fluoroquinolone group of antibiotics, which is widely used for the treatment of bacterial infections such as respiratory and urinary tract infections, skin, bone, and soft tissue infections. CIP has also been recommended drug by the World Health Organization (WHO) for the treatment of tuberculosis [6,7]. Additionally, the treatment of CIP has shown a strong potential for a possible cure against the coronavirus. These aspects lead to large manufacture and subsequent consumption of CIP, consequently leading to their exposure in natural reservoirs [8,9]. In India, amongst all antibiotics, ciprofloxacin has been detected in raw wastewater in concentrations as high as 28-32 mg/L [10]. From different case studies reported in the literature, the concentration of ciprofloxacin detected in hospital wastewater as 101 µg/L [11], municipal wastewater around 1.265 µg/L [12], Brazilian hospital effluent around 65 µg/L [13], rural and urban hospital wastewater in Vietnam as 42.8 and 36.5 µg/L [14], respectively. Most of the earlier studies showed the occurrence of antibiotics in the range of ng/L to μg/L but due to massive consumption of antibiotics in recent years, the occurrence range in wastewater is expected to shift to a higher range of mg/L. As a consequence of the existence of antibiotics in general, and CIP, in particular, in the aquatic environment has raised concerns about antibiotic-resistant pathogens [15,16].

Conventionally, physical, chemical, biological methodologies are practiced for the removal of antibiotics from wastewater [17]. Although, adsorption can offer high removal, it has serious drawback in the form of adsorbent cost and secondary waste generation [18,19]. Various studies have been reported on the degradation of ciprofloxacin from wastewater using different photocatalysts at different initial concentrations of ciprofloxacin [20–23]. Recently, Z- scheme photocatalysis has being used for degradation of varieties of pollutants using solar light active Z-scheme [24]. Although photocatalysis can offer 100% degradation of ciprofloxacin, it requires very high operational as well as maintenance cost for its use at a commercial scale. Recently, ultrasound mediated electrochemical advanced oxidation processes (EAOPs) such as electrocoagulation, electro-Fenton, and electrooxidation have found increased attention among the many other water and wastewater treatment technologies [25,26].

Cavitation is one of the advanced oxidation processes (AOPs) which generates oxidizing species in-situ and is considered as a greener process that can be used for the treatment of wastewaters [27]. Few literature studies are reported on the use of ultrasound for degradation of ciprofloxacin [28–30] which have drawbacks of low cavitational yield, higher energy requirements, and high cost of operation. Hydrodynamic cavitation (HC) is found to be suitable in terms of cost, scale up, energy efficiency, and ease in operation as compared to acoustic cavitation for the degradation of complex pollutants present in wastewater. In the case of hydrodynamic cavitation, cavities get generated by varying pressure within the flow which can be achieved through geometric constrictions and are well discussed in the literature [31]. The conventional reactor configurations in hydrodynamic cavitation are orifice, venturi, and high-speed rotor-stator assembly while vortex diode is comparatively a newer geometrical configuration. The application of vortex diode for the effluent treatment was suggested for mineralization of various pollutants along with the design of vortex diode

[27,32,33]. A typical design of vortex diode consists of a tangential inlet and axial outlet connected smoothly to the vortex chamber. The fluid enters through a tangential port at high pressures, forms vortex flow causing sudden pressure drop to such an extent that part of liquid flashes into vapor generating cavities, followed by cavity growth prior to their collapse. The collapse of the cavities or the implosion generates localized high temperature and pressure conditions, causing water to cleave homolytically generating active radicals such as H•, HO•, HOO•, and 2O•; the hydroxyl radicals being strong oxidizing species responsible for the oxidation of organic pollutants. Vortex diode is superior in terms of swirling flow, larger opening area- thereby less prone to clogging, less energy-intensive, and can offer much higher efficiency in the degradation of pollutants. Different studies were reported for the use of vortex diode in the degradation of pollutants such as dyes and solvents and also for successfully treating real industrial wastewaters for reduction in COD and ammoniacal nitrogen [34–36]. However, no work has been reported yet on its application in the degradation of antibiotics. Recently, Mukherjee et al. [37] reported the use of a rotational hydrodynamic cavitating device for the degradation of ciprofloxacin at a very low initial concentration of 0.05 mg/L, which required high energy. A 45% CIP degradation was achieved in 60 min using only hydrodynamic cavitation whereas, intensified approaches of HC+O_3, HC+H_2O_2, and HC+Fenton resulted in 91.4%, 85.6%, and 87.6% degradation within 30 min. The pharmaceutical industries require treating wastewater streams containing higher concentrations of API pollutants. Hence, there is a need for developing a sustainable methodology for the degradation of these persistence classes of organic pollutants from wastewaters at different levels of concentrations and different points of effluent release.

The present study, for the first time, reports the degradation of ciprofloxacin antibiotic using hydrodynamic cavitation by vortex flow-based vortex diode as a cavitating device over a wide range of concentration, from low (10 mg/L) initial concentrations of ciprofloxacin to comparatively high (100 mg/L) concentration. Systematic studies were carried out to evaluate the effects of various process parameters such as pressure drop across the device, initial concentration of pollutant (ciprofloxacin), as well as process intensification by aeration, and by addition of hydrogen peroxide. The degradation kinetics and cavitational yields were evaluated using the per-pass degradation model. The results of this work, effects of process intensifications, especially that for high degradation efficiency and practically completely mineralization without intermediates can be highly useful for devising an effective effluent treatment strategy for industry and wastewater treatment practices.

6.2 Materials and Methods

6.2.1 Materials

Ciprofloxacin ($C_{17}H_{18}FN_3O_3$ >98%, MW 367.80 g/mol), anhydrous, in crystalline powder form was procured from Sisco Research Laboratory Pvt. Ltd., Mumbai. Hydrogen peroxide (30% w/v, AR grade) was purchased from MOLYCHEM, Mumbai. Acetonitrile (≥99.9%, HPLC grade) was procured from Avantor Performance Materials India Limited. Formic acid (≥99.9%, HPLC grade) was purchased from Loba Chemie Pvt. Ltd.

6.2.2 Methodology

All the experiments were carried out using a hydrodynamic cavitation pilot plant, capacity 1 m^3/h, with vortex diode as a cavitating device. A cylindrical vertical recirculation tank with the conical bottom of the working capacity of 25L was employed for the wastewater holding and a vertical multistage centrifugal pump (Model CNP make CDLF2-6, SS316, 2 m^3/h at 45 MWC), rating 0.75 kW (1 hp), 2900 RPM, discharge pressure 0–5 bar) was used for pumping the liquid with flow control. The line connecting to the suction of the centrifugal pump from the bottom of the recirculation tank is equipped with Y-type strainer (CF 8M, ACME Engineering Production Corporation). Seamless SS316 tubing of size 0.75inch OD is used for the process fluid flow. Flow transmitter (KRONE, H250) with analog display, range 150-1500 LPH was used to measure the mainline flow rate while the temperature was measured using RTD (EUREKA Eng. Enterprises India; 0–200° C), fitted at downstream of cavitation reactor, inserted into recirculation tank. The cavitating device used in the present study was a vortex diode (Chamber diameter 66 mm, Throat diameter 11 mm, SS316) operated in reverse flow mode. A cooling coil (SS316) was provided into the recirculation tank for temperature control of the system. Horner make, HMI display is used for data logging with the provision of a sim card to access data from any location. The whole assembly is mounted on CS powder-coated skid with adjustable wheels for portability. The schematic representation and actual photograph of the experimental setup were reported in our earlier work [38].

In view of the limited information for treatment methodologies employing higher concentrations and also for the relevance to industry, the degradation studies of ciprofloxacin using vortex diode as a cavitating device were carried out using synthetic wastewater for two initial concentrations of ciprofloxacin-10 and 100 mg/L.

Based on the inception of cavitation for vortex diode at ~0.48 bar [39], the effect of pressure drop on ciprofloxacin degradation was studied for different pressure conditions such as ΔP as 0.5, 1, 1.5, and 2 bar for both the initial concentrations of ciprofloxacin (10 and 100 mg/L). Process intensification using aeration was studied by bubbling air in the tank, employing an air pump (SOBO AQUARIUM SB-9905, 2 Nozzle, 4.2W, Max. 5.5 L/min × two output); aeration by inserting a tube (SS316) into the recirculating tank from the top. The other process intensification approach involves the combination of HC and H_2O_2 using different molar ratios of CIP: H_2O_2 as 1:100, 1:300, 1:500, 1:700, 1:1000, and 1:1500 for both the initial concentrations of 10 mg/L as well as 100 mg/L. All the experiments were conducted for 180 min and the sample was withdrawn periodically, 30 min intervals, for the degradation monitoring. The pH of wastewater before and after treatment was in the range of 6.6 to 7.8 with only a minor change observed during the experiment.

6.2.3 Analysis

The degradation of CIP was monitored by measuring Total organic carbon (TOC, SHIMADZU make, TOC-L series TOC analyzer) and also by High Performance Liquid Chromatography (HPLC, Agilent, 1260 infinity series, C-18 column (4.6×250 mm)). A mobile phase of acetonitrile (80%) and 0.1 % formic acid in deionized water (DI) (20%) was used as an eluent for the separation under reverse-phase conditions at a flow rate of 0.8 mL/min. Detection of CIP was performed at a wavelength of 280 nm. The standard calibration graph was plotted for CIP (R^2 value = 0.99) for estimation of unknown CIP concentration during the treatment. The by-products formed during the degradation of CIP were identified using liquid chromatography–mass spectroscopy (LC–MS) technique.

6.3 Results and discussion

6.3.1 Effect of pressure drop on degradation kinetics of CIP

The pressure drop across the cavitation device is an important parameter that determines the efficiency of the treatment. In any cavitating device, the cavitation regime can be confirmed by identifying cavitation inception point. It was observed that the inception of cavitation occurs at 0.48 bar for vortex diode [39], also confirmed by another independent studies [40]. Thus, HC reactor was operated in the cavitation regime. Recently, the formation of OH radicals was reported using a terephthalic acid photoluminescence approach [41].

Four different pressure drop conditions were selected such as ΔP of 0.5, 1, 1.5, and 2 bar to evaluate the degradation efficiency at low and high concentrations of CIP. It was ensured that the process is operated in the cavitation regime. For a lower concentration of CIP (C_0 = 10 mg/L), the highest TOC reduction of 35% was obtained at ΔP of 1 bar while at a higher concentration of CIP (C_0 = 100 mg/L), about 16% TOC reduction was obtained after 180 min. The values for % TOC reduction for different pressure drop conditions at low and high CIP concentrations are given in Table 6.1. Based on the values of TOC reduction at different pressure drops, ΔP of 1 bar condition was considered as an optimum pressure drop condition for both high and low CIP concentrations and was considered for further studies.

The pressure drop and OH radical formation are related to the geometrical design of the vortex diode. Typically, the intensity of cavitation is important for the degradation of pollutants and certainly the nature of pollutant has crucial role apart from the geometry of the reactor. While the mechanism of degradation is essentially the same in different reactor configurations, the requirement of pressures for different configurations is quite different for effecting similar levels of degradation and here the performance of vortex diode, as a cavitating device requiring comparatively lower pressure drop compared to other conventional devices such as orifice or venturi [27,42]. It was also seen that the optimum value of pressure drop is different for different types of pollutants which necessities a detailed investigations related to the optimization of pressure drop for the selected pollutants.

The lower pressure drop requirement for vortex diode is in agreement to that reported in previous studies [35,36], compared to the conventional devices such as orifice, venturi, etc. Also, from earlier literature reports, it is evident that the optimum value of pressure drop required is different for different pollutants which justifies the optimization study of pressure drop for the selected pollutant to achieve a high extent of degradation.

Table 6. 1: TOC reduction and rate constant data for CIP using vortex diode

Concentration, C_0 (mg/L)	ΔP, Bar	% TOC reduction after 180 min	1st order rate constant, $K \times 10^3$ (min^{-1})
10	0.5	21	1.3
	1	35	2.6
	1.5	27	1.7
	2	18	1.1
100	0.5	13	0.8
	1	16	1.1
	1.5	8	0.5
	2	6	0.4

The reactions pertaining to the degradation in hydrodynamic cavitation can be assumed as pseudo first order and kinetics of CIP degradation can be evaluated using simple power law model which is given below,

$$C = C_0 e^{-kt} \qquad (6.\ 1)$$

Where, C_0 and C represent CIP concentrations before and after treatment, ‘t’ is time (min) and ‘k’ is first order rate constant (min^{-1}).

The rate constants values are given in Table 6.1 for both low and high concentrations of CIP using vortex diode as a cavitating device. It was observed that high values of rate constants were obtained at ΔP 1 bar as 2.6×10^{-3} (min^{-1}), 1.1×10^{-3} (min^{-1}) at CIP concentrations of 10 and 100 mg/L respectively. It is evident that the extent of degradation is quite higher at a lower concentration of CIP than that at a higher concentration. The decrease in the degradation with an increase in the pollutant concentration can be attributed to similar concentration availability of generated OH radicals for low and high pollutant concentrations. The results are consistent with many literature reports on the decrease in degradation with an increase in pollutant concentration [43–46]. Suryawanshi et al. [43] reported higher COD removal at lower initial concentrations for degradation of solvents using cavitation for acetone, methyl ethyl ketone, and toluene in the range of 100-500 ppm. Similarly, decreased rate constant from 2.2×10^{-3} min^{-1} to 1.3×10^{-3} min^{-1} was observed for an increase in the initial concentration of dichlorvos from 10 to 50 ppm [44]. Rajoriya [46] also observed similar trend for degradation of reactive blue 13 dye using cavitation and reported decrease in % decolorization from 47% to 19% with an increase in the initial concentration of dye from 30 to 60 ppm. In the present work also, %TOC reduction was higher at low CIP concentration than that obtained at high concentration. It should be noted that though the percentage degradation decreases with an increase in the initial concentration, the actual amount of the pollutant removed is higher at higher initial concentrations.

6.3.2 Effect of aeration

Aeration is one of the simplest forms of process intensification in hydrodynamic cavitation, where air can be introduced into the fluid, through simple bubbling to a sparger design. In this work, a simple form of bubbling air using a tube inserted in the holding tank fluid was used. The design of the holding tank incorporates inclined return/recycle of water dipped in pool of water to ensure intense mixing/ turbulence in the tank. An optimized pressure drop of ΔP of 1 bar was employed for comparison of the results of process intensification. At CIP concentration of 10 mg/L, about 16% TOC reduction and 6% CIP degradation were obtained after 180 min of treatment time whereas, at CIP concentration of 100 mg/L about 7% TOC reduction and 24% CIP degradation were obtained. Thus, cavitation coupled with aeration for CIP degradation showed only marginal improvements, especially for the CIP degradation. The synergistic coefficient in aeration was calculated by using a formula,

$$\text{Synergistic coefficient} = \frac{k_{(\mathrm{HC+Aeration})}}{k_{\mathrm{HC}}+k_{\mathrm{Aeration}}} \qquad (6.\ 2)$$

The values of synergistic coefficient obtained for low concentration of 10 mg/L and high concentration of 100 mg/L were less than one (0.23 and 0.30 respectively). The results indicate no synergism for the intensified approach of aeration for both low and high initial concentrations of CIP degradation. The process intensification in the form of aeration using hydrodynamic cavitation was earlier reported for ammoniacal nitrogen removal [36] and solvent degradation [35]. It is conventionally believed that the process intensification in the form of aeration may provide additional nuclei thereby positively impacting the formation of more oxidizing species and consequently resulting in fruitful collapse with more degradation of pollutants in wastewater. The effects of aeration in the different studies reported in the literature for different pollutants were not consistent and while enhancement in the degradation due to aeration was reported in some studies because of increased oxidation due to air/oxygen, negligible effect of aeration was also reported in some studies[35,47]. Further, when significant enhancement in degradation due to the addition of oxygen was reported, the same was not observed with aeration[47,48]. The negative effect of aeration observed in the present study can be attributed to possible effects other than oxidation, such as physical carryover of the cavities that can reduce the cavitational effect.

6.3.3 Process intensification using the addition of H_2O_2

Hydrogen peroxide (H_2O_2) is a strong oxidizing agent and commonly used form of process intensification along with hydrodynamic cavitation for degradation of API pollutants [49,50]. H_2O_2 on decomposition yields only water and oxygen. Hydrodynamic cavitation along with hydrogen peroxide provides additional oxidizing species which further enhances the degradation of pollutants. The hybrid approach of cavitation with the addition of hydrogen peroxide was studied at different loadings of H_2O_2 using the molar ratios of CIP: H_2O_2 as 1:100, 1:300, 1:500, 1:700, 1:1000, and 1:1500. The extent of CIP degradation obtained for the different molar ratios is shown in Figure 6.1. To evaluate the combined effect of hydrodynamic cavitation with the addition of H_2O_2 for CIP degradation, synergistic coefficient was calculated by using the formula as,

$$\text{Synergistic coefficient} = \frac{k_{(HC+H2O2)}}{k_{HC}+k_{H2O2}} \tag{6. 3}$$

At an initial CIP concentration of 10 mg/L, cavitation alone shows about 21% CIP degradation with 6% TOC reduction after 180 min while when the hydrodynamic cavitation is coupled with H_2O_2, the extent of CIP degradation was 80% at a molar ratio of CIP: H_2O_2 as 1:1000. Similarly, at a CIP concentration of 100 mg/L cavitation alone gave about 56% CIP degradation with 16% TOC reduction after 180 min while when cavitation is coupled with H_2O_2 the extent of CIP degradation was 95% at a molar ratio of CIP: H_2O_2 as 1:1000. The highest CIP degradation was obtained for 1:1000 molar ratio H_2O_2 addition for both low and high concentrations with synergistic coefficient values of 2.8 and 2.6 respectively. A comparative analysis of CIP degradation is shown in Figure 6.2. Figure 6.2 represents a comparative analysis of cavitation alone with a combination of HC+ H_2O_2. Low CIP concentration of 10 mg/L, cavitation alone results in mineralization (interpreted in the form of higher TOC reduction) whereas, in the case of HC+ H_2O_2, the extent of CIP degradation was observed to be higher as compared to mineralization. It can be seen that the extent of CIP degradation, as well as TOC reduction, is comparatively more at high concentration (100 mg/L) as compared to that with low CIP concentration (10 mg/L). This can be attributed to the fact that the process follows the reactive pathway where the reaction rate is dependent on the concentration of the species (here pollutant); the more the concentration of the species, the higher is the reaction rate.

Figure 6.3 depicts HPLC spectra for degradation of CIP using a combined approach of HC+ H_2O_2 at a molar ratio of CIP: H_2O_2 as 1:1000. It can be seen that not many prominent intermediates peaks were detected for the combined HC+ H_2O_2 approach and intermediates get eventually degraded. The findings are quite interesting and form advantage for the proposed hybrid hydrodynamic cavitation technology since the photooxidation studies reveal formation of many intermediates. Appendix II summarizes the advanced oxidation processes reported in the literature to highlight the importance of the results of this work.

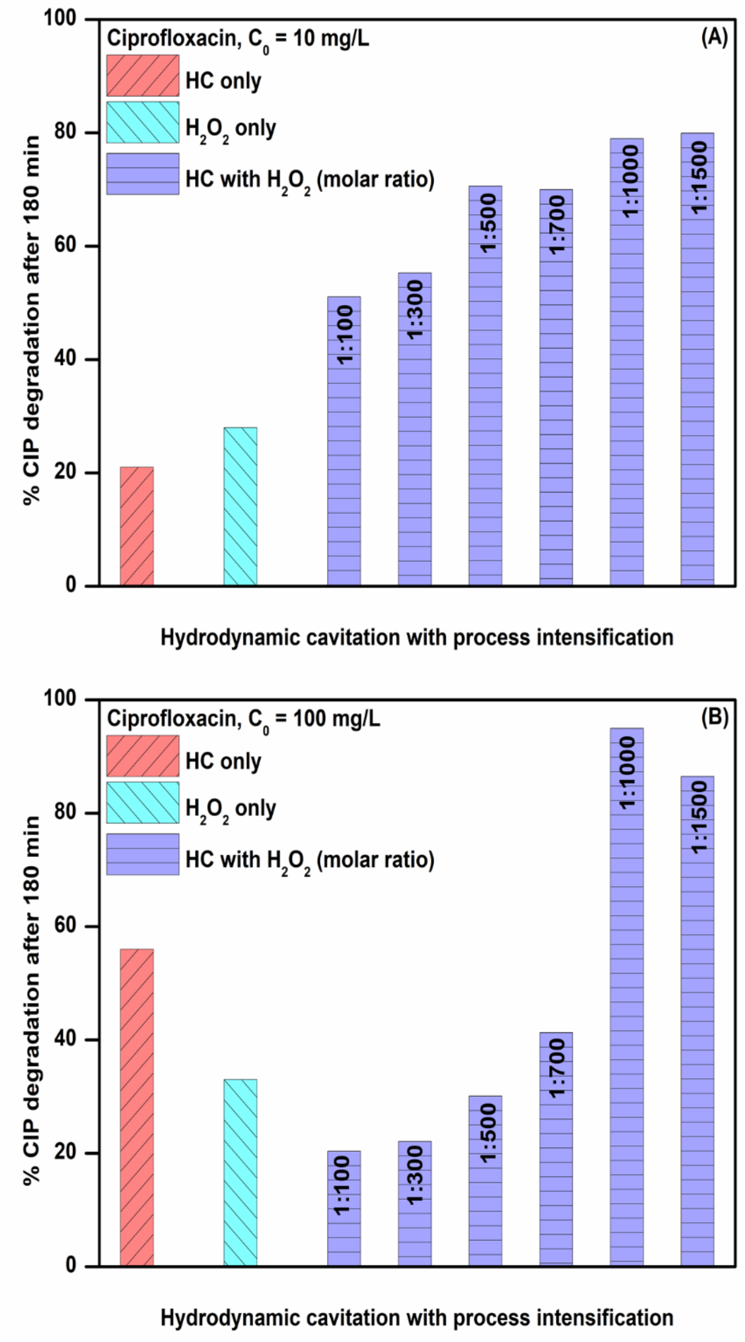


Figure 6. 1: Hybrid cavitation with the addition of H_2O_2

A. 10 mg/L, B. 100 mg/L

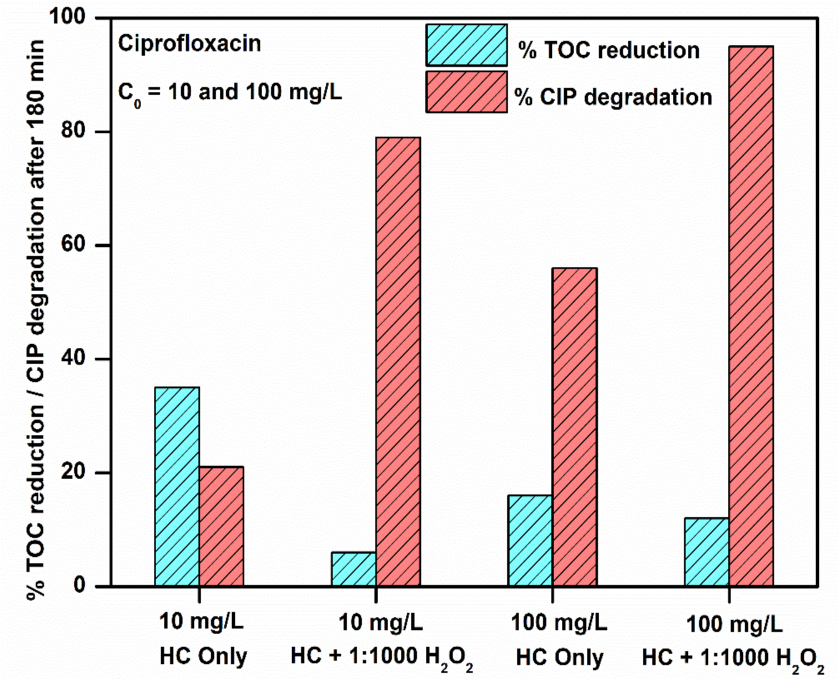
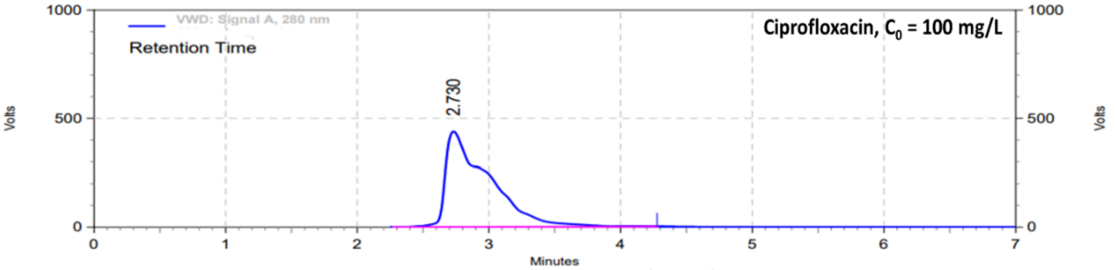
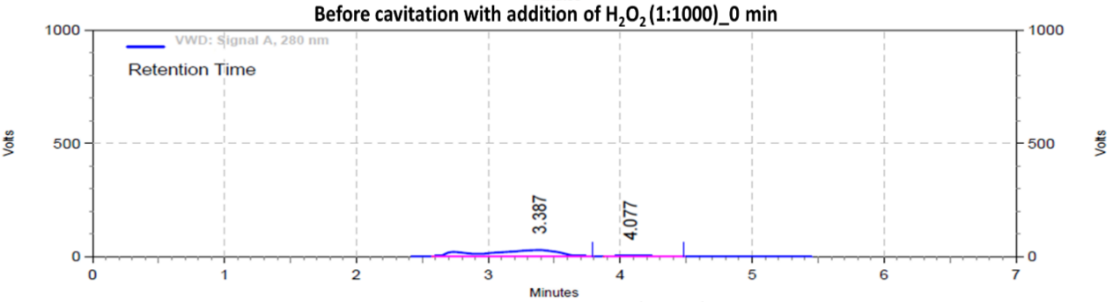


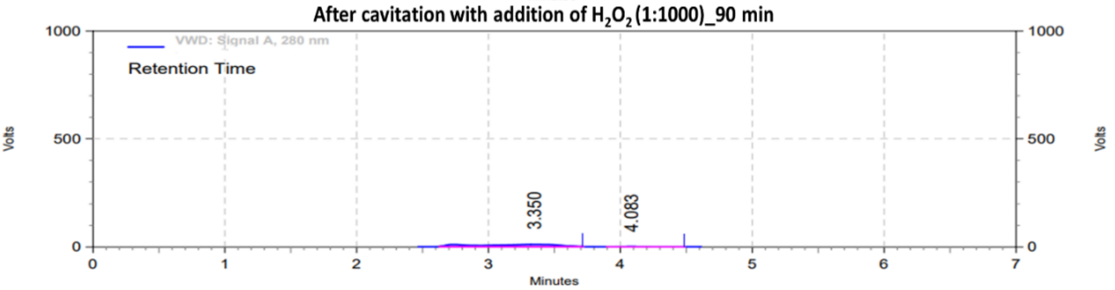
Figure 6. 2: Evaluating effect of optimum H_2O_2 dosing on CIP degradation



Before cavitation with addition of H_2O_2 (1:1000)_0 min



After cavitation with addition of H_2O_2 (1:1000)_90 min



After cavitation with addition of H_2O_2 (1:1000)_180 min

Figure 6. 3: HPLC spectra for CIP degradation (C_0 = 100 mg/L) for hybrid cavitation

6.3.4 CIP degradation mechanism

A high extent of degradations of CIP were achieved when the hydrodynamic cavitation is coupled with H_2O_2 for both lower and higher concentrations. In view of HPLC analysis (Figure 6.3) indicating not many prominent intermediates, it is instructive to investigate degradation mechanism and intermediates evaluation, using LC-MS analysis. Figure 6.4 shows LC-MS spectra for the treated sample of CIP degradation using HC+ H_2O_2 after 180 min of treatment time at CIP concentration of 100 mg/L. LC-MS analysis shows two prominent peaks at m/z 214.91, and 102.12. The likely intermediates could be 1-cyclopropyl-1,4-dihydroquinoline-3-carboxylic acid (m/z 214.91) and 4-hydroxypiperidin-1-ium (m/z 102.12). The analysis confirms that the hybrid approach of hydrodynamic cavitation with addition of hydrogen peroxide produces very few intermediates and that may also get degraded eventually with extended treatment time. Based on the analysis, the mechanism can be postulated and is shown in Figure 6.5 for process intensification approach of hydrogen peroxide.

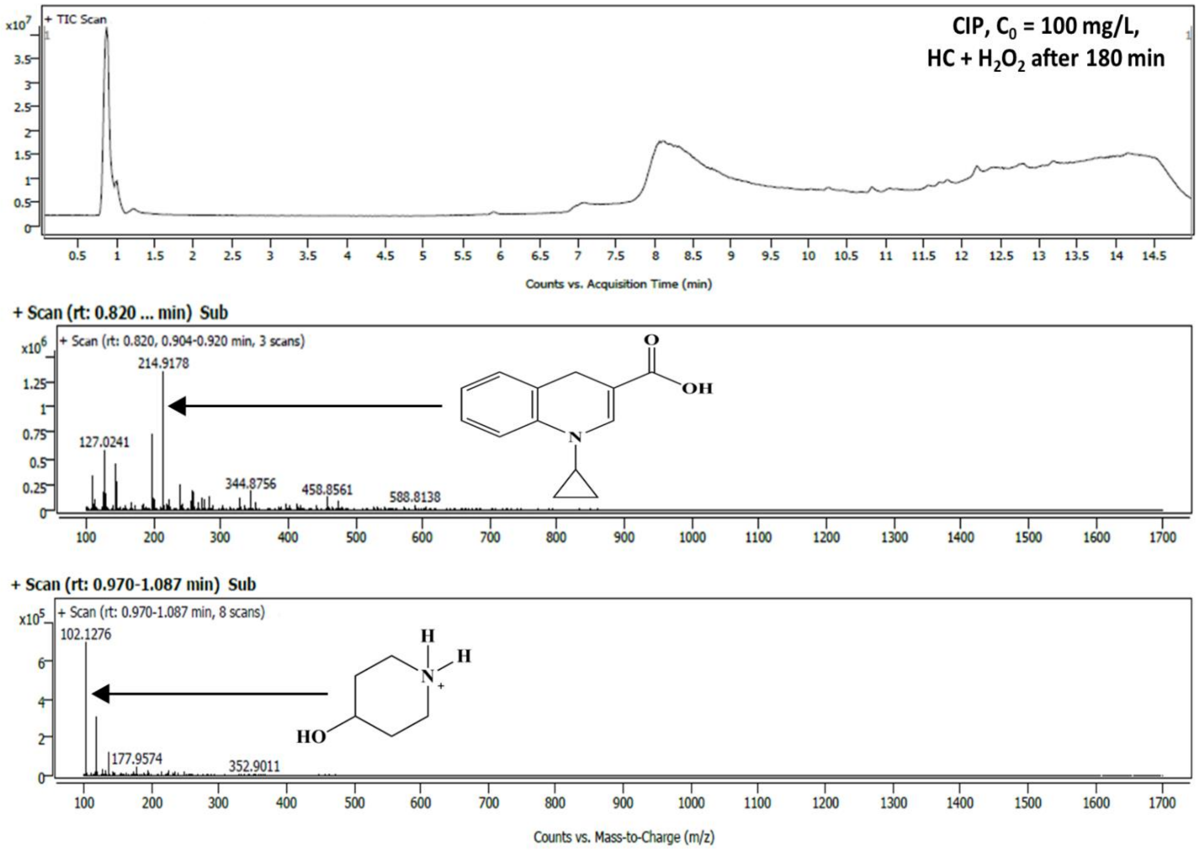


Figure 6. 4: CIP degradation by products by LC-MS spectra for hybrid cavitation

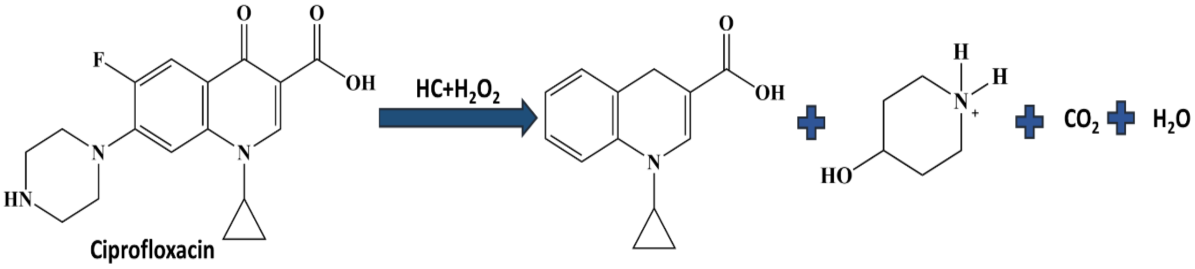


Figure 6. 5: CIP degradation mechanism for hybrid treatment approach

6.3.5 Per-pass degradation factor and cavitational yield for ciprofloxacin degradation

The conventional kinetics/ rate analysis is done typically using the power-law model. However, the recent approach which is based on the number of passes required for degradation closely resembles physicochemical behavior in the hydrodynamic cavitation process and is, therefore, most appropriate, especially at a larger scale of operation [35,36,51–54]. The per-pass degradation factor is defined as,

$$\text{Per-pass degradation factor } (\phi) = k\tau \qquad (6.4)$$

Where, τ is residence time which is a ratio of volume of the holding tank and the flow rate.

The energy dissipation rate is calculated as,

$$W = \Delta P \times Q \qquad (6.5)$$

The overall cavitational yield (amount of CIP degraded per unit energy dissipation) can be calculated as,

$$Y = \frac{V(c_0 - c)}{\Delta PQt}\ \mathrm{mg/J} \qquad (6.6)$$

Where, Y= cavitational yield, V= volume, C_0 and C= initial and final concentration of pollutant

Figure 6.6 represents the enhancement due to hybrid approach for the per-pass degradation factors as well as cavitation yield under different conditions such as hydrodynamic cavitation alone, and hybrid hydrodynamic cavitation with the addition of H_2O_2 (1:1000 molar ratio) for different CIP concentrations. It can be seen that the per-pass degradation factor is high at a high CIP concentration of 100 mg/L. The hybrid approach of hydrodynamic cavitation using vortex diode at ΔP 1 bar with the addition of H_2O_2 (1:1000 molar ratio) showed a very high enhancement in per-pass degradation factor for low concentration (566% enhancement) as compared to high concentration (283% enhancement).

The values of cavitation yield at 10 mg/L initial concentration of CIP using hydrodynamic cavitation alone, and hydrodynamic cavitation with the addition of H_2O_2 (1:1000 molar ratio) are 1.9×10^{-4} mg/J, and 7.2×10^{-4} mg/J respectively. Similarly, for a high concentration of 100 mg/L CIP concentration, the values for cavitational yield are 48.5×10^{-4} mg/J, and 86.8×10^{-4} mg/J using hydrodynamic cavitation alone, and hydrodynamic cavitation with the addition of H_2O_2 (1:1000 molar ratio) respectively. From the results, it is evident that the hybrid method is superior to the single method in terms of cavitational yield for both low (~ 4 times) and high concentrations of CIP (~2 times). The enhancement here can be attributed to the enhanced generation of hydroxyl radicals due to H_2O_2.

Mukherjee et al. [37] reported cavitational yield obtained for ciprofloxacin degradation using a rotational hydrodynamic cavitating device, where the cavitational yields obtained for different approaches such as cavitation alone, HC+ H_2O_2, HC+ Fenton's reagent, and HC+O_3 were 2.9×10^{-7}, 5.6×10^{-7}, 5.7×10^{-7}, and 6.1×10^{-7}mg/J, respectively. The reported values were significantly lower (~650-14000 times) as compared with the cavitational yield obtained in the present work. The rotational hydrodynamic cavitation reactors require operation at a very high speed (~3000 RPM), thus are energy-intensive as compared to vortex diode. The values for cavitational yield in the case of vortex diode for HC alone were in the range of 1.9×10^{-4} mg/J to 48.5×10^{-4} mg/J; for intensified approach of HC+H_2O_2, in the range of 7.2×10^{-4} mg/J to 86.8×10^{-4} mg/J for 10-100 mg/L initial CIP concentration, clearly represent significantly higher efficiency of the vortex diode and therefore, utility of vortex-based cavitation in the degradation of CIP. Thus, hydrodynamic cavitation using vortex diode as a cavitating device can be considered to be the most energy efficient alternative for the degradation of ciprofloxacin.

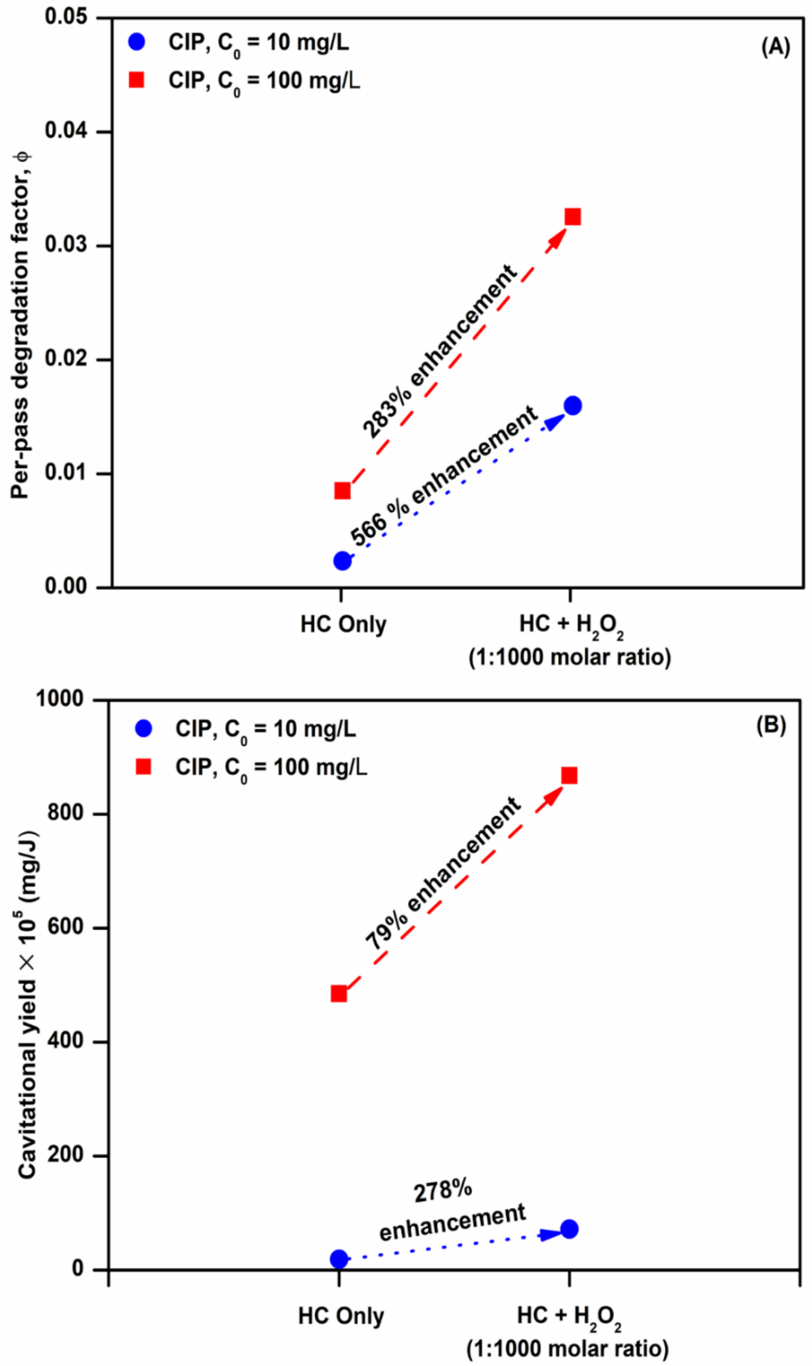


Figure 6. 6: Per-pass degradation and cavitational yield for different methodologies

A. 10 mg/L, B. 100 mg/L

6.3.6 Cost analysis

The cost of the process, hydrodynamic cavitation using vortex diode as cavitating device, for %CIP degradation can be calculated as [27],

$$\text{Cost of treatment per m}^3 \text{ of effluent} = \frac{N_C \times \Delta P \times P_E}{36\eta} \qquad (6.\ 7)$$

Where, Nc is the number of passes, ΔP is pressure drop across cavitation device, P_E is the cost of electricity and η is pump efficiency.

The techno-economic feasibility was evaluated under typical Indian conditions. The cost of electricity for the Indian scenario was assumed as Rs. 10 /kWh (1$ = 75 Rs) and pump efficiency is assumed as 66%. The total cost obtained using only hydrodynamic cavitation was 41 Rs/m^3 (0.546 $/m^3) (22 Rs/gm) for concentration of CIP as 10 mg/L whereas, the corresponding cost for 100 mg/L concentration was 0.9 Rs/gm, substantial reduction due to the effect of concentration. The total cost obtained for the process intensification approach using H_2O_2, was 38 Rs/m^3 (~0.5 $/m^3) (~8 Rs/gm) for 10 mg/L CIP concentration whereas, for 100 mg/L CIP concentration, the cost of the treatment was ~3 Rs/gm under optimized conditions. The detailed calculation has been given in Appendix III. The cost of treatment per unit weight of the pollutant is substantially less for the intensified approach due to significantly reduced number of passes and also due to the increased degradation of the pollutant, although, the cost can vary if the number of passes or the cost of additives get increased.

6.4 Conclusions

The present study successfully demonstrates near complete degradation of antibiotic ciprofloxacin using vortex flow-based cavitation device at low and high concentrations of CIP up to 100 mg/L. The process intensification using H_2O_2 could provide more than 95% degradation, very insignificant formation of intermediates compared to reported catalytic degradations, and a more predominant mineralization pathway. The important findings are listed below,

1. The present study, for the first time, demonstrated the use of vortex flow-based cavitation for antibiotics degradation.
2. The optimum pressure drop for CIP degradation was very low, 1 bar, for low to high initial CIP concentrations.

3. Vortex diode as a cavitating device, ΔP of 1 bar, low CIP concentration of 10 mg/L gave about 21% CIP degradation with 35% TOC reduction whereas, at high CIP concentration of 100 mg/L, 56% CIP degradation with 16% TOC reduction were obtained.
4. Process intensification using the addition of hydrogen peroxide showed significant enhancement in degradation compared to only a marginal improvement for intensification using aeration.
5. For the combined approach of HC+H_2O_2, CIP degradations of 79% and 95% were achieved at CIP concentrations of 10 and 100 mg/L respectively.
6. The cavitational yield for the combined approach of HC+H_2O_2 was higher (86.8×10^{-4} mg/J) as compared to that obtained for HC alone (48.5×10^{-4} mg/J) at 100 mg/L initial concentration of CIP.
7. Per-pass degradation model showed about 4-7 times improvement in per-pass degradation for cavitation with the addition of H_2O_2 (1:1000 molar ratio) as compared to the conventional hydrodynamic cavitation.
8. A reasonably low cost of treatment along with high efficiency can be achieved using hybrid cavitation with H_2O_2 as compared to the cavitation alone.

The effective use of the vortex based cavitating device in hydrodynamic cavitation and process intensification using H_2O_2 at comparatively high antibiotic loading with substantially low cost clearly highlights the techno-economic feasibility in implementing the strategy for the degradation of antibiotics.

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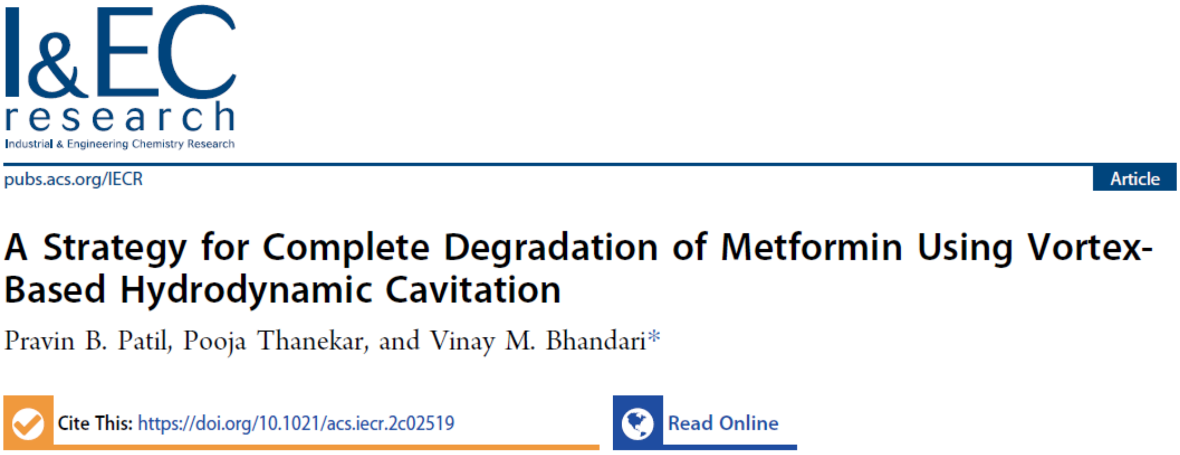
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A Strategy for Complete Degradation of Metformin Using Vortex-Based Hydrodynamic Cavitation

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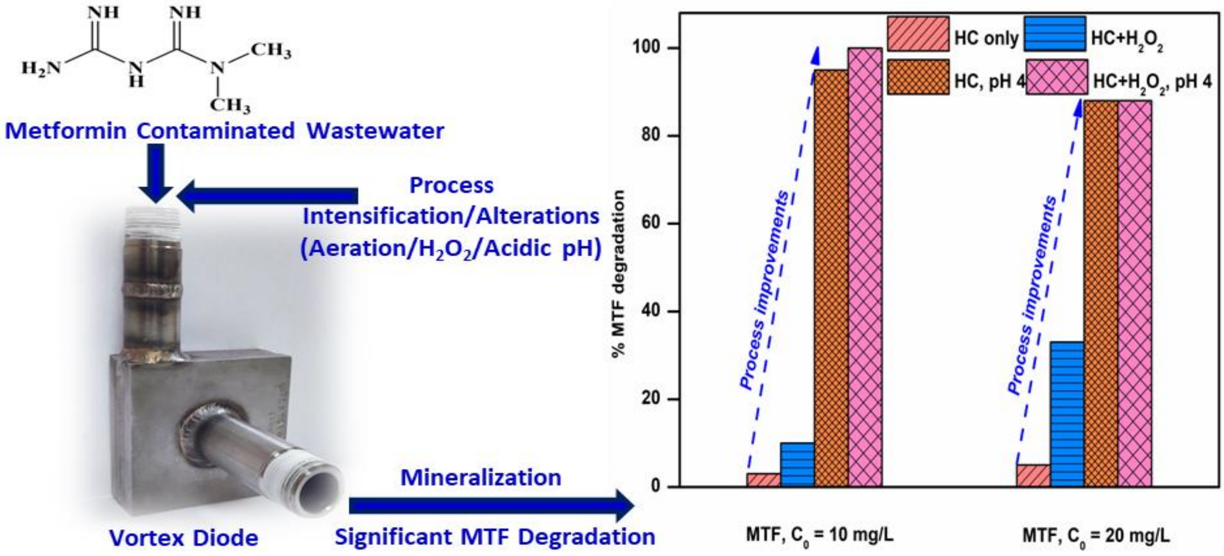
Chapter – 7



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Chapter 7

A Strategy for Complete Degradation of Metformin Using Vortex-Based Hydrodynamic Cavitation

Abstract

The present work successfully establishes degradation of metformin, an antidiabetic drug, using vortex flow-based hydrodynamic cavitation (HC) and process intensification. Studies were carried out on a pilot plant (1m^3/h) and for high initial concentrations, 10-20 mg/L. Effects of various process parameters were evaluated apart from intensifications using aeration and the addition of hydrogen peroxide. A low degradation (3-5 %) by HC at ΔP of 1 bar could be improved by process intensification using hydrogen peroxide (33%). Importantly, a very high, 95% metformin degradation, was obtained at pH 4 with excellent cavitational yields up to 162×10^{-5} mg/J, further extending to 100% degradation using HC+H_2O_2, an order of magnitude enhancement of 900%. The synergy can be drastically enhanced by process modifications. Per pass degradation enhancement was huge, 100 times, corresponding to order of magnitude cost reduction compared to conventional hydrodynamic cavitation. The established strategy can have positive implications for industrial wastewater treatment.

7.1 Introduction

Thousands of tons of pharmaceutical and personal care products are being produced worldwide since use of these in different forms has now become part of a modern lifestyle in daily use for different purposes which eventually increases the demand for the synthesis of active pharmaceutical ingredients (API) and consequently, their release in the environment in the form of API pollutants [1–3]. Most of these API pollutants are emerging contaminants causing grave environmental concerns. In recent years, the presence of API pollutants is considerable in every water matrix such as groundwater, surface water, seawater, drinking water, and wastewater (influent and effluent) [1,4]. In general, the order for the occurrence of API pollutants in relative concentrations in the environment is industrial wastewater > hospital wastewater > surface water > ground water > drinking water [5]. The surface water bodies typically have sub-ppm levels of concentrations while the industrial wastewater streams for the treatment can have significantly higher concentrations, typically in tens of ppm. Thus, the methodologies for treating different wastewaters have a varying mandate in terms of initial concentrations of the pollutants. The major route for the presence of API pollutants in the environment is the discharge of wastewaters from many pharmaceutical industries due to a lack of efficient and cost-effective treatment methodologies; the persistent to pseudo persistent nature of the pollutants reflecting into difficulty in their complete destruction by conventional treatment methodologies [6,7]. Thus, there is a need for the development of effective treatment technology, especially for the treatment of emerging API pollutants.

Metformin ($C_4H_{11}N_5$) abbreviated hereinafter as MTF, is an antihyperglycemic drug and is often prescribed worldwide as a first-line medication for type 2 diabetes. Apart from its usage in the treatment of diabetes, it is also found effective as an anticancer agent [8] as well as used in the treatment of polycystic ovary syndrome [9]. As being extensively used globally for various applications, there is an increased demand which can further lead to the increased detection of MTF in the water matrix. MTF is a highly polar compound with pKa value of 12.4 [10]. MTF is an emerging contaminant in the environment and possibly a potential endocrine disruptor in the environment [11,12]. Scheurer et al. [13] reported the occurrence of MTF in STP influents of Germany in the range of 101-121 µg/L. Trautwein et al. [14] reported the occurrence of MTF in various sources such as southern German sewage treatment plant (111,800 ng/L), multinational lake constance (102 ng/L), river Elbe (472 ng/L), river Weser (349 ng/L), marine north sea water (13 ng/L). Bradley et al. [15,16] reported values in the concentration range of 1-1000 ng/L after surveying various pharmaceuticals in different surface waters, USA, highlighting the need for a sustainable and cost-effective methodology for MTF removal to avoid water contamination of natural reservoirs.

Conventionally MTF is removed from wastewater by various methodologies such as physical, chemical, biological, or using a combination of advanced technologies. Also, many literature studies have reported MTF removal using advanced oxidation methods such as photocatalysis, Fenton, photo-Fenton, TiO_2-Fenton, etc. Zhu et al. [17] reported adsorptive removal of MTF using graphene oxide as an adsorbent and achieved 80% removal in 20 min whereas, Niaei et al. [18] reported 95.7% MTF removal in 120 min using (Fe- Z) zeolite nano-adsorbent at 10 mg/L concentration. There are various studies reported on the adsorptive removal of MTF using a variety of adsorbents such as powdered activated carbon, ion exchange resins, carbon nanotubes, chitosan, activated carbon, and organic resins [17]. Though adsorption is effective for the removal, problems associated with adsorption such as regeneration of adsorbent, secondary waste generation pose serious constraints in large-scale operations. The degradation of MTF was investigated using modified biological processes such as using Hybrid Vertical Anaerobic Biofilm-Reactor (HyVAB) [19], activated sludge [20], and phytoremediation approach by *Typha latifolia* plants [21]. All these modified biological approaches resulted in 74-98% removal efficiency however, the time required for degradation is very high (14-28 days) which makes the process inefficient/ impractical at a high concentration of MTF and for real life application.

The removal of MTF using the photo-Fenton process was reported recently with only 24 % removal in 60 min [22], while 99% degradation in 27 min was reported using the intensification in the form of electro-Fenton process [23]. The use of photocatalysts was also reported widely with varying efficiencies, TiO_2 in presence of UV light with 41% TOC degradation within 60 min [24], 97% removal in 240 min using a solar photocatalytic process [25], Carbuloni et al. [26] investigated the photocatalytic degradation of MTF using TiO_2-ZrO_2 catalyst and found more than 50% degradation in 120 min with the formation of intermediates which were non-toxic to Lactuca sativa seeds. Quintao et al. [27] investigated the degradation of MTF by direct photolysis, photocatalysis, ozonation, and chlorination and found 60% efficiency using chlorination and ozonation whereas, direct photolysis (UV-C) and heterogeneous photocatalysis (TiO_2/UV-C) resulted in lower removal efficiencies of 9.2% and 31%, respectively. The mineralization rate was low for all different approaches (0.72-20%) indicating the formation of by-products. Wols et al. [28] studied the degradation of 40 selected pharmaceuticals, including MTF using a combined approach of UV/H_2O_2 and reported lower degradation efficiency for metformin as compared to other pharmaceuticals. Badran et al. [29] reported wet air oxidation for a very high initial concentration of 16 g/L and found ~40 % TOC reduction in 120 min at 180° C and pressure above 50 bar. Although AOPs such as Fenton, photo- Fenton, photocatalysis, UV, and H_2O_2 indicate very high removal at a lab-scale, there are limitations, in terms of techno-economic feasibility or cost-effectiveness for implementation for industrial scale applications.

Cavitation is a specific form of advanced oxidation process which involves in situ generations of oxidizing species which can be harnessed for a variety of physicochemical transformations and is suitable in the treatment of wastewater contaminated varieties of pollutants [30]. However, there are no reports on the degradation of metformin using any forms of cavitation; acoustic or hydrodynamic cavitation. Hydrodynamic cavitation has proven its effectiveness over acoustic cavitation in various aspects such as energy requirement, cost of operation, and scalability. In hydrodynamic cavitation, different geometric constrictions are used for the generation of cavities, and the devices are classified as those with moving parts and without moving parts. The high-speed rotor-stator assembly, a device with moving elements, is energy-intensive and not the first choice for cavitation [31]. The devices without moving parts mainly include conventional forms such as orifice and venturi which are linear flow-based devices while the vortex diode a recently developed device works on vortex phenomena [32,33]. The vortex diode device employs tangential entry for the flow in the chamber for the formation of the vortex. Due to strong swirling flow, the low-pressure region formed at the center of the vortex which leads to the formation of vapor-filled cavities, and cavities escape from the axial port. Further, escaped cavities realize high pressure and collapse takes place in the downstream region leading to homolytic cleavage of the water molecules and formation of oxidizing species such as hydroxyl radicals [34]. The vortex diode offers several advantages over conventional linear flow-based devices such as early inception of cavities, larger opening area (less choking), higher efficiency, and is less energy-intensive with increased/easy scalability. The pressure drop across the cavitating device contributes mainly to the operating cost of the treatment process and since the vortex diode requires a lower pressure drop (~3 times), in range of 0.5 -2 bar, compared to most other conventional devices such as orifice-requiring pressure drop typically 5 bar or even more, it represents a cost-effective approach [35–37]. Thus, hydrodynamic cavitation using a vortex diode as a cavitating device can be considered an alternative to the existing treatment methodologies.

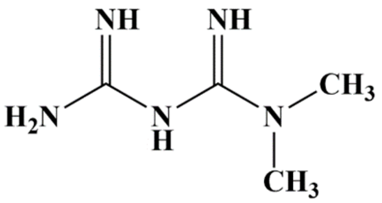
The present work, for the first time, reports the degradation of the antihyperglycemic drug, metformin by hydrodynamic cavitation using a vortex diode as a cavitating device at a pilot-plant scale (capacity,1m^3/h). The operating parameters such as the effect of pressure, initial concentration apart from process intensifications of aeration, and addition of H_2O_2, were studied and the effect of pH on MTF degradation was also evaluated. The degradation kinetics was studied by using the per pass degradation model and cavitational yields were compared under different process conditions. The cost analysis established the techno-economic feasibility of the developed methodology. The results of this work will be useful as an effective effluent treatment strategy for the degradation of antidiabetic drugs in general and metformin in particular apart from industrial wastewater treatment.

7.2 Experimental

7.2.1 Materials

Metformin hydrochloride (CAS: 1115-70-4; Purity >99.96%), in crystalline solid form was procured from BLD Pharmatech (India) Pvt Ltd, Telangana. Hydrogen peroxide (50% w/v, AR grade) was purchased from Molychem, Mumbai. Methanol (≥99.9%, HPLC grade) was procured from Avantor Performance Materials India Limited. Nitric acid (69%, Emparata ®) from Merck and Potassium hydroxide from Qualigens were obtained. The chemical structure and physicochemical properties of MTF are shown in Table 7.1 as below,

Table 7. 1: Chemical structure and physicochemical properties of Metformin

Structure	Name	Metformin
	IUPAC name	3-(diaminomethylidene)-1,1-dimethylguanidine
	Mol mass (g/mol)	129.16
	pKa	12.4
	Solubility	~200 g/L
	Melting Point	223-226 °C
	Boiling Point	224.1 °C

7.2.2 Methodology

An experimental set-up with a vortex flow-based cavitation device, vortex diode, is shown in Figure 7.1. The setup details have already been reported in our earlier reports (Patil and Bhandari, [36]) and hence only essential aspects are discussed here for immediate reference and to avoid repetition. The setup consists of storage tank (25L capacity), a Y type strainer (CF 8M, ACME Engineering Production Corporation) for filtering dirt and impurities of large size, a vertical multistage centrifugal pump (Model CNP make CDLF2-6, SS316, 2 m^3/h at 45 MWC; rating 0.75 kW (1 hp), 2900 RPM, discharge pressure 0–5 bar with non-flame proof motor), and SS316 seamless tubes of OD 0.75 inch with appropriate OD fittings. Flow transmitter (KRONE, H250), range 150-1500 LPH with integral analog indicator was used to measure mainline flow rate while the temperature was measured using RTD (EUREKA Eng. Enterprises India; 0–200° C) which is fitted in the downstream region of cavitation reactor and into the recirculating tank. The entire assembly was mounted on a carbon steel powder-coated assembly with wheels.

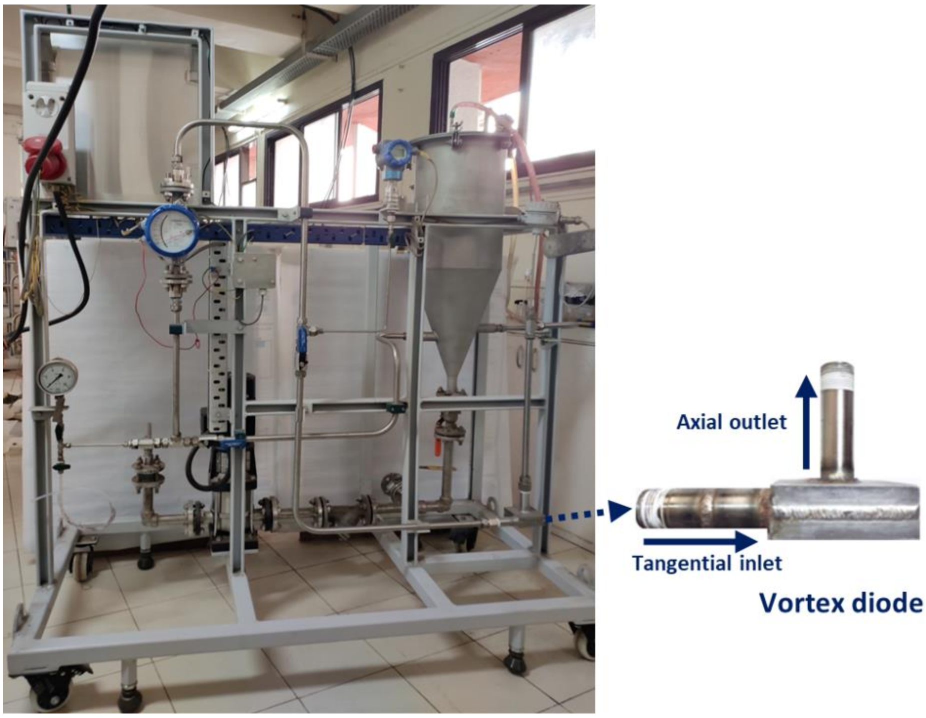


Figure 7. 1: Hydrodynamic cavitation pilot plant and Vortex Diode ($1m^3/h$)

The degradation studies were carried out using a vortex diode as a cavitating device on synthetic wastewater using predetermined initial concentrations of MTF (10 and 20 mg/L). The temperature was maintained in the range of 35-40°C using a water circulation in a circular coil (SS316) inserted into the feed tank. Based on earlier studies on the inception of cavitation for vortex diode at ~0.48 bar [38], the effect of pressure drop was studied in the range of 0.5 to 2 bar for both the initial concentrations. The process intensification in the form of aeration was studied by simply bubbling air in the recirculating tank using an air pump (SOBO AQUARIUM SB-9905, 2 Nozzle, 4.2W, Max. 5.5 L/min). Another process intensification approach was evaluated by the addition of hydrogen peroxide at different molar ratios with respect to the initial concentration of MTF, MTF:H_2O_2 in the range 1:100 to 1:1500. For the experiments without pH adjustments, the pH of the wastewater before and after was in the range of 6.3 to 6.8 with marginal change observed during the experiment. The effect of pH was investigated for acidic pH of 4 and using basic pH of 8 (acidic pH adjustment was done using 1 M nitric acid solution while basic pH was adjusted using 0.1 M potassium hydroxide solution). All the experiments were performed for a treatment time of 180 min and samples were withdrawn periodically, after every 30 min interval for analysis. Reproducibility of the experiments was confirmed and was satisfactory.

7.2.3 Analysis

The MTF degradation was monitored by measuring Total organic carbon (TOC, SHIMADZU make, TOC-L series TOC analyzer) at different intervals and also by High-Performance Liquid Chromatography (HPLC, Agilent, 1260 infinity series, C-18 column (4.6×250 mm)). A mobile phase of methanol (30%) and deionized water (DI) (70%) was used as an eluent for the separation under reverse-phase conditions at a flow rate of 0.8 mL/min. Detection of MTF was performed at a wavelength of 233 nm. The standard calibration graph was plotted for MTF (R^2 value = 0.99) for estimation of unknown MTF concentration during the treatment. The formation of by-products for MTF degradation using different process alterations was identified using the liquid chromatography-mass spectroscopy (LC-MS) technique.

7.3 Results and discussion

7.3.1 Effect of pressure drop and degradation kinetics of MTF

The inception of cavitation in vortex diode is reported experimentally earlier by Suryawanshi et al. [38] at ~0.48 bar and also by Ranade et al. [39] at 0.5-0.8 bar by acoustic analysis. Therefore, the effect of pressure drop was studied in the range 0.5-2 bar for vortex diode since the optimum pressure drop value is different for different systems. Beyond the optimum pressure drop, formation of cavity cloud may occur which adversely affects cavitational intensity. Since the optimum pressure drop depends on the reactor configurations and the type of pollutants and also due to the inability for theoretical prediction of optimum pressure drop, the effect of pressure drop needs to be experimentally evaluated in each case. The experimental conditions of this work ensure the cavitation regime to evaluate degradation efficiency of MTF under different conditions of initial concentrations and pH of the solution. It was experimentally observed that for the conditions of neutral pH, there was no significant variation in the extent of TOC reduction n of MTF for the different pressure drops of 0.5, 1, 1.5 and 2 bar for the initial concentration of 10 mg/L as shown in Figure 7.2. Similar results were also obtained for the higher concentration of 20 mg/L. Hence, an optimized pressure drop of 1 bar was decided for all the experiments related to the degradation of MTF using hydrodynamic cavitation for the both initial concentrations. The maximum TOC reduction of 14% was obtained at a pressure drop of 1 bar for both MTF concentrations.

The reactions in hydrodynamic cavitation can be assumed to be pseudo first-order and kinetics of MTF degradation can be evaluated using a simple power-law model as,

$$C = C_0e^{-kt} \qquad (7.\ 1)$$

Where, C_0 and C are the MTF concentrations before and after the treatment, ‘t’ is time (min) and ‘k’ is rate constant (min^{-1}). Table 7.2 gives the k values for both the initial concentrations of 10 and 20 mg/L and also for different process alterations using hydrodynamic cavitation. For the optimum pressure drop, ΔP of 1 bar the corresponding k values for initial concentrations, 10 and 20 mg/L were 0.2×10^{-3} min^{-1} and 0.3×10^{-3} min^{-1} respectively.

Many literature studies support the typical degradation behaviour of cavitation in which the extent of degradation of pollutants increases with the increase in the pressure drop till the optimum, beyond which it decreases for all types of cavitating devices, however, optimized value is varied based on the type of cavitating devices, nature of pollutants, etc. Suryawanshi et al. [40] reported the optimized pressure drop of 0.5 bar for degradation of solvents using a vortex diode as a cavitating device whereas, Dixit et al. [35] reported 1.5 bar as the optimum pressure drop for degradation of naproxen, a pharmaceutical pollutant. However, for conventional devices such as orifice, venturi, etc the value of optimized pressure drop is higher than that required for vortex diode. Kumar et al. [41] reported that the maximum decolorization of ternary dye wastewater was achieved at an inlet pressure of 6 bar using an orifice as a cavitating device whereas, Raut-Jadhav et al. [42] reported optimized inlet pressure of 15 bar for circular venturi as a cavitating device for degradation of insecticide. It was reported that beyond 15 bar of inlet pressure (optimized condition), a lower extent of degradation was achieved. However, in the present case, with an increase in the pressure drop from 0.5- 2 bar, not much difference in the extent of degradation/TOC reduction was observed.

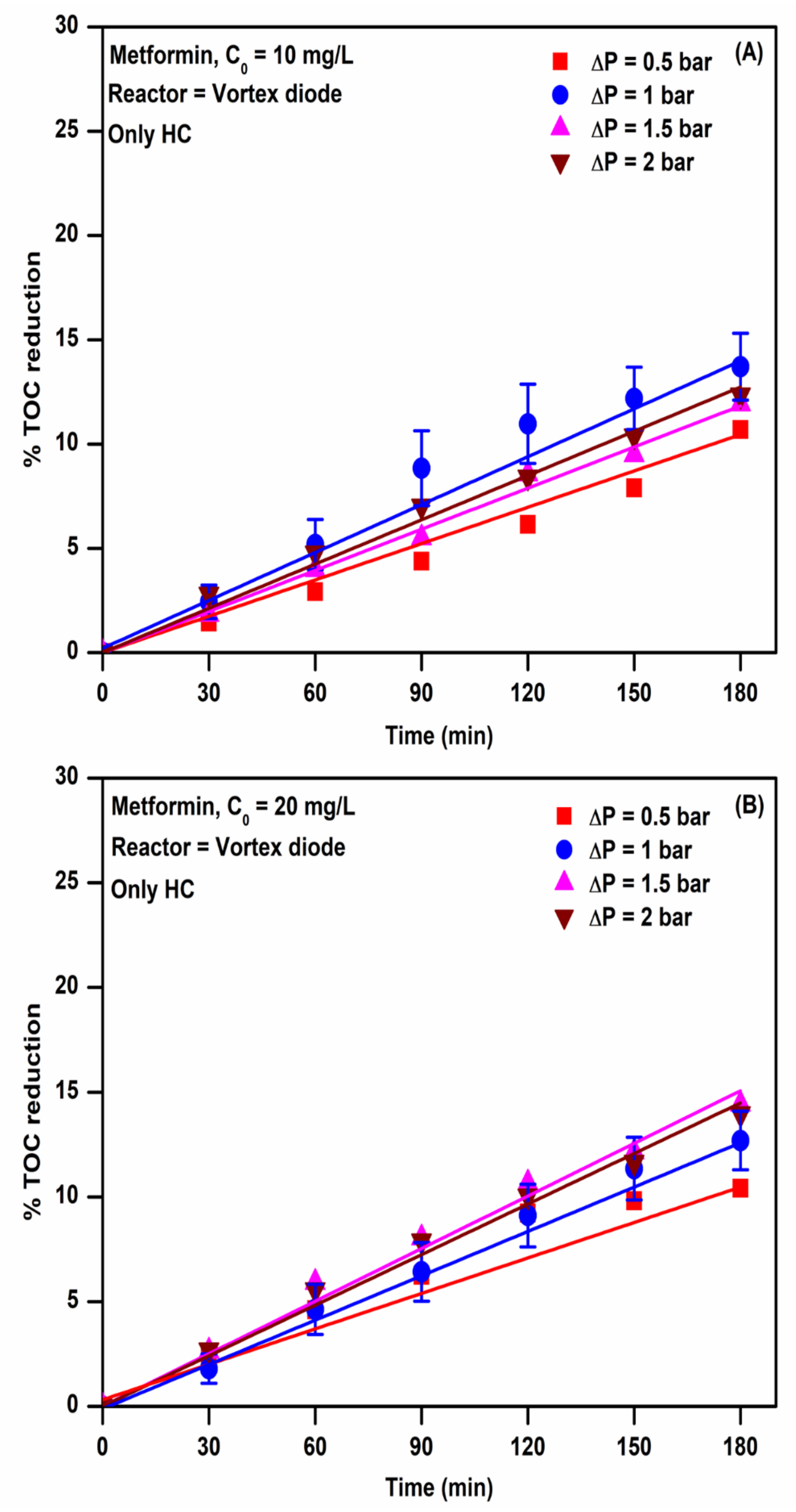


Figure 7. 2: Effect of pressure drop A. C_0 = 10 ppm, B. C_0 = 20 ppm (pH: 6.3-6.8)

7.3.2 Effect of Aeration

The effect of aeration was reported in various studies to exploit possible increased oxidation due to the addition of air/oxygen. The effect of aeration appears to be pollutant specific, indicating the necessity for the evaluation of this type of process intensification in metformin degradation. The process intensification approach of aeration was studied at optimum pressure drop condition of ΔP, 1 bar by bubbling air in a recirculating tank of cavitation reactor for both MFT concentrations, 10 and 20 mg/L. It was observed that the extent of TOC reduction of only 7% and 10% could be achieved for the MTF concentrations of 10 and 20 mg/L respectively. The extent of degradation obtained for the combined HC+aeration showed contribution of only cavitation and no effect of aeration due to this intensification approach.

The process intensification approach of aeration for cavitation has been found beneficial in some cases where the additional nuclei generation enhances the degradation of pollutants depending on the nature of pollutants. The effect of aeration as process intensification was reported in earlier studies for ammoniacal nitrogen removal [34] and solvent degradation [37,40] by hydrodynamic cavitation. Patil et al. [37] reported 100% enhancement in degradation of octanol solvent using a process intensification approach of aeration. However, in the same study, the authors highlighted the selective effect, since for other solvents such as DMF and cyclohexanol, the enhancement due to aeration was not satisfactory. Suryawanshi et al. [40] also reported marginal improvement (~10%) in the extent of degradation of solvents using cavitation coupled with aeration. Similar to the enhanced ammoniacal nitrogen removal [34] and octanol degradation [37] due to aeration, a significant enhancement in COD, TOC, and color reduction of textile dyeing industry effluent due to cavitation coupled with the addition of oxygen was reported by Rajoriya et al. [43] and reported the effective use of oxygen as process intensification than air. Joshi et al. [44] reported ~3 times enhancement by HC+oxygen (40%) in COD reduction of industrial wastewater as compared to HC+air (15%) approach. Thus, the effect of aeration can be confirmed to be pollutant specific with limited sensitivity to device or process conditions. The nature of the pollutant appears to be the only critical parameter in exploiting intensification due to aeration.

7.3.3 Effect of addition of H_2O_2

The process intensification approach of the addition of H_2O_2 can also provide significant improvements due to the powerful nature of oxidizing agent that provides additional hydroxyl radical apart from the cavitational effect resulting in enhancement of the rate of degradation [3,45]. Hydrodynamic cavitation along with the addition of H_2O_2 for degradation of some of the pharmaceutical pollutants was well reported by Thanekar et al. [46,47] and Dixit et al. [35] Due to the cavitational effect, a number of events take place such as generation of hydroxyl radicals, dissociation of H_2O_2 etc. The role of reactive species in the MTF degradation in the system of HC and HC + H_2O_2 can be explained in the following chain reactions [42,48,49].

$$H_2O \longrightarrow {}^{\cdot}OH + H^+ + e^-$$

$$H_2O_2 \longrightarrow {}^{\cdot}OH + {}^{\cdot}OH$$

$${}^{\cdot}OH + H_2O_2 \longrightarrow HO_2{}^{\cdot} + H_2O$$

$${}^{\cdot}OH + HO_2{}^{\cdot} \longrightarrow H_2O + O_2$$

$$HO_2{}^{\cdot} + H_2O_2 \longrightarrow {}^{\cdot}OH + H_2O + O_2$$

$$MTF + {}^{\cdot}OH / H_2O_2 \longrightarrow \text{Degradation by-products}$$

$$MTF + {}^{\cdot}OH / H_2O_2 \longrightarrow CO_2 + H_2O$$

The hybrid approach of cavitation with the addition of hydrogen peroxide was investigated at different molar ratios of MTF: H_2O_2 as, 1:100, 1:300, 1:500, 1:700, 1:1000, and 1:1500 and for both initial concentrations of MTF as 10 and 20 mg/L. The extent of MTF degradation obtained for different molar ratios of MTF: H_2O_2 is shown in Figure 7.3. It is evident that the individual approaches such as cavitation and hydrogen peroxide reported only marginal degradation percentage (3-5%), whereas, cavitation coupled with H_2O_2, has shown significant increase in the extent of degradation for the molar ratios from 1:100 to 1:500 for both MTF concentrations, 10 and 20 mg/L. A maximum extent of degradation of 10% and 31% were achieved at a molar ratio of MTF: H_2O_2 as 1:500 for MTF concentrations of 10 and 20 mg/L respectively. Further enhancement up to 33% was achieved for molar ratio of 1:700 and for

MTF concentration of 20 mg/L. The corresponding rate constants values are provided in Table 7.2. The higher degradation efficiency can be attributed to possible reactive pathway with increased availability of the oxidizing agents due to H_2O_2 for the increased demand in the case of higher concentrations.

To evaluate the combined effect of hydrodynamic cavitation with the addition of H_2O_2 for MTF degradation, the synergistic coefficient was calculated by using the formula as,

$$\text{Synergistic coefficient} = \frac{k_{(HC+H2O2)}}{k_{HC}+k_{H2O2}} \qquad (7.\ 2)$$

The values of synergistic coefficient were 2 and 4.2 for the initial MTF concentration of 10 and 20 mg/L respectively (Table 7.2) which confirms the synergism of the combined approach of HC and H_2O_2. The synergism can be attributed to the dissociation of H_2O_2 into OH radicals in addition to the OH radicals due to cavitation which ultimately intensifies the degradation process. However, higher loadings of H_2O_2 (beyond optimum), acts as a scavenger which reduces the degradation efficiency. In the present work, with the increase in the molar ratio up to 1:1500, beyond the optimum molar ratio (1:700), the extent of degradation decreases as shown in Figure 7.3, due to the scavenging effect of hydrogen peroxide. Although the role of H_2O_2 has already been proven, the optimum loading of H_2O_2 is primarily dependent on the nature of pollutants present in wastewater which also brings out the necessity for experimental investigation.

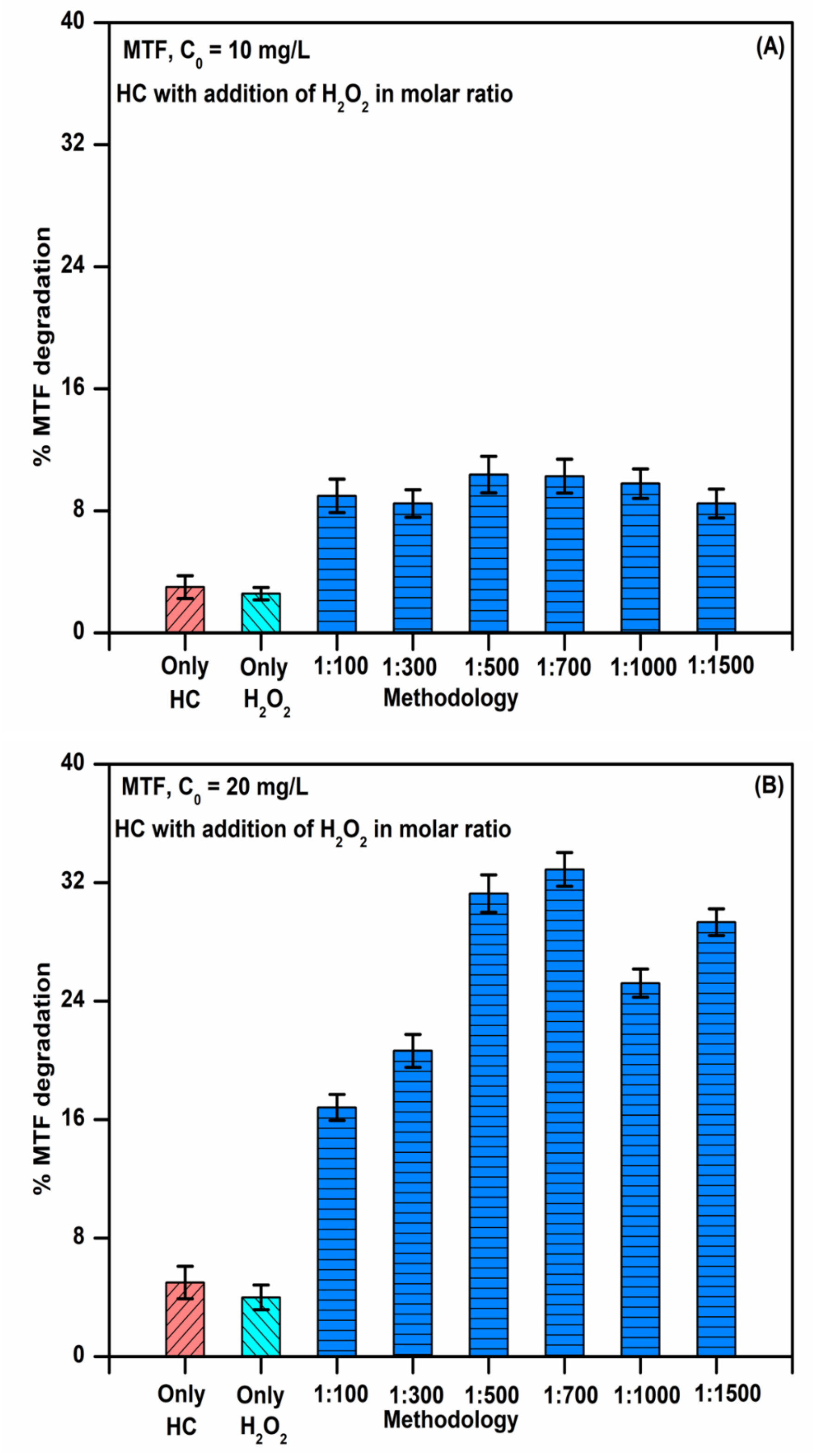


Figure 7. 3: Process Intensification using addition of H_2O_2

A. C_0 = 10 mg/L, B. C_0 = 20 mg/L (ΔP: 1 bar, pH 6.3-6.8, time 180 min)

7.3.4 Effect of pH on metformin degradation

The effect of operating pH on the extent of degradation of MTF was investigated in the range pH 2 to 8, for different HC process alterations using a vortex diode as a cavitating device operated at a pressure drop of 1bar. The obtained results have been depicted in Figure 7.4. The pH adjustments for acidic and basic conditions were done using 1 M nitric acid solution and 0.1 M potassium hydroxide solution respectively. The experimental results reveal that under acidic conditions (at pH 4), MTF degradations by HC were 95% and 88% with rate constants, 17.3×10^{-3} min^{-1} and 12.2×10^{-3} min^{-1} corresponding to initial MTF concentrations of 10 and 20 mg/L respectively. However, under the basic condition of pH 8, degradation was hugely reduced and the corresponding values were 6% and 4% for the initial MTF concentrations of 10 and 20 mg/L. The experimental investigation for only agitation at pH 4 (without cavitation) indicated only marginal degradation (<2%).

The results clearly highlight pH as one of the most important operating parameters in hydrodynamic cavitation process for API pollutant degradation. Many researchers have reported the effect of pH on the degradation of various pollutants such as dyes [50], pharmaceuticals [46], and pesticide [51] using cavitation. The degradation mechanism using hydrodynamic cavitation involves either thermal/pyrolytic decomposition of pollutant moiety trapped inside the cavity and/or attack of hydroxyl radicals on pollutant molecule trapped at the gas-liquid interface and in bulk [50]. In the case of degradation of pollutants, the attack of hydroxyl radical is found as the main mechanism which ultimately depends on the orientation (molecular or ionic state) of the pollutant molecule in the solution.

Metformin is a weakly basic in nature (pKa 2.8 and 11.5) and gets ionized in a pH range from 4-10 [52]. At pH 4, MTF occurs predominantly in the molecular form which gets trapped at the hydrophobic gas-liquid cavity interface and is hence found more susceptible to degradation resulting in the maximum extent of degradation of MTF by cavitation (95%). Also, to validate the proposed hypothesis, the experiments were performed to evaluate the extent of degradation at pH 2, which indicated a complete degradation in 30 min for both 10 mg/L and 20 mg/L MTF concentration compared to 180 min for pH 4 (and negligible degradation for pH 6.5). Thus, there is clear effect of pH modification on degradation.

However, at pH 8, due to ionization, it becomes hydrophilic in nature increasing difficulty in degrading as the hydroxyl radicals are short-lived and not likely to degrade pollutant moiety in bulk solution [53]. The present research shows very important observation that hydrodynamic cavitation using vortex diode at pH 4 can provide huge enhancement (3000%) than that compared with only cavitation without any pH adjustment.

The effect of pH was also investigated for the combined approach of HC+H_2O_2 for both initial concentrations of MTF as 10 and 20 mg/L and using previously optimized H_2O_2 loading. From Figure 7.4, it can be seen that HC+H_2O_2 approach resulted in complete degradation (100%) at pH 4 for MTF concentration of 10 mg/L while the corresponding degradation at 20 mg/L was 88%. A significant enhancement in MTF degradation (900%) was achieved with pH adjustment to 4 for a corresponding combined approach of HC+H_2O_2 without any pH adjustment. Also, the experiments of adding H_2O_2 without cavitation at pH 4 and 8 were performed to compare the degradation efficiency obtained for the hybrid approach and there was practically no degradation obtained for both initial concentrations of MTF.

The strategy of manipulation of synergy using different experimental conditions and the corresponding values of the synergistic coefficient are given in Table 7.2. Based on the degradation rate constants obtained for different experimental conditions, synergistic coefficients were calculated. It is clear that the higher synergistic coefficients can be achieved with pH modifications, and in metformin degradation using the pH 4. Significantly higher synergetic coefficients were obtained as 86.5 and 40.6 respectively for pH modifications (at pH 4) for cavitation process for both initial concentrations of MTF. For HC intensified with hydrogen peroxide synergistic coefficient values were 2.8 and 1 for initial concentrations of 10 mg/L and 20 mg/L respectively. However, significantly lower values of synergistic coefficients were obtained for HC at pH 8 for both initial concentrations of MTF.

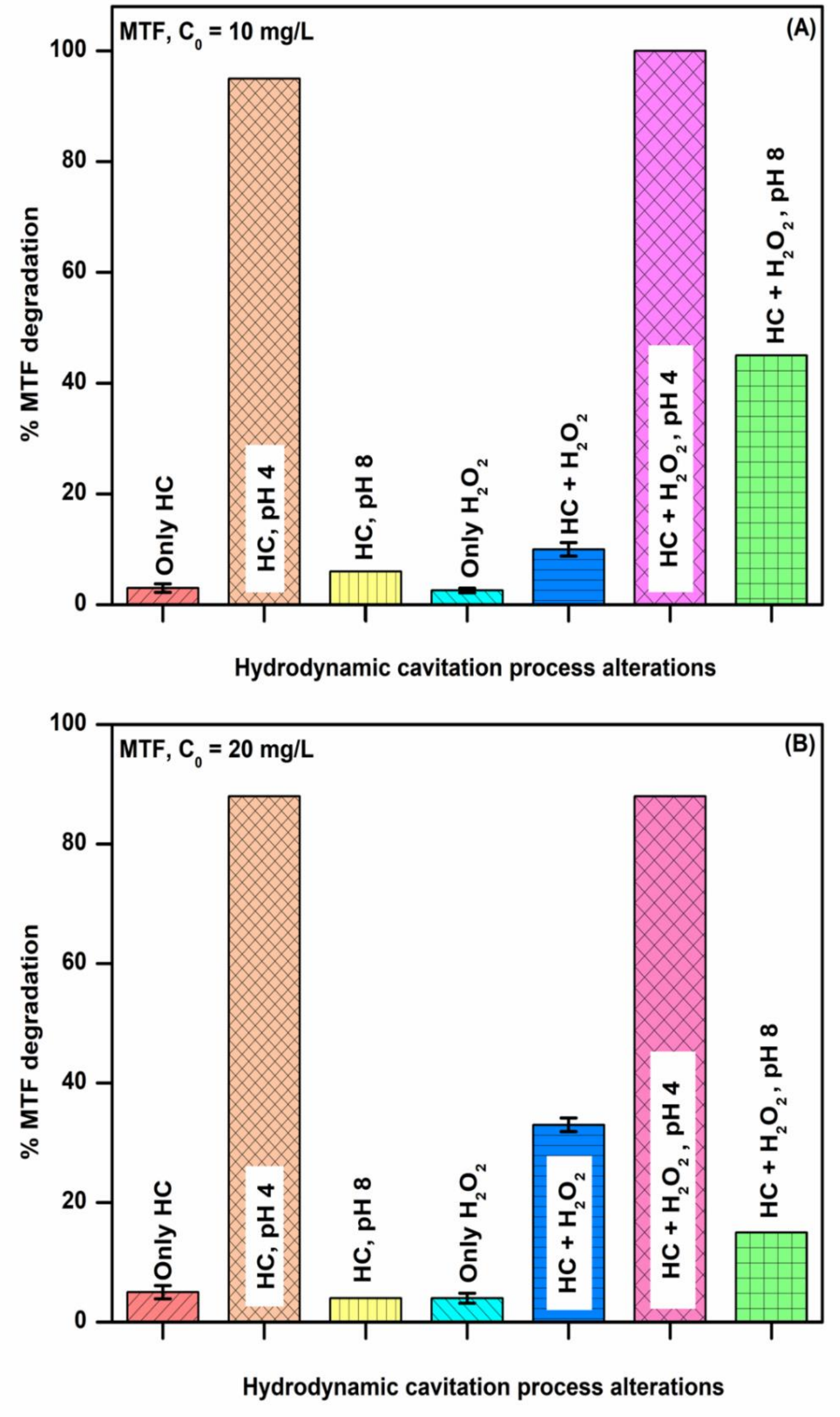


Figure 7. 4: Improving MTF degradation using different process alterations

A. C_0 = 10 mg/L, B. C_0 = 20 mg/L (ΔP: 1 bar, time 180 min)

Table 7. 2: Degradation of MTF, rate constants, and synergistic coefficients for different process alterations

MTF Concentration, mg/L	Cavitation process alterations	% MTF degradation after 180 min	1^{st} order rate constant, $k \times 10^3$ (min^{-1})	Synergistic coefficient
10	Only HC	3	0.2	-
	HC @ pH 4	95	17.3	86.5
	HC @ pH 8	6	0.3	1.5
	HC+ Aeration	<2	-	-
	Only H_2O_2	2	0.1	-
	Only Aeration	<2	-	-
	Only pH 4 and 8	<2	-	-
	HC+H_2O_2(1:500)	10	0.6	2
	HC+H_2O_2(1:500) @ pH 4	100	48.7	2.8
	HC+H_2O_2(1:500) @ pH 8	45	3.4	11.3
20	Only HC	5	0.3	-
	HC @ pH 4	88	12.2	40.6
	HC @ pH 8	4	0.2	0.6
	HC+ Aeration	<2	-	-
	Only H_2O_2	4	0.2	-
	Only Aeration	<2	-	-
	Only pH 4 and 8	<2	-	-
	HC+H_2O_2(1:700)	33	2.1	4.2
	HC+H_2O_2(1:700) @ pH 4	88	12.6	1
	HC+H_2O_2(1:700) @ pH 8	15	0.9	4.5

7.3.5 Mechanism of metformin degradation

The results of metformin degradation using different formats of hydrodynamic cavitation reveal interesting observations in the degradation behaviour. It is instructive to investigate therefore the mechanism and the forms of degradation. In this regard, efforts were made to identify the by-products using LC-MS analysis, for the different approaches such as HC alone as well as an intensified approach using H_2O_2 performed under acidic conditions of pH 4 where the maximum extent of degradations of 95% and 100 % were achieved after 180 min respectively.

Figure 7.5 shows LC-MS spectra for the treated sample of HC alone using pH 4, after 180 min of treatment time. Two prominent peaks were observed at *m/z* 119.02, and 158.00. The compounds detected were N-Nitro-N-aminoguanidine (*m/z* 119.02), 3,5-Dinitro-1H-pyrazole (*m/z* 158.00), and metformin (*m/z* 130.10). The minor peak detected of metformin (*m/z* 130.10) indicated its presence in a trace amount which supports the nearly complete (95%) degradation of MTF using HC alone using acidic conditions. Figure 7.6 shows LC-MS of degradation products of MTF for another process format- using HC with the addition of H_2O_2 where, complete MTF degradation was achieved after 180 min. Two prominent peaks were observed at *m/z* 190.94, and 126.07. The peak of metformin (*m/z* 130.10*)* which was completely disappeared, confirms complete (100%) degradation of MTF using HC+ H_2O_2. Quintao et al. [27] investigated the degradation products of MTF using photolysis, photocatalysis, ozonation and chlorination and observed that though the complete degradation was achieved within 30 min, many intermediates get formed which were persistent even after prolonged treatment. However, in the present work, hydrodynamic cavitation produces a few intermediates that also can get eventually degraded with extended treatment time.

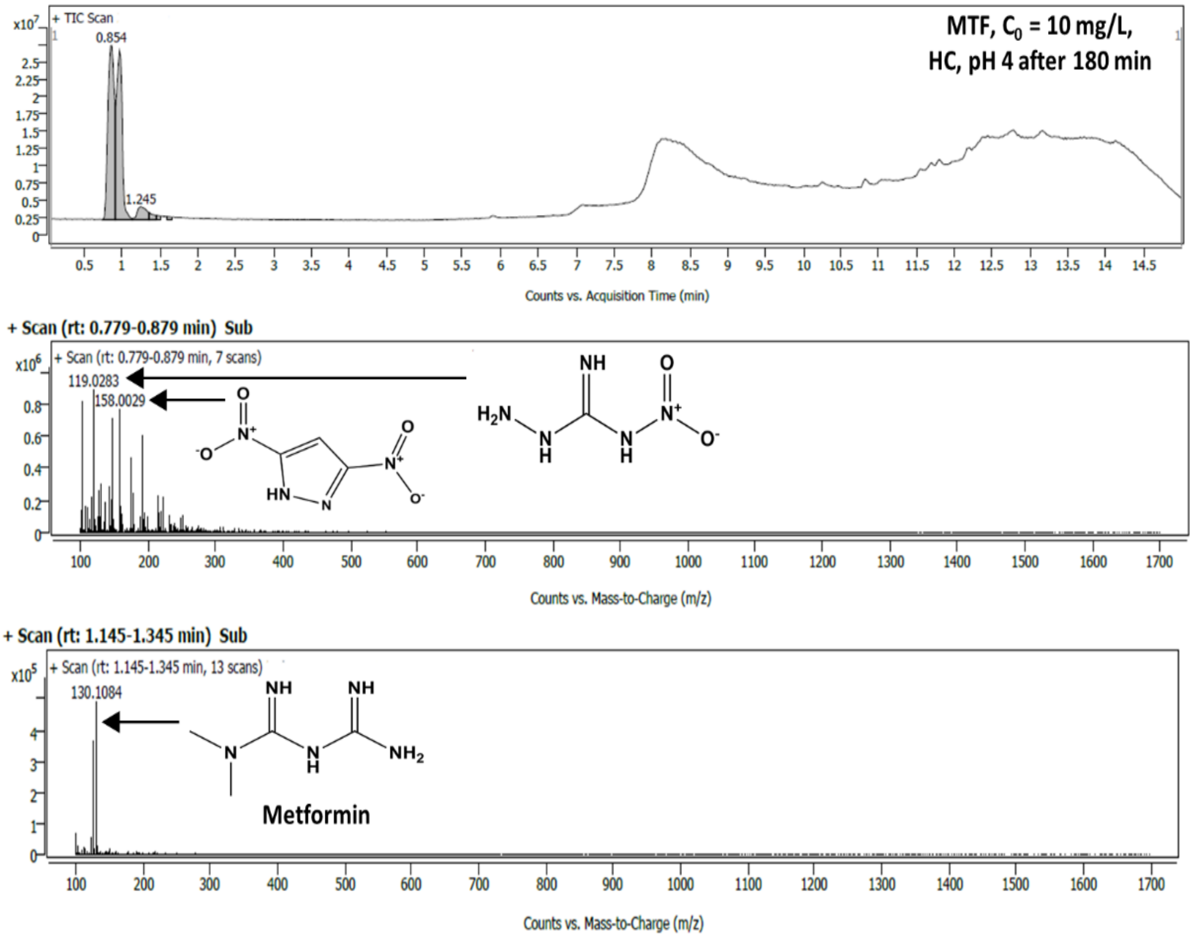


Figure 7. 5: LC-MS spectra for MTF degradation by HC (pH 4)

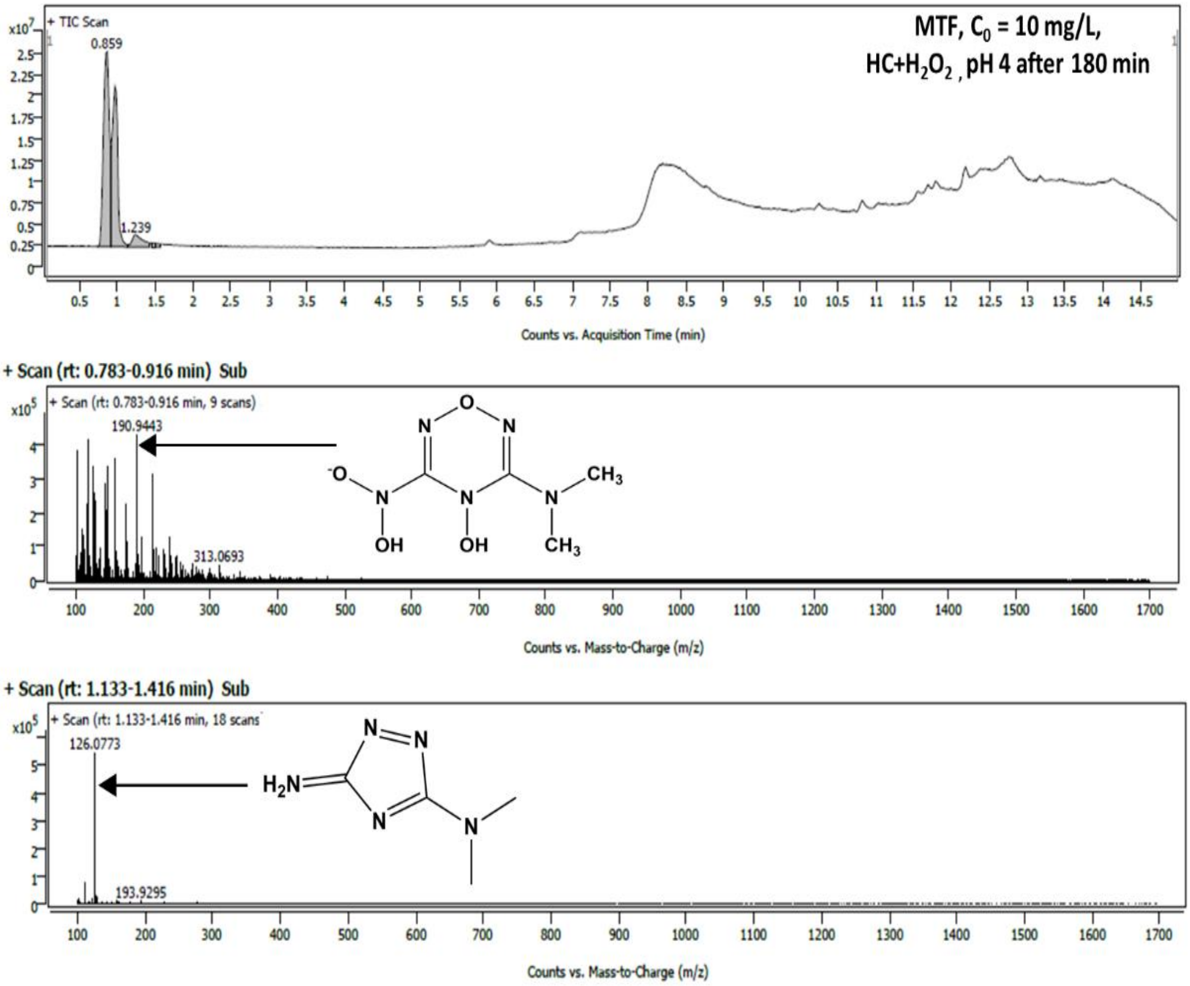


Figure 7. 6: LC-MS spectra for MTF degradation by HC with addition of H_2O_2 (pH 4)

Based on the analysis, the mechanism can be postulated and the envisaged possible intermediates are shown in Figure 7.7 for different process alterations based on hydrodynamic cavitation. It can be seen that the cavitation alone produced no by-products other than metformin which were confirmed by HPLC analysis and represents a more predominant mineralization pathway with only water and carbon dioxide as the products. However, cavitation with pH 4 as well as a hybrid approach of $HC+H_2O_2$ under acidic conditions resulted in byproduct formation with complete degradation of Metformin (100%).

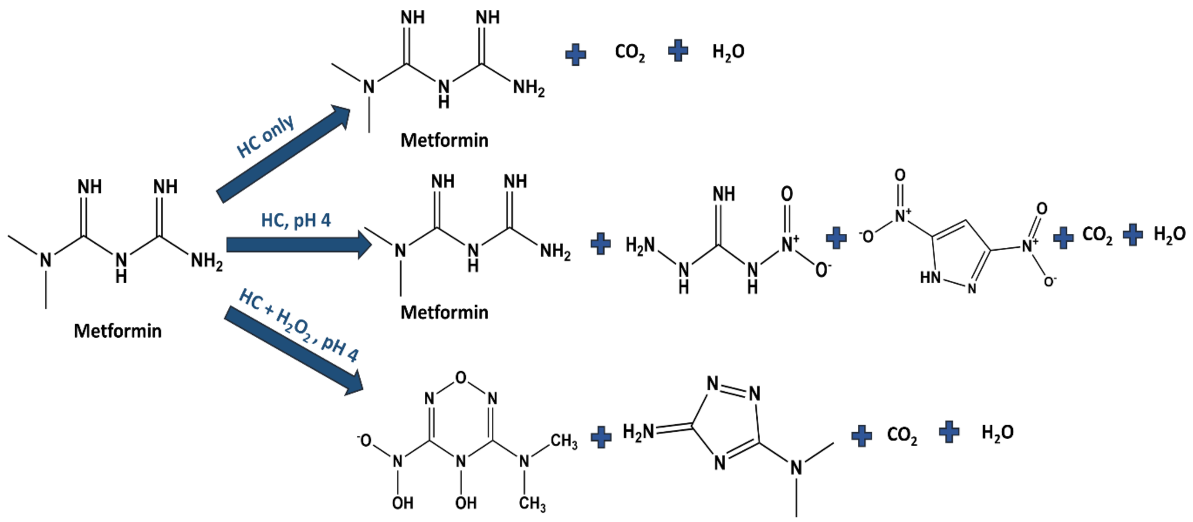


Figure 7. 7: Metformin degradation- Possible intermediates for different process alterations

7.3.6 Per pass degradation and cavitational yield

Typically, the kinetics of degradation is reported based on power-law which delivers change in concentration with respect to time. However, the per pass degradation model for hydrodynamic cavitation provides a clearer physical picture in terms of flow/ pressure drop characteristics, energy dissipation, and finally evaluating the performance of the cavitation process in the form of cavitational yield; and therefore, more realistic. It accounts for concentration effects, pressure drop across cavitation device, and the nature of the cavitating device is reflected in the per pass degradation model which closely resembles with physico-chemical behaviour of the hydrodynamic cavitation process and hence found more suitable, especially at a large scale of operation [37,54–57]. The per-pass degradation factor is defined as,

$$\text{Per-pass degradation factor } (\phi) = k\tau \qquad (7.\ 3)$$

Where, τ is residence time which is a ratio of volume of the holding tank and the flow rate.

The power dissipation is calculated as,

$$W = \Delta P \times Q \qquad (7.\ 4)$$

Where, ΔP is pressure drop across the cavitating device ($P_1 - P_2$) (bar), and Q is the flow rate (L/h)

The overall cavitational yield (amount of pollutant/MTF degraded per unit energy dissipation) can be calculated as,

$$Y = \frac{V(c_0 - c)}{\Delta PQt} \text{ mg/J} \qquad (7.5)$$

Where, Y= cavitational yield (mg/J), V= volume (L), C_0 and C= initial and final concentration of pollutant (mg/L)

The per pass degradation factors were calculated for different process alterations of cavitation and the obtained values were represented in Figure 7.8. It can be seen that significantly higher per pass degradation factor was obtained for hydrodynamic cavitation with the addition of H_2O_2 and also for hydrodynamic cavitation using acidic pH of 4 for both initial MTF concentrations of 10 mg/L and 20 mg/L. The values of per pass degradation are very low for the three formats of cavitation, viz. only HC (3×10^{-4}), HC using pH 8 (6×10^{-4}), and HC intensification using hydrogen peroxide (11×10^{-4}) for lower initial concentration of 10 mg/L while corresponding values for 20 mg/L were, 6×10^{-4}, 4×10^{-4}, 41×10^{-4} respectively. However, significant enhancement in per pass degradation factors was obtained by altering the pH to acidic (pH 4) and the values were 303×10^{-4} and 945×10^{-4} respectively corresponding to a huge enhancement of the order of 100 and 85 times for the two cavitation process formats of HC and HC intensified with hydrogen peroxide, specifically for the lower initial concentration of 10 mg/L. Similarly, for an initial concentration of 20 mg/L, per pass degradation factors were 217×10^{-4} and 213×10^{-4} respectively corresponding to an enhancement of the order of 35 and 4. The experimental observations pertaining to the pH can be attributed to the ionization effect due to pH and for effect of concentration. It is indicated that molecular form is more amenable for the degradation over ionized form.

Cavitational yield expresses the desired chemical change, in this case, degradation of MTF per unit energy dissipation (Eq. 7.5). The values of cavitational yields obtained for different process alterations have been depicted in Figure 7.8. The higher values of cavitational yields, 96×10^{-5} mg/J and 162×10^{-5} mg/J were obtained using cavitation with pH adjustment to 4 for both MTF concentrations of 10 and 20 mg/L respectively. However, further enhancement in cavitational yields, 101×10^{-5} mg/J and 166×10^{-5} mg/J were achieved for HC+ H_2O_2 with pH adjustment to 4 for both MTF concentrations of 10 and 20 mg/L respectively. The comparatively lower cavitational yields, 3×10^{-5} mg/J and 10×10^{-5} mg/J were achieved using an individual approach of cavitation without any pH adjustment for both MTF concentrations of 10 and 20 mg/L respectively. Based on the obtained results of cavitational yields for different process alterations, the hydrodynamic cavitation with acidic pH 4 gave significant enhancement in cavitational yield in the range of ~3 to 32 times than that individual operation of hydrodynamic cavitation for both initial concentrations of 10 and 20 mg/L.

Both the terms**,** per pass degradation and cavitational yield are correlated and represent the effectiveness of the process. The terms are useful in understanding the phenomenon, especially for the hydrodynamic cavitation and for different types of the reactors, for analysing/ comparing the literature data and also from the point of view of future research/ investigations on different types of devices. While the per pass degradation factor is more useful for the implementation of hydrodynamic cavitation at various scales, cavitational yield can be more relevant term to evaluate the energy effectiveness of the process.

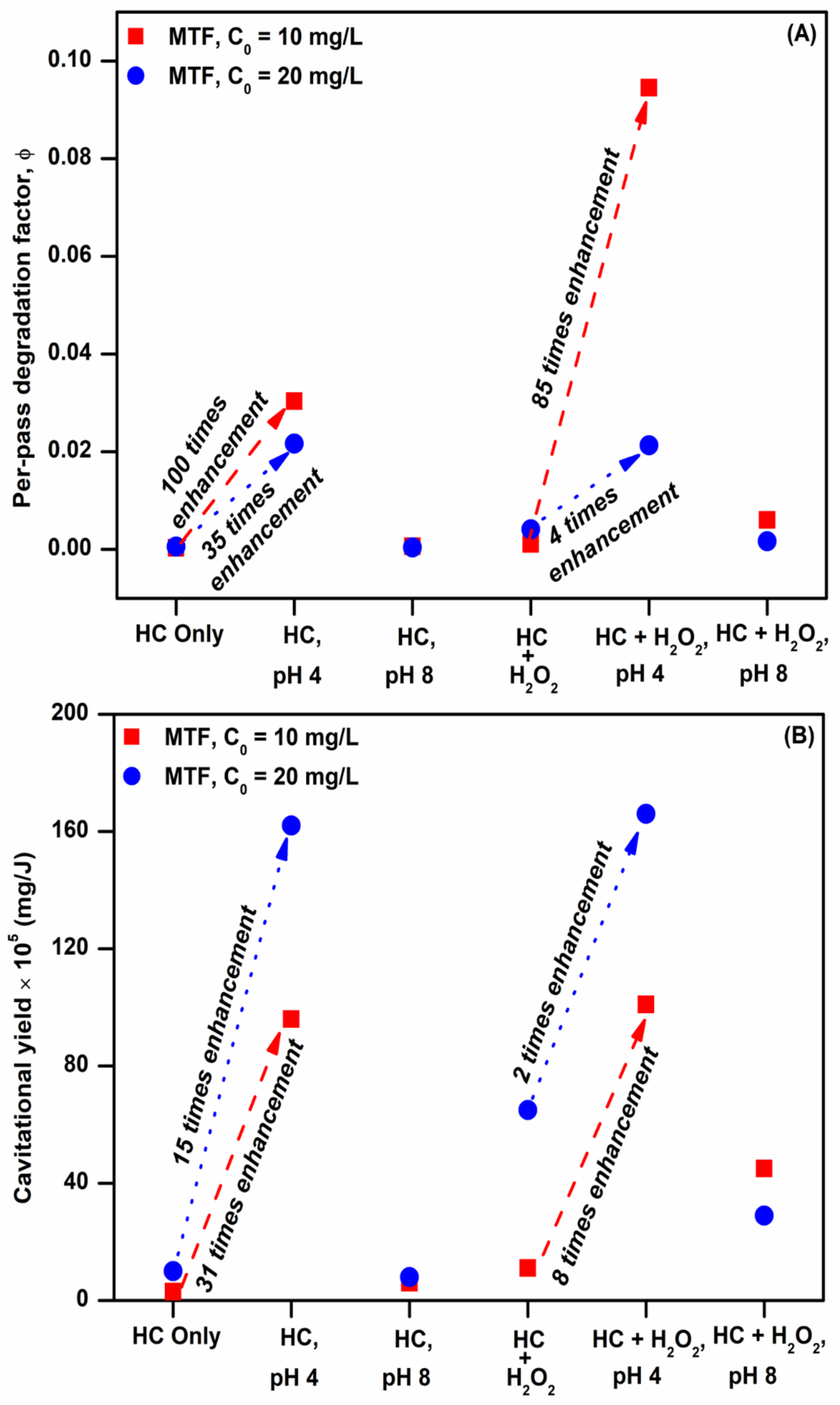


Figure 7. 8: Per-pass degradation and cavitational yield for different process alterations

A. C_0 = 10 mg/L, B. C_0 = 20 mg/L (ΔP: 1 bar, time: 180 min)

7.3.7 Cost analysis

The cost of the treatment by hydrodynamic cavitation using vortex diode as cavitating device based on MTF degradation % can be calculated as [33],

$$\text{Cost of treatment per } m^3 \text{ of effluent} = \frac{N_C \times \Delta P \times P_E}{36\eta} \qquad (7.\ 6)$$

Where, Nc is the number of passes, ΔP is pressure drop across the cavitation device, P_E is the cost of electricity and η is pump efficiency. The number, 36, in the denominator is due to the conversion of energy units for calculating cost per unit volume of effluent.

The cost calculation was done in the context of the Indian scenario. The cost of electricity for the Indian scenario was assumed as Rs 10 /kWh (1$ = 75 Rs) while pump efficiency was assumed as 66% considering commercial operating conditions (flow rates above $10m^3/h$). The calculated cost for different relevant process alterations (for close to complete degradation) are given in Table 7.3. For optimum pressure drop of 1 bar using vortex diode, the cost of treatment for only hydrodynamic cavitation was 41 Rs/m^3 (0.55 $/$m^3$), however, only for 3-5 % reduction, therefore not relevant from application point of view, whereas, with simple pH adjustment for hydrodynamic cavitation, the cost of the treatment was reduced drastically. The cost analysis for the combinations of HC+H_2O_2 with pH adjustments and only HC+ pH adjustments, and by incorporating the cost of additives, indicated low costs of 75 Rs/m^3 and 45 Rs/m^3 respectively for MTF initial concentration of 10 mg/L. It is interesting to note that though, addition of hydrogen peroxide assists in the overall degradation, the cost of HC without hydrogen peroxide and with similar pH adjustment is substantially lower and therefore a better approach for practical consideration. The cost analysis depicted order of magnitude cost reduction for the modified hybrid approach using pH adjustments of this study as compared to only vortex-based HC and only HC+H_2O_2 hybrid approach.

Table 7. 3: Cost analysis for different process alterations

MTF Concentration, mg/L	**Methodology**	**% MTF degradation**	**Cost in Rs/m^3**	**Cost in Rs/gm**
10	Only HC	3	Not Relevant	Not Relevant
	HC + H_2O_2 (1:500) @ pH4	100	75	45
	HC @ pH 4	95	45	5
20	Only HC	5	Not Relevant	Not Relevant
	HC + H_2O_2 (1:700) @ pH 4	88	131	8
	HC @ pH 4	88	45	3

Thus, the modified hybrid approach of cavitation using a vortex diode as a cavitating device and hydrogen peroxide with pH adjustment can be considered as an efficient and viable alternative to the degradation of metformin to the existing methodologies representing superior cavitational yield, high efficiency, and drastically increased cost-effectiveness.

7.4 Conclusions

The present work clearly demonstrated the effective use of hydrodynamic cavitation with vortex diode as a cavitating device for the degradation of metformin, an extensively used antidiabetic drug. Hydrodynamic cavitation alone, using a low pressure drop of only 1 bar, yields only 3-5 % of degradation while process intensification using hydrogen peroxide gave up to 33% of metformin degradation. The hybrid hydrodynamic cavitation process can be further modified using pH alteration resulting in very high, 88-95% metformin degradation, under acidic pH of 4 with an excellent cavitational yields of the order of 162×10^{-5} mg/J for the reasonably higher initial concentrations of 10- 20 mg/L. Further, complete degradation of MTF was achieved using HC+H_2O_2 under acidic pH of 4 with order of magnitude enhancement of 900%. Significantly higher synergistic coefficients can be achieved with simple pH modifications (pH 4) resulting in the process efficiency. Per pass degradation could be enhanced up to 100 times reflecting drastic reduction in the process cost compared to the conventional hydrodynamic cavitation. The results confirm that the use of vortex flow-based device in hydrodynamic cavitation and process intensification with acidic pH condition results in significant degradation of MTF with low treatment cost providing techno-economical alternative for degradation of antidiabetic drug and industrial wastewater treatment.

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Solvent-assisted cavitation for enhanced removal of organic pollutants - Degradation of 4-aminophenol

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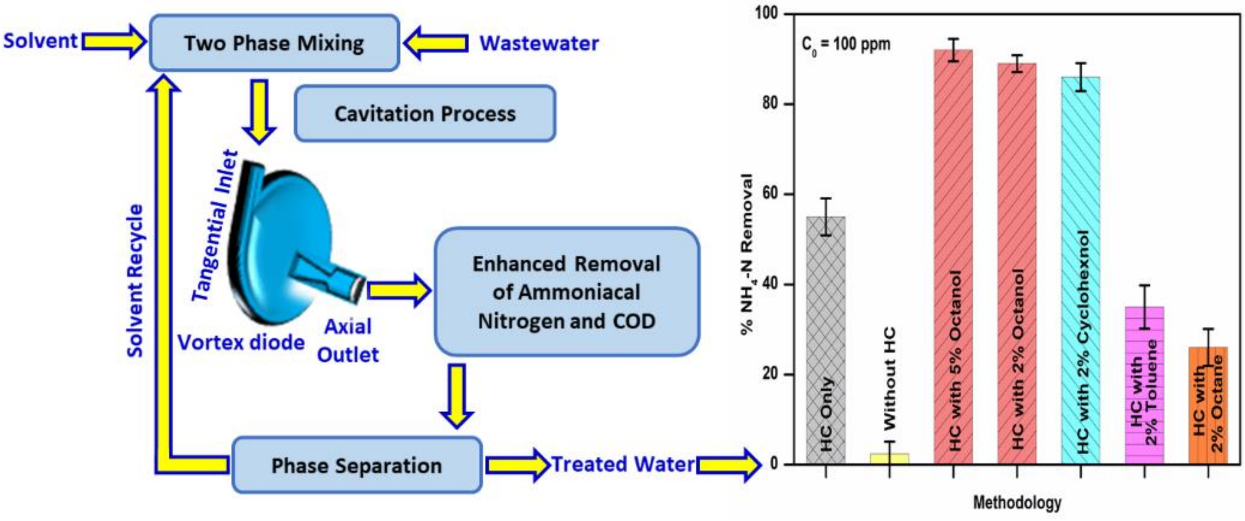
Chapter - 8



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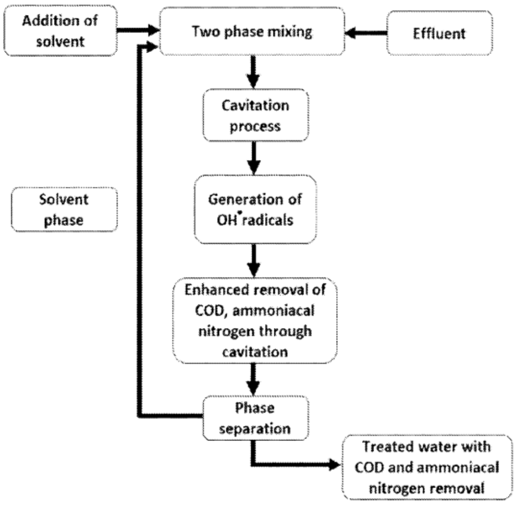

Fig 1

(57) Abstract: The present invention discloses a solvent assisted cavitation process for the removal of pollutants from waste water comprising treating waste water in a batch or continuous process in a cavitation device fed with 1-10% of an immiscible solvent resulting in a reduction in concentration of ammoniacal nitrogen and/or COD in the waste water.

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Chapter 8

Solvent-Assisted Cavitation for Enhanced Removal of Organic Pollutants – Degradation of 4-aminophenol

Abstract

A new approach of solvent-assisted cavitation process was proposed for degradation of organic pollutants. The process envisages use of suitable solvent as an additive, (1-5% v/V), in the conventional cavitation process to enhance the pollutant removal efficiency. A proof of concept was provided for removal of ammoniacal nitrogen with significantly improved efficiency using solvent-assisted hydrodynamic cavitation (HC) compared to conventional HC. Efficacy of the process was studied on a pilot plant scale (1m^3/h) and using vortex flow based vortex diode as a cavitating device. Degradation studies were carried out using a model pollutant, 4-aminophenol and four different solvents as additives, 1-octanol, cyclohexanol, 1-octane and toluene. Relatively polar solvents were found to increase the efficiency of the pollutant removal (>65%) and also increase the rates to an extent of more than 200%, compared to only HC. A very high removal of ammoniacal nitrogen, more than 90%, was obtained for solvents 1-octanol and cyclohexanol, indicating importance of selection of solvent. Per-pass degradation model showed 3 to 4 times increase in the per pass degradation for polar solvents compared to cavitation alone. The results confirm no role of conventional solvent extraction and no contamination of wastewater due to the use of solvent as an additive in the process. Further, the cost was 2 to 3 times lower compared to conventional HC. The interesting observations in the proposed process can fuel further research to provide possible improvements in existing methodologies of wastewater treatment, in general and for removal of ammoniacal nitrogen, in particular.

8.1 Introduction

Removal of ammoniacal nitrogen from wastewaters for environmental pollution control is an important problem in many industries such as dyes and textile, specialty chemicals and so on due to high ammoniacal nitrogen content. Industries such as fisheries that produce wastewaters with high biological oxygen demand (BOD), suitable for treating using conventional biological treatment methods, typically end up in treated wastewaters containing much higher ammoniacal nitrogen than the recommended norms of below 30-50 mg/L [1]. Ammoniacal nitrogen (NH_4-N), nitrogenous organic matter which can be converted to ammonia, is a measure of the amount of ammonia, a toxic pollutant. Conventional wastewater treatment methodologies generally focus on the removal of chemical oxygen demand (COD)/ total organic carbon (TOC) and biological oxygen demand (BOD) to meet the desired pollution control norms. The removal of ammoniacal nitrogen has received comparatively less attention. The conventional methods for the removal of ammoniacal nitrogen include biological, physical, and chemical methods, in isolation or in combination. Available technologies include adsorption, chemical precipitation, membrane filtration, reverse osmosis, ion exchange, air stripping, breakpoint chlorination and biological nitrification and denitrification [2]. A large number of treatment methods such as coagulation, adsorption focus on physical removal of pollutants, consequently generating secondary waste. Number of adsorbents were reported with varying success, such as zeolite [3–6], minerals [7], limestone [8], natural and waste materials such as shell, refuse concrete and cement [9], nanomaterials [10] and ion exchange resins [11]. Precipitation of ammoniacal nitrogen as magnesium ammonium phosphate was reported for the treatment of tannery wastewaters [12]. The biological methodologies for ammoniacal nitrogen removal include conventional nitrification/denitrification, partial nitritation, ANAMMOX (anaerobic ammonium oxidation) [13,14], and its combined system CANON (completely autotrophic nitrogen removal over nitrite) for use at industrial scale. Biological methods typically require high residence time and are sensitive to temperature fluctuations and may require additional carbon sources for their smooth operation at large scale operation [15]. Advanced oxidation processes (AOPs) and their combinations such as Fenton, Photo Fenton, Photocatalysis, UV/H_2O_2, and ozone are also reported for ammoniacal nitrogen removal from wastewaters.

Advanced oxidation processes typically have high cost of treatment compared to cavitation, in general (mainly due to catalyst and processing) [16] and can also produce undesirable intermediates [17,18]. Pravin et al. [19] successfully demonstrated effective removal of ammoniacal nitrogen using process intensification with treatment cost as low as 0.01 to 0.1 $/m^3. Membrane based processes have limitations in wastewater treatment, generate secondary waste apart from high cost. Methodologies such as cavitation can degrade the organic pollutants to achieve degradation of organics to the extent of mineralization and that the secondary waste generation can be partly/ completely eliminated. In view of the constraints of most of existing methodologies, high costs of treatment apart from limitations on extent of pollutants removal with ease of operation, it is instructive to develop newer methodologies for removal of organic pollutants, specifically for ammoniacal nitrogen removal.

Hydrodynamic cavitation, is the most practical form of cavitation processes in general for industrial applications compared to acoustic, optic or particle cavitation processes [20]. Cavitation involves *in situ* generation of oxidizing species, by homolytically cleaving water molecule and consequently oxidising the organic pollutants for complete mineralization. In view of the ease of operation and scale-up, hydrodynamic cavitation is an attractive alternative compared to other conventional advanced oxidation processes in wastewater treatment.

Cavitation is a physico-chemical process where the physical component requires formation, growth and violent collapse (implosion) of cavities in microseconds. Consequent to cavities collapse, extreme temperature and pressures are experienced at the point of implosion; pressure about ~1000 atm and temperatures ~10000k. Under these extreme conditions, water splits, a homolytic cleavage, generating hydroxyl radicals required for the oxidation of organics- chemical process [20]. Hydrodynamic cavitation processes make use of different cavitating devices such as linear flow based devices e.g. orifice, venturi and rotational flow/ vortex flow based devices such as vortex diode (non-moving element type) or high speed rotor stator assembly (moving element type). In recent years, vortex diode that employs vortex flow and has no moving elements has been shown to be useful in many wastewater treatment applications [19,21–23]. It was found to be superior to conventional cavitation devices such as orifice, venturi in applications such as dye removal [24], apart from many other applications such as solvent degradation [22,25,26], microbial disinfection [27–29], ammoniacal nitrogen removal [19,30,31], biomass valorisation [32,33], desulphurization of transportation fuels [34] etc. The hydrodynamic cavitation process has been well discussed in many of the above literature apart from the design details for various forms of devices.

The application of cavitation processes for the wastewater treatment has not been largely successful in real life operations in spite of large number of studies on various types of cavitation processes, cavitating devices and process intensifications. It is essential that newer ways and process modifications be investigated to increase the efficiency in the removal of different types of organic pollutants and for reducing the cost of operation apart from ease of operation and scalability. In this context, the present study reports, for the first time, a new approach of solvent-assisted cavitation for the enhanced degradation of organic pollutants, using suitable solvent as an additive (1-5% v/V). Degradation of 4-aminophenol as a model nitrogen compound was discussed in detail. The nature of solvent was investigated using relatively polar solvents such as octanol and cyclohexanol and non-polar solvents such as octane and toluene. The removal kinetics was evaluated using the per-pass degradation model. The solvent can be easily separated, recycled and reused. The findings of this work would provide a newer approach of solvent-assisted cavitation for the industrial wastewater treatment, in general and for removal of ammoniacal nitrogen, in particular.

8.2 Conceptual Development of the Process

A solvent-assisted cavitation process for the removal of pollutants from waste water envisages treating wastewater and a suitable immiscible solvent as an additive, in a small volume percent of 1-5%, using a cavitation process for the degradation of pollutants. The process involves the following steps:

1. Addition of suitable solvent as an additive in a wastewater tank.
2. Allowing the wastewater to be treated using the cavitation device for the required time to obtain the wastewater with reduced levels of COD and/or ammoniacal nitrogen.
3. Separating the solvent from water and possible recycle and reuse.
4. To obtain treated water with the desired COD and/or ammoniacal nitrogen removal.

The entire operation can be essentially carried out at ambient conditions. The proposed methodology envisages use of any suitable solvent, alone or in combinations, which is immiscible with water. While, in principle, any type of cavitation process can be applied, hydrodynamic cavitation can be a better option in view of the reported literature on wastewater treatment. Also, in hydrodynamic cavitation, the cavitating device can be selected from any type e.g. orifice, venturi, vortex diode etc. The process can be carried out in a batch or continuous mode or in combination with other wastewater treatment methods like adsorption, coagulation and oxidation for meeting the prescribed norms of pollution control and/or for cost-effectiveness.

A schematic flow diagram of the proposed process, based on the steps outlined as above, is given in Figure 8.1A, depicting mixing suitable solvent with the wastewater stream in the desired proportions and carrying out the cavitation process in an usual manner for the oxidation of organic pollutants by generating oxidising species such as hydroxyl radicals or hydrogen peroxide. The objective is to enhance the performance of the conventional cavitation process using solvent additive- solvent expected to assist through generation of additional cavities for improved cavitation and possibly by providing conducive environment, by increased localized organic pollutant concentration at the interface due to the solvent-pollutant affinity.

Advanced Oxidation Processes (AOP) are well known for the degradation of pollutants and for the treatment of wastewaters. However, it is evident from the discussion above and Figure 8.1, no AOP has any resemblance with the solvent-assisted cavitation process for the treatment of wastewaters. The commonly used Fenton oxidation requires use of iron catalyst and hydrogen peroxide in acidic medium which is entirely different from this new process that requires no catalyst or such conditions. Further, no AOP refers to the use of solvent in degradation of wastewaters using cavitation. The conventional solvent extraction process refers to the removal of species in its original physical form in a different phase (e.g. solvent extraction) or removal of its modified form (e.g. reactive extraction, dissociation extraction). The present work refers to destruction of the species using a solvent additive in cavitation (1-5%), completely different from extraction process. This can be viewed as “Transformed advanced oxidation process using solvent for degradation of pollutants”.

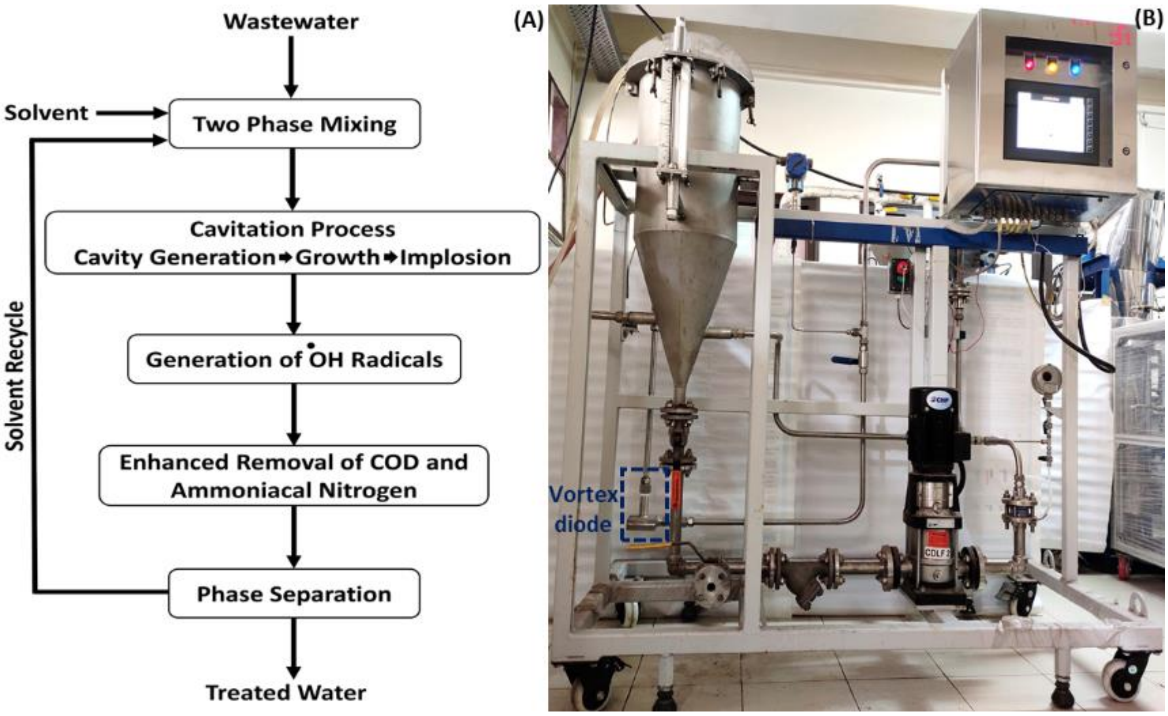


Figure 8. 1: Solvent-assisted hydrodynamic cavitation process (A) Flow diagram (B) Experimental set-up

8.3 Experimental

Four different solvents, 1-octanol, cyclohexanol, 1-octane and toluene (HPLC grade, >99%, Loba Chemie) were used. Reagent grade 4-Aminophenol ($H_2NC_6H_4OH$; 99%) was obtained from Sigma Aldrich. The analysis of ammoniacal nitrogen, removal as NH_4-N, was carried out using Spectroquant® Pharo 100 spectrophotometer (MERCK, India), wavelength range 320-1100 nm while for total organic carbon, SHIMADZU TOC-L series of TOC analyzer was used. The degradation by way of mineralization is thus reflected in the TOC removal.

The essential parts of the experimental set up (Figure 8.1B) include a vertical cylindrical feed cum recirculation tank (SS316) with working capacity of ~25 litres, pumping arrangement for the wastewater, cavitating device and controls/ measurements of process parameters. A vertical multistage centrifugal pump (Model CNP make CDLF2-6, SS316, 2 m^3/h at 45 MWC), rating 0.75 kW (1 hp), 2900 RPM, discharge pressure 0–5 bar with non-flame proof motor was used and flow was controlled by ¾" NB valves (Wesmec Engineering Pvt ltd). SS316 seamless tubes of 0.75 inch diameter with appropriate fitting were part of the flow system. Flow transmitter (KRONE, H250), range 150-1500 LPH with integral analog indicator was used to measure mainline flow rate while temperature was measured using RTD (EUREKA Eng. Enterprises India; 0–200° C) inserted into the feed tank. A cooling coil (SS316) was used in the feed tank for precise temperature control. Horner make HMI display was used for data logging with provision of sim card for data monitoring and transfer from any location. Whole assembly was mounted on carbon steel powder coated skid with wheels.

The removal of ammoniacal nitrogen was studied using 4-aminophenol as a model nitrogen containing compound. Initial concentration of 100 mg/L was used for all the experiments, unless specified. A volume of 12 L of synthetic wastewater was typically used with predetermined solvent volume fraction (2 and 5%) as an additive. Vortex diode was used as a cavitating device (SS316, Chamber diameter 66 mm) and experiments were carried out using predetermined pressure drop. The solvent was separated after each cavitation experiment by simple layer separation using separating funnel. The removal of ammoniacal nitrogen and reduction in total organic carbon was monitored by sampling at periodic time intervals. For observing the extent of degradation and the rate behaviour, the experiments were carried out for 180 min and samples were withdrawn at 30 min interval for analysis. In view of cavitation inception, based on earlier studies, at 0.48 bar for the vortex diode [34], the pressure drop condition of 0.5 bar or above was selected for all the experiments to ensure the operation in the cavitation regime.

The samples of both aqueous phase and solvent phase before and after the cavitation were analysed for para-aminophenol in the two phases and also for any formation of intermediates using HPLC technique (Agilent, 1260 infinity series, equipped with UV visible detector and wavelength, λ=210 nm, C-18 column (4.6×250 mm)). The mobile phase was in the ratio of 95:5 with aqueous buffer and acetonitrile with flow rate 0.8 ml/min. Aqueous buffer was prepared by addition of 4 ml of phosphoric acid, 50 ml of methanol in 1 lit HPLC grade water [35].

8.4 Results and discussion

8.4.1 Effect of nature solvent and solvent volume fraction

The effects of pressure drop and initial concentration of the pollutants have been well reported in hydrodynamic cavitation [34] and also for the removal of ammoniacal nitrogen [19]. Accordingly, pressure drop, ΔP of 0.5 bar was used for evaluating the efficacy of solvent-assisted hydrodynamic cavitation process.

The solvent-assisted cavitation process invariably depends on the selection of the solvent, similar to solvent extraction. The nature of solvent, polarity of the solvent are expected to play important role in the new process. In the case of removal of ammoniacal nitrogen, for the representative pollutant, p-amino phenol, four different solvents were evaluated from slightly polar to non-polar solvent classes. The four solvents included n-octanol, cyclohexanol, toluene and octane.

The extent of removal of ammoniacal nitrogen using only hydrodynamic cavitation was ~55%. It was observed that the solvents, octanol and cyclohexanol have significant effect in increasing the efficiency of degradation whereas, the solvents toluene and octane have adverse impact on the removal efficiency.

The positive effect of solvent volume fraction was validated using 2% and 5% volume fraction of octanol, since it gave increased efficiency (Figure 8.2A). A very high removal of 92% was obtained with 5% v/V of octanol (k, 15×10^{-3},min^{-1}) while in the case of 2% v/V of octanol 89% ammoniacal nitrogen removal was obtained (k, 12.4×10^{-3}, min^{-1}). Similarly, high extent of removal of 86%, was obtained for cyclohexanol (2%), in 180 min (Figure 8.2B). Another interesting observation that can be made from Figure 8.2 is that there is significant increase in the rate of degradation process when the solvent volume fraction is increased and the difference in this regard is highlighted in Figures. 8.2A and B. Thus, in the solvent-assisted cavitation process, the degradation of pollutants can be accomplished by manipulating the process parameters such as solvent nature/polarity, solvent volume fraction etc. Similar to the conventional cavitation processes, the other parameters such as nature of cavitation process (acoustic/ hydrodynamic), pressure drop, nature of cavitating device in hydrodynamic cavitation etc. may also influence the performance. In view of the reported literature on the effects of pressure drop, nature of cavitating device and cavitation process type, only the pertinent parameters are highlighted in this work and effects of other parameters are believed to be similar to those reported in the literature, though need to be separately investigated for quantitative analysis and comparison. Overall, solvent-assisted cavitation process can provide significantly increased efficiency and substantially increased rates of degradation. The nonpolar solvents, octane and toluene (2% v/V) gave ammoniacal nitrogen removal only about 26% and 35% respectively, far lower than that obtained using only cavitation (Figure 8.3A and Figure 8.3B).

The results clearly highlight not just the effect of nature of solvent, but also the importance of solvent volume fraction in the solvent-assisted cavitation process for improved removal of ammoniacal nitrogen. These aspects need detailed investigations for appropriate selection of the solvent.

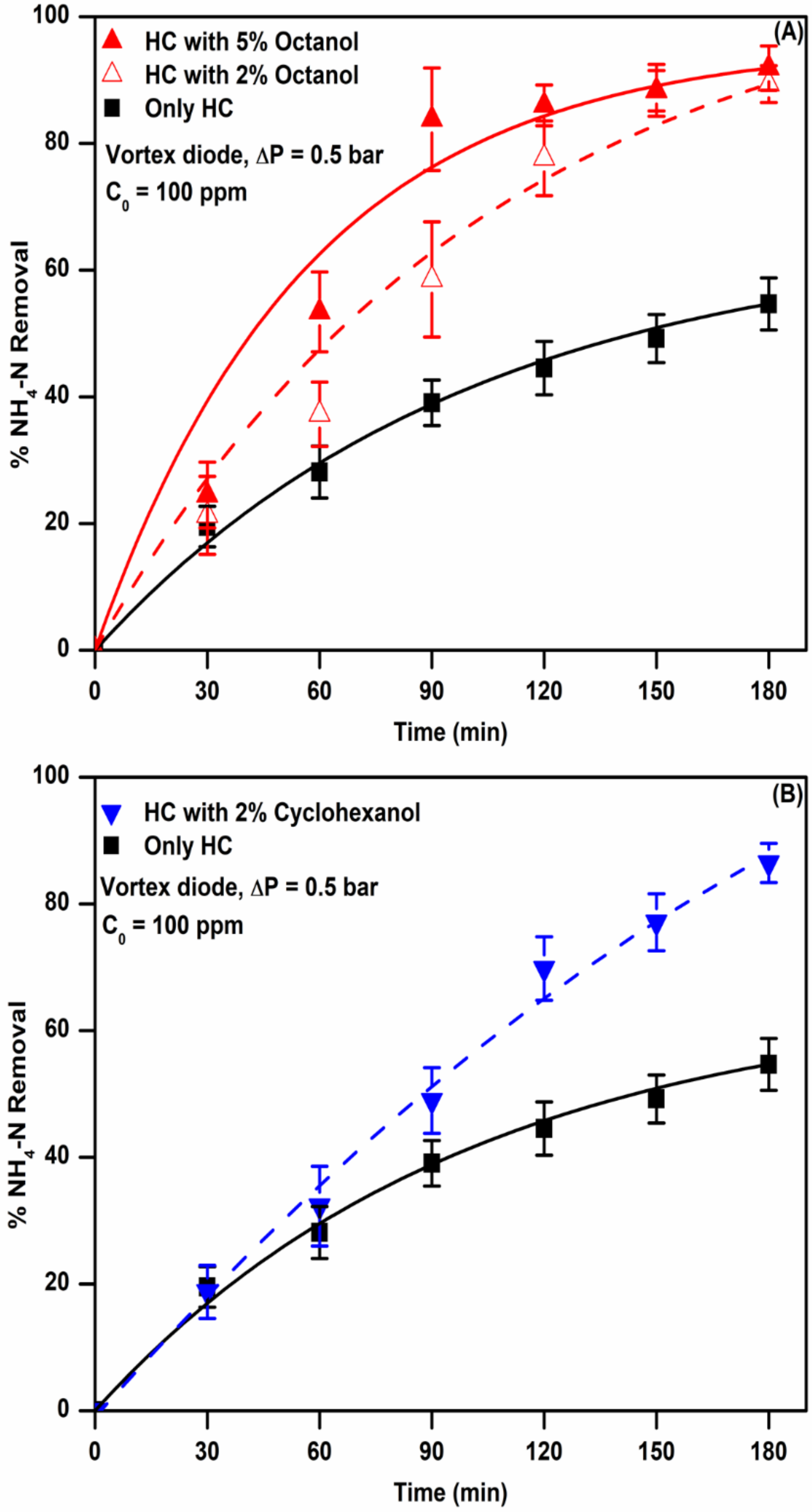


Figure 8. 2: Removal of ammoniacal nitrogen using solvents (A) Octanol (B) Cyclohexanol

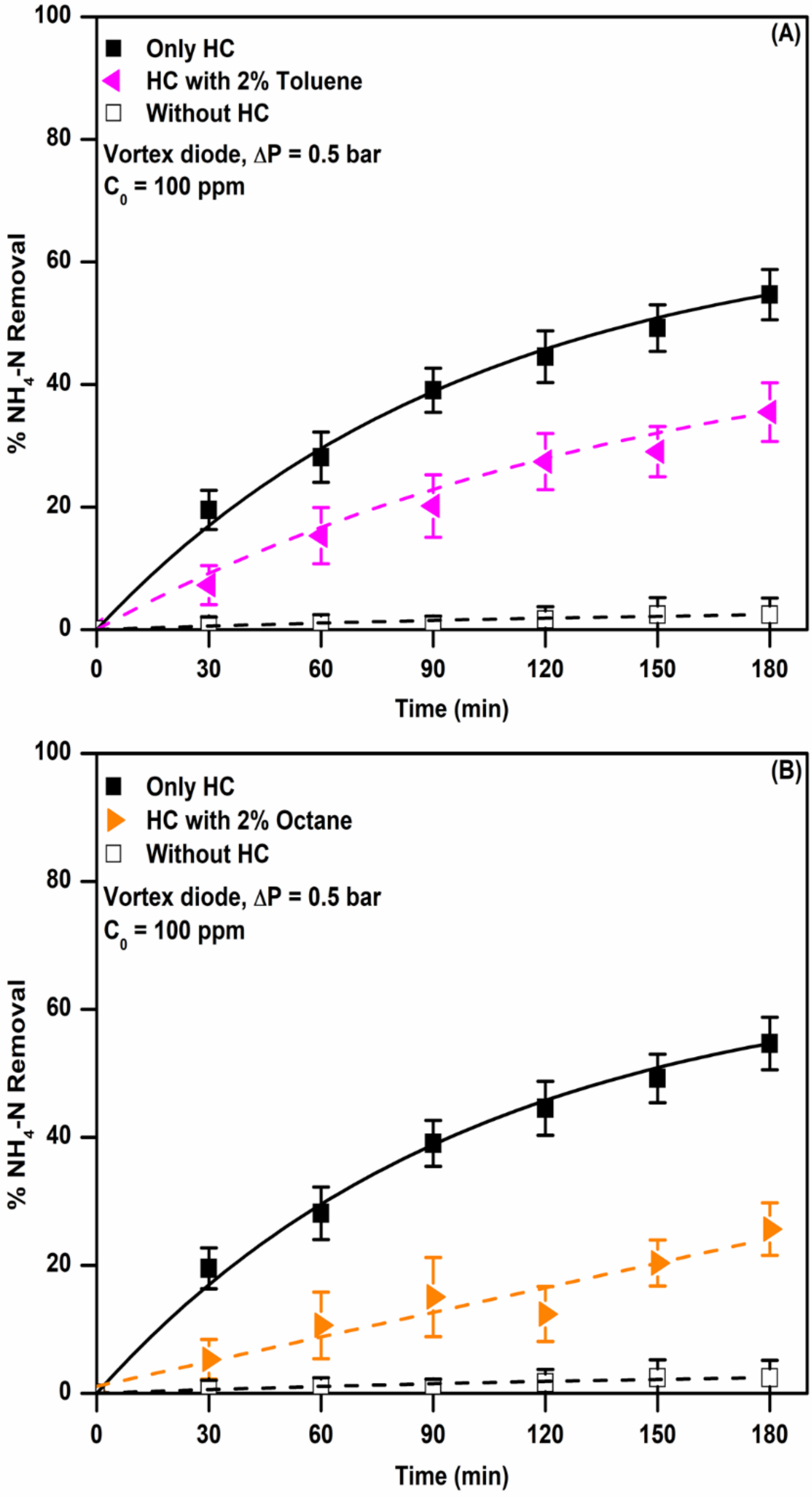


Figure 8. 3: Removal of ammoniacal nitrogen using solvents (A) Toluene (B) Octane

8.4.2 Kinetics of degradation

The kinetics of the degradation was studied for the initial concentration of 100 mg/L of 4-aminophenol and for different volume fraction of solvents in water. A pseudo first order model was considered, where,

$$C = C_0 e^{-kt} \tag{8. 1}$$

C_0 and C denote the initial ammoniacal nitrogen concentration and concentration at any time, t, “t” is time (min), and k is an apparent rate constant (min^{-1}) of the reaction. The fit of the model was found good with $R^2>0.98$ for all the k value estimates. The values of the rate constant are given in Table 8.1. For only hydrodynamic cavitation using vortex diode, pressure drop of 0.5 bar, the k value was 4.7×10^{-3} min^{-1} while for cavitation with 2% and 5% octanol it was 12.4×10^{-3} min^{-1} and 15×10^{-3} min^{-1} respectively. The k values in case of 2% cyclohexanol, octane and toluene were 9.9×10^{-3} min^{-1}, 1.5×10^{-3} min^{-1} and 2.5×10^{-3} min^{-1} respectively. It was observed that the increase in the removal rate was significant when cavitation was carried out with relatively polar solvents such as octanol and cyclohexanol while in the case of non-polar solvents, such as octane and toluene, the removal rate was lower compared to the cavitation alone.

Table 8. 1: Rate constant for different solvents (4-aminophenol (100 mg/L); vortex diode; ΔP, 0.5 bar)

Methodology	**% NH_4-N Removal after 180 min**	**1st Order Rate Constant $k \times 10^3$ (min^{-1})**
HC only	55	4.7
Without HC	2.4	0.1
HC with 2% n-Octanol	89	12.4
HC with 5% n-Octanol	92	15
HC with 2% Cyclohexanol	86	9.9
HC with 2% n-Octane	26	1.5
HC with 2% Toluene	35	2.5

In the case of octanol, with a volume fraction of 2%, the removal rate was significantly increased by 2.5 times than cavitation alone while increasing volume fraction to 5% gave more than 3 times increase in the rate of ammoniacal nitrogen removal. For cyclohexanol, 2% volume fraction gave ~ 2 times enhancement in the removal rate compared to the cavitation alone. Thus, the developed methodology can be viewed as a transformed advanced oxidation process using solvent for degradation of the pollutants.

8.4.3 Per-pass degradation and cavitational yield

In recent years, use of per-pass degradation model in describing the hydrodynamic cavitation behaviour for different reactors has gained significance due to the physical understanding and for its ability to represent close to real life operation [25,27–29]. The per-pass degradation factor is described as,

$$\text{Per-pass degradation factor } (\phi) = k\,\tau \tag{8. 2}$$

Where, τ is residence time which is defined as ratio of volume in holding tank and flowrate through cavitation reactor.

Figure 8.4 shows comparative analysis of per-pass degradation for the cavitation device, vortex diode at $\Delta P = 0.5$ bar for cavitation alone and with the addition of different polar and nonpolar solvents and also for different solvent ratios. Cavitation with relatively polar solvents such as octanol and cyclohexanol shows almost doubling of the per-pass removal while there was no improvement for cavitation with the addition of non-polar solvents such as octane and toluene compared to cavitation alone, as discussed in the earlier section.

The energy dissipation rate is calculated as,

$$W = \Delta P \times Q \tag{8. 3}$$

The overall cavitational yield (amount of ammoniacal nitrogen degraded per unit energy dissipation) can be obtained as,

$$Y = \frac{V(C_0 - C)}{\Delta P Q t} \text{ mg/J} \tag{8. 4}$$

The value of the cavitational yield in the case of hydrodynamic cavitation without solvent was 11.4×10^{-4} mg/J while in the case of octanol it was 14.5×10^{-4} mg/J and 16×10^{-4} mg/J for 2% and 5% volume fraction respectively. The values in case of 2% volume fraction of cyclohexanol, octane and toluene were 14.3×10^{-4} mg/J, 5×10^{-4} mg/J and 7.5×10^{-4} mg/J respectively. The model, therefore, correlates increase in the cavitational yield for the relatively polar solvents.

The cavitation device will certainly have an important role in the process. However, the objective of this work is to provide the proof of concept for the solvent-assisted hydrodynamic cavitation for the degradation of the organic pollutants/ removal of ammoniacal nitrogen using any cavitation process, in general and hydrodynamic cavitation, in particular. Hence, though the selection of cavitating device will impact the overall performance of the process, the enhancement due to the novel process so as to obtain solvent-assisted cavitation for wastewater treatment will maintain, irrespective of the type of the cavitating device. It is however, required that further investigations be carried out for different cavitation reactors to further assess the practical relevance of the process in the wastewater treatment.

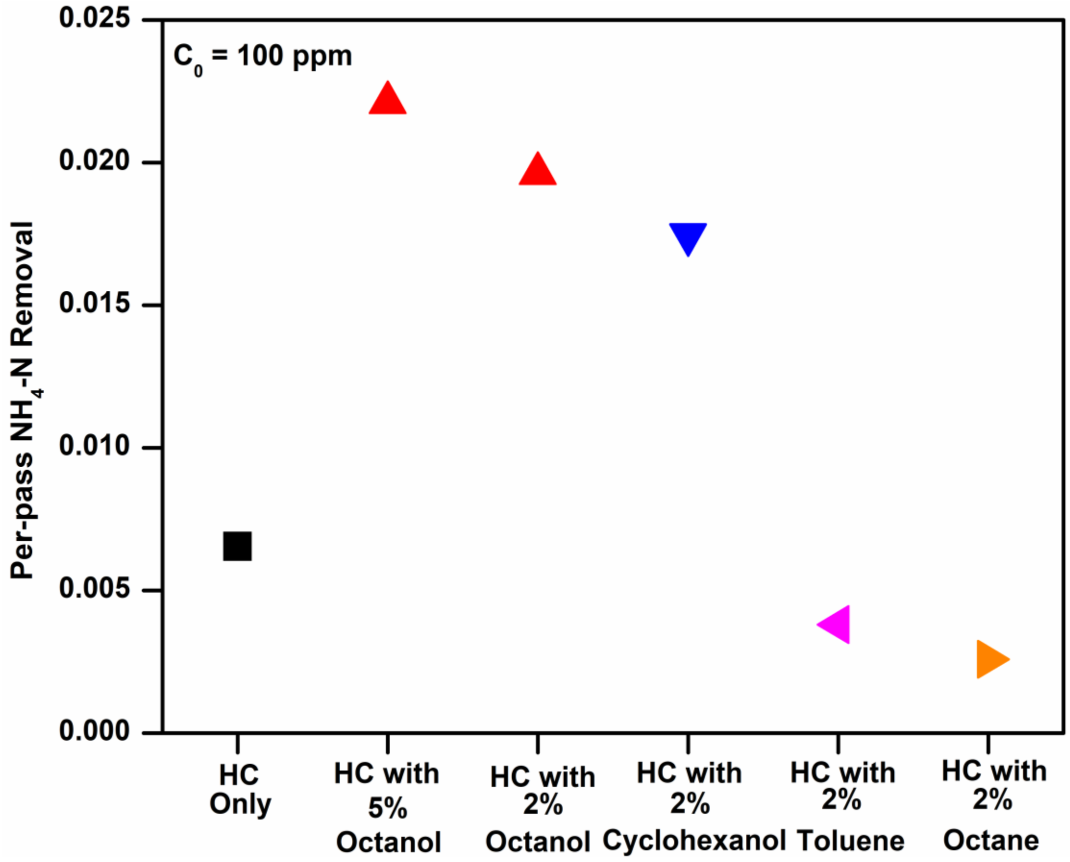


Figure 8. 4: Per-pass NH_4-N removal, C_0 = 100 ppm

8.4.4 Differentiating solvent assisted cavitation and solvent extraction processes

The reported work in the literature pertaining to the solvent and wastewater can be broadly classified into two parts:

1. Solvent use in solvent extraction process.
2. Different processes for degradation of solvents

The use of solvent extraction process for treating large volumes of wastewaters is not common due to correspondingly large quantities of solvent requirements and operational difficulties. Further, small concentrations of pollutants make it less suitable and economically not viable. A combination of solvent extraction and freeze thaw for oil recovery from petroleum refinery wastewater was recently reported by Hu et al. [36]. Requirement of high volume ratio of toluene/wastewater was suggested for the recovery of nitrotoluenes from wastewater by solvent extraction [37]. Recently, extraction and fractional distillation was reported for the removal of organic compounds from wastewater of oil industry [38].

A number of studies have been reported for the degradation of solvents by advanced oxidation processes in wastewater treatment- solvents of the type acetone, toluene and so on, typically by employing O_3/UV process [39–41], by Fenton process [42], by sonochemical and photochemical oxidation [43] or such multiple combinations using different oxidising agents such as hydrogen peroxide [44–46]. Degradation of solvents using cavitation processes was sparsely reported in the literature [22,25,26].

The solvent extraction process, typically employs physical separation of the targeted species or its reacted form from wastewater to the solvent phase. Dissociation extraction is one such example, although such approaches have limited practical utility.

The degradation of solvents using advanced oxidation processes typically have Fenton process type catalyst and other reagent requirements apart from low concentrations of solvents, largely in ppm range. Cavitation methodologies reported for the degradation of solvents also involve low concentrations of different solvents.

The novelty in the developed solvent-assisted cavitation process can be visualized in the form of solvent additive being used for enhanced degradation of organic pollutants. Water is a continuous phase while solvent is a dispersed phase. During the cavitation, cavities can form from both water as well as from solvent and the oxidation reactions can take place at the interface in accordance with the availability of the pollutant species. The vapour filled cavities of solvent and water exist only for a small duration of time (microseconds); essentially a transition state. Physical extraction of the organic pollutant may occur in the solvent, though equilibrium distribution is less likely due to transient nature and existence. Degradation of the pollutant and subsequent mineralization by the oxidation process makes the solvent-assisted cavitation completely different from the conventional extraction process as well as from the conventional cavitation process. The use of solvent for assisting the degradation of the pollutants is not reported so far in any form of cavitation processes and obtaining significant enhancement in the degradation of pollutants using the solvent-assisted cavitation process can be construed as a novelty in the process that can have practical utility and applications in wastewater treatment, especially when no additional pollution due to the use of solvent additives is observed or can be achieved.

8.4.5 Mechanism of the Solvent- assisted cavitation process

Cavitation is known to generate cavities that grow in size and eventually implode to enable formation of hydroxyl radicals through water cleaving at extreme conditions of temperature and pressure at the point of implosion. In the conventional process, therefore, the number of cavities and productive implosions of the cavities are most crucial for generation of the oxidising radicals and consequently degradation of organic pollutants via oxidation. With the 3 zone theory in cavitation, it is also possible that when the pollutant is near the bubble implosion interface, there are high chances of pyrolytic break down [20]. It was recently reported that any process intensification that can increase the number of cavities can aid/ enhance the degradation performance, e.g. aeration, and also that the degradation mechanism of p-aminophenol involves oxidation with final oxidation products as benzoquinone, water and NOx [19]. In this work, therefore, elucidation of the mechanism of the solvent-assisted cavitation is specifically attempted.

It is believed that the addition of solvent as an additive in the solvent-assisted cavitation incorporates the third component in the system in both liquid and vapour phases- water containing organic pollutants, vapour filled cavities/ vapours of both aqueous as well as organic, and third component in the form of the additional solvent as the organic liquid phase and solvent vapour phase. In the conventional cavitation process, the cavities inherently get formed in the aqueous phase and bring the organic moiety into the cavities or at the point of implosion for the degradation to take place. It is postulated that the addition of appropriate solvent as an additive result into generation of additional cavities due to solvent flashing into vapour and also subsequent collapse of these cavities, though the complete mechanism is rather not clear at this point of time. It is possible that the organic moiety may easily migrate into the solvent and therefore more chances of it to degrade due to the increased implosions of different cavities. Since all types of solvents are not suitable to enhance the degradation behaviour, it is believed that the affinity to solvent is crucial. The advantage, over and above the conventional hydrodynamic cavitation, in enhancing the degradation of pollutants and also the disadvantage or adverse impact due to some solvents in this regard, both the effects are clearly depicted in Figure 8.5A where positive effect is observed in terms of enhancing the rate as well as overall degradation for the two solvents, octanol and cyclohexanol, and negative or adverse impact in terms of reduced degradation is obtained for the two solvents, toluene and octane.

Figure 8.5B depicts the variation in the relative polarity for the four solvents. The enhancement in degradation with relatively polar solvents such as octanol and cyclohexanol can be attributed to increased localized concentration of the pollutant at the solvent interface compared to the pollutant concentration in the aqueous phase. Consequently, the increased concentration at the point of implosion increases the rates of degradation and also increases overall degradation efficiency. Compared to the effect of relatively polar solvents, the pollutant species going into non-polar solvent is likely to get insulated from hydroxyl radicals, subsequently reducing the local concentration of pollutant for oxidation which consequently results in lower rates of degradation and lowered efficiency compared to not only relatively polar solvents, but also that for only hydrodynamic cavitation. Thus, it can explain the increased degradation for the relatively polar solvents and reduced degradation efficiency for the non-polar solvents as compared to the conventional cavitation (~ 62% increase for 2%

octanol, 56% for cyclohexanol in contrast to lowered degradation for toluene, (-36%) and for octane (-53%)).

The solvent physical properties such as viscosity and surface tension will also impact the cavity formation and therefore, the cavitation process. These aspects need to be investigated in detail for complete elucidation of the mechanism of the solvent-assisted cavitation process.

The developed process is distinctly different from the conventional solvent extraction. In the solvent extraction, there is a physical distribution of the species in two phases, aqueous and organic; extraction in the solvent takes place thereby depleting the concentration from the aqueous phase. Further, in the solvent extraction process, there is no degradation of the species or more specifically mineralization. In the present work, the analysis of both the solvent and aqueous phases before and after the cavitation confirmed that the removal is not through extraction of the organic pollutant in the solvent. Figure 8.6 shows the HPLC analysis of the solvent and the aqueous phase prior to and after the cavitation (180 min), for the experiment with 2% octanol. A sharp peak of 4-aminophenol can be seen in the aqueous phase before and after cavitation indicating its predominant concentration in the aqueous phase and only a minor distribution of 4-aminophenol (~2%) in solvent phase was observed. Further, no major by-products formation was seen after the cavitation. There was no pollutant increase due to the use of the solvent. The solvent-assisted cavitation process is essentially carried out at ambient conditions and considering the higher boiling points of the solvents (Toluene, 111 ^{o}C; n-Octane, 125 ^{o}C; Cyclohexanol, 161 ^{o}C and Octanol, 195 ^{o}C), the loss of solvent due to vaporization is expected to be negligible. Preliminary analysis by physical separation showed highest recovery for n-octane in the range of 96-98% (2 % v/V) and lowest recovery for cyclohexanol, 75-78%; lower recovery can be attributed to the difficulty in the separation as a separate layer. The ease of separation of solvent depends on the miscibility and characteristics of the solvent and solvent selection is important similar to that in the case of solvent extraction. Also, no pollution due to the use of solvent additive was confirmed from the TOC analysis; reduced TOC after the treatment. The results clearly substantiate the suggested mechanism of the solvent assisted cavitation.

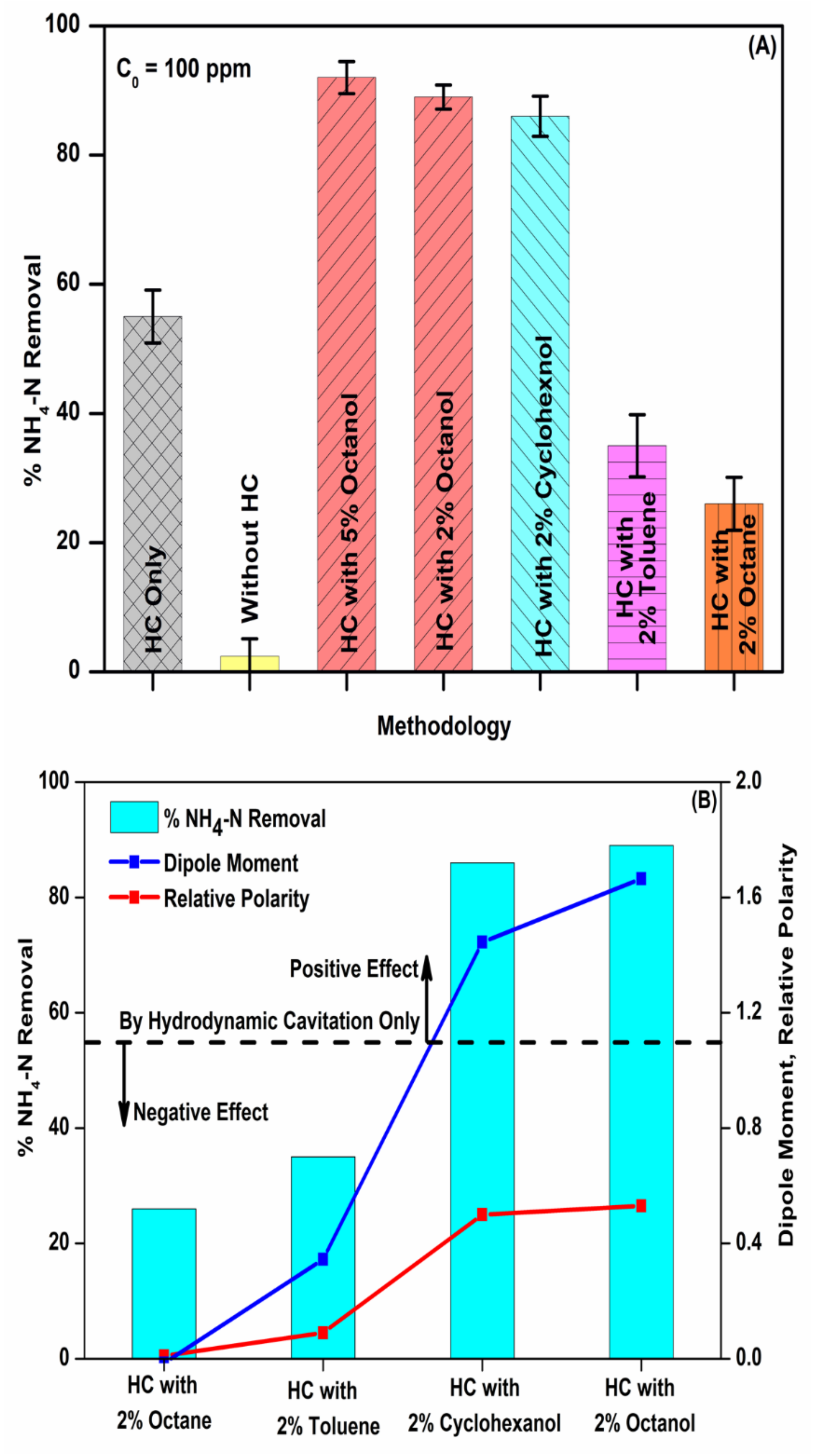
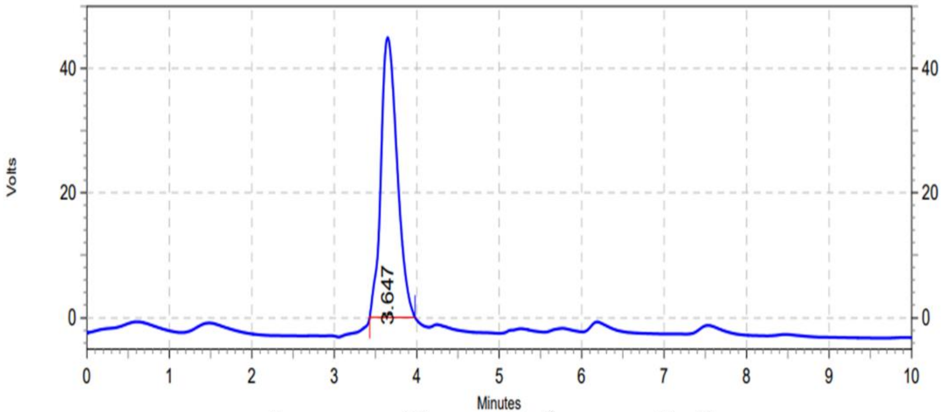
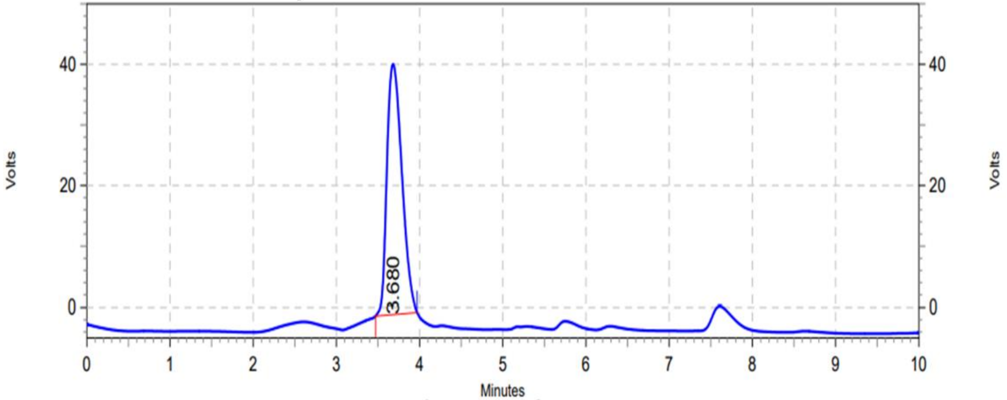


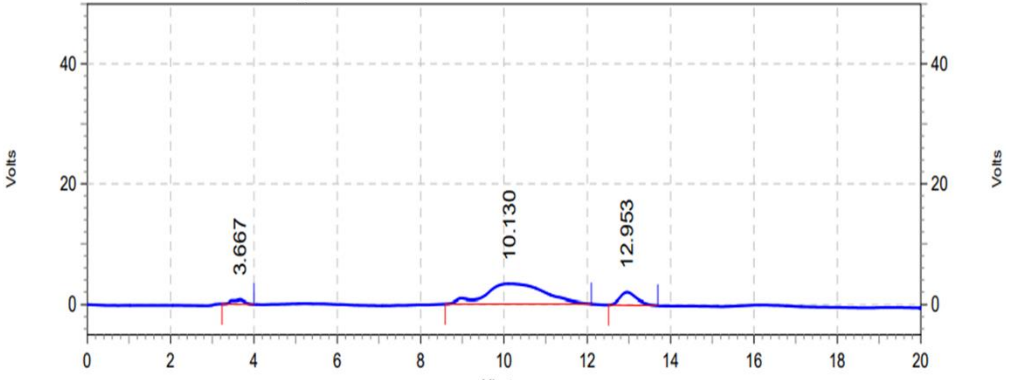
Figure 8. 5: Correlating solvent polarity with degradation efficiency



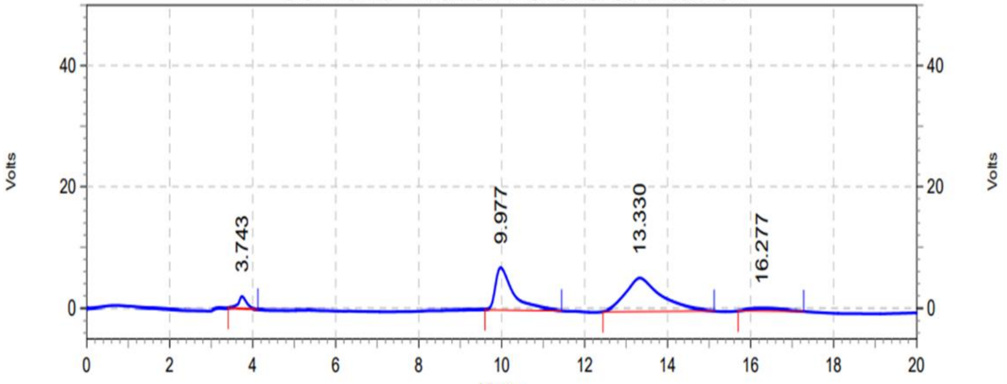
Aqueous Phase: Before cavitation



Aqueous Phase: After cavitation



Solvent Phase: Before cavitation



Solvent Phase: After cavitation

Figure 8. 6: HPLC results indicating degradation of para-aminophenol

8.4.6 Cost analysis for solvent assisted ammoniacal nitrogen removal

The cost of treatment per unit volume of effluent by hydrodynamic cavitation can be calculated as [1],

$$\text{Cost of treatment per m}^3 \text{ of effluent} = \frac{N_c \times \Delta P \times P_E}{36\eta} \qquad (8.\ 5)$$

Where, Nc is number is the number of passes, ΔP is pressure drop across cavitation device, P_E is the cost of electricity and η is the pump efficiency.

In view of the negligible solvent usage/loss, the cost of the solvent was neglected in the present analysis. However, solvent cost may have to be accounted, if required, for the solvent/ recovery. Assuming the cost of electricity for typical Indian scenario as Rs. 10 /kWh (1$ = 70 Rs) and pump efficiency at 66% (commercial high flowrates, above 10 m^3/h), the cost of treatment by the hydrodynamic cavitation alone using the vortex diode at ΔP = 0.5 bar was found to be 24 Rs/m^3 (0.34$/$m^3$), while for the solvent assisted cavitation using 2 and 5% octanol it was 11 Rs/m^3 (0.15$/$m^3$) and 8 Rs/$m^3$ (0.11$/$m^3$) respectively. The cost in the case of 2% cyclohexanol was 13 Rs/m^3 (0.18$/$m^3$). It is clear that the solvent assisted hydrodynamic cavitation using vortex diode as the cavitating device for ammoniacal nitrogen removal reduces cost by approximately 2-3 times compared to the hydrodynamic cavitation alone.

Thus, the solvent-assisted cavitation process for the wastewater treatment appears to be quite attractive alternative compared to the cavitation alone, both in terms of efficiency and cost of operation.

8.5 Conclusion

A newer approach of solvent-assisted cavitation process is proposed for the degradation of organic pollutants and use of suitable solvent, as an additive (1-5% v/V), is reported for the first time specifically for the enhanced removal of organic pollutants, in general and ammoniacal nitrogen, in particular. The proposed process was found to have higher efficiency in the removal of ammoniacal nitrogen compared to the conventional cavitation. The important findings are,

1. Vortex flow-based cavitation reactor was found to be highly effective for the removal of ammoniacal nitrogen.
2. Solvent-assisted cavitation process retains the advantages of conventional cavitation processes by employing mild operating conditions such as low pressure drop of 0.5 bar while accomplishing higher levels of degradation of organic pollutants.
3. Solvent characteristics are important for obtaining enhancement in the removal of pollutants and relatively polar solvents such as octanol and cyclohexanol were found to be highly effective compared to non-polar solvents e.g. toluene and octane.
4. A very high ammoniacal nitrogen removal to the extent of 90% could be obtained for relatively polar solvents- octanol and cyclohexanol; an enhancement of 65% over and above the conventional hydrodynamic cavitation under similar conditions.
5. Removal rate was also significantly enhanced by 2 to 3 times than individual operation of hydrodynamic cavitation depicting high efficacy of the new process.
6. Non-polar solvents, as additives, were found to diminish the effect of hydrodynamic cavitation, possibly due to insulating effect for the pollutant moiety.
7. The developed process appears to have significantly low cost compared to conventional hydrodynamic cavitation and more than 200% cost reduction was achieved.

The results can provide impetus to further research for possible improvements in the existing cavitation technologies and process intensification methodologies in the wastewater treatment, in general and for the removal of ammoniacal nitrogen, in particular.

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Chapter – 9

Conclusions and Future Scope

Chapter 9

Conclusions and Future Scope

9.1 Conclusions

Industrial wastewater treatment is an important research area in view of the serious challenges posed by difficult removal of refractory pollutants and new emerging organic pollutants that are difficult to remove/ degrade using the conventional wastewater treatment technologies. Application of technologies such as hydrodynamic cavitation have not found many applications in real life wastewater treatment, in spite of the simplicity of the process, high efficiency and lower cost compared to many advanced oxidation processes. The present research mainly focuses on the newer studies that would provide new impetus for the application of hydrodynamic cavitation, in general, and using vortex diode as a cavitation device, in particular for various less explored application of industrial wastewater treatment, specifically for the removal of ammoniacal nitrogen, removal of solvents and removal of API pollutants. Several process intensification approaches in the form of aeration, addition of oxidising agents such as hydrogen peroxide etc. are also explored and evaluated in detail with cost analysis to prove efficacy of the process and application in real wastewater treatment. A new process, solvent-assisted cavitation for the increased removal of organic pollutants is also developed for the first time and a proof of concept is established and validated using experimental data.

The important findings of the research can be summarized as below:

Improving Efficiency for Removal of Ammoniacal Nitrogen from Wastewaters using Hydrodynamic Cavitation

1. A new methodology is established for improving the effectiveness of hydrodynamic cavitation especially using vortex diode as a cavitating device in wastewater treatment, specifically for the removal of ammoniacal nitrogen.

2. Initial concentration has significant impact on the removal and quantity of ammoniacal nitrogen removed increases with the increase in the concentration for the same pressure drop and reactor conditions.
3. Overall, 9-45% removal using vortex diode for pressure drop of only 0.5 bar.
4. Improvement, up to 8 times, can be obtained using simple process intensification by sparging air or oxygen and overall removal of over 80% could be accomplished, in the case of vortex diode at significantly low pressure drop (0.5 to 2 bar compared to orifice- up to 5 bar).
5. Superiority of vortex diode as a cavitation reactor over conventional device-orifice and order of magnitude increase in the cavitational yield using aeration was demonstrated.
6. The methodology of improving efficiency gets reflected in significant cost reduction due to process intensification, ranging from 200% to more than 1100%,
7. A plausible mechanism to elucidate effect of aeration clearly highlighted role of oxygen for degradation by cavitation.
8. Successful application of the technology for the treatment of real industrial wastewaters from distillery industry having high ammoniacal nitrogen content.

Wastewater Treatment and Process Intensification for Degradation of Solvents using Hydrodynamic Cavitation

1. The vortex flow in cavitation was found to offer superior performance (cavitational yield) compared to orifice- Low pressure drop conditions i.e. 0.5 bar for vortex diode and 2 bar for orifice were most effective in solvent degradation.
2. Process intensification in the form of aeration was highly effective in improving the degradation efficiency; only marginal improvement by addition of oxidizing agent such as hydrogen peroxide.
3. A reduction in TOC to the extent of 74% could be achieved for octanol (200 ppm) using aeration with cavitational yield of 1202×10^{-4} mg/J for vortex diode, yield ~10 times higher than that for orifice.

4. The degradation depends on the nature of solvent and it was revealed that low values of dielectric constant ($\varepsilon<10$) favour degradation.
5. Successful validation using real effluent treatment.

Intensified Hydrodynamic Cavitation using Vortex Flow Based Cavitating Device for Degradation of Ciprofloxacin

1. The present study, for the first time, demonstrated the use of vortex flow-based cavitation for antibiotics degradation.
2. The optimum pressure drop for CIP degradation was very low, 1 bar, for low to high initial CIP concentrations.
3. Vortex diode as a cavitating device, ΔP of 1 bar, low CIP concentration of 10 mg/L gave about 21% CIP degradation with 35% TOC reduction whereas, at high CIP concentration of 100 mg/L, 56% CIP degradation with 16% TOC reduction were obtained.
4. Process intensification using the addition of hydrogen peroxide showed significant enhancement in degradation compared to only a marginal improvement for intensification using aeration.
5. For the combined approach of HC+H_2O_2, CIP degradations of 79% and 95% were achieved at CIP concentrations of 10 and 100 mg/L respectively.
6. The cavitational yield for the combined approach of HC+H_2O_2 was higher (86.8×10^{-4} mg/J) as compared to that obtained for HC alone (48.5×10^{-4} mg/J) at 100 mg/L initial concentration of CIP.
7. Per-pass degradation model showed about 4-7 times improvement in per-pass degradation for cavitation with the addition of H_2O_2 (1:1000 molar ratio) as compared to the conventional hydrodynamic cavitation.
8. A reasonably low cost of treatment along with high efficiency can be achieved using hybrid cavitation with H_2O_2 as compared to the cavitation alone.
9. The effective use of the vortex based cavitating device in hydrodynamic cavitation and process intensification using H_2O_2 at comparatively high antibiotic loading with

substantially low cost clearly highlights the techno-economic feasibility in implementing the strategy for the degradation of antibiotics.

A Strategy for Complete Degradation of Metformin using Vortex-Based Hydrodynamic Cavitation

1. The present work clearly demonstrated the effective use of hydrodynamic cavitation with vortex diode as a cavitating device for the degradation of metformin, an extensively used antidiabetic drug.
2. Hydrodynamic cavitation alone, using a low pressure drop of only 1 bar, yields only 3-5 % of degradation while process intensification using hydrogen peroxide gave up to 33% of metformin degradation.
3. The hybrid hydrodynamic cavitation process can be further modified using pH alteration resulting in very high, 88-95% metformin degradation, under acidic pH of 4 with an excellent cavitational yields of the order of 162×10^{-5} mg/J for the reasonably higher initial concentrations of 10- 20 mg/L.
4. A complete degradation of MTF was achieved using HC+H_2O_2 under acidic pH of 4 with order of magnitude enhancement of 900%.
5. Significantly higher synergistic coefficients can be achieved with simple pH modifications (pH 4) resulting in the process efficiency. Per pass degradation could be enhanced up to 100 times reflecting reduction in the process cost compared to the conventional hydrodynamic cavitation.
6. The results confirm that the use of vortex flow-based device in hydrodynamic cavitation and process intensification with acidic pH condition results in significant degradation of MTF with low treatment cost providing techno-economical alternative for degradation of antidiabetic drug and industrial wastewater treatment.

Solvent-Assisted Cavitation for Enhanced Removal of Organic Pollutants - Degradation of 4-Aminophenol

1. A new approach of solvent-assisted cavitation process is proposed for the degradation of organic pollutants and use of suitable solvent, as an additive (1-5% v/V), is developed specifically for the enhanced removal of organic pollutants, in general and ammoniacal nitrogen, in particular.
2. Vortex flow-based cavitation reactor was found to be highly effective for the removal of ammoniacal nitrogen.
3. Solvent-assisted cavitation process retains the advantages of conventional cavitation processes by employing mild operating conditions such as low pressure drop of 0.5 bar while accomplishing higher levels of degradation of organic pollutants.
4. Solvent characteristics are important for obtaining enhancement in the removal of pollutants and relatively polar solvents such as octanol and cyclohexanol were found to be highly effective compared to non-polar solvents e.g. toluene and octane.
5. A very high ammoniacal nitrogen removal to the extent of 90% could be obtained for relatively polar solvents- octanol and cyclohexanol; an enhancement of 65% over and above the conventional hydrodynamic cavitation under similar conditions.
6. Removal rate was also significantly enhanced by 2 to 3 times than individual operation of hydrodynamic cavitation depicting high efficacy of the new process.
7. Non-polar solvents, as additives, were found to diminish the effect of hydrodynamic cavitation, possibly due to the insulating effect for the pollutant moiety.
8. The developed process appears to have a significantly low cost compared to conventional hydrodynamic cavitation and more than 200% cost reduction was achieved.
9. The results provide impetus to further research for improvements in the existing cavitation technologies and process intensification methodologies in the wastewater treatment, in general and for the removal of ammoniacal nitrogen, in particular.

Overall Conclusions

The thesis provides effective strategies for industrial wastewater treatment and for the degradation of various organic pollutants with very high efficiency, especially using vortex diode as a cavitating device in hydrodynamic cavitation process. Newer insights and different process intensifications/alterations envisaged in this thesis provide methodologies for driving complete degradation of the pollutants and for increased efficiencies. The application of the developed methodologies of vortex diode for removal of organic pollutants was successfully established and validated using real industrial wastewaters which is convincing for its use in real world. The techno-economic feasibility, the ease of operation, ease of scale-up and lower capital/ land requirements can additionally prove to be excellent features in this regard.

9.2 Plan of Future Work

Industrial wastewater treatment is a complex subject and huge research is required in this area to establish, improve and develop technologies. This is especially important in view of the fact that no generalized solutions are available in view of unique character of each wastewater. Thus, no matter what the guidelines are provided by the specific research on synthetic wastewater treatment methodologies, its application to real industrial wastewaters is not straightforward and needs to be validated in most cases. Future work needs to acknowledge and incorporate these aspects for successful applications.

The future plan of work requires:

1. Studies in different configurations of cavitating devices, process intensifications and process integration with the conventional treatment technologies.
2. Extensive studies are required on degradation/ removal of different organic pollutants, in isolation, and in combination along with effects of parameters such as TDS, TSS, and other pollutants in the wastewaters.
3. It is necessary to devise guidelines for selection and optimization of process parameters for efficient degradation of pollutants from different classes such as solvents, nitrogen containing compounds, pesticides, dyes of different types such as

cationic, anionic, reactive, azo dyes etc., API pollutants of different types such as antibiotics etc.

4. Development of newer processes/ process modifications such as solvent assisted cavitation process; optimization of these processes for the removal of different organic pollutants as mentioned in Point 3 above and for the reactor configurations as mentioned in Point 1 above.
5. Computational Fluid Dynamics studies (CFD) for theoretically evaluating the flow patterns and establishing the cavitation regimes. Developing criteria for the selection of process/ process parameters and for prediction of the process performance.

Appendices

Appendix I: List of start-up companies working on cavitation

Sr.No.	Name of company	Remarks
1.	Biobang, 2019 [1]	Application of cavitation for digestion of all biomass in biogas and biomethane plants for agricultural, industrial and municipal solid waste field
2.	CaviMax, 2019 [2]	ROTOCAV reactor configuration used for various applications such as, 1. Biodiesel production 2. Biomass pretreatment 3. CaviMax farm e.a.t - (enhanced animal feed technology) - liquid pig feeding system 4. Green chemistry / sustainable chemical reactions 5. Extractions from organic biomatrices 6. Cosmetics industry 7. Food industry 8. Edible oil refining
3.	Cavitation Technologies, Inc. 2007 [3]	1. Focuses on processing liquids, fluidic mixtures, emulsions and suspended solids 2. Applications in various domains such as edible oil refining, algal oil extraction and renewable fuel production, biodiesel, alcoholic beverage enhancement, water treatment and expeditious petroleum upgrading
4.	Dynaflow Inc., 2019 [4]	Dynaflow Inc. conducts a full range of research, development, and consulting studies on cavitation including analytical, numerical and experimental work

5.	GermSAFE Technology, 2019 [5]	Academic spin-off from ICT Mumbai working on water disinfection
6.	VIVIRA Process Technologies Pvt. Ltd., 2015 [6]	VIVIRA is a spin-off based on NCL's technology. Uses a novel and patent protected vortex diode-based cavitation for treatment of variety of effluents

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Appendix II: Literature studies on degradation of Ciprofloxacin (CIP)

Sr. No.	Methodology	Initial CIP conc.	Operating conditions/ Methods/Preparations	Remarks	Ref.
1.	Adsorption	5 mg/L	Biogenic palladium nanoparticles Treatment Time: 24 h; pH 3.6	87.7% CIP removal	[1]
2.	Adsorption	22 mg/L	Zero-valent iron (ZVI) at a pH of 2.5 condition	80% CIP removal	[2]
3.	Adsorption	10 mg/L	SI-Ti_3C_2Tx M Xene nanosheets	90% CIP removal in 15-20 min at pH 5.5 Regeneration by electrochemical approach	[3]
4.	Photocatalysis	10 mg/L	Flower-like porous CNT/$PbBiO_2Br$ photocatalysts; Treatment time 40 min; ultraviolet light irradiation	47% CIP removal by pure PbBiO2Br; 86% CIP removal by CNT/PbBiO2Br;	[4]
5.	Photocatalysis	10 mg/L	Ag_2O/Ag_2CO_3/multi-walled carbon nanotube (MWNTs) composite photocatalysts; Treatment time 60 min; under visible light irradiation	76% of CIP removal by Ag_2O/Ag_2CO_3/MWNTs composite photocatalysts	[5]
6.	Photocatalysis	1 mg/L	$BiFeO_3$ nanocomposites; pH 6; $BiFeO_3$ 2.5 g/L; temperature 30° C, Treatment time: 46 min	100% CIP removal	[6]
7.	Photocatalysis	2 mg/L	Persulfate-mediated Photocatalytic Degradation in two water matrices; distilled	98% degradation with the RSW matrix at the natural pH of the solution with no dissolved organic	[7]

			water (DW) and raw surface water (RSW); Treatment time: 120 min	carbon (DOC) removal whereas, at acidic pH of the solution (pH 3), 56% DOC removal was obtained	
8.	Ultraviolet radiation (UV-C) driven oxidation	0.1 mg/L	UV-C driven; H_2O_2 10 mg/L; Treatment time 15 min	100 % degradation using a combined approach of UV-C/ H_2O_2	[8]
9.	Electro-peroxone using sacrificial iron anode	20 mg/L	Treatment time: 40 min; pH = 3; ozone dosage 33.1 mg/L; applied current 180 mA	100% degradation CIP	[9]
10	Sono-catalysis	10 mg/L	Enzyme loading: 0.02% (w/v) Temperature: 60 °C; frequency:22 kHz; duty cycle 50%; agitation 200 rpm	51% degradation	[10]
11	Hydrodynamic cavitation	0.05 mg/L	Skid-mounted rotating hydrodynamic cavitation (RHC) reactor Treatment time: 30 min;	Degradation of CIP (%) RHC+ O_3: 91.4%; RHC+ H_2O_2: 85.6%; RHC+ Fenton: 87.6%; Only RHC: 44.8%;	[11]
12.	Hydrodynamic cavitation	10 mg/L and 100 mg/L	Vortex diode cavitating device Pilot plant scale :1 m^3/h; Treatment time: 180 min;	For 10 mg/L: Degradation of CIP (%) HC: 21%, HC+H_2O_2: 79%	**Present work**

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Appendix III: Sample cost calculation

Cost of treatment per m^3 of effluent = $\frac{N_C \times \Delta P \times P_E}{36\eta}$

Where, N_c = number of passes; ΔP = pressure drop; P_E = cost of electricity.

Cost of electricity assumed for Indian scenario as Rs 10 /KWh (1$ = 75 Rs)

The pump efficiency η is assumed 66% considering commercial flow rates (above 10 m^3/h)

For initial concentration of CIP= 10 mg/L

CIP degradation (21%) using only HC approach

Pressure drop, ΔP = 1 bar, C_0= 10 mg/L, Treatment time 180 min, No of passes= 97

Total Cost of treatment per m^3 of effluent = $\frac{97\times1\times10}{36\times0.66}$

= Rs 41/m^3 ~ Rs.22 /gm

CIP degradation corresponding to HC using hybrid HC+ H_2O_2 approach

Pressure drop, ΔP = 1 bar, C_0= 10 mg/L, Treatment time 180 min, No of passes= 24

Cost of H_2O_2 (30%) = 30 Rs/L

Cost of additives (H_2O_2) for C_0 =10 mg/L (1:1000 molar ratio)

Total quantity of H_2O_2 required for 1 m^3 = 0.92 L

Total Cost of treatment per m^3 of effluent = $\frac{24\times1\times10}{36\times0.66}$ + Cost of H_2O_2

= Rs 38 /m^3 ~ Rs.8 /gm

Abstract

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Title of the thesis: Studies in Degradation/Removal of Pollutants/Organics Using Cavitation

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Wastewater treatment, especially industrial wastewater treatment, is critical in recent times for protecting environment and life. It is required that harmful pollutants be removed by using appropriate technologies. Also, due to the scarcity of water, it is imperative that efficient and techno-economical methodologies be developed not just for wastewater treatment, but for water recycle and reuse. Hydrodynamic cavitation process is one such promising alternative to existing methods in this regard. The present research focuses on degradation/removal of different organic pollutants by hydrodynamic cavitation using vortex flow-based cavitation device, vortex diode and linear flow-based cavitation device, orifice, on a pilot plant scale ($1m^3/h$). Removal of ammoniacal nitrogen, degradation of solvents and API pollutants was studied in detail. The quantitative data on influence of various parameters such as initial concentration, total dissolved solids, aeration and addition of hydrogen peroxide on removal of ammoniacal nitrogen/ degradation of organic pollutants is presented together for the first time. The data is processed using the per-pass degradation (removal) factor model and dependence of per-pass removal factor on pressure drop across the cavitation device (energy dissipation rates) is presented. The data is also used to calculate cavitation yield and corresponding treatment costs. A number of case studies of real life industrial effluents are also included to facilitate application of the presented results to practice. Significant improvement, of the order of magnitude (up to 8 times), in removal of ammoniacal nitrogen could be obtained by sparging air or oxygen in hydrodynamic cavitation and a very high removal of above 80% could be achieved, using vortex diode. The removal of ammoniacal nitrogen was also effective in the industrial wastewaters where up to 75% removal could be obtained. Removal of harmful solvents is pertinent issue in many chemical and pharmaceutical industries. The vortex diode required lower pressure drop and is superior to orifice and process intensification using aeration is most effective in solvent degradation also. A reduction in TOC to an extent of 74% could be achieved for octanol (200 ppm) using aeration with cavitational yield of 1202×10^{-4} mg/J for vortex diode, yield ~10 times of orifice. The nature of solvent is important and low values of dielectric constant (ε <10) favour degradation. The present work, for the first time, establishes degradation behavior of API pollutants such as ciprofloxacin (CIP), a widely used fluoroquinolone group of antibiotics and metformin, an antidiabetic drug, using vortex flow based hydrodynamic cavitation for low to high concentrations. Process intensification using H_2O_2 resulted in ~ 200% enhancement in the CIP degradation and reasonably low cost with high efficiency compared to the conventional cavitation. Similarly, a very high, 95% metformin degradation, was obtained at pH 4 with excellent cavitational yields up to 162×10^{-5} mg/J, further extending to 100% degradation using $HC+H_2O_2$, an order of magnitude enhancement of 900%. A new approach of solvent-assisted cavitation process was proposed for degradation of organic pollutants. The process envisages the use of suitable solvent as an additive, (1-5% v/V), in the conventional cavitation process to enhance the pollutant removal efficiency. A proof of concept was provided for the removal of ammoniacal nitrogen with significantly improved efficiency. Relatively polar solvents were found to increase the efficiency of the pollutant removal (>65%) and also increase the rates to an extent of more than 200%, compared to only HC. A very high removal of ammoniacal nitrogen, more than 90%, was obtained. The interesting observations in the proposed process can fuel further research to provide possible improvements in existing methodologies of wastewater treatment, in general. Overall, the present research has resulted in newer insights in removal of pollutants and methodologies for industrial wastewater treatment.

List of Publications, Patents, Conference presentations (oral/poster), emanating from the thesis work

Publication (s)

1. **Pravin B. Patil**, Vinay M. Bhandari, Vivek V. Ranade, Improving Efficiency for Removal of Ammoniacal Nitrogen from Wastewaters using Hydrodynamic Cavitation, Ultrason. Sonochem. 70 (2021), 105306, https://doi.org/10.1016/j.ultsonch.2020.105306 **Impact factor – 9.33 (2021)**
2. **Pravin B. Patil**, Vinay M. Bhandari, Vivek V. Ranade, Wastewater Treatment and Process Intensification for Degradation of Solvents using Hydrodynamic Cavitation. Chem. Eng. Process. - Process Intensif. 166 (2021), 108485. https://doi.org/10.1016/j.cep.2021.108485 **Impact factor – 4.26 (2021)**
3. **Pravin B. Patil,** Pooja Thanekar, Vinay M. Bhandari, Intensified hydrodynamic cavitation using vortex flow based cavitating device for degradation of ciprofloxacin, Chem. Eng. Res. Des. 187 (2022) 623–632. https://doi.org/10.1016/j.cherd.2022.09.027 **Impact factor – 4.11 (2021)**
4. **Pravin B. Patil,** Pooja Thanekar, Vinay M. Bhandari, A Strategy for Complete Degradation of Metformin Using Vortex-Based Hydrodynamic Cavitation, Ind. Eng. Chem. Res. (2022). https://doi.org/10.1021/acs.iecr.2c02519 **Impact factor - 4.32 (2021)**
5. **Pravin B. Patil**, Vinay M. Bhandari, Solvent-assisted Cavitation for Enhanced Removal of Organic Pollutants - Degradation of 4-aminophenol, J. Environ. Manage. 311 (2022), 114857, https://doi.org/10.1016/j.jenvman.2022.114857 **Impact factor – 8.91 (2021)**

Patents

1. Bhandari V. M. and **Patil P. B.**, Solvent Assisted Cavitation for Wastewater Treatment, 2019-INV-0055; Appl. No. 201911050122, (2019).
2. Bhandari V. M. and **Patil P. B.**, Solvent Assisted Cavitation for Wastewater Treatment, Application No: PCT/IN2020/051007, **WO 2021/111476 A1** (2021).
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Conference Presentations (Oral/Poster)

1. **Pravin B. Patil**, Vinay M. Bhandari, "Degradation of n-Octanol using Hydrodynamic Cavitation". National Science Day, CSIR-NCL, Pune, 28th February, 2018. (Poster)

   Abstract

   The degradation of n-Octanol by hydrodynamic cavitation was investigated using newer form of cavitating device- vortex diode and conventional device, orifice. The degradation studies were carried out on pilot plant having capacity 1m^3/h and degradation was monitored by measuring reduction in chemical oxygen demand (COD) and total organic carbon (TOC) at periodic intervals. For initial concentration of 50 ppm, ~10% reduction in COD and ~20% reduction in TOC was observed after 120 min. Improvement to the extent of 50% could be obtained using process intensification in the form of aeration that enhances oxidation of the pollutant species. Though the degradation levels for both vortex diode and orifice are similar, orifice requires substantially higher pressure drop compared to vortex diode, indicating higher energy requirement. The results of present study clearly indicate that hydrodynamic cavitation, especially using vortex diode as cavitating device can be promising technology for the degradation of solvents.

   Key words: Wastewater treatment, Pollution, Solvent removal, Vortex diode

2. **Pravin B. Patil**, Priyanka Shivde, Vinay M. Bhandari, “Sustainable Environmental Technologies for Industrial Wastewater Treatment- A Case Study". 4th International Conference on Recent Advancements in Chemical, Environmental and Energy Engineering (RACEEE-2019),14 & 15th February, 2019, SSN College of Engineering, Chennai. (Oral)

   Abstract

   Industrial wastewater treatment is a challenge, especially for India and developing/ adopting sustainable, techno-economically feasible technologies for highly polluting sectors such as dyes/textile, fine and specialty chemicals, petrochemical and fertilizer etc. is imperative for protecting environment. The conventional methods such as coagulation, adsorption, biological treatment or oxidation largely have limitations either in terms of efficacy or in cost of treatment. In the present work, a process integration approach has been discussed for the treatment of one API and specialty chemicals industry wastewater by employing CSIR-NCL’s hydrodynamic cavitation process using vortex diode (patented) and process integration using adsorption process for effecting complete treatment of wastewater that can not only meet discharge standards for effluent prescribed by the Government, but the treated water can also be recycled and reused. Hydrodynamic cavitation using vortex diode indicated ~40% reduction in COD/TOC from the initial COD of 1200 mg/L that can be further increased to 80% using process intensification. The FTIR analysis of the wastewater samples before and after cavitation implied complete mineralization of the organics and no formation of intermediates was observed, as against that in photocatalytic degradation. The results clearly highlight that vortex flow for generating cavitation can be an excellent alternative for improving techno-economic feasibility in the existing effluent treatment plant. Further, adsorption using modified carbon adsorbents can also effectively remove the COD and a very high breakthrough capacity was obtained. Both cavitation and adsorption were found to effectively remove the colour of effluent from initial dark yellow to colourless. In view of low CAPEX and OPEX for cavitation using vortex diode, hydrodynamic cavitation followed by adsorption can provide a practical and sustainable alternative to the existing treatment methods of industrial wastewaters.

Keywords: Cavitation, Adsorption, Oxidation, Effluent treatment, Pollution

3. **Pravin B. Patil**, Vinay M. Bhandari, "Degradation Studies for Organic Solvents using Hydrodynamic Cavitation". Water Symposium, WICTRE, IIT Bombay, 26th March, 2019. (Poster)

Abstract

Hydrodynamic cavitation for the degradation of organic solvents was investigated in detail using two different cavitating devices- orifice and a newer form of cavitating device, vortex diode (Patented by CSIR-National Chemical Laboratory, Pune). Vortex diode employs vortex flow for cavitation and is found to be more efficient as compared to conventional devices such as orifice and venturi. Further, the cavitation process can be intensified using aeration or by addition of external oxidising agent such as hydrogen peroxide. Degradation of an organic solvents, n- octanol, cyclohexanol in terms of reduction in total organic carbon (TOC) was studied on a pilot plant scale having capacity of $1 m^3/h$. Effect of initial concentration, pressure drop, aeration, addition of oxidising agents were studied for both vortex diode and for orifice. The results revealed that efficiency of solvent removal varies substantially with the change in physical operating conditions, nature of the solvent and nature of the cavitating device. Higher end solvents were found to have low efficiency of degradation as compared to MEK and toluene. The efficiency can be further enhanced using process intensification in the form of aeration. For octanol, the degradation was close to 35% which could be increased to 74%, over 100% improvement, with process intensification. Further, lower pressure drop in vortex diode is more favourable for degradation. Vortex diode requires significantly lower pressure drop than orifice for comparable extent of degradation. The results of this study are important for solvent removal using hydrodynamic cavitation and would have bearing on the treatment of solvent containing wastewaters.

Keywords: Vortex diode, Effluent treatment, Pollution, Wastewater, Industry

4. **Pravin B. Patil**, Vinay M. Bhandari, "Ammoniacal Nitrogen Removal by using Hydrodynamic Cavitation- Effect of TDS and Real Industrial Case Studies". DAE-BRNS sponsored Ninth Biennial Symposium on Emerging Trends in Separation Science& Technology (eSESTEC-2020) Bhabha Atomic Research Centre, Mumbai 400 085, March 22-26th, 2021 (ePoster)

Abstract

Industrial wastewater treatment specifically for the removal of ammoniacal nitrogen is an important problem for many industries such as dyes, food, fertilizer, distilleries and requires cost effective sustainable solutions. Hydrodynamic cavitation, using different geometrical configurations, can be highly effective in such cases. The present study reports pilot plant scale studies (capacity, 1 m^3/h) on synthetic wastewater with 4-aminophenol as model nitrogen containing organic compound and two real industrial effluents with high ammoniacal nitrogen content using hydrodynamic cavitation. Effects of initial concentration (100-500 ppm), pressure drop (0.5-5 bar) and nature of cavitating device (linear and vortex flow) were evaluated along with effect of TDS (500 ppm-2000 ppm), effect of hydrogen peroxide addition (up to 5 times initial AN concentration) and aeration. Increase in TDS impacts adversely, in general. The overall reduction in the ammoniacal nitrogen using hydrodynamic cavitation alone was up to 45%, similar for both linear and vortex flow cavitation and only a marginal (~5%) improvement was obtained using hydrogen peroxide as an additional oxidant. Significant removal of more than 80% ammoniacal nitrogen was obtained by means of sparging air or oxygen in hydrodynamic cavitation. The efficacy of cavitation with aeration was also evaluated and validated using two real industrial effluents from distillery, having a very high ammoniacal nitrogen content (>2000 ppm). Hydrodynamic cavitation using vortex diode could reduce up to ~75% ammoniacal nitrogen removal, though with longer time of treatment compared to synthetic wastewater treatment. Again, the extent of removal was quite similar in both vortex diode and orifice, however, the pressure was substantially higher for orifice than vortex diode as a cavitating device. The developed methodology of hydrodynamic cavitation with aeration and vortex diode as cavitating device was found superior

compared to conventional cavitation device and can be highly effective in industrial wastewater treatment especially for removal of ammoniacal nitrogen.

Key words: Wastewater treatment, cavitation, oxidation, 4-aminophenol, ammoniacal nitrogen

5. **Pravin Patil**, Maya Mane, Divya Dixit, Pooja Thanekar and Vinay Bhandari, "Vortex Diodes as Vortex Flow Based Cavitation Devices for Wastewater Treatment Applications- Newer Designs and Applications"MMETFP2021 (International Symposium on Materials of the Millennium: Emerging Trends and Future Prospects) Pandit Deendayal Energy University, Gandhinagar, Gujarat, India, 19-21th November, 2021. (Oral)

Abstract

In recent years, vortex diode that employ vortex flow for generating cavitation have gained prominence in the wastewater treatment, mainly for the reasons that it employs simple mechanical design with no moving elements, easy fabrication and high efficiency apart from ease of installation and operation with increased cost effectiveness. Unlike conventional devices like orifice or venturi, the cavitation realised in vortex diode is due to strongly swirling flows. Therefore, for an equivalent capacity of cavitation devices, the diameter of vortex diode is larger than the diameter in orifice or venturi (~ 2.5 times), making it less susceptible to clogging. Due to the absence of moving elements, vortex diodes consume less energy compared to high speed rotor type devices that also pose operational difficulties. The design of Vortex diode is only slightly more complicated compared to conventional designs and has three essential components- an inlet tangential port to impart tangential flow, a disc-shaped chamber for generating vortex and cylindrical axial port for the exit of fluid. The design variations include variations in diameter and height of chamber along with curved surface and providing internals. In the present work, degradation studies were carried for two dyes, Congo red and Bismarck brown at initial concentration of 100 ppm using vortex diode at ΔP 0.5 bar. Three geometrical configurations, Insert I, II and III were tested. Colour removal, up to 50% could be observed. For Bismarck brown, ~ 50% for removal of COD was obtained and up to 75% could improvement could be observed by use of different insert designs. In water treatment, a very high removal of harmful bacteria was obtained using the vortex diodes; 100% disinfection. The newly designed materials of vortex diode can find many useful applications in future, especially in the area of water and wastewater treatment.

Keywords: Cavitation, Environmental Pollution, Technology, Dye Removal, Disinfection

Achievements

- Director’s commendation award with citation for research publication in chemical engineering/technology-2020 for the paper entitled, “Improving Efficiency for Removal of Ammoniacal Nitrogen from Wastewaters using Hydrodynamic Cavitation", CSIR-NCL, Pune.
- NATIONAL CHEMICAL LABORATORY RESEARCH FOUNDATION - KEERTHI SANGORAM MEMORIAL ENDOWMENT AWARD for “Best Research Scholar of the year 2021” in Engineering Sciences.

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Improving efficiency for removal of ammoniacal nitrogen from wastewaters using hydrodynamic cavitation

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ABSTRACT

The present study reports significant improvements in the removal of ammoniacal nitrogen from wastewater which is an important problem for many industries such as dyes and pigment, distilleries and fisheries. Pilot plant studies (capacity, 1 m^3/h) on synthetic wastewater using 4-amino phenol as model nitrogen containing organic compound and two real industrial effluents of high ammoniacal nitrogen content were carried out using hydrodynamic cavitation. Two reactor geometries were evaluated for increased efficiency in removal-orifice and vortex diode. Effect of initial concentration (100–500 mg/L), effect of pressure drop (0.5–5 bar) and nature of cavitating device (linear and vortex flow for cavitation) were evaluated along with effect of salt content, effect of hydrogen peroxide addition and aeration. Initial concentration was found to have significant impact on the extent of removal: ~ 5 g/m^3 removal for initial concentration of 100 mg/L and up to 12 g/m^3 removal at high concentration of 500 mg/L. Interestingly, significant improvement of the order of magnitude (up to 8 times) in removal of ammoniacal nitrogen could be obtained by sparging air or oxygen in hydrodynamic cavitation and a very high removal of above 80% could be achieved. The removal of ammoniacal nitrogen by vortex diode was also found to be effective in the industrial wastewaters and results on two different effluent samples of distillery industry indicated up to 75% removal, though with longer time of treatment compared to that of synthetic wastewater. The developed methodology of hydrodynamic cavitation technology with aeration and vortex diode as a cavitating device was found to be highly effective for improving the efficiency of the conventional cavitation methods and hence can be highly useful in industrial wastewater treatment, specifically for the removal of ammoniacal nitrogen.

1. Introduction

A large number of chemical and allied industries generate huge amounts of wastewaters which require effluent treatment prior to discharge for meeting stringent norms on Chemical Oxygen Demand (COD), Biological oxygen demand (BOD) and Ammoniacal Nitrogen (NH_4-N). Industrial wastewater treatment is important for the sustainability of environment and ecology and at times can threaten the very existence of the industry, if the pollution norms are not complied with. The conventional wastewater treatment largely focuses on the managing COD or BOD levels. In comparison, the subject of removal of ammoniacal nitrogen has received sparse attention barring standard biological methods of treatment. The nitrogen content, measured in the form of ammoniacal nitrogen, is a serious problem in many industrial wastewaters due to limitations of both biological and conventional physico-chemical methods. Ammoniacal nitrogen is a measure for the nitrogenous organic matter as ammonia, a toxic pollutant that can directly poison humans and upset the equilibrium of water ecology systems. The ammoniacal nitrogen is required to be below 30–50 mg/L [1], though the limit can vary depending on location. There are many industries such as dyes and pigment, nitrogenous fertilizers, specialty chemicals that generate wastewaters having high ammoniacal nitrogen (1500–3000 mg/L) and demand specific solutions for wastewater treatment. Similarly, industries such as fisheries generate huge volumes of wastewaters, easily treatable using conventional biological treatment methods but end up in “treated wastewater” having high ammoniacal nitrogen of the order of 400–600 mg/L that needs to be again brought down to well below 50 mg/L using cost-effective physico-chemical methods.

The ammoniacal nitrogen from effluent is conventionally removed

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Nomenclature

C_0	Initial concentration, (mg/L or ppm)
C	Final concentration, (mg/L or ppm)
g	Gravitational acceleration, m/s^2
k	Rate constant, min^{-1}
N_C	Number of passes required for treatment
P	Pressure, bar
P_E	Cost of electricity per kWh, Rs.
Q	Flow Rate, liter/h
t	Time, min
V	Volume, Liter
V_G	Superficial gas velocity, m/s
W	Energy dissipation rate, W
Y	Cavitational yield, mg/J
Ø	Per-pass degradation factor
ΔP	Pressure drop, bar
η	Efficiency of the pump

using biological, physical, chemical methods or combination of these methods. Adsorption, chemical precipitation, membrane filtration, reverse osmosis, ion exchange, air stripping, breakpoint chlorination and biological nitrification/ denitrification are commonly employed in this regard [2]. Physico-chemical treatment or ion exchange/adsorption are widely used for the reasons of being stable, easy to maintain and reliable. Aguilar [3] investigated physico-chemical removal of ammoniacal nitrogen by coagulation-flocculation using activated silica powdered activated carbon and precipitated calcium carbonate. The removal of ammonia was found to be rather low (3–17%). However, the removal of albuminoid nitrogen (nitrogen in the form of proteins) was appreciable (74–89%). Studies are also reported on effectiveness of variety of materials such as clay and zeolite [4–8], limestone [7]; natural and waste materials such as waste paper, refuse cement and concrete [9] for removal of ammoniacal nitrogen. Advanced oxidation processes including photocatalytic processes were also reported for model and industrial wastewater treatment [10,11]. Destructive methods such as catalyst dependent advanced oxidation processes, though can reduce ammoniacal nitrogen, have significantly high cost of operation compared to most other processes. However, for refractory pollutants, due to non-biodegradability and also because of severe limitations of conventional treatment, application of advanced oxidation methods is often required to meet the pollution control norms. The oxidation processes employ oxidizing agents such as hydroxyl radicals, ozone, hydrogen peroxide that react with the pollutant resulting into partial or total degradation through mineralization of species. Persulfates based oxidation processes are also gaining attention in recent years and have been well reviewed recently [12–15]. The severe process conditions in terms of pressure/ temperature/catalyst and therefore cost intensive nature of these methods restrict their application due to economic viability. Thus, it is essential to evaluate newer methods and devices that have potential to offer techno-economically feasible option, specifically for ammoniacal nitrogen reduction. Hydrodynamic cavitation can offer one such useful alternative in the existing treatment of industrial wastewaters for reducing the ammoniacal nitrogen [1,16–21]. While the use of vortex diode and hydrodynamic cavitation is reported in the literature, systematic studies to evaluate effects of various process parameters along with cost consideration are essential from practical point of view and for implementation in real life applications pertaining to the effluent treatment, which is the main objective of this study. Further, the methodology can be effectively integrated with other conventional methods of treatment.

In the present work, we report removal of ammoniacal nitrogen using hydrodynamic cavitation with 4-amino phenol as model nitrogen containing organic pollutant. Two different devices were evaluated for their efficacy in the removal of ammoniacal nitrogen- orifice, a conventional cavitating device that employ linear flow, and vortex diode-employing vortex flow for cavitation. Influence of aeration and addition of hydrogen peroxide on intensifying removal of ammoniacal nitrogen was investigated. The efficacy of the developed methodology was also validated for real industrial wastewater treatment. The quantitative data on influence of initial concentration, total dissolved solids, aeration and addition of hydrogen peroxide on removal of ammoniacal nitrogen is presented together for the first time. The data is processed using the per-pass degradation (removal) factor model and dependence of per-pass removal factor on pressure drop across the cavitation device (energy dissipation rates) is presented. The data is also used to calculate cavitation yield and corresponding treatment costs. Two case studies of real life industrial effluents are also included to facilitate application of the presented results to practice. The results presented in this work will be useful for selection of cavitation device and appropriate process parameters for applying hydrodynamic cavitation for treatment of waste water containing ammoniacal nitrogen.

2. Applications of fluidic devices without moving parts

Cavitation fluidic devices may be broadly grouped into two types: devices with and without moving parts. The first class of devices is typically comprised of a rotating impeller and stator. These devices are rather expensive and incur a higher maintenance overhead. Cavitation devices without moving parts have significantly lower costs, and are considered to be the most promising route for realizing the full potential of hydrodynamic cavitation. Cavitation devices without moving parts can be further classified into two broad types: those based on linear flow, and those based on rotational flows. In linear flow cavitation devices such as an orifice or Venturi, the working fluid is forced through a restriction, such that low pressure and therefore cavitation is realized. In rotational flow devices, low-pressure cavitating region is generated around axis of rotation. In this second scenario, the cavitating zone can be sufficiently removed from solid surfaces so as to eliminate the risk of associated damage to the device [19].

Hydrodynamic cavitation demands specific designs of cavitating devices for creating low pressure regions in the flow domain, mainly by increasing the linear velocity of liquid by forcing the flow through constrictions such as orifice or venturi (conventional devices) or by increasing the rotational velocity of liquid by forcing it in the form of vortex flow through a device like vortex diode which has an outlet port from the center of vortex. The schematic of hydrodynamic cavitation process using vortex diode is shown in Fig. 1. The process integration in the form of aeration (optional) is also indicated. In the conventional devices, constrictions are designed such that velocity at the throat (smallest flow area zone) is large enough to generate cavities that subsequently collapse in a region further downstream of constriction resulting in the desired effect. In the latter case, dimensions of the cavitating device- vortex diode, and outlet port are designed such that low-pressure region are generated because of the highly swirling flow in the vortex diode chamber to generate cavities which subsequently escape the chamber via outlet port and then collapse as they enter high pressure region. The performance of cavitation depends on number density and collapse intensity of generated cavities.

2.1. Cavitation process and hydrodynamic cavitation

Cavitation is an advanced oxidation process that involves both physical and chemical changes. The physical process mainly involves formation, growth and collapse of micro bubbles (cavities) within a liquid. The cavities subsequently collapse (implosion) and as a consequence, very high pressure (as high as 1000 atm) and temperature (as

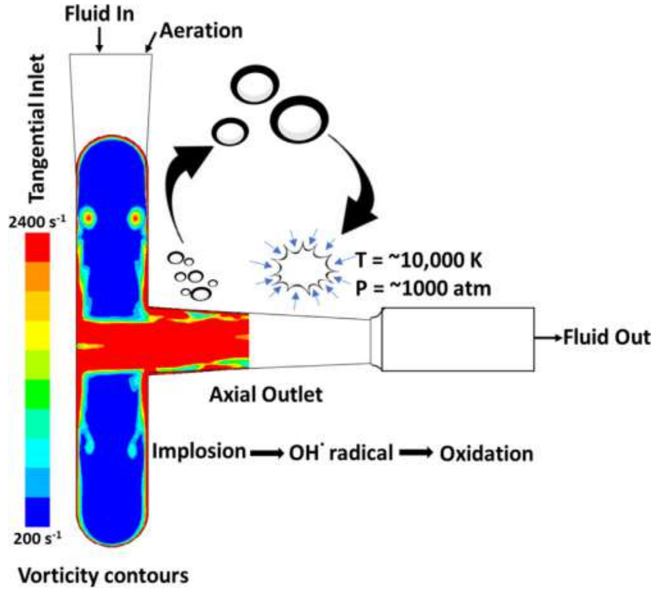

Fig. 1. Schematic of hydrodynamic cavitation process using Vortex Diode.

high as 10,000 K or more) get generated locally at the point of collapse. The extreme temperature and pressure conditions at the location of cavity collapse (implosion), generate oxidizing species such as hydroxyl radicals that can chemically oxidize and destroy refractory pollutants. Under ideal conditions, the products of oxidation of organic pollutants are water and carbon dioxide implying complete mineralization. The phenomenon can be exploited for variety of applications, especially in wastewater treatment, disinfection of water and for chemical reactions [18,22–29].

The application of hydrodynamic Cavitation using tangential flow (Vortex Diode) in wastewater treatment and other applications was reported extensively by Ranade and coworkers in recent years [18,21,28,30,31]. The design of Vortex diode is more complicated compared to conventional designs and has three essential components: an inlet tangential port to impart tangential flow, a disc-shaped chamber for generating vortex and cylindrical axial port for the exit of fluid [32]. There are several design variations that are possible which mainly include variations in diameter and height of chamber along with curved surface and providing internals. The vortex establishes a large pressure drop across the device. The flow characterization in vortex diode is well discussed in the literature and will not be repeated here [27,30,33,34]. Recently [1,20,35,36], have discussed degradation of organics such as dyes, solvents and degradation of organics from real industrial wastewater. However, no systematic studies have been reported specifically for removal of ammoniacal nitrogen using hydrodynamic cavitation. In this work, we have used vortex based cavitation device reported in the literature [18,19,30,32] for the removal of ammoniacal nitrogen, evaluated its efficacy under various process conditions and have tried to significantly enhance the removal efficiency using process intensification for overall reduction in the cost of treatment.

3. Experimental

3.1. Materials

Reagent grade 4-Aminophenol ($H_2NC_6H_4OH$; 99%) was obtained from Sigma Aldrich. Hydrogen peroxide (30%) was obtained from MERCK India. Sodium chloride (NaCl, greater than 99%) was obtained from Sigma-Aldrich. Air, Helium and Oxygen (all 99.99% pure) cylinders were procured from M/s Vadilal Gas, India. Single nozzle air pump (SOBO AQUARIUM SB-108, Max. 3 L/min) was also used for comparison. A synthetic wastewater solution of 4-Aminophenol was prepared using double distilled water for different known concentrations.

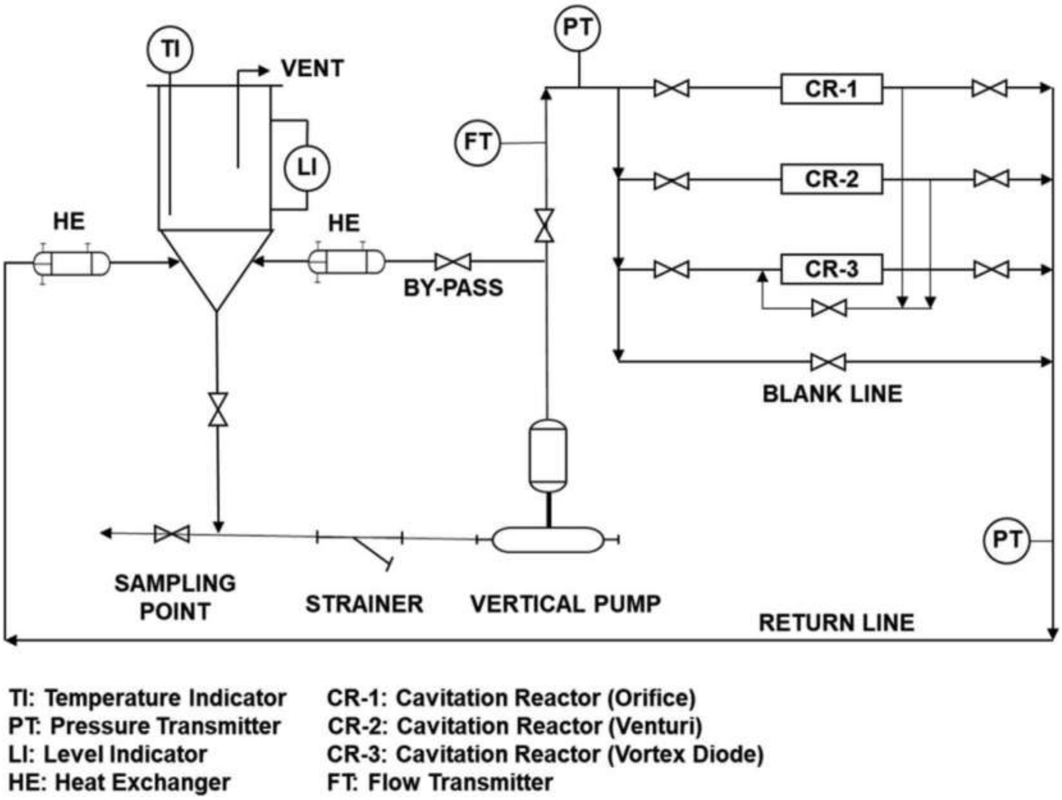

Fig. 2. Schematic of Hydrodynamic Cavitation Set-up.

Spectroquant® Pharo 100 spectrophotometer (MERCK, India) of wavelength range 320–1100 nm was used for analysis of COD and Ammoniacal nitrogen.

The details of experimental set-up were reported earlier [28,31] and only essential aspects are repeated here for immediate and easy reference and to avoid repetition. The main elements of the hydrodynamic cavitation pilot plant (Fig. 2) include a 50-liter storage tank with a conical bottom, a vertical multistage 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, control valves and cavitating devices in the main line. A bypass line to main flow is used to control the flow rate. Nominal Pipe diameter was 3/4 inch. Flow transmitters and pressure transmitters are used to record flow and pressure (KROHNE, H250, Honeywell ST 700). The set-up is equipped with temperature measurement (RTD make EUREKA Eng. Enterprises India; 0–200 C) and control system. Two cavitating devices were used-orifice (single hole, circular with 3 mm diameter) and a vortex diode [30] (fabricated locally; chamber diameter 66 mm, Throat diameter 11 mm, Material of construction- SS 316) operated in reverse flow mode. For the process intensification study, prior to sending the fluid to cavitation device, an arrangement was made for gas bubbling by inserting a tube in the tank and using air pump or air cylinder, oxygen cylinder or helium cylinder (typically air was bubbled using a single nozzle air pump, SOBO AQUARIUM SB-108 with maximum flow rate of 3 L/min).

The removal of ammoniacal nitrogen was investigated mainly using a synthetic wastewater system with 4-aminophenol as model nitrogen compound and for different concentrations in the range of 100–500 mg/L. In view of the inception of cavitation at $<$ 0.5 bar for vortex diode and $\sim$ 1.25 bar for orifice [31], the pressure drop conditions for vortex diode were selected from 0.5 bar and above and for orifice 2 bar and above. Cavitation number for the considered operating range for orifice was less than 1 (Cavitation number of 0.75 corresponding to the flow rate of 0.41 m^3/h and 0.35 corresponding to the flow rate of 0.59 m^3/h, at pressure drop of 2 and 5 bar respectively). The usual definition of Cavitation number is not applicable to the vortex diode. We have ensured that both the devices are operated in cavitating regime. Experiments were conducted for 120 min and samples were withdrawn at periodic intervals and analyzed for ammoniacal nitrogen. The pH of the solution was observed to be in the range of 6.9–7.3, indicating no appreciable change.

4. Results and discussions

4.1. Effect of initial concentration and removal kinetics

The results of initial concentration effect on reduction in ammoniacal nitrogen are presented in Fig. 3 for two different reactor configurations, vortex diode and orifice. It was observed that initial concentration has significant impact on the removal. While a good removal of ammoniacal nitrogen could be obtained for Vortex diode (up to 45%) at lower concentration of 100 mg/L, it was less than 20% at high concentration of 500 mg/L. The corresponding extent of removal, for orifice was only marginally lower, however, required substantially higher pressures compared to vortex diode.

The influence of initial concentration on percentage removal of pollutant is similar to that reported in the literature [37–39]. The initial concentration of pollutant influences the vapour and dissolved gas content of the cavity during collapse, similar to that reported [40] and therefore influences overall hydroxyl radical generation rate. The overall extent of degradation depends on concentrations of generated hydroxyl radicals as well as concentration of pollutant. It should be noted that though percentage degradation decreases with increase in initial concentration, the actual amount of pollutant degraded increases with increase in initial pollutant concentration.

In order to study the kinetics of removal, a pseudo-first order kinetics was considered. The reduction in ammoniacal nitrogen could be represented as,

$$C = C_0 e^{-kt} \qquad (1)$$

where C_0 and C indicate ammoniacal nitrogen concentration before and after the treatment, “t” is time (min), and k is an apparent rate constant (min^{-1}) of the reaction. Since removal predominantly occurs in the first 60 min, the rate data was fitted accordingly. The values of rate constants are given in Table 1. For lower concentration of 100 ppm, k value obtained in case of vortex diode was 7.18×10^{-3} min^{-1} and 6.61×10^{-3} min^{-1} for ΔP of 0.5 and 2 bar respectively. Similarly, in case of orifice, the k value was 5.41×10^{-3} min^{-1} and 5.05×10^{-3} min^{-1} for ΔP of 2 and 5 bar respectively. It is evident that the extent of removal was quite higher in case of vortex diode compared to orifice, especially at lower concentration of 100 ppm. At higher concentration of 200 and 500 ppm, values of apparent rate constant, k, decrease for both vortex diode and orifice as compared to low-100 ppm concentration.

4.2. Effect of pressure drop

Pressure drop across the cavitating device is one of the most important parameter that not only determines the efficiency of removal but also decides the cost of operation. The results on the effect of

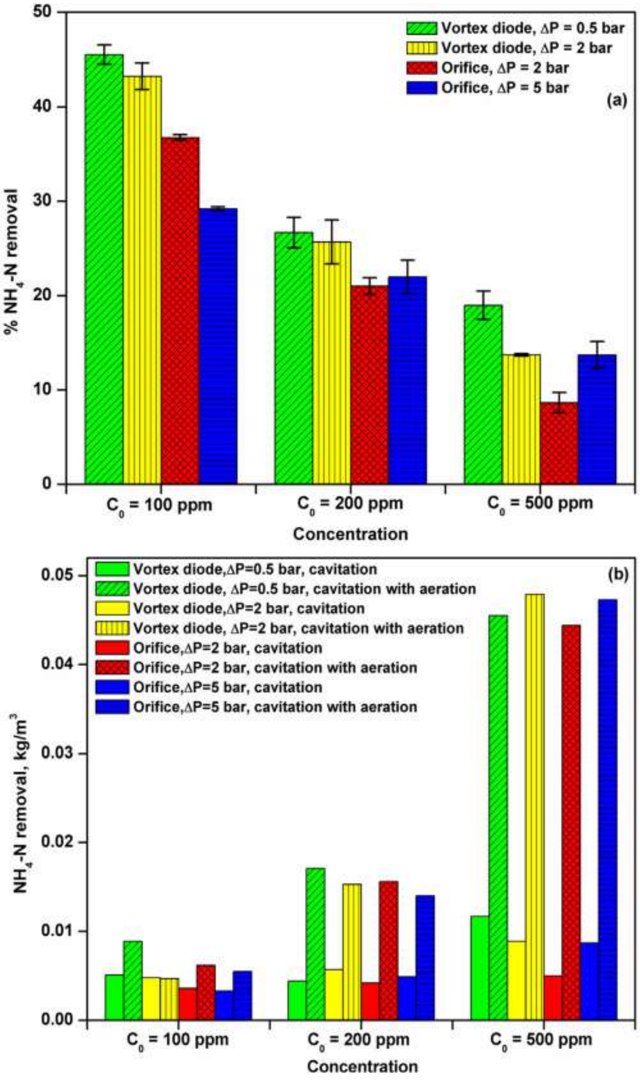

Fig. 3. Effect of initial concentration on removal of NH_4-N.

Table 1
Rate constant data for removal of NH_4-N with Vortex diode and Orifice.

Reactor	Initial conc. (ppm)	% NH_4-N removal (120 min)	Apparent rate constant $k \times 10^3$ (min^{-1})
Vortex diode			
ΔP = 0.5 bar	100	45.5	7.1
	200	26.7	2.9
	500	18.9	2.1
ΔP = 2 bar	100	43.2	6.6
	200	25.7	2.9
	500	13.7	1.5
Orifice			
ΔP = 2 bar	100	36.7	5.4
	200	21.0	2.3
	500	8.67	1.1
ΔP = 5 bar	100	29.2	5.0
	200	21.9	2.0
	500	13.7	1.6

pressure drop are shown in Fig. 4 for both vortex diode (0.5 and 2 bar) and orifice (2 and 5 bar) and for different initial concentrations. The results clearly reveal significantly higher rates of removal for the vortex diode compared to conventional orifice at all the concentration. Further, low pressure drop is favored in both the reactors, especially at low concentrations and the effect is also dictated by the reactor geometry (corresponding to their point of inception of cavitation). In all the cases, the performance of vortex diode was superior to conventional device-orifice for the removal of ammoniacal nitrogen; both rate as well as in terms of extent of removal. The present results highlight another important aspect concerning the pressure drop; the reduction/removal somewhat insensitive to increase in pressure drop across cavitation device up to a certain level and then decreases at very high pressure drops. This also agrees well with many reports which indicate existence of optimum pressure drop [28,41,42].

4.3. *Effect of total dissolved solids*

The hydrodynamic cavitation, by virtue of its dependence on the cavity implosion, is expected to be influenced by presence of dissolved solids; however, no systematic studies have been reported in this regard. In order to evaluate the effect, experiments were carried out using initial concentration of PAP as 100 and 500 ppm and using added initial dissolved salt concentration of 500 ppm and 2000 ppm (NaCl concentration). The results using vortex diode as a cavitating device are shown in Fig. 5. The results indicate marginal effect of TDS at low salt concentrations while the effect is more pronounced at higher values of TDS. However, within the typical prescribed limits of TDS (< 2100 ppm), effectiveness of the hydrodynamic cavitation for the removal of ammoniacal nitrogen is clearly evident.

4.4. *Intensification by addition of H_2O_2*

Conventional forms of process intensifications include addition of strong oxidizing agents such as hydrogen peroxide or ozone. Since no studies are available for removal of ammoniacal nitrogen in this regard, representative forms of process intensification have been chosen for studying their impact on removal of ammoniacal nitrogen. Fig. 6 shows some of the results with the intensification using hydrogen peroxide (30%) as additional or external- to be specific, oxidizing agent on removal of ammoniacal nitrogen (hydrogen peroxide formation is also expected in the normal course of cavitation). In the external addition, the dose of hydrogen peroxide was investigated at the level of five times than concentration of pollutant. It was observed that there is no significant improvement and at low ammoniacal concentration of 100 mg/L, vortex diode and orifice yields about 50% and ~ 40% ammoniacal nitrogen removal at ΔP of 0.5 and 2 bar respectively, while at higher concentration of 500 mg/L about ~ 30% removal in ammoniacal nitrogen was obtained. The results indicate that process intensification in the form of hydrogen peroxide does not significantly increase the removal.

The Synergistic coefficient for hydrodynamic cavitation and H_2O_2 was calculated by using formula as given below,[39]

$$\text{Synergistic coefficient} = \frac{k_{(HC+H_2O_2)}}{k_{HC} + k_{H_2O_2}}$$

Synergistic coefficient values less than one confirmed the above observation of no synergism for hydrodynamic cavitation with addition of H_2O_2.

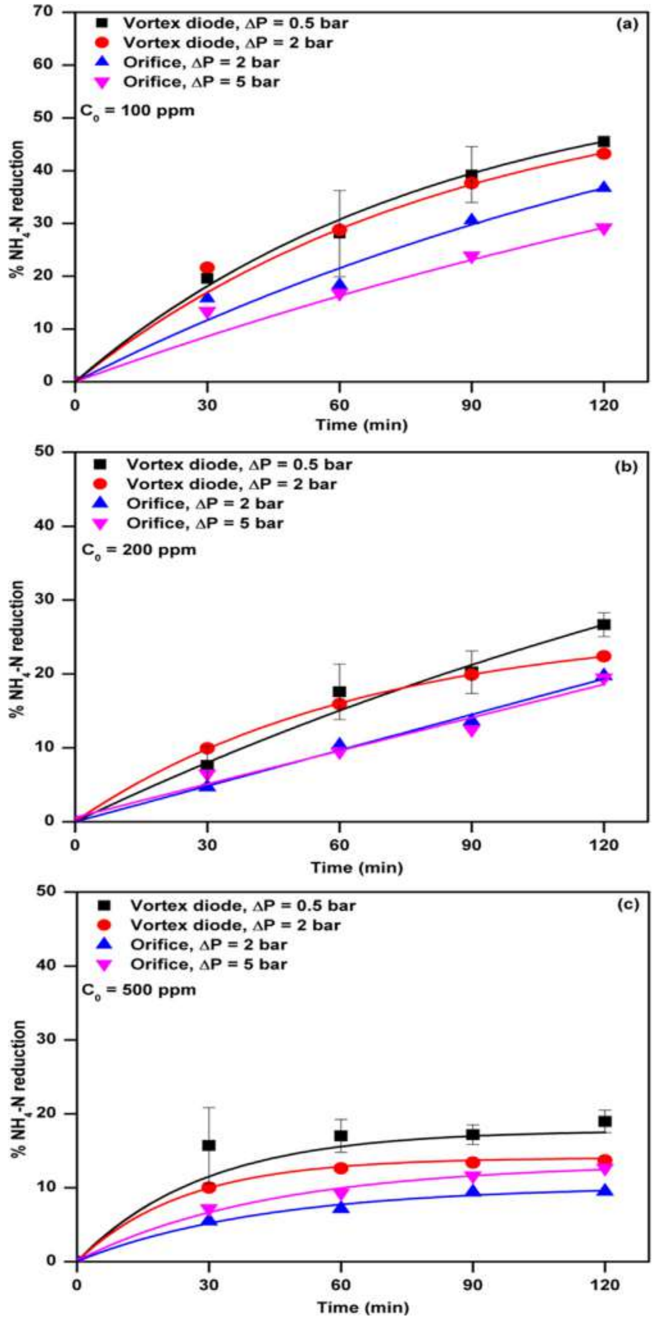

Fig. 4. Effect of Pressure Drop for different initial concentrations (a) 100 ppm (b) 200 ppm (c) 500 ppm.

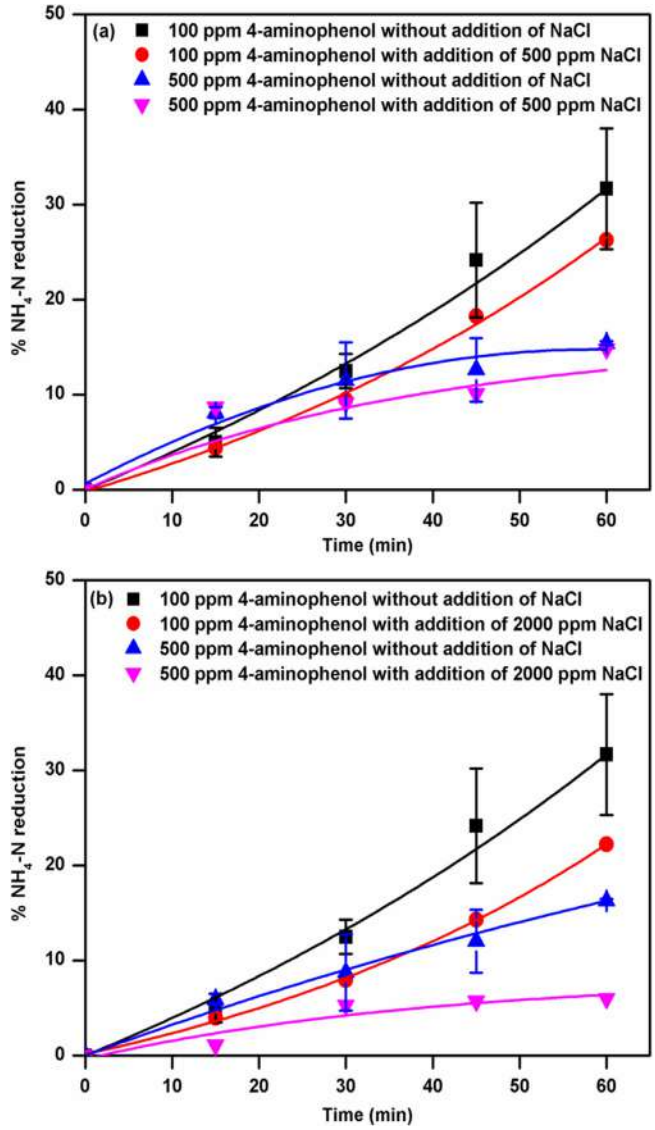

Fig. 5. Effect of dissolved solids on hydrodynamic cavitation (a) Low TDS (b) High TDS.

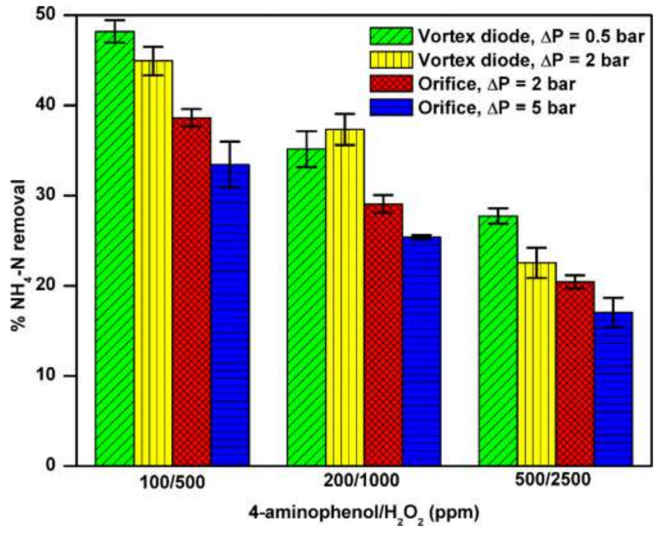

Fig. 6. Effect of addition of H_2O_2.

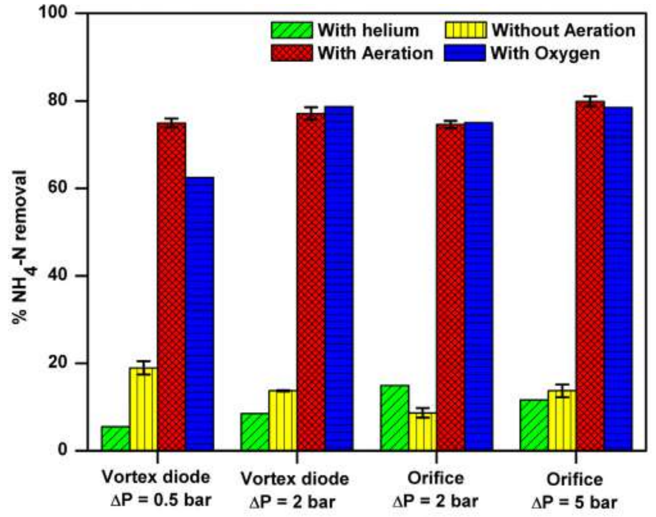

Fig. 7. Increased efficiency due to aeration on NH_4-N removal (C_o = 500 ppm).

4.5. *Intensification using aeration*

Simple form of process intensifications such as aeration can be useful for the reason that cavities constitute vapor, air and other gases which therefore can influence the behavior in term of implosion or oxidation or both. Aeration may cause,

1. Early inception of cavitation
2. Increased number of cavities, thereby increasing probability of reaction
3. Increase number of oxidizing radicals (due to enhanced availability of oxygen)

To evaluate the effect of aeration, experiments were carried out with and without aeration (air was sparged through the effluent storage tank). Independent experiments were also carried out with bubbling of helium and pure oxygen, instead of air. Since, the extent of removal is less at high initial concentrations, a concentration of 500 ppm ammoniacal nitrogen was selected to explore the enhancement. The results of process intensification studies are shown in Fig. 7. A very high removal of ammoniacal nitrogen was obtained (4 to 10 times), by aeration that was otherwise not possible by normal cavitation. About ~ 80% removal was obtained using aeration at 500 mg/L concentration. Suryawanshi et al. [28] reported ~ 10% enhancement in COD reduction due to aeration for the removal of solvents and suggested that the nature of the pollutant species may be important in this regard. Thus, process intensification in the form of aeration was not very effective for the removal of COD from the wastewaters. In view of the present results, a substantially different mechanism may be expected for the removal of ammoniacal nitrogen.

The results of the experiments using oxygen and helium independently are also shown in Fig. 7. As can be expected, bubbling of oxygen produces more or less similar effect as bubbling of air. In fact, the close similarity of the two clearly indicates role of oxygen in the enhancement rather than any of the physical factors mentioned above. Bubbling of the inert gas such as helium (used only for establishing proof-of-concept and is not required in any form for real application) has not shown any positive impact on cavitation. The observations, therefore, clearly imply chemical form of the process intensification due to increased availability of oxygen as the critical component in the removal of ammoniacal nitrogen. Naturally, it is believed that the removal occurs via formation of NOx and water in the process similar to that of CO_2 and water in COD reduction.

The removal mechanism is believed to include set of reactions due to collapse of cavities [43], resulting in generation of oxidizing species followed by possible formation of intermediates such as ketone, 4-benzoquinone imine and finally product of oxidation as benzoquinone, water and NOx [44]. This implies no significant reduction in the COD as the carbon number get only partly reduced, as has been confirmed in the present study, where separate COD measurement indicated average COD reduction of only 15%. However, more detailed investigations are required to establish the exact mechanism in this regard.

4.6. Per-pass removal

Instead of using an apparent first order kinetic constant to represent removal, it may be useful to use per-pass degradation factor to describe hydrodynamic cavitation experiments presented in this work [21]. The per-pass degradation factor is defined as,

$$\text{Per-pass degradation factor } (\emptyset) = k\,\tau \tag{2}$$

where, τ is residence time defined as a ratio of volume of holding tank and flow rate through cavitation device.

The energy dissipation rate,

$$W = \Delta P * Q \tag{3}$$

The overall cavitational yield (amount of ammoniacal nitrogen degraded per unit energy dissipation) can be written as,

$$Y = \frac{V\,(C_0 - C)}{\Delta PQt}\,\text{mg/J} \tag{4}$$

Fig. 8 shows values of per pass degradation factor and energy dissipation rate for the different conditions. At higher pressure drop conditions for vortex diode at 2 bar and orifice at 5 bar, the energy dissipation rate is quite high than low pressure drop conditions. This clearly demonstrates that lower pressure drop conditions are more favorable for both vortex diode and orifice from the cavitational yield perspective. The vortex diode at 0.5 bar shows maximum per-pass degradation compared to all other pressure drop conditions.

4.7. Comparative analysis of per-pass degradation factor- without aeration and with aeration

It is instructive to quantify the effect on enhancement using per-pass degradation factor for different cases such as removal without aeration and with aeration. The analysis in this regard is shown in Fig. 9. It is evident from the values of per-pass degradation factor that aeration leads to improvement in hydrodynamic cavitation. With increasing C_0, the improvement by aeration became larger. The analysis also quantitatively reveals effectiveness, especially at low pressure drops and differentiates the impact of reactor geometry.

4.8. Reactor geometry and cavitational yield

From the results obtained for ammoniacal nitrogen removal, it is clear that the reactor geometry has a strong influence on the removal behavior. This can be quantified in terms of cavitational yield for different reactors which is the ratio of amount of pollutant degraded and product of pressure drop, flow rate and time. This analysis can be more useful since there is large uncertainty associated with the characterization of the cavitation behavior due to difficulty in obtaining number/quantity of cavities, size of the cavities or size distribution that can imply quality of the cavities and effects of various known and unknown parameters such as presence of organics, dissolved solids, other impurities, liquid viscosity, surface tension, temperature and so on. Thus, the overall performance is largely attributed to the visible and measurable parameters such as pressure drop, reactor configuration. Fig. 10 provides values of cavitational yield for different reactors- vortex diode and orifice. A comparison is also made for the large enhancement obtained for the process intensification using aeration. The energy dissipated by aeration can be given by g × V_G (J/kg), where g is gravitational acceleration (9.81 m/s^2) and V_G is superficial gas velocity (m/s). In the present work, under experimental conditions, the energy consumption due to aeration was found to be less than 1% of the total energy consumption and hence, for simplifying and ease of comparison, energy dissipated by aeration is neglected. The values of cavitational yields were 49.2×10^{-4} mg/J and 31.4×10^{-4} mg/J for vortex diode at 0.5 bar pressure drop, 100 ppm initial concentration and for with and without aeration. The corresponding values for orifice were 8.4×10^{-4} mg/J and 4.9×10^{-4} mg/J respectively. For the initial concentration of 500 ppm, the same values for vortex diode and orifice were 261.0×10^{-4} mg/J and 73.8×10^{-4} mg/J and 59.8×10^{-4} mg/J and 6.75×10^{-4} mg/J respectively. It is evident that vortex diode as a cavitation reactor is superior to the conventional device-orifice. It can also be seen that the cavitation yield is higher for higher initial concentration. Also, cavitational yield increases significantly (up to 10 times) using aeration.

4.9. Cost considerations in removal of ammoniacal nitrogen using hydrodynamic cavitation

In view of the high efficacy of hydrodynamic cavitation technology for the treatment of industrial wastewaters containing high ammoniacal nitrogen, it would be prudent to estimate approximate costs associated with the treatment method. The cost of treatment can be obtained as [1]:

$$\text{Cos}\,t\ of\ treatment\ per\ m^3\ of\ effluent = \frac{N_c \times \Delta P \times P_E}{36\eta}$$

For the removal of ammoniacal nitrogen with and without aeration, the cost is estimated for the Indian scenario assuming the cost of electricity as Rs. 10 per kWh (1$ = ~70 Rs). Pump efficiency was assumed as 66%. For the similar levels of removal and for the process conditions found most favorable in the present work, 0.5 bar ΔP and vortex diode, the cost of treatment is 7 Rs/m^3 (~0.1$/$m^3$), without aeration and 2 Rs/m^3 (~0.02$/$m^3$) for process intensification with aeration (assuming negligible cost of aeration).

The corresponding costs for the orifice are 30 and 7 Rs/m^3 (approx. 0.42 and 0.1 $/$m^3$ respectively), at 2 bar ΔP without and with aeration respectively. For a high concentration of 500 ppm, the estimated costs are 7 Rs/m^3 (~0.1$/$m^3$) and 0.60 Rs/$m^3$ (~0.008$/$m^3$) for vortex diode without and with aeration while corresponding values for orifice are 30 and 3 Rs/m^3 (approx. 0.42 and 0.04 $/$m^3$ respectively). Thus, the treatment cost for vortex diode is significantly lower as compared to

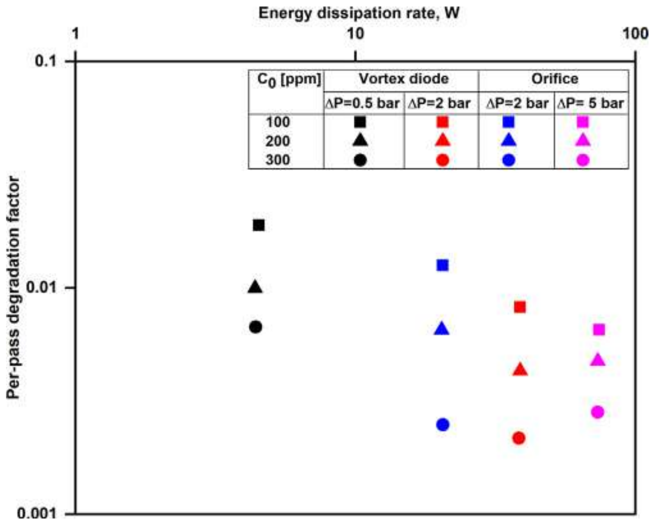

Fig. 8. Per pass degradation factor and energy dissipation rate at different concentrations.

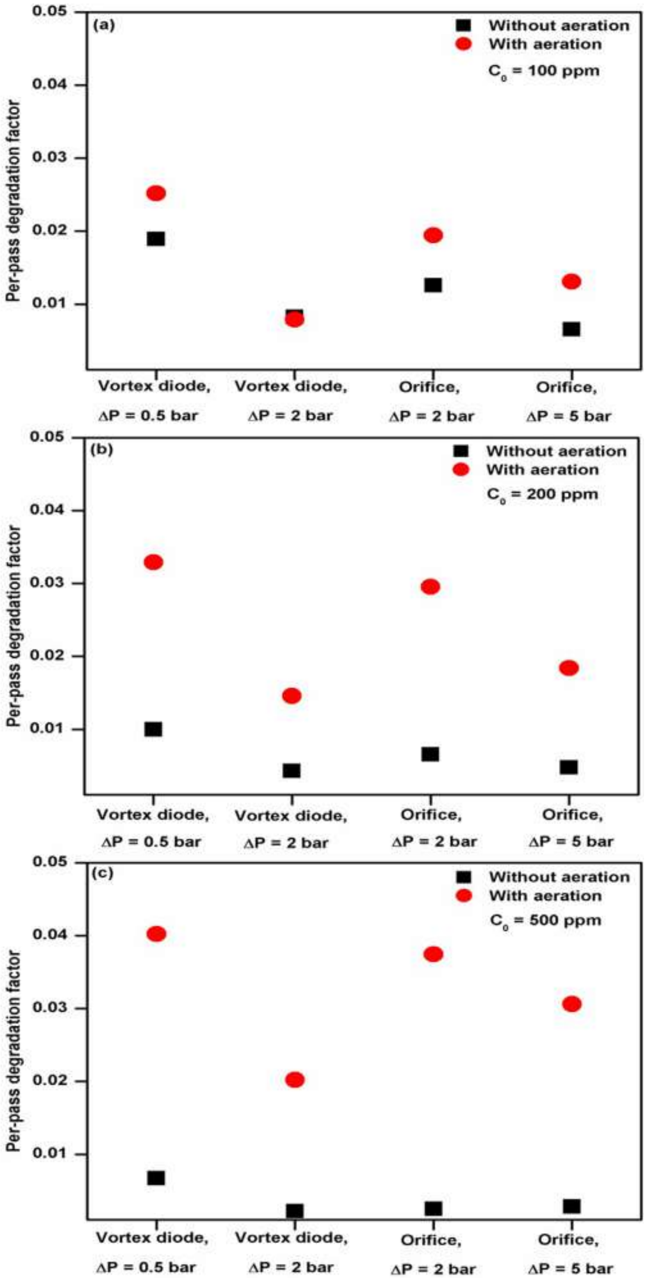

Fig. 9. Per pass degradation factors depicting effect of aeration.

the orifice used in this work.

The high effectiveness of vortex diode in the treatment of wastewaters is largely due to the flow pattern- vortex flow in the design of cavitation reactor. The rotational flow in such case is effective in removal at lower pressure drop conditions as compared to the linear flow based conventional cavitation devices.

5. Removal of ammoniacal nitrogen from real industrial wastewater- two case studies

Two different industrial wastewater samples mainly having the problem of high ammoniacal nitrogen were procured from a local distillery industry. The first sample was partially treated spent wash with initial COD of 75875 ppm and initial ammoniacal nitrogen content of 2050 ppm. The sample was dark brown in colour with intense odor. pH of the sample was 7. The second sample was of condensate water, after the biological treatment of distillery wastewater and had ammoniacal nitrogen content of 2880 ppm.

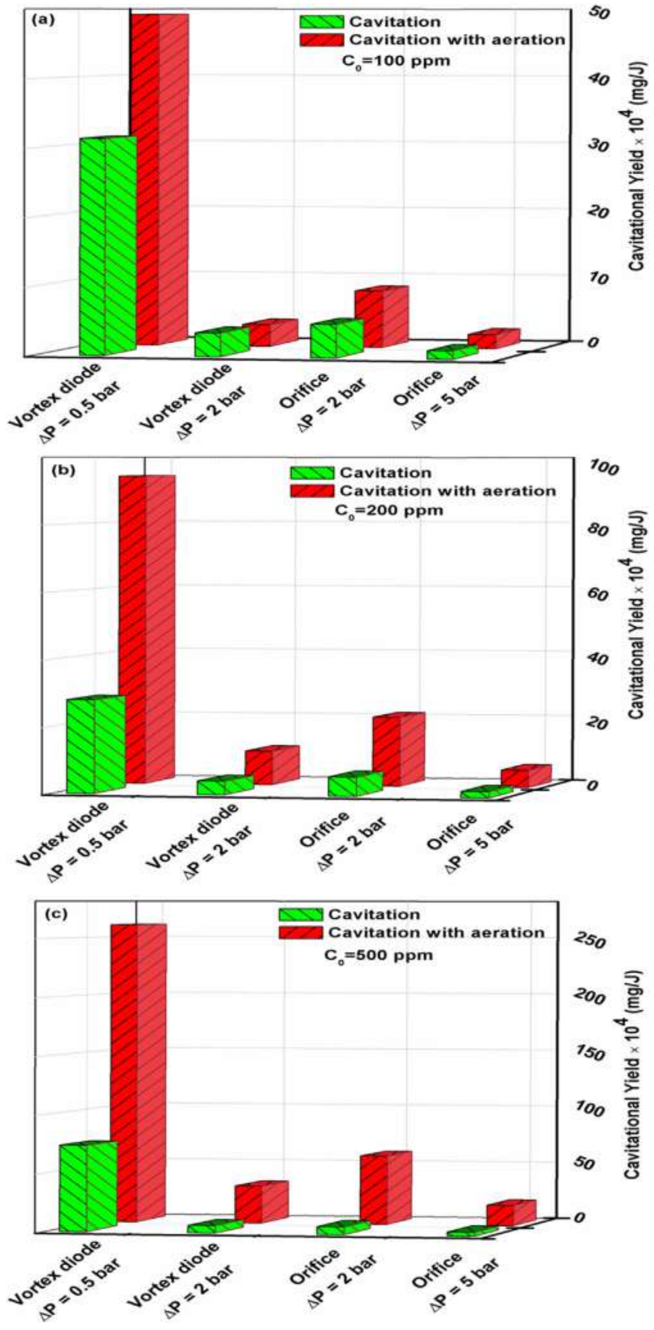

Fig. 10. Cavitational yield for vortex diode and orifice; with and without aeration.

Both the samples were specifically evaluated for the removal of ammoniacal nitrogen using vortex diode and employing a pressure drop of 0.5 bar and 2 bar respectively, conditions chosen on the basis of preliminary investigations. The reduction in the ammoniacal nitrogen for the spent wash sample was ~ 36% in 60 min, indicating efficacy of the hydrodynamic cavitation technique in treating real industrial wastewater. The treatment of condensate water however was quite difficult and a high reduction of the order of 75% could be obtained (Fig. 11) only after prolonged treatment (~10 h), indicating relatively high cost of the treatment of such wastewaters. This difficulty in the treatment can be largely attributed to the nature of highly refractory compounds that remained in the wastewaters even after the biological treatment.

The results on the real industrial wastewater treatment are similar to those reported by Bhandari et al. [20] for real industrial wastewater

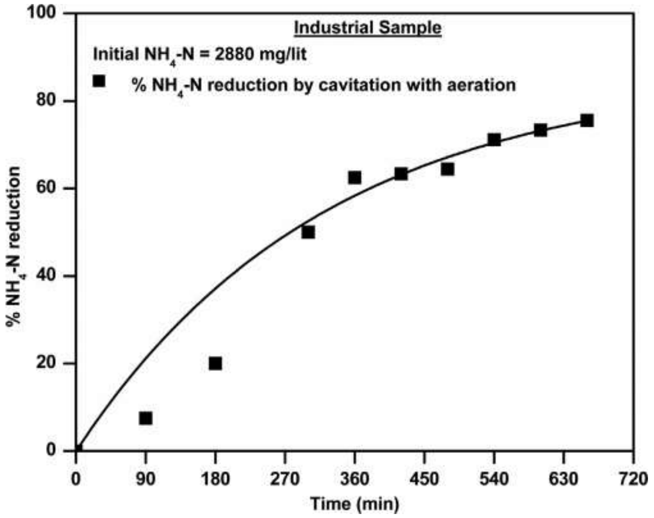

Fig. 11. Ammoniacal nitrogen reduction in real life- distillery industrial wastewater.

treatment of fertilizer industry where ~ 37% reduction in the ammoniacal nitrogen was reported for wastewaters of high ammoniacal nitrogen content (530–1330 ppm) and ~ 87% reduction for the low ammoniacal nitrogen (276 ppm) containing wastewater. The present study on distillery wastewater samples however had significantly higher ammoniacal nitrogen content and hydrodynamic cavitation was found to be effective in treating real industrial wastewaters even at such high levels of concentrations. Essentially, higher removal to desired extent can be achieved using prolonged treatment time or using appropriate process intensification.

6. Conclusion

The present study clearly establishes methodology for improving the effectiveness of hydrodynamic cavitation especially using vortex diode as a cavitating device in wastewater treatment, specifically for the removal of ammoniacal nitrogen. Initial concentration has significant impact on the removal and quantity of ammoniacal nitrogen removed increases with the increase in the concentration for the same pressure drop and reactor conditions. Overall, 9–45% removal could be obtained only using hydrodynamic cavitation depending upon the initial concentration and reactor geometry, high removal using vortex diode for pressure drop of only 0.5 bar. Interestingly, significant improvement, up to 8 times, can be obtained using simple process intensification by sparging air or oxygen and overall extent of removal of over 80% could be accomplished, again high improvement in the case of vortex diode at significantly low pressure drop (0.5 to 2 bar compared to orifice- up to 5 bar). For the initial concentration of 500 ppm, with and without aeration, the values of cavitational yield for vortex diode at pressure drop of 0.5 bar were 261.0×10^{-4} mg/J and 73.8×10^{-4} mg/J and for orifice at pressure drop of 2 bar were 59.8×10^{-4} mg/J and 6.75×10^{-4} mg/J, clearly proving superiority of vortex diode as a cavitation reactor over conventional device-orifice and demonstrating order of magnitude increase in the cavitational yield using aeration. The methodology of improving efficiency gets reflected in significant cost reduction due to process intensification, ranging from 200% to more than 1100%, an crucial and important aspect from industrial application point of view. A plausible mechanism to elucidate effect of aeration clearly highlighted role of oxygen for degradation by cavitation. The application of the technology for the treatment of real industrial wastewaters from distillery industry having high ammoniacal nitrogen content was equally effective in reducing ammoniacal nitrogen proving efficacy of the developed technique. The insight obtained in this study and the results are useful for real life industrial wastewater treatment and hydrodynamic cavitation technology with aeration appears to be a highly promising technology for the removal of ammoniacal nitrogen, in terms of efficiency, ease of operation, easy scale-up and cost effectiveness. The cavitating devices and aeration may be used alone or in combinations with existing established effluent treatment processes to facilitate water recycling and reuse.

Author contributions

V.M.B. and P. B. P conceived and developed the idea along with experimental methodology/result analysis. P.B.P. conducted all the experiments and analyzed the data. V.V.R. contributed to the data analysis. All three authors were involved in the preparation of the manuscript.

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Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: 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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Wastewater treatment and process intensification for degradation of solvents using hydrodynamic cavitation

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ABSTRACT

Industrial wastewater treatment for removal of small concentrations of harmful solvents is pertinent issue in many chemical and pharmaceutical industries. The present work evaluates removal of three common solvents by hydrodynamic cavitation (nominal capacity, $1m^3/h$). Solvent degradation of three solvents viz. octanol, dimethyl formamide and cyclohexanol was studied in the concentration range of 50-200 mg/L and for the pressure drop range of 0.5-5 bar. The vortex based cavitation device (vortex diode) was compared with that of linear flow based device (orifice). Process intensification in the form of aeration and addition oxidizing agent- hydrogen peroxide was also evaluated for synergistic effect. The vortex diode required lower pressure drop and is superior to orifice and process intensification using aeration is most effective. A reduction in TOC to the extent of 74% could be achieved for octanol (200 ppm) using aeration with cavitational yield of 1202×10^{-4} mg/J for vortex diode, yield ~10 times of orifice. The degradation depends on the nature of solvent and it was revealed that low values of dielectric constant ($\varepsilon<10$) favour degradation. The kinetics was evaluated using rate model based on per-pass degradation factor. The process techno-economic feasibility is useful in industrial wastewater treatment.

Nomenclature

C_0 Initial concentration, (mg/L or ppm)
C Final concentration, (mg/L or ppm) k Rate constant, min^{-1}
N_C Number of passes required for treatment
P Pressure, bar
P_E Cost of electricity per kWh, Rs.
Q Flow Rate, liter/h t Time, min
V Volume, Liter
W Energy dissipation rate, W
Y Cavitational yield, mg/J
Ø Per-pass degradation factor
ΔP Pressure drop, bar
η Efficiency of the pump
ε Dielectric constant

1. Introduction

Industrial wastewater treatment is a serious environmental concern due to rapid industrialization in general, and rise of fine chemicals/pharmaceutical industries, in particular, posing challenges in treating wastewaters for removal of specific organics such as solvents and specialty molecules. Apart from sustainability of the environment, water scarcity is also important driving force for industrial wastewater treatment, recycle and reuse. In view of its importance, a very large number of studies have been reported in the literature for the removal of chemical oxygen demand (COD) or total organic carbon (TOC) using different techniques, mainly coagulation, adsorption, oxidation, membrane separation, biological degradation and so on typically belonging to the class of physical, chemical and biological methods of treatment [1]. However, specific and detailed investigations on removal of different solvents in effluent water are lacking. Solvents are commonly used in many chemical and pharmaceutical industries at various stages of operations and naturally end up in wastewater in small concentrations, even after recovery. Solvent waste is recognised as a hazardous waste [2] and conventional methodologies have severe limitations in the removal/degradation due to various reasons apart from poor biodegradability. Consequently, even after secondary treatment, solvents traces can remain in wastewater. Suryawanshi *et al.* [3] reported degradation studies of acetone, methyl ethyl ketone and toluene using

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cavitation with better removal for only toluene and marginal improvement using aeration. Extended work for higher concentrations, removal of acetone, ethyl acetate and isopropyl alcohol was reported using cavitation [4]; both the studies indicating viability of hydrodynamic cavitation technique for degradation of solvents. In view of large number of solvents being commercially used and limited information in the literature on degradation, differences due to nature of solvents (MW, structure, protic and aprotic nature etc.), number of processes/ reactor configurations and so on, it is instructive to evaluate degradation of various solvents to arrive at practical strategy for their removal.

The technology scenario for wastewater treatment is complex and a large number of methodologies, from simple to highly complex, from low cost to highly cost intensive options add to difficulties in selection of methods. Further, any one method is rarely sufficient in meeting the effluent standards for discharge or for water recycle and reuse and therefore a combination of many methods is practically required resulting into significantly increased cost of treatment. Also, most of the conventional methods generate secondary waste and therefore compared to recovery or physical removal methods, destructive technologies are especially suitable for the wastewater treatment in view of small concentrations of harmful pollutants. Compared to physical and biological methods, chemical methods have a very large variation from concept to application strategy, especially for oxidation processes that employ simple oxidation to complex forms such as catalytic processes with different catalysts, Fenton oxidation, photo-oxidation, UV/H_2O_2, Ozone, cavitation and electro-oxidation. The increased complexity of the advanced oxidation processes (AOPs) and their combination have their own effectiveness and limitations for the removal of difficult pollutants, essentially require higher cost with increased complexity [5,6,7,8,9,10]. Cavitation, one form of advanced oxidation processes, is a destructive method of treatment which provides in situ generation hydroxyl radicals for the oxidation of the pollutants. It can be regarded as a greener process since complete mineralization of contaminants is possible. Further, hydrodynamic cavitation in this regard can offer ease of operation, multiple reactor geometries, easy scalability and lower cost of treatment.

The principle of cavitation process is well discussed in the literature wherein, flow of liquid through low pressure region resulting into formation, growth and subsequent adiabatic collapse of cavities/microbubbles (~10-100 microns) in liquid. Consequent to cavity implosion, extreme conditions get generated at localized points- hot spots with temperature of ~10000 K and pressures of ~1000 atm. The result is homolytic cleavage of water molecules generating hydroxyl radicals, a strong oxidizing agent that can oxidise organics to the extent of complete mineralization, final product being water and carbon dioxide. Though four principal types of cavitation e.g. acoustic, hydrodynamic, optic and particle cavitation are known, only hydrodynamic cavitation appears practical for wastewater treatment at this point of time, both from chemistry and engineering viewpoint. Different cavitation reactor geometries such as orifice, venturi, high speed rotor-stator assembly are commonly used while vortex diode is a recently discussed and also commercialized reactor configuration. Orifice type devices employ linear flow and generate cavities using small constrictions in the path of liquid, therefore are prone to clogging, erosion consequently not very suitable for wastewater treatment. Unlike conventional HC devices like orifice or venturi, the cavitation realised in vortex diode does not depend on small constrictions. The cavitation is realised by strongly swirling flows. Therefore, for an equivalent capacity of cavitation devices, smallest diameter of vortex diode is significantly larger than smallest diameter in orifice or venturi (without going into details, it is approximately 2.5 times larger). Therefore, vortex diode is much less susceptible to clogging by particles or fibrous materials compared to venturi or orifice. High speed rotor type devices are energy intensive and also pose operational difficulties. In view of these, the recent device based on vortex flow, vortex diode that does not have moving elements and also requires significantly lower energy appears to be most promising alternative to conventional cavitation reactors [1,3,11,12,13]. The design is simple with tangential entry and axial exit connected to vortex chamber (Fig. 1). A strong swirling flow causes low pressure region at center of the vortex leading to formation of vapour filled cavities and subsequent collapse after realizing high pressure at downstream region leading to formation of hot spots. The vortex-based cavitation device was evaluated earlier in variety of applications such as dye removal [14], ammoniacal nitrogen removal [12,13,15], microbial disinfection [16,17,18], biomass valorization [19], and desulphurization of transportation fuels [20].

In present study, in an attempt to provide a more complete platform for theoretical and practical assessment for solvent degradation, we report degradation of three solvents using hydrodynamic cavitation; two different cavitation reactors- employing vortex flow (vortex diode) and linear flow (orifice); two process intensification strategies using aeration and hydrogen peroxide addition; kinetics of degradation and cost evaluation for techno-economic feasibility analysis. This study, for the first time, has underlined the effect of dielectric constant of the solvent in degradation of the solvent in cavitation processes. Though dielectric constant is related to polarity, we believe that specific data presented in this work will provide a basis for further research on relating key solvent properties to degradation performance and treatment parameters. The solvent, 1-Octanol is widely used in perfume and flavouring industry, solvent dimethyl formamide (DMF) is widely used in pharmaceutical, pesticide, leather and surface coating industry while cyclohexanol is widely used as plasticizer, in soap and detergent industry. A detailed investigation is carried out for all the three solvents at different concentrations and different pressure drop across cavitation reactors. The per-pass degradation factor model [4] was applied to evaluate degradation behaviour and cavitational yield.

2. Experimental

The solvents, 1-Octanol, cyclohexanol (HPLC grade from Loba Chemie) and DMF (HPLC grade from Merck) were used for degradation study. Hydrogen peroxide (50%) was obtained from MERCK India. Air pump (SOBO AQUARIUM SB-9905, 2 Nozzle, 4.2W, Max. 5.5 L/min × two output) was used for aeration. SHIMADZU TOC-L series of TOC analyzer was used for analysis of total organic carbon.

The degradation studies were carried out using synthetic wastewater containing known predetermined concentration of individual solvent in water. The block diagram and actual experimental setup is shown in Fig. 2, many details of which are already reported earlier [3,20,13] and hence to avoid repetition only essential components are discussed here. The experiments were carried out using 20 L of wastewater solution in the storage tank (50 L capacity). A vertical multistage 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 is used and flow is controlled by ¾" NB valves (valve industries ltd). Flow transmitter (KROHNE, H250) is used to measure flow in the main line while pressure transmitter (Honeywell ST 700) is provided at both upstream and downstream section of cavitation reactor to measure the pressure. Temperature is measured using RTD (EUREKA Eng. Enterprises India; 0–200°C) while temperature control is carried out by using recirculating chiller (JULABO FL1701) at bypass line. Two cavitation reactors include, orifice (Circular 3mm single hole, SS316) and vortex diode (Chamber diameter 66 mm, Throat diameter 11 mm, SS316). For aeration, vertical cylindrical tube is inserted into the tank before sending fluid through cavitation reactor which is connected to air pump (SOBO AQUARIUM SB-9905, 2 Nozzle, 4.2W, Max. 5.5 L/min × two output) smoothly by silicon tubing with provision of air flow rate control by small adjusting valve. The degradation of solvent was monitored by monitoring reduction in total organic carbon, TOC. In view of cavitation inception for vortex diode at 0.48 bar and for orifice at ~1.25 bar [20], the pressure drop conditions were selected as 0.5 and 2 bar for vortex diode and 2 and 5 bar for orifice respectively to ensure that both the

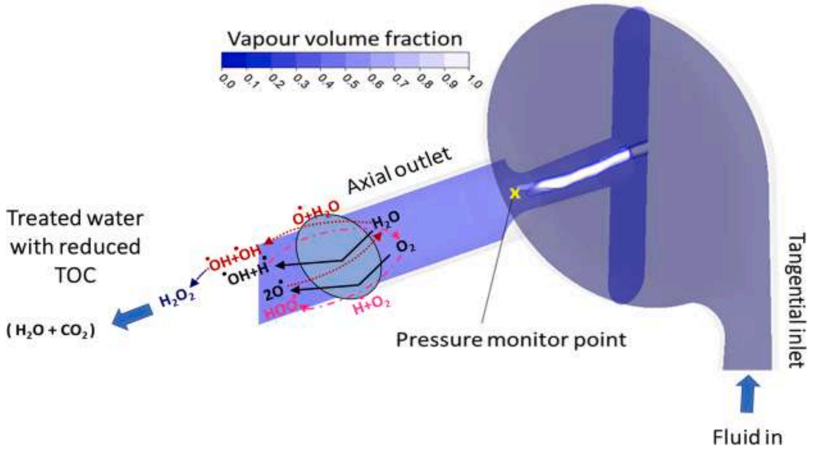

Fig. 1. Schematic of vortex diode

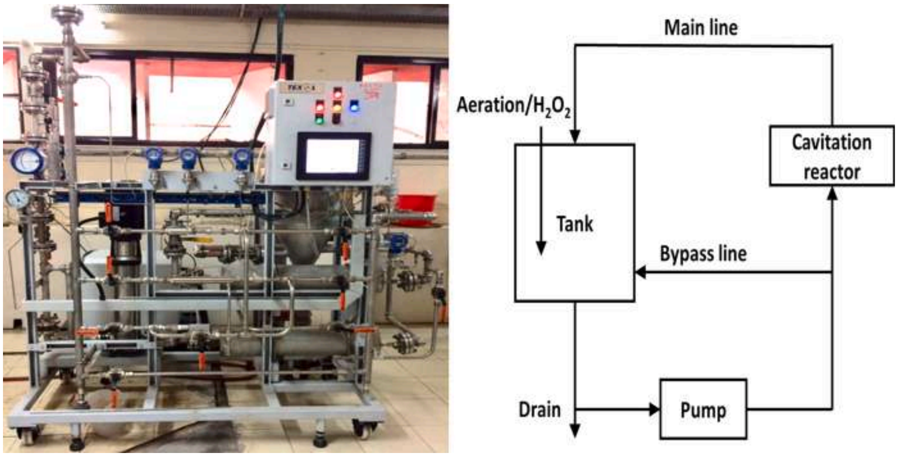

Fig. 2. Schematic of hydrodynamic cavitation pilot plant and experimental setup

cavitation reactors operate in cavitation regime.. Experiments were conducted for 60 min and samples were withdrawn at 15 min interval. The pH of sample was observed to be in the range 6.7-7.4 showing a marginal change during the experiment.

3. Results and discussion

3.1. *Effect of initial concentration*

The effect of initial concentration for the three different solvents, octanol, DMF and cyclohexanol, at initial concentration of 50 and 200 ppm is elucidated in Fig. 3 along with a comparison for the two different reactors-vortex diode and orifice. The effect of initial concentration of solvent is quite significant and amount of solvent degraded increases with solvent concentration. Since the overall extent of degradation is a function of concentrations of hydroxyl radicals and pollutant, though percentage degradation decreases with increase in initial concentration, the solvent amount degraded increases with increase in initial pollutant concentration. Octanol gave ~ 21% TOC reduction at 50 ppm using vortex diode which increased to ~ 37% at 200 ppm initial concentration in 60 min; indicating more than 70% improvement in degradation. The corresponding TOC reduction by using orifice was also quite similar, however, requiring substantially higher pressures compared to vortex diode.

The effect of concentration for DMF and cyclohexanol was quite similar, though the values of degradation were substantially lower as compared to that obtained with octanol at both lower and higher concentrations. DMF shows 12% TOC reduction in 60 min at both 50 and 200 ppm initial concentration while cyclohexanol shows 7% and 2% TOC reduction after 60 min at 50 and 200 ppm respectively.

The concentration of solvent and the nature of the solvent are both important for the viability of hydrodynamic cavitation technique for solvent degradation. Higher values of degradation for lower ranges of concentrations are crucial since effluents typically have low pollutant concentrations. Further, increased degradation with higher concentrations is useful to establish viability of the process in the entire concentration range. The higher initial concentration influences vapour and gas content of cavity during collapse subsequently impacting degradation rate [21]. The results show that the amount of pollutant degraded is more at higher concentration, which is quite important and relevant for real effluent treatment.

The experimental observation reveals that concentration decreases exponentially with time, suggesting use of simple power law model for kinetics of degradation. The reactions in hydrodynamic cavitation can be assumed to be pseudo first order and the kinetics can be evaluated using the following simple mathematical expression.

$$C = C_0 e^{-kt} \tag{1}$$

Where, C_0 and C is the pollutant concentration before and after treatment, ‘t’ is time (min) and ‘k’ is first order rate constant (min^{-1}).

The fit of the model is good (R^2 value >0.98). Table 1 lists the k values for different solvents at lower and higher concentration for the two reactor configurations, vortex diode and orifice. For low concentration of 50 ppm and lower pressure drop condition, the k values for

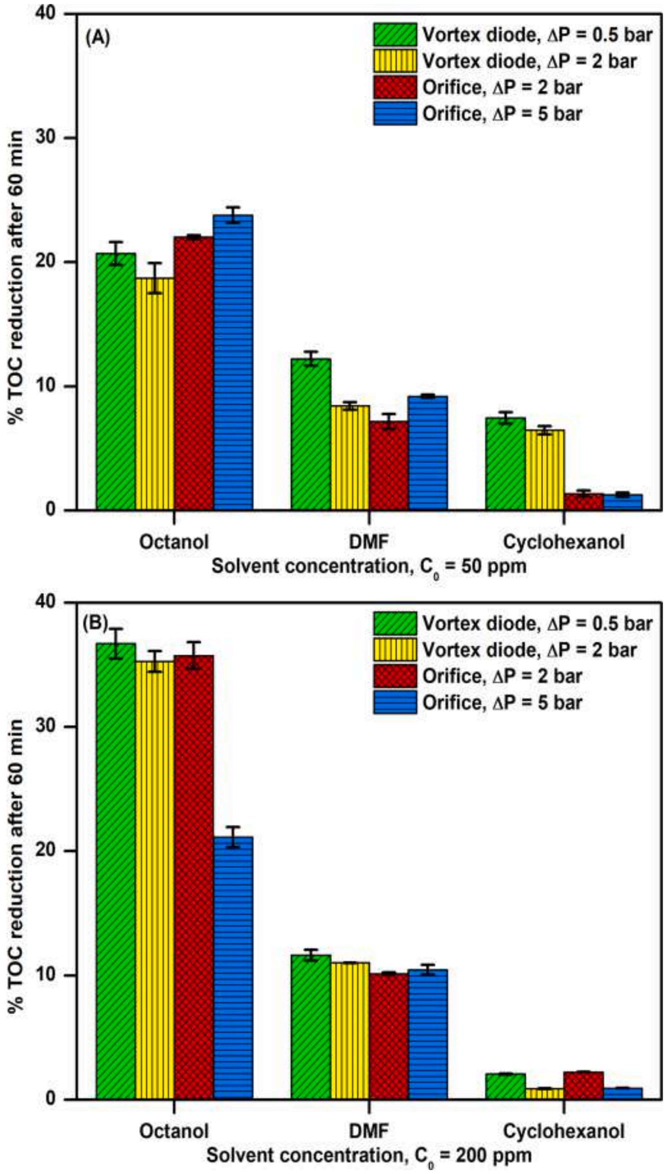

Fig. 3. Effect of initial concentration of solvents (A) C_0 = 50 ppm, (B) C_0 = 200 ppm

octanol, DMF and cyclohexanol were 3.9×10^{-3} (min^{-1}), 2.2×10^{-3} (min^{-1}) and 1.3×10^{-3} (min^{-1}) for vortex diode and 3.9×10^{-3} (min^{-1}), 1.2×10^{-3} (min^{-1}) and 0.2×10^{-3} (min^{-1}) for orifice. While at higher concentration of 200 ppm, the k values for octanol, DMF and cyclohexanol were 7.6×10^{-3} (min^{-1}), 2×10^{-3} (min^{-1}) and 0.3×10^{-3} (min^{-1}) for vortex diode and 7.5×10^{-3} (min^{-1}), 1.8×10^{-3} (min^{-1}) and 0.4×10^{-3} (min^{-1}) for orifice. The rate data clearly highlights the impact of concentration and nature of the solvent in degradation using hydrodynamic cavitation without use of the catalyst or process intensification. Therefore, these results can be construed as primary findings in investigating application of hydrodynamic cavitation for solvent degradation and for evaluating reactor configurations.

Table 1
Rate constant data for different solvents (Octanol, DMF and Cyclohexanol)

Solvent	Reactor	ΔP, Bar	% TOC reduction after 60 min		1st order rate constant, K × 10^3 (min^{-1})	
			50 ppm	200 ppm	50 ppm	200 ppm
Octanol	Vortex diode	0.5	21	37	3.9	7.6
	Vortex diode	2	19	35	3.5	7.3
	Orifice	2	22	36	3.9	7.5
	Orifice	5	24	21	4.6	4
DMF	Vortex diode	0.5	12	12	2.2	2
	Vortex diode	2	8	11	1.4	2
	Orifice	2	7	10	1.2	1.8
	Orifice	5	9	11	1.6	1.8
Cyclohexanol	Vortex diode	0.5	7	2	1.3	0.3
	Vortex diode	2	6	1	1.1	0.1
	Orifice	2	1	2	0.2	0.4
	Orifice	5	1	1	0.2	0.2

3.2. *Effect of pressure*

The pressure drop is one of the most important parameter in the application of hydrodynamic cavitation technique dictating energy requirement and consequently cost of the operation. Different reactor configurations require different ranges of pressures in this regard. Our previous work on vortex diode has confirmed low pressure drop requirement for the vortex flow operation using vortex diode compared to linear flow device, orifice [13]. The present study, for ease of comparison with the reported data in the literature and also in view of inception of cavitation at ~0.48 bar for vortex diode and ~1.2 bar for orifice, employed similar conditions of pressure drop, the range of ΔP from 0.5 to 2 bar for vortex diode and ΔP in the range 2 and 5 bar for orifice. The cavitation number for orifice was less than one; 0.75 and 0.35 for 2 bar and 5 bar respectively whereas, in case of vortex diode, the usual definition of cavitation number is not applicable. The selected range of pressures therefore ensures cavitation. The effect of pressure drop for solvent degradation is shown in Fig. 4 for 50 ppm and 200 ppm initial concentrations. As discussed earlier, octanol gave ~ 21% TOC reduction at 50 ppm using vortex diode which increased to ~ 37% at 200 ppm initial concentration in 60 min; indicating more than 70% improvement in degradation at ΔP of 0.5 bar. For similar/ corresponding TOC reduction, substantially higher pressures were required for orifice, ΔP of 2 bar, compared to vortex diode. The highest values of degradation for the three solvents, octanol, DMF and cyclohexanol, using vortex diode were 37%, 12% and 7% respectively and the corresponding values for the orifice were 36%, 10% and 2%, however at significantly higher pressures compared to vortex diode. The results clearly highlight the increased efficacy of using vortex diode or vortex flow in cavitation, and lower energy consumption. The results also indicate that lower pressure drop condition is more or less equally good in the degradation of solvents especially for vortex diode configuration; orifice requiring substantially higher pressure drop compared to vortex diode to obtain similar extent of degradation in all the cases. Further, the effect of pressure drop is more pronounced in orifice, a linear flow based device for which similar positive impact of increased pressure has been well reported [3]. The degradation behaviour agrees well with that reported in the literature. However, for these solvents and in the range of pressure drop of this study, no identifiable flattening of the trend was observed indicating no choked cavitation as found in previous reports. Therefore, the operation can be performed by further increasing pressures for both the devices. However, increased number of passes would adversely impact the cost of operation. Per-pass degradation is a useful concept in the analysis of hydrodynamic cavitation operations in this regard.

3.3. *Process intensification using aeration*

The process intensification using aeration was earlier reported as

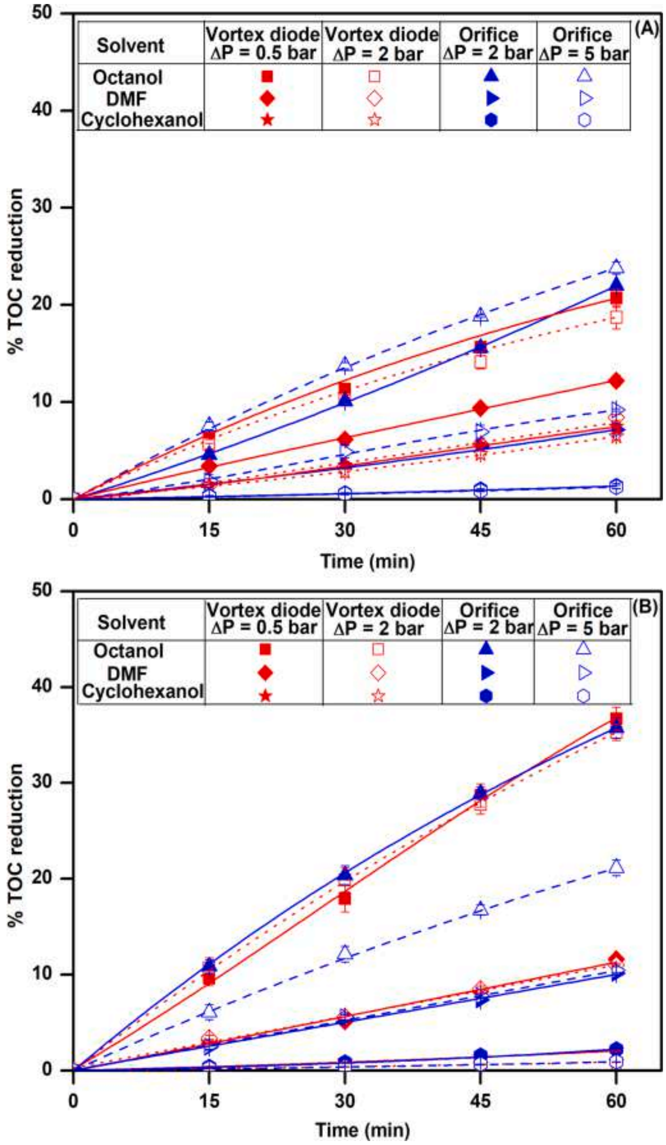

Fig. 4. Effect of pressure on solvent degradation (A) $C_0 = 50$ ppm, (B) $C_0 = 200$ ppm

highly effective in enhancing the removal of ammoniacal nitrogen [13], though its effect in solvent degradation was not that impressive [3]. Process intensification in the form of aeration is expected to enhance the efficiency of hydrodynamic cavitation due to possible generation of additional nuclei for reaction (number of cavities), for early inception of cavitation apart from improving the quality of the cavities (size/enlargement), consequently contributing to the fruitful collapse (implosion) of cavities and subsequent increased degradation rate and efficiency of hydrodynamic cavitation. In the present study, aeration was effected by bubbling air in the effluent tank prior to liquid passing through cavitation reactor.

The results of degradation of different solvents with and without aeration and for the two reactor configurations are shown in Figs. 5 and 6. The difference in the rate for vortex diode is highlighted in Fig. 6 for solvent octanol, where highest impact of process intensification was observed. The values of extent of degradation for the three solvents, octanol, DMF and cyclohexanol using only hydrodynamic cavitation were 21%, 12% and 7% at initial concentration of 50 ppm and at ΔP of 0.5 bar for vortex diode which could be enhanced to the extent of 35%, 19% and 10% using aeration. The same values at 200 ppm initial concentration were 37%, 12% and 2% which could be enhanced to the

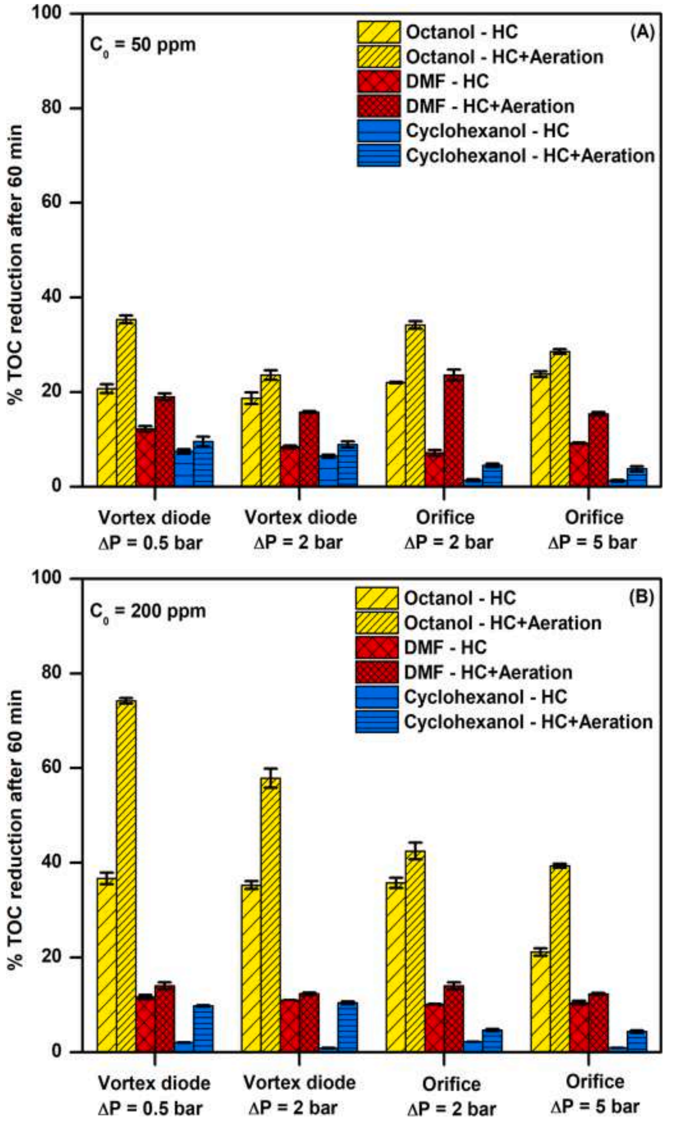

Fig. 5. Effect of aeration on solvent degradation, (A) $C_0 = 50$ ppm (B) $C_0 = 200$ ppm

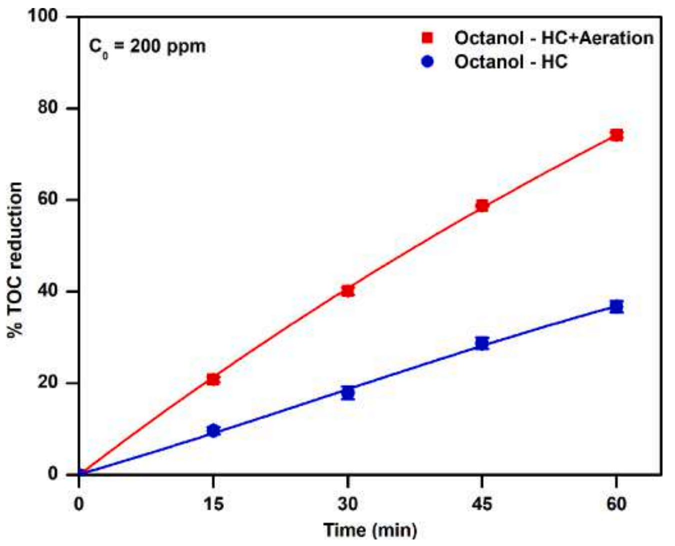

Fig. 6. Enhancement in TOC reduction for Octanol/ Vortex diode, ΔP = 0.5 bar

extent of 74%, 14% and 10% using aeration. A marked difference is evident due to nature of the solvent, octanol showing significant benefits of process intensification. The values for orifice, a cavitation reactor that employs linear flow, for the initial concentration of 50 ppm and at ΔP of 2 bar for the three solvents are 22%, 7% and 1% respectively while the enhancement due to aerations yields the values as 34%, 24% and 5% respectively and for initial concentration of 200 ppm 36%, 10% and 2% which could be improved to the extent of 42%, 14% and 5% respectively. The values for higher pressure drop ΔP of 5 bar and initial concentration of 50 ppm for orifice were 24%, 9% and 1% without aeration and 29%, 15% and 4% with aeration while for 200 ppm, 21%, 11 and 1% without aeration and 39%, 12% and 4% with aeration. Thus, for the solvent octanol, a highest degradation enhancement of 100% could be obtained with useful degradation efficiency of 74%. For other solvents, though order of magnitude enhancement could be obtained due to process intensification, the values of degradation efficiency were not satisfactory, in general.

Suryawanshi *et al.* [3] reported only ~10% improvement in COD removal by aeration as compared to without intensification. Sarvothaman *et al.* [4] found close to 100% increase in the per-pass degradation factor by means of aeration in the solvent degradation. Recently, Thanekar and co-workers also reported significant improvement due to aeration in their study on degradation of benzene by hydrodynamic cavitation coupled with aeration using orifice, with 98.9% reduction [22]. From the analysis of the data on different solvents of this study and that reported in the literature, it is evident that the usefulness of the process intensification in the form of aeration largely depends on the nature of the solvent as the physical effect due to aeration in the form of improvement in quantity/quality of the cavities would essentially be similar for all the solvents. Since, *a priori* prediction of the effect of solvent nature in this regard for hydrodynamic cavitation is not possible by any theoretical means at this point of time, it is imperative that experimental investigations on various solvents be carried out to develop empirical guidelines that can help in translating the findings for real life applications apart from forming basis for theoretical framework development.

To evaluate combined effect of hydrodynamic cavitation and aeration, synergistic coefficient was calculated by using formula [23],

$$\text{Synergistic coefficient} = \frac{k_{HC+Aeration}}{k_{HC} + k_{Aeration}} \tag{2}$$

The obtained values of synergistic coefficient revealed increased effectiveness of process intensification using the combined approach of hydrodynamic cavitation with aeration thereby in obtaining increased degradation as compared to only hydrodynamic cavitation. For octanol, where highest ~74% TOC reduction was seen, a high value of synergistic coefficient, 2.41, was obtained. For other solvents such as DMF and cyclohexanol, the synergistic coefficient values were expectedly lower though improved degradation was observed using aeration. The values of synergistic coefficient in case of DMF and cyclohexanol were 0.8 and 1.31 respectively.

3.4. *Process intensification using addition of H_2O_2*

Hydrogen Peroxide is one of the most powerful known oxidising agents and is used extensively in not just for oxidation reactions, but also in the form of process intensification in cavitation, especially for effluent treatment [24,25]. The conventional mechanism of hydrodynamic cavitation involves generation, *in situ*, of strong oxidising species such as hydroxyl radicals and also hydrogen peroxide followed by oxidation of organic pollutants and therefore, any further addition of hydrogen peroxide, as process intensification, is believed to generate synergistic effect with the conventional cavitation process, enhancing concentration of oxidising species that contribute to the degradation and increase the efficiency of degradation.

Hydrogen peroxide (50%) was used with external addition of hydrogen peroxide in 1:5 molar ratio (5 moles of H_2O_2 for 1 mole of solvent) for different solvent concentrations. The results of process intensification using hydrogen peroxide are presented in Fig. 7, for all the three solvents and also for different initial solvent concentrations. It is evident that, though the trend shows increase in the efficiency of degradation, the magnitude of increase in not very high. Interestingly, process intensification in the form of aeration gave huge improvement for solvent-octanol, while process intensification in the form of hydrogen peroxide addition did not have any specific preference for the solvent in this regard. This can be attributed to possible effectiveness of hydrodynamic cavitation technique in generating oxidising agents in sufficient concentration and further increase in the concentration of oxidising species may not be useful. In general, hydrodynamic cavitation will assist H_2O_2 to disassociate and sometimes increased concentration of $^{\cdot}OH$ radicals will also lead to self-quenching. Overall effect depends on the relative rate of reaction between $^{\cdot}OH$ radicals; in this scenario, reaction between 2 $^{\cdot}OH$ radicals, and between $^{\cdot}OH$ radical & organic pollutant. If reactivity of organic pollutant is high, addition of hydrogen peroxide is expected to show improvement, else, it may not. The indifference with respect to different solvents also indirectly point to this reasoning.

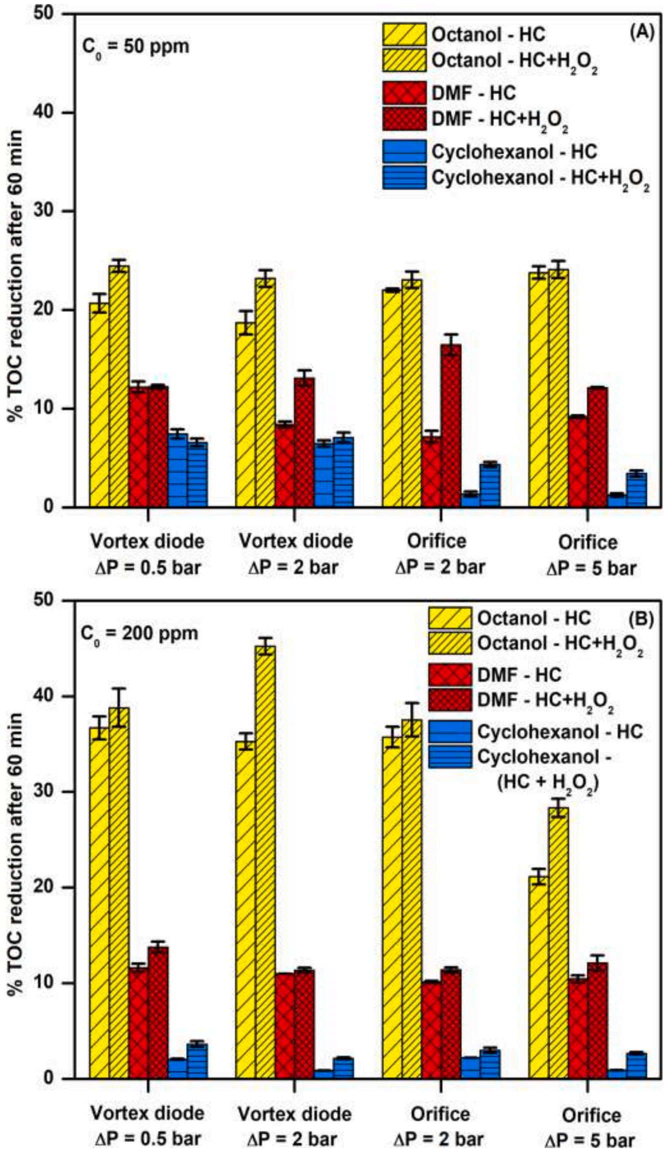

Fig. 7. Effect of addition of H_2O_2 addition (A) C_0 = 50 ppm, (B) C_0 = 200 ppm

To evaluate combined effect of hydrodynamic cavitation with addition of hydrogen peroxide, synergistic coefficient was calculated by using formula [23],

$$\text{Synergistic coefficient} = \frac{k_{HC+H_2O_2}}{k_{HC} + k_{H_2O_2}} \tag{3}$$

It was confirmed that hydrodynamic cavitation with addition of hydrogen peroxide shows only a marginal improvement in TOC reduction and therefore limited synergism with the value of synergistic coefficient close to 1. The present study, in the ranges of the parameters, reactor configurations and for the three solvents, indicates ineffectiveness of process intensification in the form of hydrogen peroxide addition for practical and useful benefits.

3.5. Effect of reactor geometry, Per-pass degradation factor model and cavitational yield

The conventional approach for degradation kinetics is by using chemical reaction model for kinetics. However, a more rigorous approach would be that using a model that closely resembles the physico-chemical working of the hydrodynamic cavitation process. The use of per-pass degradation factor in hydrodynamic cavitation is therefore more appropriate in description and for implementation at a larger scale [4,16,17,18]. The per pass degradation can be defined as:

$$\text{Per} - \text{pass} \quad \text{degradation} \quad \text{factor}(\phi) = k\,\tau \tag{4}$$

Where, τ is residence time which is ratio of volume of holding tank and flow rate through cavitation device.

The energy dissipation rate is calculated as,

$$W = \Delta P \times Q \tag{5}$$

Fig. 8 shows values of per-pass degradation factor and energy dissipation at different conditions. At higher pressure drop conditions of vortex diode and orifice (ΔP = 2 and 5 bar) energy dissipation rate is very high compared to lower pressure drop conditions. The fig. 8 clearly shows vortex diode with ΔP of 0.5 bar gives maximum per-pass degradation factor for octanol, cyclohexanol and DMF at both lower and

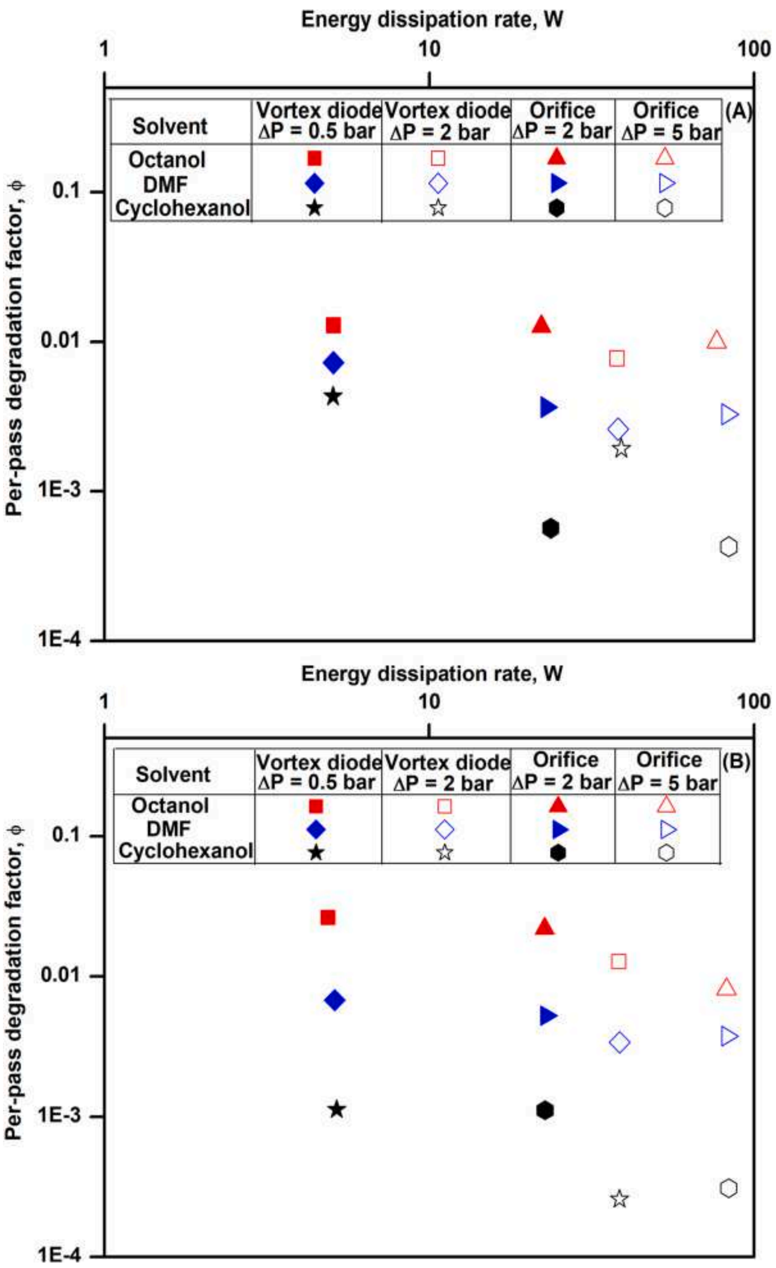

Fig. 8. Per-pass degradation factor for solvents (A) C_0 = 50 ppm, (B) C_0 = 200 ppm

higher concentration.

The overall cavitational yield (amount of solvent degraded per unit energy dissipation) can be written as,

$$Y = \frac{V(C_0 - C)}{\Delta PQt}\,\mathrm{mg}\Big/\mathrm{J} \qquad (6)$$

The extent of degradation is different for different geometrical configuration and can be quantified by means of cavitational yield which is ratio of amount of pollutant degraded and product of pressure drop, flow rate and time. Fig. 9 represents cavitational yield for different rectors – vortex diode and orifice. There was significant improvement by process intensification by means of aeration hence it is instructive to make comparison of the data, with and without aeration, using vortex diode and orifice for octanol, cyclohexanol and DMF at 50 and 200 ppm. Among the three solvents there was significant improvement in case of octanol at both low and high concentrations by aeration especially at lower pressure drop conditions for vortex diode and orifice. The values of cavitational yield for octanol at 50 and 200 ppm were 31.5×10^{-4} mg/J, 503.6×10^{-4} mg/J with cavitation and 58.1×10^{-4} mg/J, 1202.6×10^{-4} mg/J with aeration using vortex diode while for orifice 6×10^{-4} mg/J, 94.9×10^{-4} mg/J with cavitation and 14.2×10^{-4} mg/J, 119.7×10^{-4} mg/J with aeration. It is evident from the analysis of values of cavitational yield that vortex diode is superior to conventional orifice due to high cavitational yield.

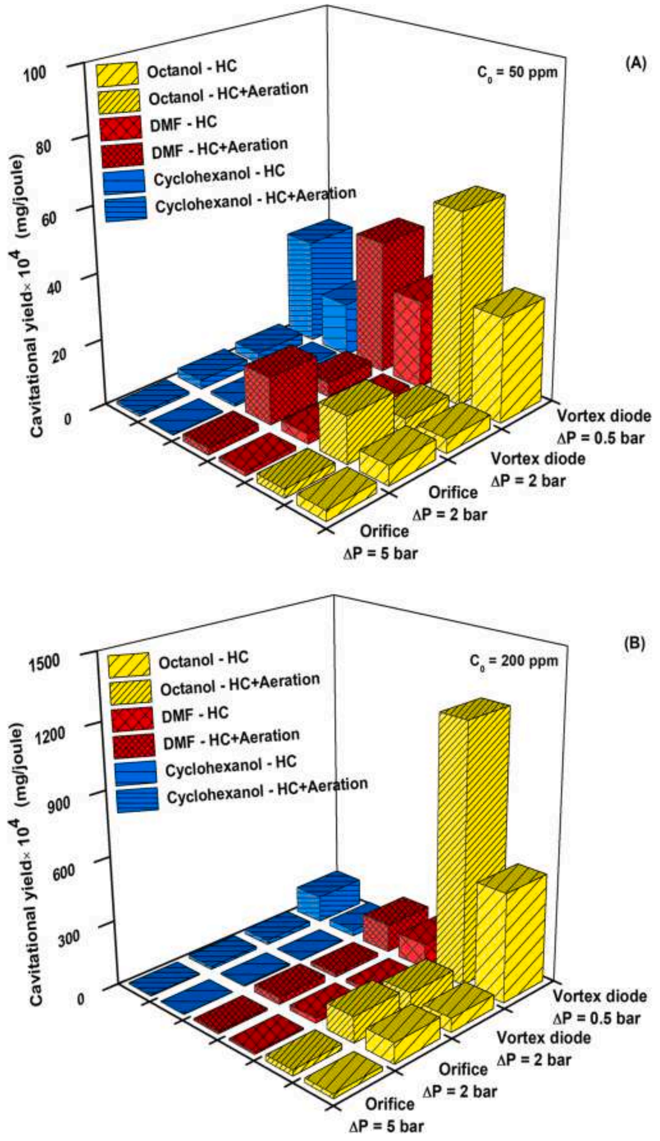

Fig. 9. Comparative analysis of cavitational yield with and without aeration (A) $C_0 = 50$ ppm, (B) $C_0 = 200$ ppm

3.6. Nature of solvent and effect of dielectric constant

The overall degradation depends on various factors such as molecular weight, molecular structure and size, polarity, pKa, vapour pressure (or boiling point), pH and reactivity (functional groups in the organic molecules) [3]. Since $^{\cdot}$OH radicals are very reactive, their life time is quite small. If organic pollutants have affinity towards vapour bubble, those pollutants will have better contact with $^{\cdot}$OH radicals. Volatile pollutant may also get vaporised in bubble and may thermally degrade (rather than degradation via $^{\cdot}$OH radicals). It is a quite complex mechanism and any simple relationship may not be deciphered at this point of time due to limited availability of data. Chakinala and co-workers could obtain only 58% degradation of phenol using hydrodynamic cavitation in 105 minutes and for the initial concentration of ~237 ppm [26]. Similarly, up to 54% degradation in 90 minutes was reported for degradation of p-nitrophenol [27]. Though the experimental processing and parameters were quite different in these studies, the important suggestion with regard to degradation was that higher degradation in p-nitrophenol could be attributed to its higher mass compared to phenol.

A rather unnoticed parameter so far, the dielectric constant of the solvents, appears to be an important parameter impacting solvent degradation and has not been seriously looked into in any of the previous studies. Higher values of dielectric constant indicate increased polarity. After comparing degradation of various solvents with dielectric constant, ε, values ranging from 2.4 to 40 and degradation using hydrodynamic cavitation, it was apparent that the solvents having low values of dielectric constant are prone to degradation compared to those solvents with higher values of dielectric constant (Fig. 10). Suryawanshi *et al.* [3] reported highest degradation to the extent of 78% for toluene (ε 2.38) in comparison with other two solvents MEK (ε 18.85) and acetone (ε 20.07) where degradation was only 29 and 27% respectively in 180 minutes. Similarly, Sarvothaman *et al.* [4] reported a high degradation efficiency of 80% in 240 minutes for ethyl acetate (ε 6.02) compared to acetone and IPA (ε 19.92). Therefore, solvents such as toluene, ethyl acetate and n-octanol with dielectric constant 10 or much lower can be relatively easily destroyed to an extent of 80%, whereas solvents such as DMF (ε 36.71) tend to yield degradation efficiency of only ~10% under similar conditions. Comparatively low degradation efficiency for cyclohexanol (ε 13.4) can be attributed to its aromatic nature and attached strong hydroxyl group, possibly providing resistance to degradation. The hypothesis suggested here appears to agree well with literature data on different solvent degradation [3,4]. It is to be noted that not many systematic studies on solvent degradation using hydrodynamic cavitation are reported in the literature. Use of limited data on various solvents including that from the present study, it can be stated that high degradation was possible for toluene, ethyl acetate and octanol solvents which have low dielectric constant values among other solvents studied so far. Since the cavitation mechanism is concerned with generation of cavities within the aqueous medium, in water having a high dielectric constant of 80, the nature of solvent species as pollutant moiety can be highly relevant apart from solvent being *protic* or *aprotic*. However, this effect of dielectric constant and that of aromatic structure or linear chain structure has not been systematically investigated and requires detailed study. Therefore, it can be only reaffirmed that the plausible mechanism of physical and chemical degradation may involve contribution of various complex interactions due to mass, structure and functional characteristics of the organic moiety.

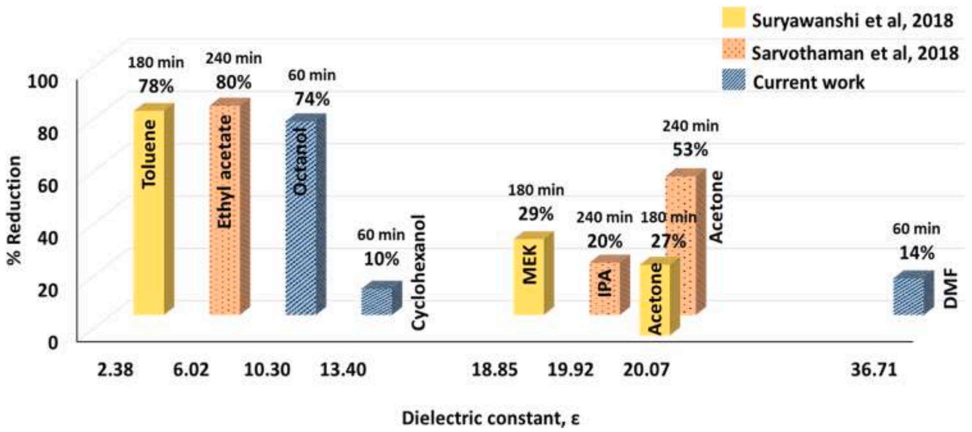

Fig. 10. Effect of solvent dielectric constant on degradation efficiency.

3.7. Cost analysis

Typically, the cost of treatment by hydrodynamic cavitation per unit volume of effluent can be calculated as [1],

$$\text{Cost of treatment per m}^3\text{ of effluent} = \frac{N_c \times \Delta P \times P_E}{36\eta} \tag{7}$$

Where, Nc is the number of passes, ΔP is pressure drop across cavitation device, P_E is cost of electricity and η is pump efficiency.

A representative cost analysis was carried for the degradation of various solvents to evaluate techno-economic feasibility of the technique. The cost of electricity in India was assumed at Rs. 10 /kWh (1$ = 70 Rs) and pump efficiency at 66%. Using the comparable levels of degradation and process conditions and for the best data of the present work- octanol; 0.5 bar and vortex diode, the cost of treatment is 4 Rs/m^3 (0.0571$/$m^3$), without aeration and 1.68 Rs/m^3 (0.024 $/$m^3$) by process intensification using aeration. The corresponding costs for orifice at ΔP of 2 bar are 17 and 14 Rs/m^3 (0.242 $/$m^3$) and (0.2 $/$m^3$), without and with aeration respectively. It is clear that treatment cost by using vortex diode is significantly lower compared to orifice showing rotational flow cavitation device is superior compared to linear flow device. While technical effectiveness and limitations of solvent degradation are evident from the results under different conditions, it is interesting to note that an order of magnitude, to the extent of 2-3 times reduction in the cost of treatment is possible using simple process intensification in the form of aeration and using suitable form of cavitation reactor.

4. Case study-Real Industrial Effluent from API Intermediate manufacturer

Industrial wastewater from API intermediate manufacturer having problem of high organics and colour in final stream of wastewater was procured from local industry. The initial TOC of sample was 257.8 ppm with light brown colour and total dissolved solids of ~60,000 mg/lit. The pH of sample was 6.72 with small concentration of solvents in wastewater. The sample was specifically tested for organics degradation and colour removal by hydrodynamic cavitation using vortex diode as cavitating device on pilot plant of capacity 1m^3/h and in combination with aeration and addition of hydrogen peroxide.

Initially sample was tested by using vortex diode at different pressure drops such as 0.5, 1 and 2 bar respectively. The combined approach of cavitation with aeration and cavitation with addition of hydrogen peroxide (1:10 ratio) with respect to initial concentration of effluent was investigated and the photographs reflecting treatment results are shown in Fig 11. The reduction in TOC was ~45% after prolonged treatment (HC followed by HC +aeration followed by HC+H_2O_2) of ~6 hours. The prolonged treatment required may be due to presence of various other organics-difficult to degrade type, metals such as Ni, Fe, and some inorganics such as sodium sulphate, sodium chloride which are found in final stream of effluent. The colour removal was less using only cavitation or cavitation coupled with aeration as compared to that using hydrogen peroxide where drastic colour removal was obtained. Further, no significant changes were found in pH or in suspended solids. The strategy and the results for the treatment of real industrial effluent clearly demonstrate efficacy of hydrodynamic cavitation with vortex diode as cavitating device along with process intensification- aeration and addition of oxidizing agent such as hydrogen peroxide for possible treatment of industrial effluent contaminated with organics and for colour removal.

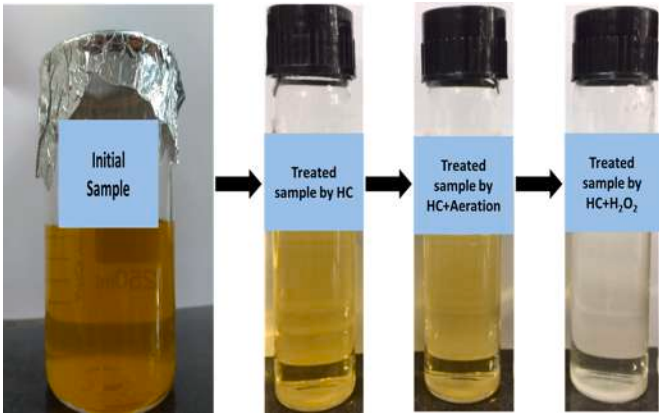

Fig. 11. Case study of real industrial wastewater treatment by hydrodynamic cavitation

5. Conclusion

The present study clearly underlined the differences in the degradation behaviour of the three solvents, octanol, DMF and cyclohexanol using hydrodynamic cavitation techniques due to nature of the solvent apart from highlighting differences due to reactor configurations- linear flow based and vortex flow based cavitation. Different forms of process intensifications were also successfully evaluated for increasing the efficiency of degradation. The important findings are:

1 The vortex flow in cavitation was found to offer superior performance (cavitational yield) compared to orifice- Low pressure drop conditions i.e. 0.5 bar for vortex diode and 2 bar for orifice were most effective in solvent degradation.

2 Process intensification in the form of aeration was highly effective in improving the degradation efficiency; only marginal improvement by addition of oxidizing agent such as hydrogen peroxide.
3 A reduction in TOC to the extent of 74% could be achieved for octanol (200 ppm) using aeration with cavitational yield of 1202×10^{-4} mg/J for vortex diode, yield ~10 times higher than that for orifice.
4 The degradation depends on the nature of solvent and it was revealed that low values of dielectric constant ($\varepsilon<10$) favour degradation.
5 The strategy for degradation was also confirmed to be useful for real effluent treatment.

The substantially low cost of solvent degradation indicates techno-economic feasibility in implementation of the hydrodynamic cavitation in industrial wastewater treatment. The presented results and approach will be useful for further investigations on effluent treatment of water contaminated by various solvents.

Author Contributions

V.M.B. and P. B. P conceived and developed the idea along with experimental methodology/result analysis. P.B.P. conducted all the experiments and analyzed the data. V.V.R. contributed to the review and suggestions. All three authors were involved in the preparation of the manuscript.

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. The authors (VMB and PBP) declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Intensified hydrodynamic cavitation using vortex flow based cavitating device for degradation of ciprofloxacin

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ABSTRACT

The present work, for the first time, establishes degradation behavior of ciprofloxacin (CIP), a widely used fluoroquinolone group of antibiotics, using vortex flow based hydrodynamic cavitation (HC) for low to high concentrations of CIP (10 and 100 mg/L). Effect of pressure on the degradation of CIP and TOC reduction was investigated on pilot plant scale (capacity 1 m^3/h). Process intensifications using aeration as well as hydrogen peroxide (H_2O_2) were also investigated. While aeration did not yield any significant enhancement, process intensification using H_2O_2 resulted in ~ 200% enhancement in the CIP degradation as compared to HC alone. Excellent degradations, to an extent of 79 & 95%, were achieved corresponding to high cavitational yields of 7.2×10^{-4} mg/J and 86.8×10^{-4} mg/J for CIP concentrations of 10 and 100 mg/L respectively using the process intensified approach of HC and H_2O_2, not reported so far for cavitating devices without moving elements. The developed methodology demonstrated 4–7 times improvement in per-pass degradation and low cost with high efficiency compared to the conventional cavitation. The results clearly highlight utility of the process intensified approach using H_2O_2 for the degradation of CIP even at high concentrations, specifically important for pharmaceutical industries requiring zero liquid discharge norms.

1. Introduction

In recent years, new emerging pollutants such as pharmaceuticals, in the form of active pharmaceutical ingredients (API), have been in the spotlight of the scientific community as they may cause significant human health and environmental side effects, even at low concentrations (ng/L to µg/L) (Alfonso-muniozguren et al., 2021; Deblonde et al., 2015). The usage of antibiotics, among the various pharmaceuticals, has been tremendously increased and as a result, their concentrations in wastewaters becoming a serious emerging environmental issue -either in the form of the parent compound or as metabolites in natural reservoirs including surface water, groundwater, as well as wastewater treatment plant effluent (Ahmed et al., 2015; Le-Minh et al., 2010). A majority of these compounds are recalcitrant or bio-refractory, in that they cannot be degraded using most of the conventional treatment methodologies (Zupanc et al., 2013). A much serious concern is in the form of wastewaters generated in the manufacturing plants involving significantly high concentrations of API pollutants, order of magnitude higher than those found in the commonly researched surface water streams having very low concentrations in µg/L. In

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Nomenclature

CIP	Ciprofloxacin.
C_0	Initial concentration, (mg/L or ppm).
C	Final concentration, (mg/L or ppm).
k	Rate constant, min^{-1}.
N_C	Number of passes required for treatment.
P	Pressure, bar.
P_E	Cost of electricity per kWh, Rs.
Q	Flow Rate, L/h.
t	Time, min.
V	Volume, L.
W	Energy dissipation rate, W.
Y	Cavitational yield, mg/J.
ϕ	Per-pass degradation factor.
ΔP	Pressure drop, bar.
η	Efficiency of the pump.

view of the stringent norms of zero liquid discharge for many of the pharmaceutical industries, it is imperative that suitable methodologies be evaluated for the treatment for wastewater streams containing high concentrations of API pollutants.

Ciprofloxacin (CIP) belongs to the fluoroquinolone group of antibiotics, which is widely used for the treatment of bacterial infections such as respiratory and urinary tract infections, skin, bone, and soft tissue infections. CIP has also been recommended drug by the World Health Organization (WHO) for the treatment of tuberculosis (Zhang et al., 2018; Patel, 2014). Additionally, the treatment of CIP has shown a strong potential for a possible cure against the coronavirus. These aspects lead to large manufacture and subsequent consumption of CIP, consequently leading to their exposure in natural reservoirs (Correia et al., 2017; Marciniec et al., 2020). In India, amongst all antibiotics, ciprofloxacin has been detected in raw wastewater in concentrations as high as 28–32 mg/L (Bhagat et al., 2020). From different case studies reported in the literature, the concentration of ciprofloxacin detected in hospital wastewater as 101 µg/L (Rodrigues-Silva et al., 2019), municipal wastewater around 1.265 µg/L (Chen et al., 2021), Brazilian hospital effluent around 65 µg/L (Martins et al., 2008), rural and urban hospital wastewater in Vietnam as 42.8 and 36.5 µg/L (Lien et al., 2016), respectively. Most of the earlier studies showed the occurrence of antibiotics in the range of ng/L to µg/L but due to massive consumption of antibiotics in recent years, the occurrence range in wastewater is expected to shift to a higher range of mg/L. As a consequence of the existence of antibiotics in general, and CIP, in particular, in the aquatic environment has raised concerns about antibiotic-resistant pathogens (Kummerer, 2003; Deng et al., 2019).

Conventionally, physical, chemical, biological methodologies are practiced for the removal of antibiotics from wastewater (de Ilurdoz et al., 2022). Although, adsorption can offer high removal, it has serious drawback in the form of adsorbent cost and secondary waste generation (He et al., 2020; de et al., 2014). Various studies have been reported on the degradation of ciprofloxacin from wastewater using different photocatalysts at different initial concentrations of ciprofloxacin (Wang et al., 2019, 2016; Mostafaloo et al., 2020; Olmez-Hanci and Arslan-Alaton, 2020). Recently, Z- scheme photocatalysis has being used for degradation of varieties of pollutants using solar light active Z-scheme (Hassani et al., 2021). Although photocatalysis can offer 100% degradation of ciprofloxacin, it requires very high operational as well as maintenance cost for its use at a commercial scale. Recently, ultrasound mediated electrochemical advanced oxidation processes (EAOPs) such as electrocoagulation, electro-Fenton, and electrooxidation have found increased attention among the many other water and wastewater treatment technologies (Hassani et al., 2022; Ghanbari et al., 2020).

Cavitation is one of the advanced oxidation processes (AOPs) which generates oxidizing species in-situ and is considered as a greener process that can be used for the treatment of wastewaters (Ranade and Bhandari, 2014). Few literature studies are reported on the use of ultrasound for degradation of ciprofloxacin (de Bel et al., 2011; Sutar and Rathod, 2015; Xiao et al., 2014) which have drawbacks of low cavitational yield, higher energy requirements, and high cost of operation. Hydrodynamic cavitation (HC) is found to be suitable in terms of cost, scale up, energy efficiency, and ease in operation as compared to acoustic cavitation for the degradation of complex pollutants present in wastewater. In the case of hydrodynamic cavitation, cavities get generated by varying pressure within the flow which can be achieved through geometric constrictions and are well discussed in the literature (Gogate and Pandit, 2004). The conventional reactor configurations in hydrodynamic cavitation are orifice, venturi, and high-speed rotor-stator assembly while vortex diode is comparatively a newer geometrical configuration. The application of vortex diode for the effluent treatment was suggested for mineralization of various pollutants along with the design of vortex diode (Ranade and Bhandari, 2014; Ranade et al., 2013; Pandare and Ranade, 2015). A typical design of vortex diode consists of a tangential inlet and axial outlet connected smoothly to the vortex chamber. The fluid enters through a tangential port at high pressures, forms vortex flow causing sudden pressure drop to such an extent that part of liquid flashes into vapor generating cavities, followed by cavity growth prior to their collapse. The collapse of the cavities or the implosion generates localized high temperature and pressure conditions, causing water to cleave homolytically generating active radicals such as H•, HO•, HOO•, and 2 O• the hydroxyl radicals being strong oxidizing species responsible for the oxidation of organic pollutants. Vortex diode is superior in terms of swirling flow, larger opening area- thereby less prone to clogging, less energy-intensive, and can offer much higher efficiency in the degradation of pollutants. Different studies were reported for the use of vortex diode in the degradation of pollutants such as dyes and solvents and also for successfully treating real industrial wastewaters for reduction in COD and ammoniacal nitrogen (Bhandari et al., 2016; Patil et al., 2021a, 2021b). However, no work has been reported yet on its application in the degradation of antibiotics. Recently, Mukherjee et al (Mukherjee et al., 2021). reported the use of a rotational hydrodynamic cavitating device for the degradation of ciprofloxacin at a very low initial concentration of 0.05 mg/L, which required high energy. A 45% CIP degradation was achieved in 60 min using only hydrodynamic cavitation whereas, intensified approaches of HC+O_3, HC+H_2O_2, and HC+Fenton resulted in 91.4%, 85.6%, and 87.6% degradation within 30 min. The pharmaceutical industries require treating wastewater streams containing higher concentrations of API pollutants. Hence, there is a need for developing a sustainable methodology for the degradation of these persistence classes of organic pollutants from wastewaters at different levels of concentrations and different points of effluent release.

The present study, for the first time, reports the degradation of ciprofloxacin antibiotic using hydrodynamic cavitation by vortex flow-based vortex diode as a cavitating device over a wide range of concentration, from low (10 mg/L) initial concentrations of ciprofloxacin to comparatively high (100 mg/L) concentration. Systematic studies were carried out to evaluate the effects of various process parameters such as pressure drop across the device, initial concentration of pollutant (ciprofloxacin), as well as process intensification by aeration, and by addition of hydrogen peroxide. The degradation kinetics and cavitational yields were evaluated using the per-pass degradation model. The results of this work, effects of process intensifications, especially that for high degradation efficiency and practically completely mineralization without intermediates can be highly useful for devising an effective effluent treatment strategy for industry and wastewater treatment practices.

2. Materials and methods

2.1. Materials

Ciprofloxacin ($C_{17}H_{18}FN_3O_3 > 98\%$, MW 367.80 g/mol), anhydrous, in crystalline powder form was procured from Sisco Research Laboratory Pvt. Ltd., Mumbai. Hydrogen peroxide (30% w/v, AR grade) was purchased from MOLYCHEM, Mumbai. Acetonitrile (≥99.9%, HPLC grade) was procured from Avantor Performance Materials India Limited. Formic acid (≥99.9%, HPLC grade) was purchased from Loba Chemie Pvt. Ltd.

2.2. Methodology

All the experiments were carried out using a hydrodynamic cavitation pilot plant, capacity 1 m^3/h, with vortex diode as a cavitating device. A cylindrical vertical recirculation tank with the conical bottom of the working capacity of 25 L was employed for the wastewater holding and a vertical multistage centrifugal pump (Model CNP make CDLF2–6, SS316, 2 m^3/h at 45 MWC), rating 0.75 kW (1 hp), 2900 RPM, discharge pressure 0–5 bar) was used for pumping the liquid with flow control. The line connecting to the suction of the centrifugal pump from the bottom of the recirculation tank is equipped with Y-type strainer (CF 8 M, ACME Engineering Production Corporation). Seamless SS316 tubing of size 0.75inch OD is used for the process fluid flow. Flow transmitter (KRONE, H250) with analog display, range 150–1500 LPH was used to measure the mainline flow rate while the temperature was measured using RTD (EUREKA Eng. Enterprises India; 0–200 °C), fitted at downstream of cavitation reactor, inserted into recirculation tank. The cavitating device used in the present study was a vortex diode (Chamber diameter 66 mm, Throat diameter 11 mm, SS316) operated in reverse flow mode. A cooling coil (SS316) was provided into the recirculation tank for temperature control of the system. Horner make, HMI display is used for data logging with the provision of a sim card to access data from any location. The whole assembly is mounted on CS powder-coated skid with adjustable wheels for portability. The schematic representation and actual photograph of the experimental setup were reported in our earlier work (Patil and Bhandari, 2022).

In view of the limited information for treatment methodologies employing higher concentrations and also for the relevance to industry, the degradation studies of ciprofloxacin using vortex diode as a cavitating device were carried out using synthetic wastewater for two initial concentrations of ciprofloxacin-10 and 100 mg/L.

Based on the inception of cavitation for vortex diode at ~0.48 bar (Suryawanshi et al., 2016), the effect of pressure drop on ciprofloxacin degradation was studied for different pressure conditions such as ΔP as 0.5, 1, 1.5, and 2 bar for both the initial concentrations of ciprofloxacin (10 and 100 mg/L). Process intensification using aeration was studied by bubbling air in the tank, employing an air pump (SOBO AQUARIUM SB-9905, 2 Nozzle, 4.2 W, Max. 5.5 L/min × two output); aeration by inserting a tube (SS316) into the recirculating tank from the top. The other process intensification approach involves the combination of HC and H_2O_2 using different molar ratios of CIP: H_2O_2 as 1:100, 1:300, 1:500, 1:700, 1:1000, and 1:1500 for both the initial concentrations of 10 mg/L as well as 100 mg/L. All the experiments were conducted for 180 min and the sample was withdrawn periodically, 30 min intervals, for the degradation monitoring. The pH of wastewater before and after treatment was in the range of 6.6–7.8 with only a minor change observed during the experiment.

2.3. Analysis

The degradation of CIP was monitored by measuring Total organic carbon (TOC, SHIMADZU make, TOC-L series TOC analyzer) and also by High Performance Liquid Chromatography (HPLC, Agilent, 1260 infinity series, C-18 column (4.6 ×250 mm)). A mobile phase of acetonitrile (80%) and 0.1% formic acid in deionized water (DI) (20%) was used as an eluent for the separation under reverse-phase conditions at a flow rate of 0.8 mL/min. Detection of CIP was performed at a wavelength of 280 nm. The standard calibration graph was plotted for CIP (R^2 value = 0.99) for estimation of unknown CIP concentration during the treatment. The by-products formed during the degradation of CIP were identified using liquid chromatography–mass spectroscopy (LC–MS) technique.

3. Results and discussion

3.1. Effect of pressure drop on degradation kinetics of CIP

The pressure drop across the cavitation device is an important parameter that determines the efficiency of the treatment. In any cavitating device, the cavitation regime can be confirmed by identifying cavitation inception point. It was observed that the inception of cavitation occurs at 0.48 bar for vortex diode (Suryawanshi et al., 2016), also confirmed by another independent studies (Ranade et al., 2021). Thus, HC reactor was operated in the cavitation regime. Recently, the formation of OH radicals was reported using a terephthalic acid photoluminescence approach (Eghbali et al., 2019).

Four different pressure drop conditions were selected such as ΔP of 0.5, 1, 1.5, and 2 bar to evaluate the degradation efficiency at low and high concentrations of CIP. It was ensured that the process is operated in the cavitation regime. For a lower concentration of CIP (C_0 = 10 mg/L), the highest TOC reduction of 35% was obtained at ΔP of 1 bar while at a

Table 1 – TOC reduction and rate constant data for CIP using vortex diode.

Concentration, C_0 (mg/L)	ΔP, Bar	% TOC reduction after 180 min	1^{st} order rate constant, K × 10^3 (min^{-1})
10	0.5	21	1.3
	1	35	2.6
	1.5	27	1.7
	2	18	1.1
100	0.5	13	0.8
	1	16	1.1
	1.5	8	0.5
	2	6	0.4

higher concentration of CIP (C_0 = 100 mg/L), about 16% TOC reduction was obtained after 180 min. The values for % TOC reduction for different pressure drop conditions at low and high CIP concentrations are given in Table 1. Based on the values of TOC reduction at different pressure drops, ΔP of 1 bar condition was considered as an optimum pressure drop condition for both high and low CIP concentrations and was considered for further studies.

The pressure drop and OH radical formation are related to the geometrical design of the vortex diode. Typically, the intensity of cavitation is important for the degradation of pollutants and certainly the nature of pollutant has crucial role apart from the geometry of the reactor. While the mechanism of degradation is essentially the same in different reactor configurations, the requirement of pressures for different configurations is quite different for effecting similar levels of degradation and here the performance of vortex diode, as a cavitating device requiring comparatively lower pressure drop compared to other conventional devices such as orifice or venturi (Ranade and Bhandari, 2014; Dixit et al., 2022). It was also seen that the optimum value of pressure drop is different for different types of pollutants which necessities a detailed investigations related to the optimization of pressure drop for the selected pollutants.

The lower pressure drop requirement for vortex diode is in agreement to that reported in previous studies (Patil et al., 2021a, 2021b), compared to the conventional devices such as orifice, venturi, etc. Also, from earlier literature reports, it is evident that the optimum value of pressure drop required is different for different pollutants which justifies the optimization study of pressure drop for the selected pollutant to achieve a high extent of degradation.

The reactions pertaining to the degradation in hydrodynamic cavitation can be assumed as pseudo first order and kinetics of CIP degradation can be evaluated using simple power law model which is given below,

$$C = C_0 e^{-kt} \quad (1)$$

Where, C_0 and C represent CIP concentrations before and after treatment, ‘t’ is time (min) and ‘k’ is first order rate constant (min^{-1}).

The rate constants values are given in Table 1 for both low and high concentrations of CIP using vortex diode as a cavitating device. It was observed that high values of rate constants were obtained at ΔP 1 bar as 2.6×10^{-3} (min^{-1}), 1.1×10^{-3} (min^{-1}) at CIP concentrations of 10 and 100 mg/L respectively. It is evident that the degradation rate is quite higher at a lower concentration of CIP than that at a higher concentration. The decrease in the degradation rate with an increase in the pollutant concentration can be attributed to similar concentration availability of generated OH radicals for low and high pollutant concentrations. The results are consistent with many literature reports on the decrease in degradation with an increase in pollutant concentration (Suryawanshi et al., 2018; Thanekar et al., 2018a; Sivakumar et al., 2002; Rajoriya et al., 2017). Suryawanshi et al (Suryawanshi et al., 2018). reported higher COD removal at lower initial concentrations for degradation of solvents using cavitation for acetone, methyl ethyl ketone, and toluene in the range of 100–500 ppm. Similarly, decreased rate constant from 2.2×10^{-3} min^{-1} to 1.3×10^{-3} min^{-1} was observed for an increase in the initial concentration of dichlorvos from 10 to 50 ppm (Thanekar et al., 2018a). Rajoriya (Rajoriya et al., 2017) also observed similar trend for degradation of reactive blue 13 dye using cavitation and reported decrease in % decolorization from 47% to 19% with an increase in the initial concentration of dye from 30 to 60 ppm. In the present work also, %TOC reduction was higher at low CIP concentration than that obtained at high concentration. It should be noted that though the percentage degradation decreases with an increase in the initial concentration, the actual amount of the pollutant removed is higher at higher initial concentrations.

3.2. *Effect of aeration*

Aeration is one of the simplest forms of process intensification in hydrodynamic cavitation, where air can be introduced into the fluid, through simple bubbling to a sparger design. In this work, a simple form of bubbling air using a tube inserted in the holding tank fluid was used. The design of the holding tank incorporates inclined return/recycle of water dipped in pool of water to ensure intense mixing/ turbulence in the tank. An optimized pressure drop of ΔP of 1 bar was employed for comparison of the results of process intensification. At CIP concentration of 10 mg/L, about 16% TOC reduction and 6% CIP degradation were obtained after 180 min of treatment time whereas, at CIP concentration of 100 mg/L about 7% TOC reduction and 24% CIP degradation were obtained. Thus, cavitation coupled with aeration for CIP degradation showed only marginal improvements, especially for the CIP degradation. The synergistic coefficient in aeration was calculated by using a formula,

$$\text{Synergistic coefficient} = \frac{k_{(HC+Aeration)}}{k_{HC} + k_{Aeration}} \quad (2)$$

The values of synergistic coefficient obtained for low concentration of 10 mg/L and high concentration of 100 mg/L were less than one (0.23 and 0.30 respectively). The results indicate no synergism for the intensified approach of aeration for both low and high initial concentrations of CIP degradation. The process intensification in the form of aeration using hydrodynamic cavitation was earlier reported for ammoniacal nitrogen removal (Patil et al., 2021b) and solvent degradation (Patil et al., 2021a). It is conventionally believed that the process intensification in the form of aeration may provide additional nuclei thereby positively impacting the formation of more oxidizing species and consequently resulting in fruitful collapse with more degradation of pollutants in wastewater. The effects of aeration in the different studies reported in the literature for different pollutants were not consistent and while enhancement in the degradation due to aeration was reported in some studies because of increased oxidation due to air/oxygen, negligible effect of aeration was also reported in some studies (Patil et al., 2021a; Joshi and Gogate, 2019). Further, when significant enhancement in degradation due to the addition of oxygen was reported, the same was not observed with aeration (Joshi and Gogate, 2019; Rajoriya et al., 2018). The negative effect of aeration observed in the present study can be attributed to possible effects other than oxidation, such as physical carryover of the cavities that can reduce the cavitational effect.

3.3. *Process intensification using the addition of H_2O_2*

Hydrogen peroxide (H_2O_2) is a strong oxidizing agent and commonly used form of process intensification along with hydrodynamic cavitation for degradation of API pollutants (Thanekar et al., 2020, 2018b)·H_2O_2 on decomposition yields only water and oxygen. Hydrodynamic cavitation along with hydrogen peroxide provides additional oxidizing species which further enhances the degradation of pollutants. The hybrid approach of cavitation with the addition of hydrogen peroxide was studied at different loadings of H_2O_2 using the molar ratios of CIP: H_2O_2 as 1:100, 1:300, 1:500, 1:700, 1:1000, and 1:1500. The extent of CIP degradation obtained for the different molar ratios is shown in Fig. 1. To evaluate the combined effect of hydrodynamic cavitation with the addition of H_2O_2 for CIP degradation, synergistic coefficient was calculated by using the formula as,

$$\text{Synergistic coefficient} = \frac{k_{(HC+H_2O_2)}}{k_{HC} + k_{H_2O_2}} \tag{3}$$

At an initial CIP concentration of 10 mg/L, cavitation alone shows about 21% CIP degradation with 6% TOC reduction after 180 min while when the hydrodynamic cavitation is coupled with H_2O_2, the extent of CIP degradation was 80% at a molar ratio of CIP: H_2O_2 as 1:1000. Similarly, at a CIP concentration of 100 mg/L cavitation alone gave about 56% CIP degradation with 16% TOC reduction after 180 min while when cavitation is coupled with H_2O_2 the extent of CIP degradation was 95% at a molar ratio of CIP: H_2O_2 as 1:1000. The highest CIP degradation was obtained for 1:1000 molar ratio H_2O_2 addition for both low and high concentrations with synergistic coefficient values of 2.8 and 2.6 respectively. A comparative analysis of CIP degradation is shown in Fig. 2. Fig. 2 represents a comparative analysis of cavitation alone with a combination of HC+ H_2O_2. Low CIP concentration of 10 mg/L, cavitation alone results in mineralization (interpreted in the form of higher TOC reduction) whereas, in the case of HC+ H_2O_2, the extent of CIP degradation was observed to be higher as compared to mineralization. It can be seen that the extent of CIP degradation, as well as TOC reduction, is comparatively more at high concentration (100 mg/L) as compared to that with low CIP concentration (10 mg/L). This can be attributed to the fact that the process follows the reactive pathway where the reaction rate is dependent on the concentration of the species (here pollutant); the more the concentration of the species, the higher is the reaction rate.

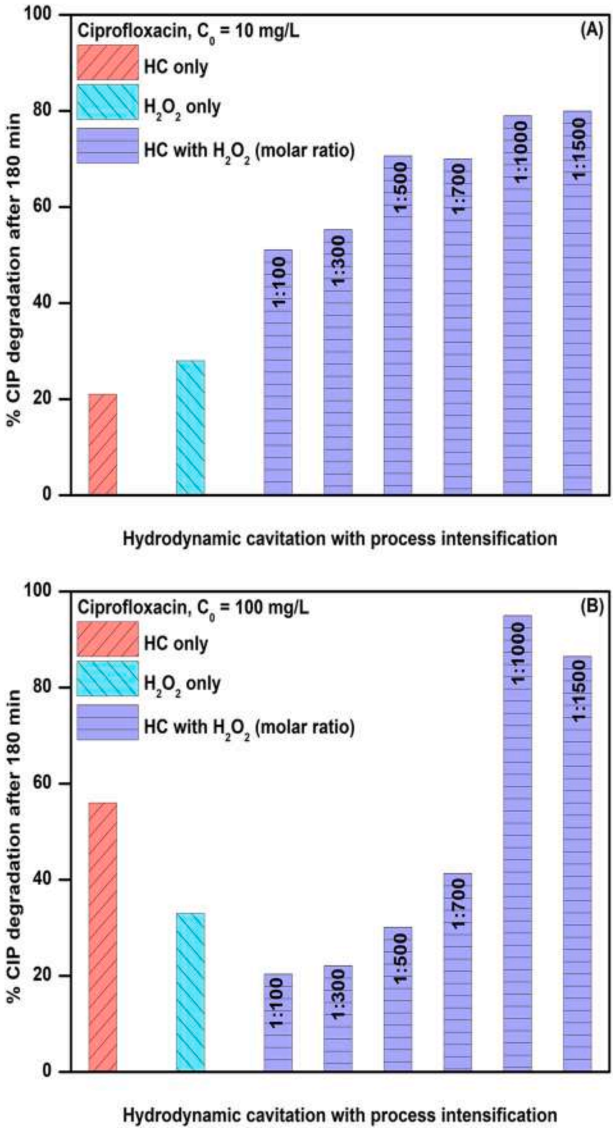


Fig. 1 – Hybrid cavitation with the addition of H_2O_2, A. 10 mg/L, B. 100 mg/L.

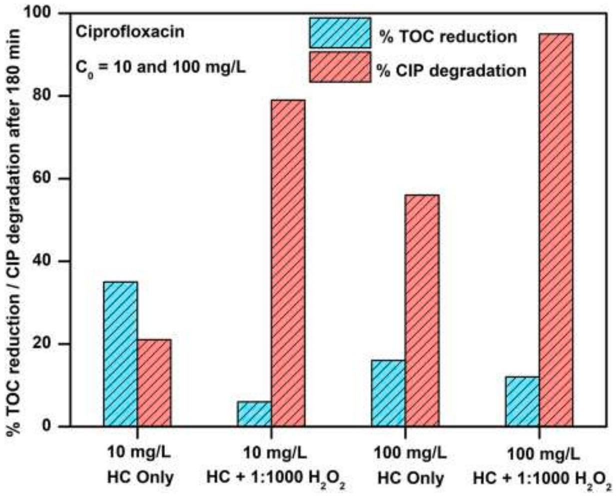
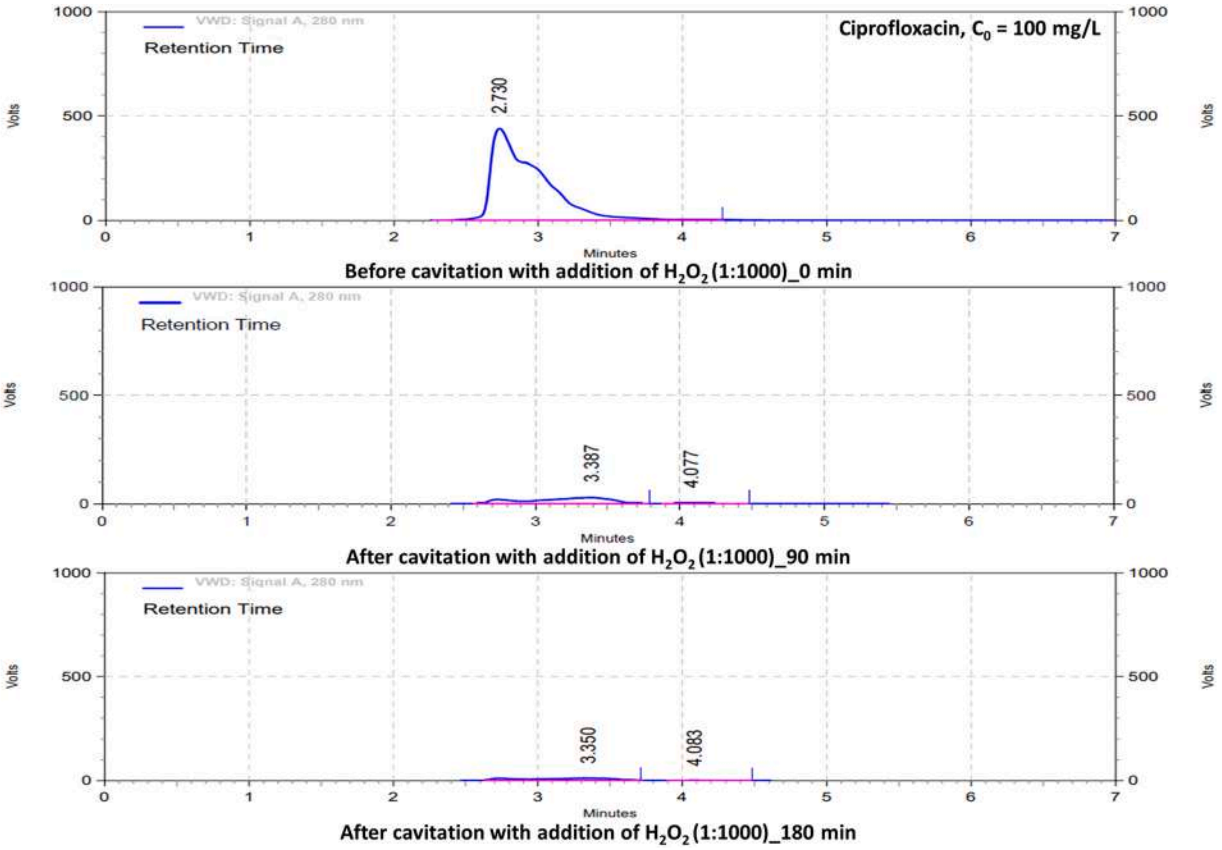


Fig. 2 – Evaluating effect of optimum H_2O_2 dosing on CIP degradation.

Fig. 3 depicts HPLC spectra for degradation of CIP using a combined approach of HC+ H_2O_2 at a molar ratio of CIP: H_2O_2 as 1:1000. It can be seen that not many prominent intermediates peaks were detected for the combined HC+ H_2O_2 approach and intermediates get eventually degraded. The findings are quite interesting and form advantage for the proposed hybrid hydrodynamic cavitation technology since the photooxidation studies reveal formation of many intermediates. Supplementary Table-1 summarizes the advanced oxidation processes reported in the literature to highlight the importance of the results of this work.



Before cavitation with addition of H_2O_2 (1:1000)_0 min

After cavitation with addition of H_2O_2 (1:1000)_90 min

After cavitation with addition of H_2O_2 (1:1000)_180 min

Fig. 3 – HPLC spectra for CIP degradation (C_0 = 100 mg/L) for hybrid cavitation.

3.4. *CIP degradation mechanism*

A high extent of degradations of CIP were achieved when the hydrodynamic cavitation is coupled with H_2O_2 for both lower and higher concentrations. In view of HPLC analysis (Fig. 3) indicating not many prominent intermediates, it is instructive to investigate degradation mechanism and intermediates evaluation, using LC-MS analysis. Fig. 4 shows LC-MS spectra for the treated sample of CIP degradation using HC+ H_2O_2 after 180 min of treatment time at CIP concentration of 100 mg/L. LC-MS analysis shows two prominent peaks at *m/z* 214.91, and 102.12. The likely intermediates could be 1-cyclopropyl-1,4-dihydroquinoline-3-carboxylic acid (*m/z* 214.91) and 4-hydroxypiperidin-1-ium (*m/z* 102.12). The analysis confirms that the hybrid approach of hydrodynamic cavitation with addition of hydrogen peroxide produces very few intermediates and that may also get degraded eventually with extended treatment time. Based on the analysis, the mechanism can be postulated and is shown in Fig. 5 for process intensification approach of hydrogen peroxide.

3.5. *Per-pass degradation factor and cavitational yield for ciprofloxacin degradation*

The conventional kinetics/ rate analysis is done typically using the power-law model. However, the recent approach which is based on the number of passes required for degradation closely resembles physicochemical behavior in the hydrodynamic cavitation process and is, therefore, most appropriate, especially at a larger scale of operation (Patil et al., 2021a, 2021b; Jain et al., 2019; Mane et al., 2020a, 2020b; Sarvothaman et al., 2018). The per-pass degradation factor is defined as,

$$\text{Per-pass degradation factor } (\phi) = k\tau \tag{4}$$

Where, τ is residence time which is a ratio of volume of the holding tank and the flow rate.

The energy dissipation rate is calculated as,

$$W = \Delta P \times Q \tag{5}$$

The overall cavitational yield (amount of CIP degraded per unit energy dissipation) can be calculated as,

$$Y = \frac{V\,(c_0 - c)}{\Delta PQt}\,\text{mg/J} \tag{6}$$

Where, Y= cavitational yield, V= volume, C_0 and C= initial and final concentration of pollutant.

Fig. 6 represents the enhancement due to hybrid approach for the per-pass degradation factors as well as cavitation yield under different conditions such as hydrodynamic cavitation alone, and hybrid hydrodynamic cavitation with the addition of H_2O_2 (1:1000 molar ratio) for different CIP concentrations. It can be seen that the per-pass degradation factor is high at a high CIP concentration of 100 mg/L. The hybrid approach of hydrodynamic cavitation using vortex diode at ΔP 1 bar with the addition of H_2O_2 (1:1000 molar ratio) showed a very high enhancement in per-pass degradation factor for low concentration (566% enhancement) as compared to high concentration (283% enhancement).

The values of cavitation yield at 10 mg/L initial concentration of CIP using hydrodynamic cavitation alone, and hydrodynamic cavitation with the addition of H_2O_2 (1:1000 molar ratio) are 1.9×10^{-4} mg/J, and 7.2×10^{-4} mg/J

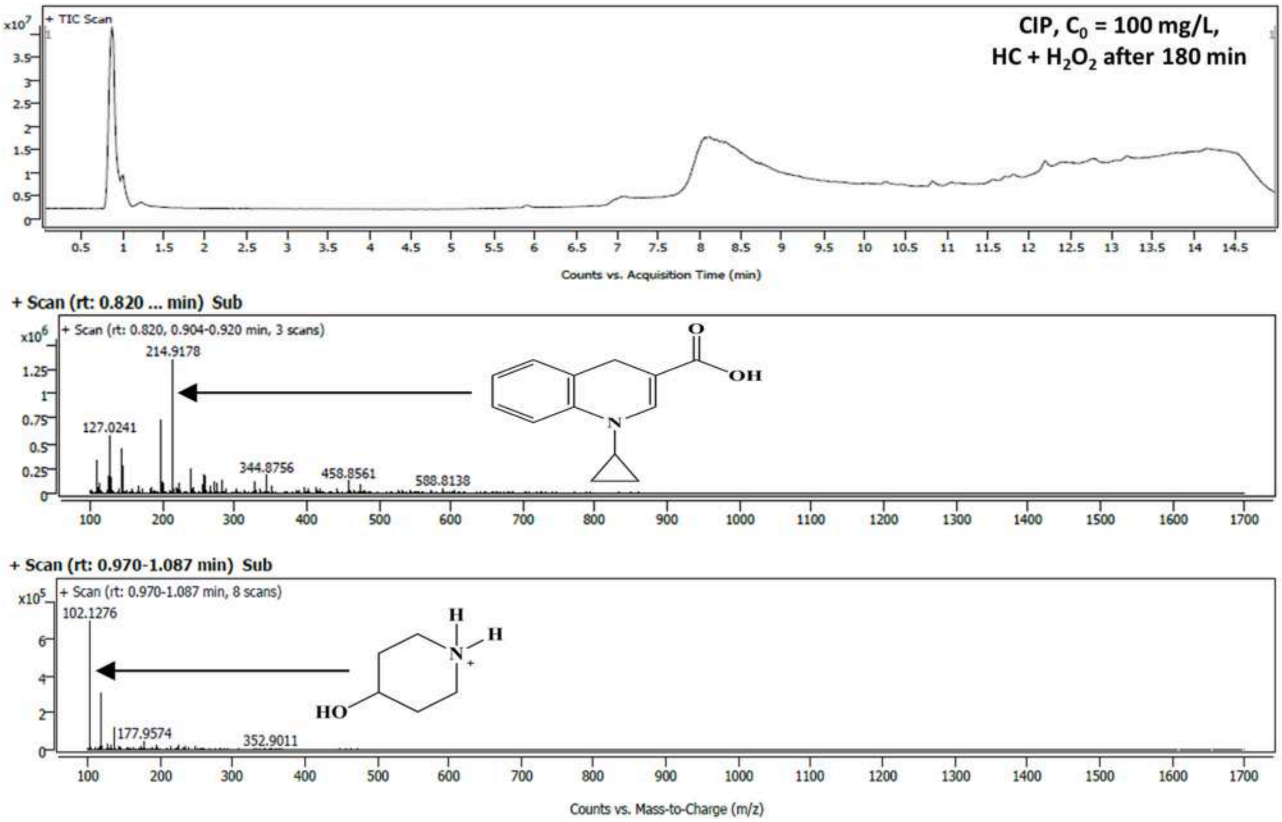


Fig. 4 – CIP degradation by products by LC-MS spectra for hybrid cavitation.

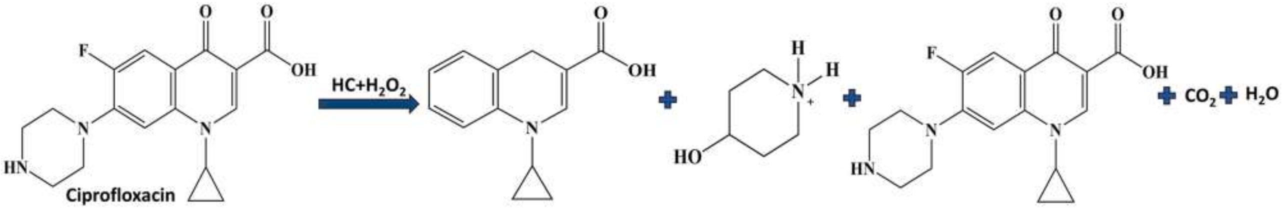


Fig. 5 – CIP degradation mechanism for hybrid treatment approach.

respectively. Similarly, for a high concentration of 100 mg/L CIP concentration, the values for cavitational yield are 48.5×10^{-4} mg/J, and 86.8×10^{-4} mg/J using hydrodynamic cavitation alone, and hydrodynamic cavitation with the addition of H_2O_2 (1:1000 molar ratio) respectively. From the results, it is evident that the hybrid method is superior to the single method in terms of cavitational yield for both low (~ 4 times) and high concentrations of CIP (~ 2 times). The enhancement here can be attributed to the enhanced generation of hydroxyl radicals due to H_2O_2.

Mukherjee et al (Mukherjee et al., 2021). reported cavitational yield obtained for ciprofloxacin degradation using a rotational hydrodynamic cavitating device, where the cavitational yields obtained for different approaches such as cavitation alone, HC+ H_2O_2, HC+ Fenton's reagent, and HC+O_3 were 2.9×10^{-7}, 5.6×10^{-7}, 5.7×10^{-7}, and 6.1×10^{-7} mg/J, respectively. The reported values were significantly lower (~650– 14,000 times) as compared with the cavitational yield obtained in the present work. The rotational hydrodynamic cavitation reactors require operation at a very high speed (~ 3000 RPM), thus are energy-intensive as compared to vortex diode. The values for cavitational yield in the case of vortex diode for HC alone were in the range of 1.9×10^{-4} mg/J to 48.5×10^{-4} mg/J; for intensified approach of HC+H_2O_2, in the range of 7.2×10^{-4} mg/J to 86.8×10^{-4} mg/J for 10–100 mg/L initial CIP concentration, clearly represent significantly higher efficiency of the vortex diode and therefore, utility of vortex based cavitation in the degradation of CIP. Thus, hydrodynamic cavitation using vortex diode as a cavitating device can be considered to be the most energy efficient alternative for the degradation of ciprofloxacin.

3.6. *Cost analysis*

The cost of the process, hydrodynamic cavitation using vortex diode as cavitating device, for %CIP degradation can be calculated as (Ranade and Bhandari, 2014),

$$\text{Cost of treatment per m}^3\text{ of effluent} = \frac{N_c \times \Delta P \times P_E}{36\eta} \tag{7}$$

Where, Nc is the number of passes, ΔP is pressure drop across cavitation device, P_E is the cost of electricity and η is pump efficiency.

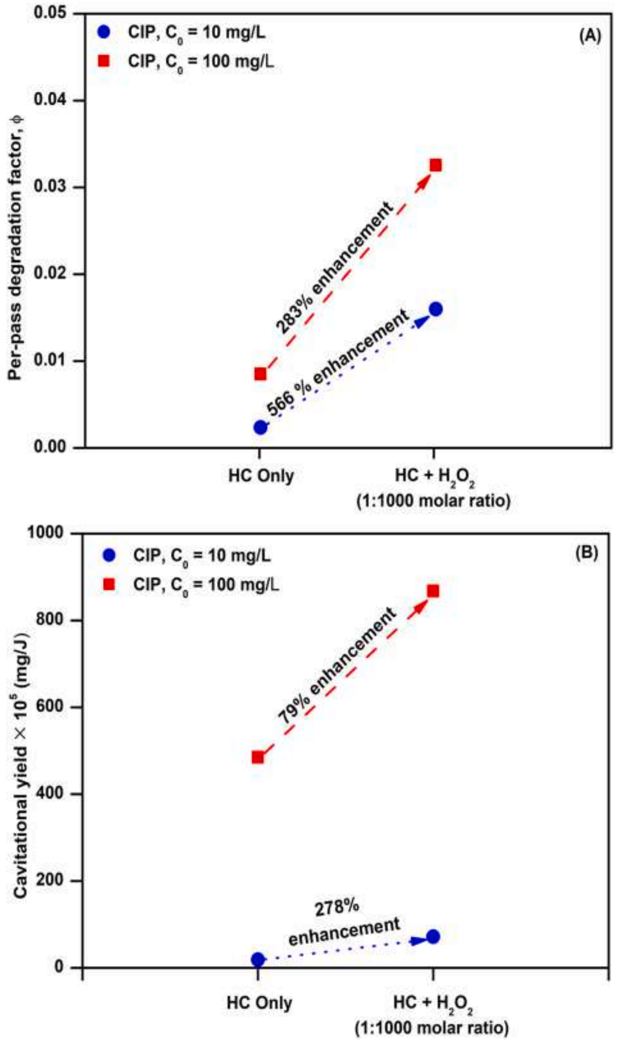


Fig. 6 – Per-pass degradation and cavitational yield for different methodologies A. 10 mg/L, B. 100 mg/L.

The techno-economic feasibility was evaluated under typical Indian conditions. The cost of electricity for the Indian scenario was assumed as Rs. 10 /kWh (1$ = 75 Rs) and pump efficiency is assumed as 66%. The total cost obtained using only hydrodynamic cavitation was 41 Rs/m^3 (0.546 \$/m^3) (22 Rs/gm) for concentration of CIP as 10 mg/L whereas, the corresponding cost for 100 mg/L concentration was 0.9 Rs/gm, substantial reduction due to the effect of concentration. The total cost obtained for the process intensification approach using H_2O_2, was 38 Rs/m^3 (~0.5 \$/m^3) (~8 Rs/gm) for 10 mg/L CIP concentration whereas, for 100 mg/L CIP concentration, the cost of the treatment was ~3 Rs/gm under optimized conditions. The detailed calculation has been given in Appendix-I. The cost of treatment per unit weight of the pollutant is substantially less for the intensified approach due to significantly reduced number of passes and also due to the increased degradation of the pollutant, although, the cost can vary if the number of passes or the cost of additives get increased.

4. Conclusions

The present study successfully demonstrates near complete degradation of antibiotic ciprofloxacin using vortex flow-based cavitation device at low and high concentrations of CIP up to 100 mg/L. The process intensification using H_2O_2 could provide more than 95% degradation, very insignificant formation of intermediates compared to reported catalytic degradations, and a more predominant mineralization pathway. The important findings are listed below,

1. The present study, for the first time, demonstrated the use of vortex flow-based cavitation for antibiotics degradation.
2. The optimum pressure drop for CIP degradation was very low, 1 bar, for low to high initial CIP concentrations.
3. Vortex diode as a cavitating device, ΔP of 1 bar, low CIP concentration of 10 mg/L gave about 21% CIP degradation with 35% TOC reduction whereas, at high CIP concentration of 100 mg/L, 56% CIP degradation with 16% TOC reduction were obtained.
4. Process intensification using the addition of hydrogen peroxide showed significant enhancement in degradation compared to only a marginal improvement for intensification using aeration.
5. For the combined approach of HC+H_2O_2, CIP degradations of 79% and 95% were achieved at CIP concentrations of 10 and 100 mg/L respectively.
6. The cavitational yield for the combined approach of HC+H_2O_2 was higher (86.8×10^{-4} mg/J) as compared to that obtained for HC alone (48.5×10^{-4} mg/J) at 100 mg/L initial concentration of CIP.
7. Per-pass degradation model showed about 4–7 times improvement in per-pass degradation for cavitation with the addition of H_2O_2 (1:1000 molar ratio) as compared to the conventional hydrodynamic cavitation.
8. A reasonably low cost of treatment along with high efficiency can be achieved using hybrid cavitation with H_2O_2 as compared to the cavitation alone.

The effective use of the vortex based cavitating device in hydrodynamic cavitation and process intensification using H_2O_2 at comparatively high antibiotic loading with substantially low cost clearly highlights the techno-economic feasibility in implementing the strategy for the degradation of antibiotics.

CRediT authorship contribution statement

V.M.B. and P.B.P. conceived and developed the idea along with experimental methodology/result analysis. P.B.P. conducted all the experiments and analyzed the data. P.T. contributed to the analysis of the results. All the authors were involved in the preparation of the manuscript.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix-I

Sample cost calculation

$$\text{Cost of treatment per m}^3\text{ of effluent} = \frac{N_c \times \Delta P \times P_E}{36\eta}$$

Where, N_c = number of passes; ΔP = pressure drop; P_E = cost of electricity.

Cost of electricity assumed for Indian scenario as Rs 10 /KWh (1$ = 75 Rs).

The pump efficiency η is assumed 66% considering commercial flow rates (above 10 m^3/h).

For initial concentration of CIP= 10 mg/L.

CIP degradation (21%) using only HC approach.

Pressure drop, ΔP = 1 bar, C_0 = 10 mg/L, Treatment time 180 min, No of passes= 97

$$\text{Total Cost of treatment per m}^3\text{ of effluent} = \frac{97 \times 1 \times 10}{36 \times 0.66}$$

= Rs 41/m^3 ~ Rs.22 /gm.

CIP degradation corresponding to HC using hybrid HC+ H_2O_2 approach.

Pressure drop, ΔP = 1 bar, C_0 = 10 mg/L, Treatment time 180 min, No of passes= 24.

Cost of H_2O_2 (30%) = 30 Rs/L.

Cost of additives (H_2O_2) for C_0 = 10 mg/L (1:1000 molar ratio).

Total quantity of H_2O_2 required for 1 m^3 = 0.92 L.

Total Cost of treatment per m^3 of effluent = $\frac{24 \times 1 \times 10}{36 \times 0.66}$ + Cost of H_2O_2.

= Rs 38 /m^3 ~ Rs.8 /gm.

Appendix B. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.cherd.2022.09.027.

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Article

A Strategy for Complete Degradation of Metformin Using Vortex-Based Hydrodynamic Cavitation

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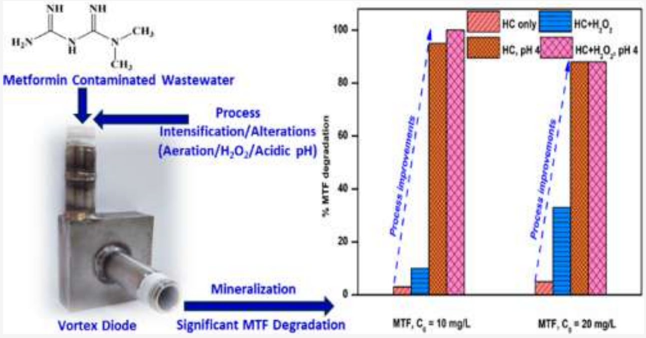
ABSTRACT: The present work successfully establishes the degradation of metformin, an antidiabetic drug, using vortex flow-based hydrodynamic cavitation (HC) and process intensification. Studies were carried out on a pilot plant (1 m^3/h) and for high initial concentrations, 10−20 mg/L. Effects of intensifications using aeration and the addition of hydrogen peroxide on various process parameters were evaluated. A low degradation (3−5%) by HC at ΔP of 1 bar could be improved by process intensification using hydrogen peroxide (33%). Importantly, a very high 95% metformin degradation was obtained at pH 4 with excellent cavitational yields up to 162 × 10^{-5} mg/J, further extending to 100% the degradation using HC+H_2O_2, an order of magnitude enhancement of 900%. The synergy can be drastically enhanced by process modifications. Per pass degradation enhancement was huge, 100 times, corresponding to an order of magnitude cost reduction compared to conventional hydrodynamic cavitation. The established strategy can have positive implications for industrial wastewater treatment.



1. INTRODUCTION

Thousands of tons of pharmaceutical and personal care products are being produced worldwide since use of these in different forms has now become part of a modern lifestyle. Their daily use increases the demand for the synthesis of active pharmaceutical ingredients (API) and consequently increases their release in the environment in the form of API pollutants.[1−3] Most of these API pollutants are emerging contaminants causing grave environmental concerns. In recent years, the presence of API pollutants is considerable in every water matrix such as groundwater, surface water, seawater, drinking water, and wastewater (influent and effluent).[1,4] In general, the order for the occurrence of API pollutants in relative concentrations in the environment is industrial wastewater > hospital wastewater > surface water > groundwater > drinking water.[5] The surface water bodies typically have subppm levels of concentrations while the industrial wastewater streams before treatment can have significantly higher concentrations, typically in tens of ppm. Thus, the methodologies for treating different wastewaters have a varying mandate in terms of initial concentrations of the pollutants. The major route for the presence of API pollutants in the environment is the discharge of wastewaters from many pharmaceutical industries due to a lack of efficient and cost-effective treatment methodologies; the persistent to pseudo-persistent nature of the pollutants reflects the difficulty of their complete destruction by conventional treatment methodologies,[6,7] and highlights the need of an effective treatment of API pollutants.

Metformin ($C_4H_{11}N_5$) abbreviated hereinafter as MTF, is an antihyperglycemic drug and is often prescribed worldwide as a first-line medication for type 2 diabetes. Apart from its usage in the treatment of diabetes, it is also found effective as an anticancer agent[8] and is also used in the treatment of polycystic ovary syndrome.[9] Because it can extensively be applied globally for various applications, there is an increased demand, and this can further lead to the increased detection of MTF in the water matrix. MTF is a highly polar compound with a pK_a value of 12.4.[10] MTF is an emerging contaminant in the environment and possibly a potential endocrine disruptor in the environment.[11,12] Scheurer et al.[13] reported the occurrence of MTF in STP influents of Germany in the range of 101−121 μg/L. Trautwein et al.[14] reported the occurrence of MTF in various sources such as southern German sewage treatment plant (111,800 ng/L), multinational lake Constance (102 ng/L), river Elbe (472 ng/L), river Weser (349 ng/L), and marine North Sea

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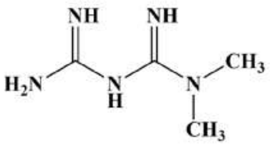
Table 1. Chemical Structure and Physicochemical Properties of Metformin

Structure	Name	Metformin
	IUPAC name	3-(diaminomethylidene)-1,1-dimethylguanidine
	Mol mass (g/mol)	129.16
	pKa	12.4
	Solubility	~200 g/L
	Melting Point	223-226 °C
	Boiling Point	224.1 °C

water (13 ng/L). Bradley et al.[15,16] reported values in the concentration range of 1−1000 ng/L after surveying various pharmaceuticals in different surface waters, USA, highlighting the need for a sustainable and cost-effective methodology for MTF removal to avoid water contamination of natural reservoirs.

Conventionally MTF is removed from wastewater by various physical, chemical, or biological methodologies, or by using a combination of advanced technologies. Also, many literature studies have reported MTF removal using advanced oxidation methods such as photocatalysis, Fenton, photo-Fenton, TiO_2−Fenton, etc. Zhu et al.[17] reported adsorptive removal of MTF using graphene oxide as an adsorbent and achieved 80% removal in 20 min, whereas Niaei et al.[18] reported 95.7% MTF removal in 120 min using (Fe-Z) zeolite nanoadsorbent at 10 mg/L concentration. There are various studies reported on the adsorptive removal of MTF using a variety of adsorbents such as powdered activated carbon, ion exchange resins, carbon nanotubes, chitosan, activated carbon, and organic resins.[17] Though adsorption is effective for the removal, problems associated with adsorption such as regeneration of adsorbent and secondary waste generation pose serious constraints in large-scale operations. The degradation of MTF was investigated using modified biological processes such as the hybrid vertical anaerobic biofilm-reactor (HyVAB),[19] activated sludge,[20] and phytoremediation by *Typha latifolia* plants.[21] All these modified biological approaches resulted in 74−98% removal efficiency; however, the time required for degradation is very high (14−28 days) which makes the process inefficient/impractical at a high concentration of MTF and for real life application.

The removal of MTF using the photo-Fenton process was reported recently with only 24% removal in 60 min,[22] while 99% degradation in 27 min was reported using intensification in the form of the electro-Fenton process.[23] The use of photocatalysts was also reported widely with varying efficiencies: TiO_2 in the presence of UV light with 41% TOC degradation within 60 min[24] and 97% removal in 240 min using a solar photocatalytic process.[25] Carbuloni et al.[26] investigated the photocatalytic degradation of MTF using TiO_2−ZrO_2 catalyst and found more than 50% degradation in 120 min with the formation of intermediates which were nontoxic to *Lactuca sativa* seeds. Quintao et al.[27] investigated the degradation of MTF by direct photolysis, photocatalysis, ozonation, and chlorination and found 60% efficiency using chlorination and ozonation, whereas direct photolysis (UV−C) and heterogeneous photocatalysis (TiO_2/UV−C) resulted in lower removal efficiencies of 9.2% and 31%, respectively. The mineralization rate was low for all different approaches (0.72−20%) indicating the formation of byproducts. Wols et al.[28] studied the degradation of 40 selected pharmaceuticals, including MTF using a combined approach of UV/H_2O_2 and reported lower degradation efficiency for metformin as compared to other pharmaceuticals. Badran et al.[29] reported wet air oxidation for a very high initial concentration of 16 g/L and found ∼40% TOC reduction in 120 min at 180 °C and pressure above 50 bar. Although AOPs such as Fenton, photo-Fenton, photocatalysis, UV, and H_2O_2 indicate very high removal at the lab-scale, there are limitations, in terms of techno-economic feasibility or cost-effectiveness for implementation for industrial scale applications.

Cavitation is a specific form of an advanced oxidation process which involves in situ generation of oxidizing species which can be harnessed for a variety of physicochemical transformations and is suitable in the treatment of wastewater contaminated varieties of pollutants.[30] However, there are no reports on the degradation of metformin using any forms of cavitation; acoustic or hydrodynamic cavitation. Hydrodynamic cavitation has proven its effectiveness over acoustic cavitation in various aspects such as energy requirement, cost of operation, and scalability. In hydrodynamic cavitation, different geometric constrictions are used for the generation of cavities, and the devices are classified as those with moving parts and without moving parts. The high-speed rotor-stator assembly, a device with moving elements, is energy-intensive and not the first choice for cavitation.[31] The devices without moving parts mainly include conventional forms such as orifice and venturi which are linear flow-based devices while the vortex diode a recently developed device works on vortex phenomena.[32,33] The vortex diode device employs tangential entry for the flow in the chamber for the formation of the vortex. Due to strong swirling flow, the low-pressure region formed at the center of the vortex leads to the formation of vapor-filled cavities, and the cavities escape from the axial port. Further, escaped cavities realize high pressure and collapse takes place in the downstream region leading to homolytic cleavage of the water molecules and formation of oxidizing species such as hydroxyl radicals.[34] The vortex diode offers several advantages over conventional linear flow-based devices such as early inception of cavities, larger opening area (less choking), and higher efficiency, and it is less energy-intensive with increased/easy scalability. The pressure drop across the cavitating device contributes mainly to the operating cost of the treatment process, and since the vortex diode requires a lower pressure drop (∼3 times), in range of 0.5−2 bar, compared to most other conventional devices such as orifice- requiring pressure drop typically 5 bar or even more, it represents a cost-effective approach.[35−37] Thus, hydrodynamic cavitation using a vortex diode as a cavitating device can be considered an alternative to the existing treatment methodologies.

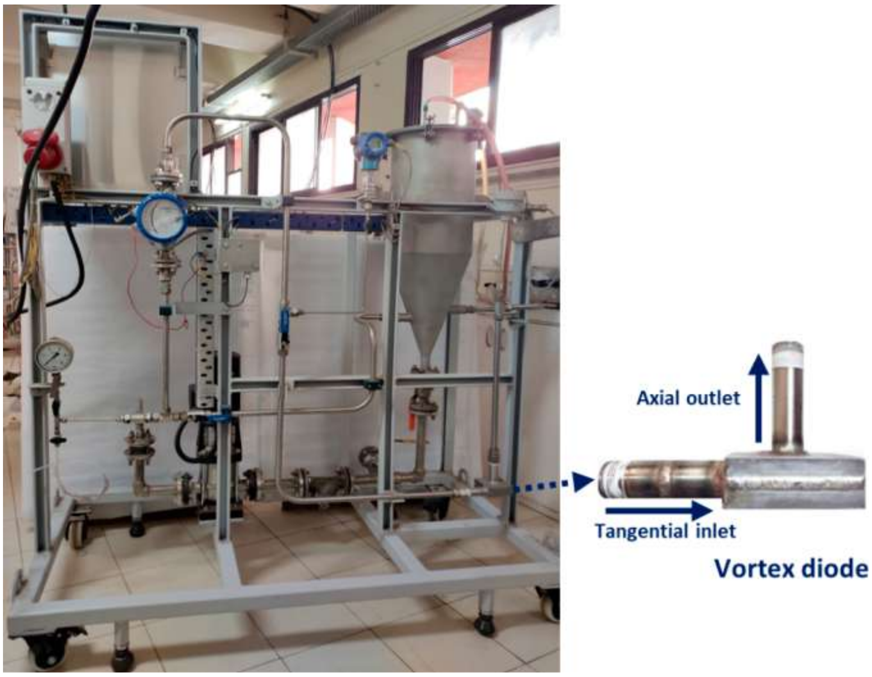


Figure 1. Hydrodynamic cavitation pilot plant and Vortex Diode (1 m^3/h).

The present work, for the first time, reports the degradation of the antihyperglycemic drug metformin by hydrodynamic cavitation using a vortex diode as a cavitating device at a pilot-plant scale (capacity, 1 m^3/h). The operating parameters, such as the effect of pressure, initial concentration apart from process intensifications of aeration, and addition of H_2O_2, were studied, and the effect of pH on MTF degradation was also evaluated. The degradation kinetics was studied by using the per pass degradation model, and cavitational yields were compared under different process conditions. The cost analysis established the techno-economic feasibility of the developed methodology. The results of this work will be useful as an effective effluent treatment strategy for the degradation of antidiabetic drugs in general and metformin in particular apart from industrial wastewater treatment.

2. EXPERIMENTAL SECTION

2.1. Materials. Metformin hydrochloride (CAS: 1115-70-4; purity > 99.96%), in crystalline solid form was procured from BLD Pharmatech (India) Pvt Ltd., Telangana. Hydrogen peroxide (50% w/v, AR grade) was purchased from Molychem, Mumbai. Methanol (≥99.9%, HPLC grade) was procured from Avantor Performance Materials India Limited. Nitric acid (69%, Emparata) from Merck and potassium hydroxide from Qualigens were obtained. The chemical structure and physicochemical properties of MTF are shown in Table 1.

2.2. Methodology. An experimental setup with a vortex flow based cavitation device, vortex diode, is shown in Figure 1. The setup details have already been reported in our earlier reports (Patil and Bhandari,[36]) and hence only essential aspects are discussed here for immediate reference and to avoid repetition. The setup consists of storage tank (25L capacity), a Y type strainer (CF 8M, ACME Engineering Production Corporation) for filtering dirt and impurities of large size, a vertical multistage centrifugal pump (model CNP, make CDLF2-6, SS316, 2 m^3/h at 45 MWC; rating, 0.75 kW (1 hp); 2900 rpm; discharge pressure 0−5 bar with nonflame proof motor), and SS316 seamless tubes of OD 0.75 in. with appropriate OD fittings. A flow transmitter (KRONE, H250), range 150−1500 LPH with integral analog indicator was used to measure the mainline flow rate, while the temperature was measured using RTD (EUREKA Eng. Enterprises India; 0−200 °C) which is fitted in the downstream region of the cavitation reactor and into the recirculating tank. The entire assembly was mounted on a carbon steel powder-coated assembly with wheels.

The degradation studies were carried out using a vortex diode as a cavitating device on synthetic wastewater using predetermined initial concentrations of MTF (10 and 20 mg/L). The temperature was maintained in the range of 35−40 °C using a water circulation in a circular coil (SS316) inserted into the feed tank. Based on earlier studies on the inception of cavitation for vortex diode at ∼0.48 bar,[38] the effect of pressure drop was studied in the range of 0.5 to 2 bar for both the initial concentrations. The process intensification in the form of aeration was studied by simply bubbling air in the recirculating tank using an air pump (SOBO AQUARIUM SB-9905, 2 Nozzle, 4.2W, Max. 5.5 L/min). Another process intensification approach was evaluated by the addition of hydrogen peroxide at different molar ratios with respect to the initial concentration of MTF, MTF/H_2O_2 in the range 1:100 to 1:1500. For the experiments without pH adjustments, the pH of the wastewater before and after was in the range of 6.3 to 6.8 with marginal change observed during the experiment. The effect of pH was investigated for acidic pH of 4 and using basic pH of 8 (acidic pH adjustment was done using 1 M nitric acid solution while basic pH was adjusted using 0.1 M potassium hydroxide solution). All the experiments were performed for a treatment time of 180 min and samples were withdrawn periodically, after every 30 min interval for analysis. Reproducibility of the experiments was confirmed and was satisfactory.

2.3. Analysis. The MTF degradation was monitored by measuring total organic carbon (TOC, SHIMADZU make, TOC-L series TOC analyzer) at different intervals and also by high-performance liquid chromatography (HPLC, Agilent, 1260

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infinity series, C-18 column (4.6 × 250 mm)). A mobile phase of methanol (30%) and deionized water (DI) (70%) was used as an eluent for the separation under reverse-phase conditions at a flow rate of 0.8 mL/min. Detection of MTF was performed at a wavelength of 233 nm. The standard calibration graph was plotted for MTF (R^2 value = 0.99) for estimation of unknown MTF concentration during the treatment. The formation of byproducts for MTF degradation using different process alterations was identified using liquid chromatography−mass spectroscopy (LC−MS).

3. RESULTS AND DISCUSSION

3.1. Effect of Pressure Drop and Degradation Kinetics of MTF. The inception of cavitation in vortex diode is reported experimentally earlier by Suryawanshi et al.[38] at ∼0.48 bar and also by Ranade et al.[39] at 0.5−0.8 bar by acoustic analysis. Therefore, the effect of pressure drop was studied in the range 0.5−2 bar for vortex diode since the optimum pressure drop value is different for different systems. Beyond the optimum pressure drop, the formation of a cavity cloud may occur which adversely affects cavitational intensity. Since the optimum pressure drop depends on the reactor configurations and the type of pollutants and also due to the inability for theoretical prediction of optimum pressure drop, the effect of pressure drop needs to be experimentally evaluated in each case. The experimental conditions of this work ensure the cavitation regime to evaluate degradation efficiency of MTF under different conditions of initial concentrations and pH of the solution. It was experimentally observed that for the conditions of neutral pH, there was no significant variation in the extent of TOC reduction of MTF for the different pressure drops of 0.5, 1, 1.5, and 2 bar for the initial concentration of 10 mg/L as shown in Figure 2. Similar results were also obtained for the higher concentration of 20 mg/L. Hence, an optimized pressure drop of 1 bar was decided for all the experiments related to the degradation of MTF using hydrodynamic cavitation for the both initial concentrations. The maximum TOC reduction of 14% was obtained at a pressure drop of 1 bar for both MTF concentrations.

The reactions in hydrodynamic cavitation can be assumed to be pseudo-first-order and kinetics of MTF degradation can be evaluated using a simple power-law model as,

$$C = C_0\, e^{-kt} \tag{1}$$

where C_0 and C are the MTF concentrations before and after the treatment, t is time (min) and k is rate constant (min^{-1}). Table 2 gives the k values for both the initial concentrations of 10 and 20 mg/L and also for different process alterations using hydrodynamic cavitation. For the optimum pressure drop, ΔP of 1 bar the corresponding k values for initial concentrations, 10 and 20 mg/L were 0.2×10^{-3} min^{-1} and 0.3×10^{-3} min^{-1}, respectively.

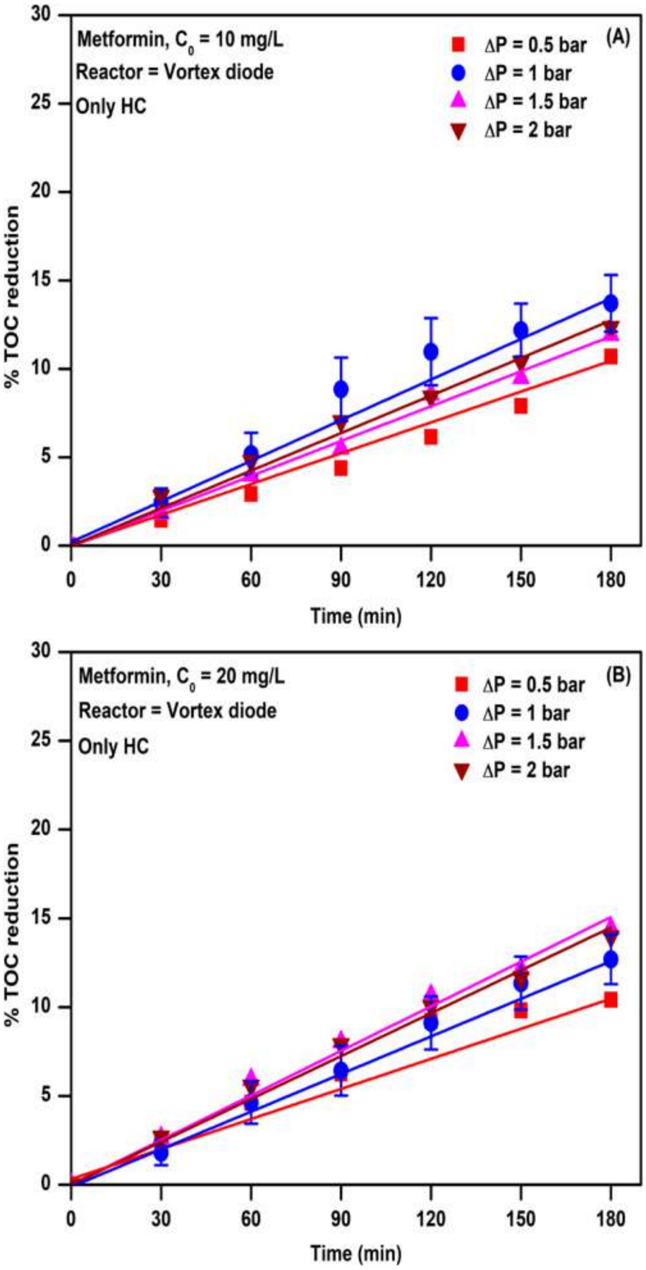

Figure 2. Effect of pressure drop: (A) C_0 = 10 ppm; (B) C_0 = 20 ppm (pH: 6.3−6.8).

Many literature studies support the typical degradation behavior of cavitation in which the extent of degradation of pollutants increases with the increase in the pressure drop until the optimum, beyond which it decreases for all types of cavitating devices; however, optimized value is varied based on the type of cavitating devices, nature of pollutants, etc. Suryawanshi et al.[40] reported the optimized pressure drop of 0.5 bar for degradation of solvents using a vortex diode as a cavitating device, whereas Dixit et al.[35] reported 1.5 bar as the optimum pressure drop for degradation of naproxen, a pharmaceutical pollutant. However, for conventional devices such as orifice, venturi, etc. the value of optimized pressure drop is higher than that required for vortex diode. Kumar et al.[41] reported that the maximum decolorization of ternary dye wastewater was achieved at an inlet pressure of 6 bar using an orifice as a cavitating device, whereas Raut-Jadhav et al.[42] reported an optimized inlet pressure of 15 bar for circular venturi as a cavitating device for degradation of insecticide. It was reported that beyond 15 bar of inlet pressure (optimized condition), a lower extent of degradation was achieved. However, in the present case, with an increase in the pressure drop from 0.5−2 bar, not much difference in the extent of degradation/TOC reduction was observed.

3.2. Effect of Aeration. The effect of aeration was reported in various studies to exploit possible increased oxidation due to the addition of air/oxygen. The effect of aeration appears to be pollutant specific, indicating the necessity for the evaluation of this type of process intensification in metformin degradation. The process intensification approach of aeration was studied at the optimum pressure drop condition of ΔP, 1 bar by bubbling air in a recirculating tank of cavitation reactor for both MTF concentrations, 10 and 20 mg/L. It was observed that the extent of TOC reduction of only 7% and 10% could be achieved for the MTF concentrations of 10 and 20 mg/L, respectively. The extent of degradation obtained for the combined HC+aeration showed the contribution of only cavitation and no effect of aeration due to this intensification approach.

The process intensification approach of aeration for cavitation was found beneficial in some cases where additional nuclei generation enhances the degradation of pollutants depending on the nature of pollutants. The effect of aeration as process intensification was reported in earlier studies for ammoniacal nitrogen removal[34] and solvent degradation[37,40] by hydrodynamic cavitation. Patil et al.[37] reported 100% enhancement in degradation of octanol solvent using a process intensification approach of aeration. However, in the same study, the authors highlighted the selective effect, since for other solvents such as DMF and cyclohexanol, the enhancement due to aeration was not satisfactory. Suryawanshi et al.[40] also reported marginal improvement (~10%) in the extent of degradation of solvents using cavitation coupled with aeration. Similar to the enhanced ammoniacal nitrogen removal[34] and octanol degradation[37] due to aeration, a significant enhancement in COD, TOC, and color reduction of textile dyeing industry effluent due to cavitation coupled with the addition of oxygen was reported by Rajoriya et al.[43] who also reported the effective use of oxygen as process intensification rather than air. Joshi et al.[44] reported ~3 times enhancement by HC+oxygen (40%) in COD reduction of industrial wastewater as compared to the HC+air (15%) approach. Thus, the effect of aeration can be confirmed to be pollutant specific with limited sensitivity to device or process conditions. The nature of the pollutant appears to be the only critical parameter in exploiting intensification due to aeration.

3.3. Effect of the Addition of H_2O_2.

The process intensification approach of the addition of H_2O_2 can also provide significant improvements due to the powerful nature of oxidizing agent that provides an additional hydroxyl radical apart from the cavitational effect resulting in enhancement of the rate of degradation.[3,45] Hydrodynamic cavitation along with the addition of H_2O_2 for degradation of some of the pharmaceutical pollutants was well reported by Thanekar et al.[46,47] and Dixit et al.[35] Due to the cavitational effect, a number of events take place such as the generation of hydroxyl radicals, dissociation of H_2O_2, etc. The role of reactive species in the MTF degradation in the system of HC and HC + H_2O_2 can be explained in the following chain reactions.[42,48,49]

$$H_2O \rightarrow \cdot OH + H^+ + e^-$$

$$H_2O_2 \rightarrow \cdot OH + \cdot OH$$

$$\cdot OH + H_2O_2 \rightarrow HO_2\cdot + H_2O$$

$$\cdot OH + HO_2\cdot \rightarrow H_2O + O_2$$

$$HO_2\cdot + H_2O_2 \rightarrow \cdot OH + H_2O + O_2$$

$$\text{MTF} + \cdot OH/H_2O_2 \rightarrow \text{degradation by-products}$$

$$\text{MTF} + \cdot OH/H_2O_2 \rightarrow CO_2 + H_2O$$

The hybrid approach of cavitation with the addition of hydrogen peroxide at different molar ratios of MTF/ H_2O_2 as, 1:100, 1:300, 1:500, 1:700, 1:1000, and 1:1500 and for both initial concentrations of MTF as 10 and 20 mg/L was investigated. The extent of MTF degradation obtained for different molar ratios of MTF: H_2O_2 is shown in Figure 3. It is evident that the individual approaches such as cavitation and hydrogen peroxide reported only marginal degradation percentage (3−5%), whereas, cavitation coupled with H_2O_2, has shown significant increase in the extent of degradation for the molar ratios from 1:100 to 1:500 for both MTF concentrations, 10 and 20 mg/L. A maximum extent of degradation of 10% and 31% were achieved at a molar ratio of MTF/H_2O_2 as 1:500 for MTF concentrations of 10 and 20 mg/L, respectively. Further enhancement up to 33% was achieved for a molar ratio of 1:700 and for MTF concentration of 20 mg/L. The corresponding rate constants values are provided in Table 2. The higher degradation efficiency can be attributed to a possible reactive pathway with increased availability of the

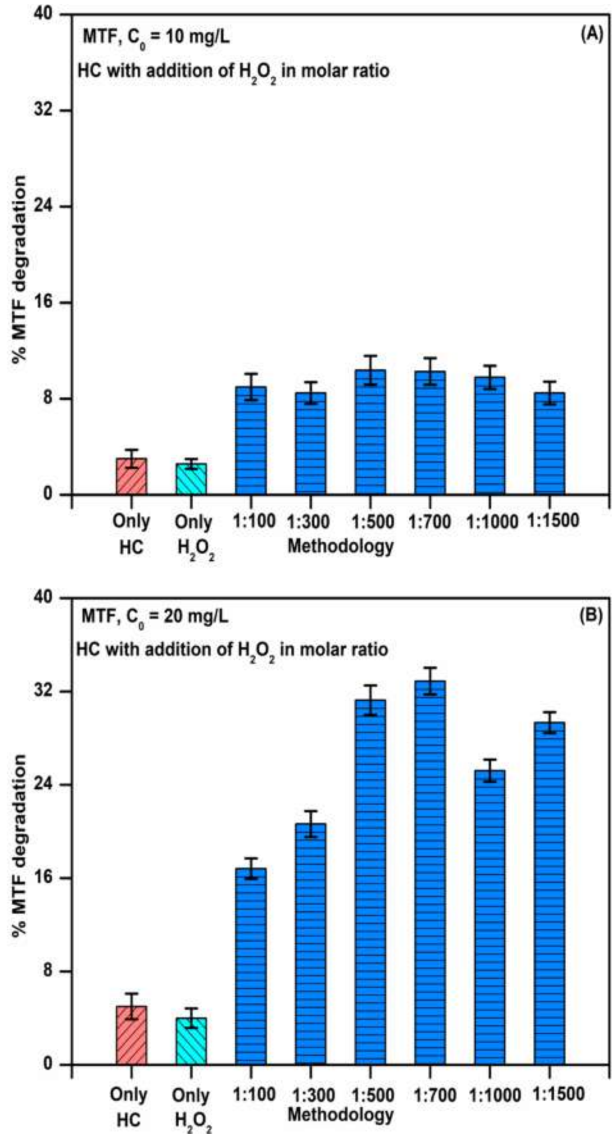

Figure 3. Process intensification using the addition of H_2O_2: (A) C_0 = 10 mg/L, (B) C_0 = 20 mg/L (ΔP, 1 bar; pH, 6.3−6.8; time, 180 min).

oxidizing agents due to H_2O_2 for the increased demand in the case of higher concentrations.

To evaluate the combined effect of hydrodynamic cavitation with the addition of H_2O_2 for MTF degradation, the synergistic coefficient was calculated by using the formula

$$\text{synergistic coefficient} = \frac{k_{(\mathrm{HC+H2O2})}}{k_{\mathrm{HC}} + k_{\mathrm{H2O2}}} \qquad (2)$$

The values of the synergistic coefficient were 2 and 4.2 for the initial MTF concentration of 10 and 20 mg/L, respectively (Table 2) which confirms the synergism of the combined approach of HC and H_2O_2. The synergism can be attributed to the dissociation of H_2O_2 into OH radicals in addition to the OH radicals due to cavitation which ultimately intensifies the degradation process. However, higher loadings of H_2O_2 (beyond optimum), acts as a scavenger which reduces the degradation efficiency. In the present work, with the increase in the molar ratio up to 1:1500, beyond the optimum molar ratio (1:700), the extent of degradation decreases as shown in Figure 3, due to the scavenging effect of hydrogen peroxide. Although the role of H_2O_2 has already been proven, the optimum loading of H_2O_2 is primarily dependent on the nature of pollutants present in wastewater which also brings out the necessity for experimental investigation.

3.4. Effect of pH on Metformin Degradation. The effect of operating pH on the extent of degradation of MTF was investigated in the range pH 2 to 8, for different HC process alterations using a vortex diode as a cavitating device operated at a pressure drop of 1 bar. The obtained results have been depicted in Figure 4. The pH adjustments for acidic and basic conditions were done using 1 M nitric acid solution and 0.1 M potassium hydroxide solution, respectively. The experimental results reveal that under acidic conditions (at pH 4), MTF degradations by HC were 95% and 88% with rate constants, 17.3×10^{-3} min^{-1} and 12.2×10^{-3} min^{-1} corresponding to initial MTF concentrations of 10 and 20 mg/L, respectively. However, under the basic condition of pH 8, degradation was hugely reduced, and the corresponding values were 6% and 4% for the initial MTF concentrations of 10 and 20 mg/L. The experimental investigation for only agitation at pH 4 (without cavitation) indicated only marginal degradation (<2%).

The results clearly highlight pH as one of the most important operating parameters in the hydrodynamic cavitation process for API pollutant degradation. Many researchers have reported the effect of pH on the degradation of various pollutants such as dyes,[50] pharmaceuticals,[46] and pesticide[51] using cavitation. The degradation mechanism using hydrodynamic cavitation involves either thermal/pyrolytic decomposition of pollutant moiety trapped inside the cavity and/or attack of hydroxyl radicals on the pollutant molecule trapped at the gas−liquid interface and in bulk.[50] In the case of the degradation of pollutants, the attack of the hydroxyl radical is found as the main mechanism which ultimately depends on the orientation (molecular or ionic state) of the pollutant molecule in the solution.

Metformin is weakly basic in nature (pK_a 2.8 and 11.5) and gets ionized in a pH range from 4 to 10.[52] At pH 4, MTF occurs predominantly in the molecular form which gets trapped at the hydrophobic gas−liquid cavity interface and is hence found more susceptible to degradation resulting in the maximum extent of degradation of MTF by cavitation (95%). Also, to validate the proposed hypothesis, the experiments were performed to evaluate the extent of degradation at pH 2, which indicated a complete degradation in 30 min for both 10 mg/L and 20 mg/L MTF concentration compared to 180 min for pH 4 (and negligible degradation for pH 6.5). Thus, there is clear effect of pH modification on degradation.

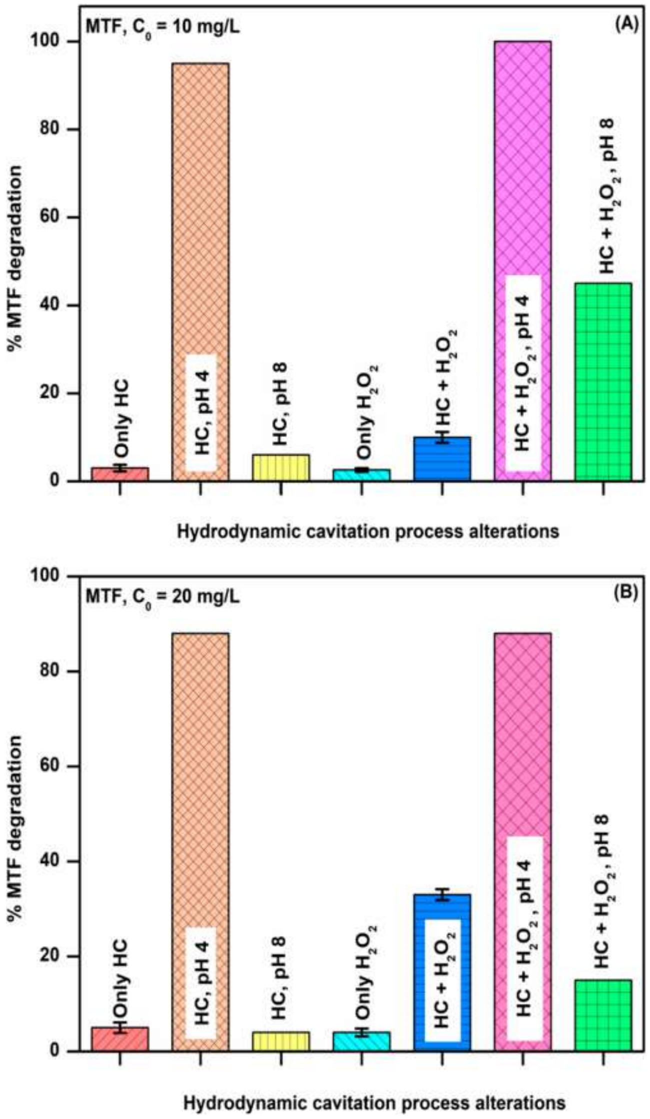

Figure 4. Improving MTF degradation using different process alterations: (A) C_0 = 10 mg/L, (B) C_0 = 20 mg/L (ΔP, 1 bar; time, 180 min).

However, at pH 8, due to ionization, MTF becomes hydrophilic in nature, degradation increases in difficulty as the hydroxyl radicals are short-lived, and the pollutant moiety is not likely to degrade in bulk solution.[53] The present research shows a very important observation that hydrodynamic cavitation using a vortex diode at pH 4 can provide a huge enhancement (3000%) compared with only cavitation without any pH adjustment.

The effect of pH was also investigated for the combined approach of HC+H_2O_2 for both initial concentrations of MTF as 10 and 20 mg/L and using previously optimized H_2O_2 loading. From Figure 4, it can be seen that the HC+H_2O_2 approach resulted in complete degradation (100%) at pH 4 for MTF concentration of 10 mg/L while the corresponding degradation at 20 mg/L was 88%. A significant enhancement in MTF degradation (900%) was achieved with a pH adjustment to 4 for

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a corresponding combined approach of HC+H_2O_2 without any pH adjustment. Also, the experiments of adding H_2O_2 without cavitation at pH 4 and 8 were performed to compare the degradation efficiency obtained for the hybrid approach, and there was practically no degradation obtained for both initial concentrations of MTF.

The strategy of manipulation of synergy using different experimental conditions and the corresponding values of the synergistic coefficient are given in Table 2. Based on the degradation rate constants obtained for different experimental conditions, synergistic coefficients were calculated. It is clear that the higher synergistic coefficients can be achieved with pH modifications, and in metformin degradation using pH 4. Significantly higher synergetic coefficients were obtained as 86.5 and 40.6, respectively, for pH modifications (at pH 4) for the cavitation process for both initial concentrations of MTF. For HC intensified with hydrogen peroxide, synergistic coefficient values were 2.8 and 1 for initial concentrations of 10 mg/L and 20 mg/L, respectively. However, significantly lower values of synergistic coefficients were obtained for HC at pH 8 for both initial concentrations of MTF.

Table 2. Degradation of MTF, Rate Constants, and Synergistic Coefficients for Different Process Alterations

MTF concn, mg/L	cavitation process alterations	% MTF degradation after 180 min	1st order rate constant, $k \times 10^3$(min^{-1})	synergistic coefficient
10	Only HC	3	0.2	
	HC @ pH 4	95	17.3	86.5
	HC @ pH 8	6	0.3	1.5
	HC+ Aeration	<2		
	Only H_2O_2	2	0.1	
	Only Aeration	<2		
	Only pH 4 and 8	<2		
	HC+H_2O_2(1:500)	10	0.6	2
	HC+H_2O_2 (1:500) @ pH 4	100	48.7	2.8
	HC+H_2O_2 (1:500) @ pH 8	45	3.4	11.3
20	Only HC	5	0.3	
	HC @ pH 4	88	12.2	40.6
	HC @ pH 8	4	0.2	0.6
	HC+ Aeration	<2		
	Only H_2O_2	4	0.2	
	Only Aeration	<2		
	Only pH 4 and 8	<2		
	HC+H_2O_2(1:700)	33	2.1	4.2
	HC+H_2O_2 (1:700) @ pH 4	88	12.6	1
	HC+H_2O_2 (1:700) @ pH 8	15	0.9	4.5

3.5. Mechanism of Metformin Degradation. The results of metformin degradation using different formats of hydrodynamic cavitation reveal interesting observations in the degradation behavior. It is instructive to investigate therefore the mechanism and the forms of degradation. In this regard, efforts were made to identify the byproducts using LC-MS analysis, for the different approaches such as HC alone as well as an intensified approach using H_2O_2 performed under acidic conditions of pH 4, where the maximum extent of degradations of 95% and 100% were achieved after 180 min, respectively.

Figure 5 shows the LC−MS spectra for the treated sample of HC alone using pH 4, after 180 min of treatment time. Two prominent peaks were observed at *m*/*z* 119.02, and 158.00. The compounds detected were *N*-nitro-*N*-aminoguanidine (*m*/*z* 119.02), 3,5-dinitro-1*H*-pyrazole (*m*/*z* 158.00), and metformin (*m*/*z* 130.10). The minor peak detected of metformin (*m*/*z* 130.10) indicated its presence in a trace amount which supports the nearly complete (95%) degradation of MTF using HC alone using acidic conditions. Figure 6 shows LC−MS of degradation products of MTF for another process format—using HC with the addition of H_2O_2 where complete MTF degradation was achieved after 180 min. Two prominent peaks were observed at *m*/*z* 190.94, and 126.07. The peak of metformin (*m*/*z* 130.10), which completely disappeared, confirms complete (100%) degradation of MTF using HC+H_2O_2. Quintao et al.[27] investigated the degradation products of MTF using photolysis, photocatalysis, ozonation, and chlorination and observed that though the complete degradation was achieved within 30 min, many intermediates were formed which were persistent even after prolonged treatment. However, in the present work, hydrodynamic cavitation produced a few intermediates that also eventually degraded with extended treatment time.

Based on the analysis, the mechanism can be postulated and the envisaged possible intermediates are shown in Figure 7 for different process alterations based on hydrodynamic cavitation. It can be seen that the cavitation alone produced no byproducts other than metformin, which was confirmed by HPLC analysis and represents a more predominant mineralization pathway with only water and carbon dioxide as the products. However, cavitation with pH 4 as well as a hybrid approach of HC+H_2O_2 under acidic conditions resulted in byproduct formation with complete degradation of metformin (100%).

3.6. Per-Pass Degradation and Cavitational Yield. Typically, the kinetics of degradation is reported based on a power-law which delivers change in concentration with respect to time. However, the per-pass degradation model for hydrodynamic cavitation provides a clearer physical picture in terms of flow/pressure drop characteristics, energy dissipation, and finally evaluating the performance of the cavitation process in the form of cavitational yield, and is therefore, more realistic. It accounts for concentration effects and pressure drop across cavitation device, and the nature of the cavitating device is reflected in the per-pass degradation model which closely resembles the physicochemical behavior of the hydrodynamic cavitation process and hence is found more suitable, especially at a large scale of operation.[37,54−57] The per-pass degradation factor is defined as

$$\text{per-pass degradation factor}(\phi) = k\tau \tag{3}$$

where τ is residence time which is a ratio of volume of the holding tank and the flow rate.

The power dissipation is calculated as

$$W = \Delta P \times Q \tag{4}$$

where, ΔP is pressure drop across the cavitating device ($P_1 - P_2$) (bar), and Q is the flow rate (L/h)

The overall cavitational yield (amount of pollutant/MTF degraded per unit energy dissipation) can be calculated as

$$Y = \frac{V(c_0 - c)}{\Delta P Q t} \quad \text{mg/J} \tag{5}$$

where Y = cavitational yield (mg/J), V = volume (L), C_0 and C = initial and final concentration of pollutant (mg/L).

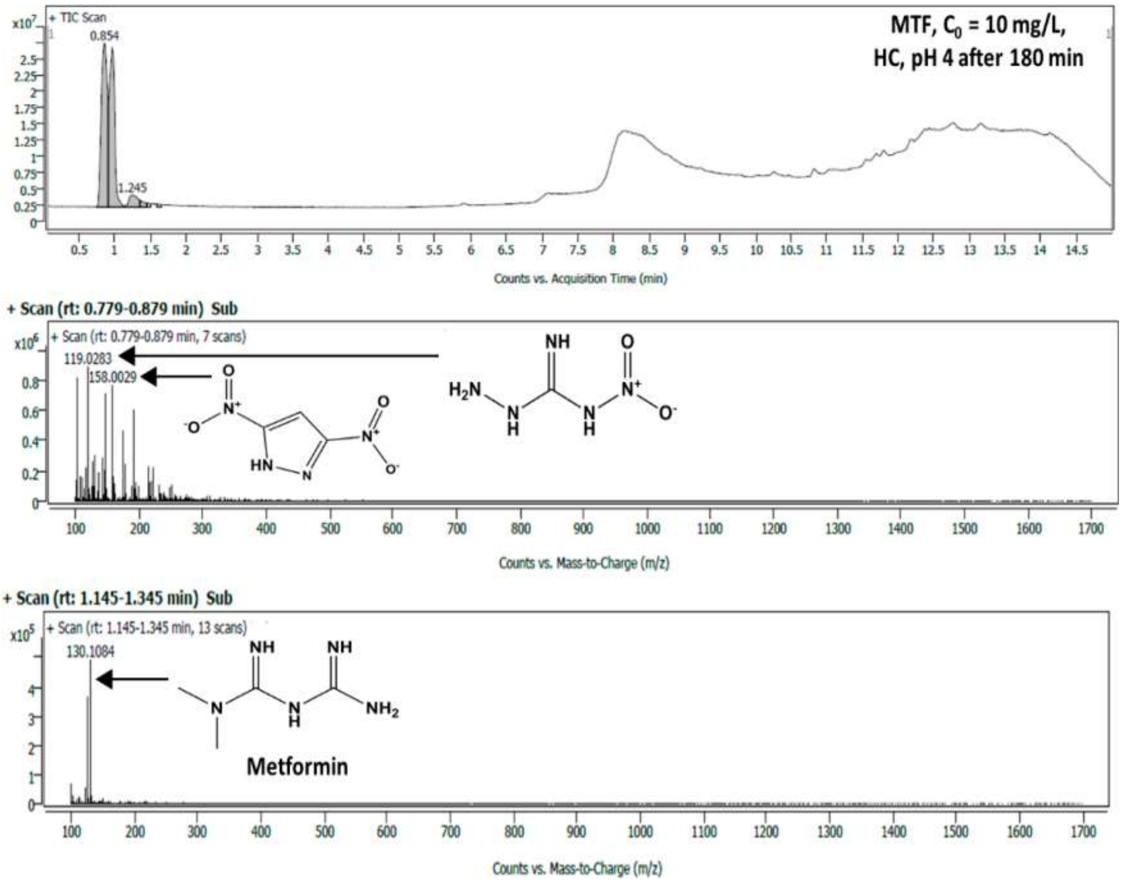

Figure 5. LC−MS spectra for MTF degradation by HC (pH 4).

The per-pass degradation factors were calculated for different process alterations of cavitation, and the obtained values were represented in Figure 8. It can be seen that a significantly higher per-pass degradation factor was obtained for hydrodynamic cavitation with the addition of H_2O_2 and also for hydrodynamic cavitation using acidic pH of 4 for both initial MTF concentrations of 10 mg/L and 20 mg/L. The values of per-pass degradation are very low for the three formats of cavitation, viz., only HC (3×10^{-4}), HC using pH 8 (6×10^{-4}), and HC intensification using hydrogen peroxide (11×10^{-4}) for lower initial concentration of 10 mg/L, while corresponding values for 20 mg/L were, 6×10^{-4}, 4×10^{-4}, and 41×10^{-4}, respectively. However, significant enhancement in per-pass degradation factors was obtained by altering the pH to acidic (pH 4), and the values were 303×10^{-4} and 945×10^{-4}, respectively, corresponding to a huge enhancement on the order of 100 and 85 times for the two cavitation process formats of HC and HC intensified with hydrogen peroxide, specifically for the lower initial concentration of 10 mg/L. Similarly, for an initial concentration of 20 mg/L, per-pass degradation factors were 217×10^{-4} and 213×10^{-4}, respectively, corresponding to an enhancement of the order of 35 and 4. The experimental observations pertaining to the pH can be attributed to the ionization effect due to pH and for effect of concentration. It is indicated that molecular form over the ionized form is more amenable for the degradation.

Cavitational yield expresses the desired chemical change, in this case, degradation of MTF per unit energy dissipation (eq 5). The values of cavitational yields obtained for different process alterations have been depicted in Figure 8. The higher values of cavitational yields, 96×10^{-5} mg/J and 162×10^{-5} mg/J were obtained using cavitation with pH adjustment to 4 for both MTF concentrations of 10 and 20 mg/L respectively. However, further enhancement in cavitational yields, 101×10^{-5} mg/J and 166×10^{-5} mg/J were achieved for HC+ H_2O_2 with pH adjustment to 4 for both MTF concentrations of 10 and 20 mg/L, respectively. The comparatively lower cavitational yields, 3×10^{-5} mg/J and 10×10^{-5} mg/J were achieved using an individual approach of cavitation without any pH adjustment for both MTF concentrations of 10 and 20 mg/L, respectively. Based on the obtained results of cavitational yields for different process alterations, the hydrodynamic cavitation with acidic pH 4 gave significant enhancement in cavitational yield in the range of ∼3 to 32 times that of the individual operation of hydrodynamic cavitation for both initial concentrations of 10 and 20 mg/L.

Both terms, per-pass degradation and cavitational yield, are correlated and represent the effectiveness of the process. The terms are useful in understanding the phenomenon, especially for the hydrodynamic cavitation and for different types of the reactors, for analyzing/comparing the literature data, and also from the point of view of future research/investigations on different types of devices. While the per-pass degradation factor is more useful for the implementation of hydrodynamic cavitation at various scales, cavitational yield can be a more relevant term to evaluate the energy effectiveness of the process.

3.7. Cost Analysis. The cost of the treatment by hydrodynamic cavitation using vortex diode as cavitating device based on MTF degradation % can be calculated as[33]

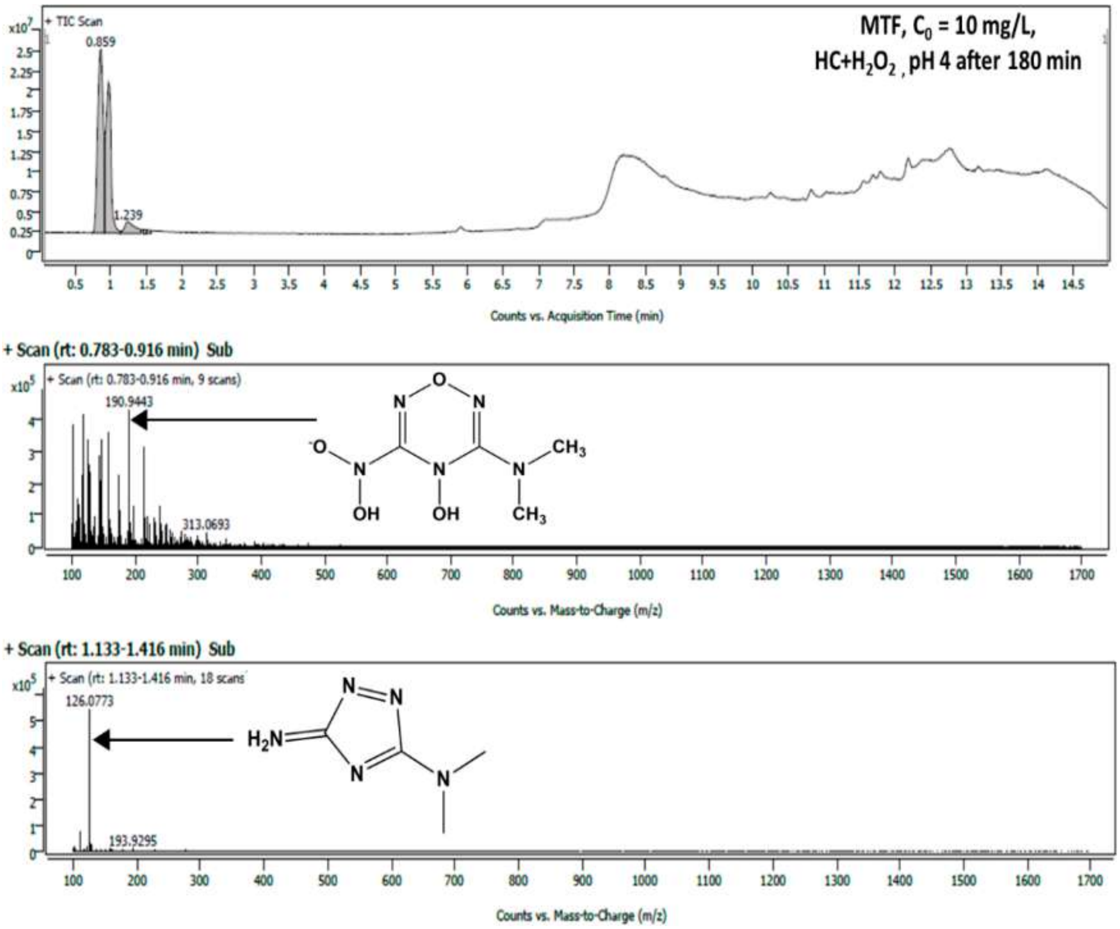

Figure 6. LC−MS spectra for MTF degradation by HC with the addition of H_2O_2 (pH 4).

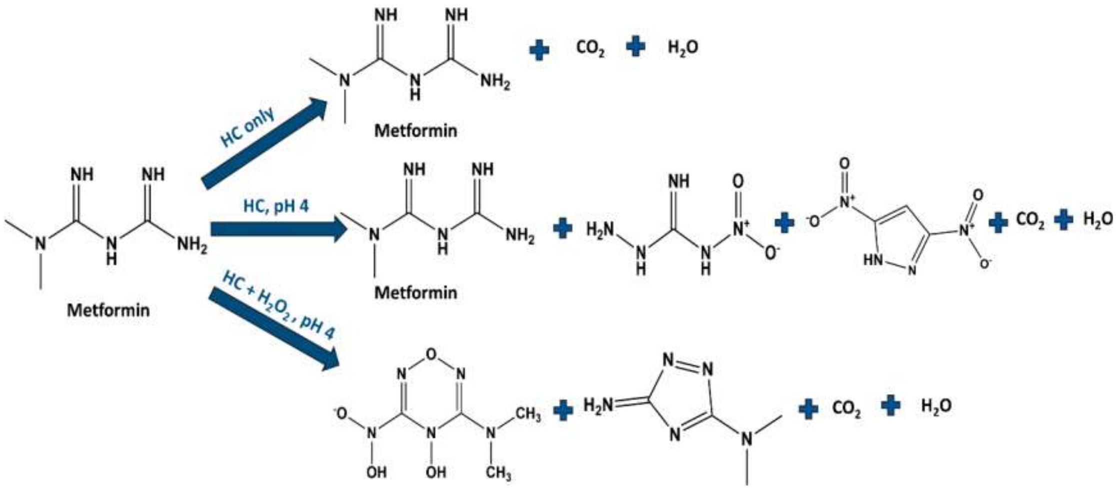

Figure 7. Metformin degradation—possible intermediates for different process alterations.

$$\text{cost of treatment per m}^3 \text{ of effluent} = \frac{N_c \times \Delta P \times P_E}{36\eta} \quad (6)$$

where N_c is the number of passes, ΔP is pressure drop across the cavitation device, P_E is the cost of electricity, and η is pump efficiency. The number 36 in the denominator is due to the conversion of energy units for calculating cost per unit volume of effluent.

The cost calculation was done in the context of the Indian scenario. The cost of electricity for the Indian scenario was assumed as Rs 10/kWh (1$ = 75 Rs) while pump efficiency was assumed as 66% considering commercial operating conditions (flow rates above 10 m^3/h). The calculated cost for different relevant process alterations (for close to complete degradation) are given in Table 3. For an optimum pressure drop of 1 bar using vortex diode, the cost of treatment for only hydrodynamic cavitation was 41 Rs/m^3 (0.55 \$/m^3), however, only for 3−5% reduction, therefore not relevant from an application point of view, whereas, with a simple pH adjustment for hydrodynamic

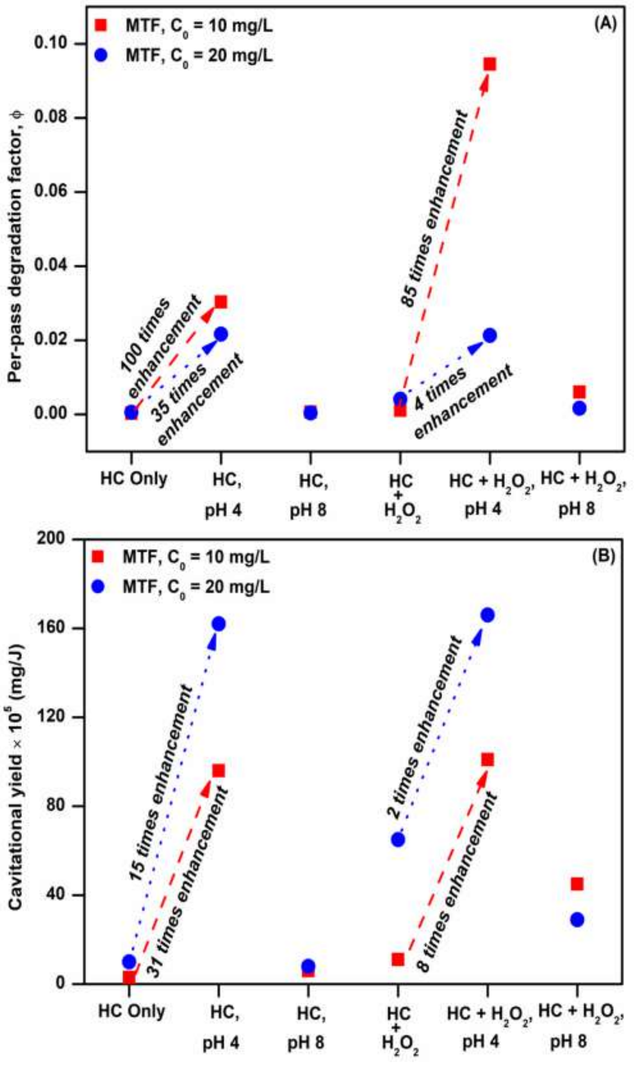

Figure 8. Per-pass degradation and cavitational yield for different process alterations: (A) C_0 = 10 mg/L, (B) C_0 = 20 mg/L (ΔP, 1 bar; time, 180 min).

Table 3. Cost Analysis for Different Process Alterations

MTF concn, mg/L	methodology	% MTF degradation	cost in Rs/m^3	cost in Rs/g
10	Only HC	3	Not Relevant	Not Relevant
	HC + H_2O_2 (1:500) @ pH4	100	75	45
	HC @ pH 4	95	45	5
20	Only HC	5	Not Relevant	Not Relevant
	HC + H_2O_2 (1:700) @ pH 4	88	131	8
	HC @ pH 4	88	45	3

cavitation, the cost of the treatment was reduced drastically. The cost analysis for the combinations of HC+H_2O_2 with pH adjustments and only HC+ pH adjustments, and by incorporating the cost of additives, indicated low costs of 75 Rs/m^3 and 45 Rs/m^3, respectively, for MTF initial concentration of 10 mg/L. It is interesting to note that though addition of hydrogen peroxide assists in the overall degradation, the cost of HC without hydrogen peroxide and with similar pH adjustment is substantially lower and therefore a better approach for practical consideration. The cost analysis depicted order of magnitude cost reduction for the modified hybrid approach using pH adjustments of this study as compared to only vortex based HC and only the HC+H_2O_2 hybrid approach.

Thus, the modified hybrid approach of cavitation using a vortex diode as a cavitating device and hydrogen peroxide with pH adjustment can be considered as an efficient and viable alternative to the degradation of metformin to the existing methodologies representing superior cavitational yield, high efficiency, and drastically increased cost-effectiveness.

4. CONCLUSIONS

The present work clearly demonstrated the effective use of hydrodynamic cavitation with vortex diode as a cavitating device for the degradation of metformin, an extensively used antidiabetic drug. Hydrodynamic cavitation alone, using a low pressure drop of only 1 bar, yields only 3−5% of degradation while process intensification using hydrogen peroxide gave up to 33% of metformin degradation. The hybrid hydrodynamic cavitation process can be further modified using pH alteration resulting in very high, 88−95% metformin degradation, under acidic pH of 4 with an excellent cavitational yields of the order of 162×10^{-5} mg/J for the reasonably higher initial concentrations of 10−20 mg/L. Further, complete degradation of MTF was achieved using HC+H_2O_2 under acidic pH of 4 with order of magnitude enhancement of 900%. Significantly higher synergistic coefficients can be achieved with simple pH modifications (pH 4) resulting in the process efficiency. Per-pass degradation could be enhanced up to 100 times reflecting drastic reduction in the process cost compared to the conventional hydrodynamic cavitation. The results confirm that the use of a vortex flow-based device in hydrodynamic cavitation and process intensification with acidic pH conditions result in significant degradation of MTF with low treatment cost providing a techno-economical alternative for the degradation of an antidiabetic drug and industrial wastewater treatment.

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Author Contributions

V.M.B. and P.B.P. conceived and developed the idea along with experimental methodology/result analysis. P.B.P. conducted all the experiments and analyzed the data. P.T. contributed to the analysis of the results. All the authors were involved in the preparation of the manuscript.

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Notes

The authors declare no competing financial interest.

■ NOMENCLATURE

MTF = Metformin
C_0 = Initial concentration, (mg/L or ppm)
C = Final concentration, (mg/L or ppm)
k = Rate constant, min^{-1}
N_C = Number of passes required for treatment
P = Pressure, bar
P_E = Cost of electricity per kWh, Rs.
Q = Flow rate, L/h
t = Time, min
V = Volume, L
W = Power dissipation, W
Y = Cavitational yield, mg/J
ϕ = Per-pass degradation factor
ΔP = Pressure drop, bar
η = Efficiency of the pump

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Solvent-assisted cavitation for enhanced removal of organic pollutants - Degradation of 4-aminophenol

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ABSTRACT

A new approach of solvent-assisted cavitation process was proposed for degradation of organic pollutants. The process envisages the use of suitable solvent as an additive, (1–5% v/V), in the conventional cavitation process to enhance the pollutant removal efficiency. A proof of concept was provided for the removal of ammoniacal nitrogen with significantly improved efficiency using solvent-assisted hydrodynamic cavitation (HC) compared to conventional HC. The efficacy of the process was studied on a pilot plant scale (1 m^3/h) and using vortex flow based vortex diode as a cavitating device. Degradation studies were carried out using a model pollutant, 4-aminophenol and four different solvents as additives, 1-octanol, cyclohexanol, 1-octane and toluene. Relatively polar solvents were found to increase the efficiency of the pollutant removal (>65%) and also increase the rates to an extent of more than 200%, compared to only HC. A very high removal of ammoniacal nitrogen, more than 90%, was obtained for solvents 1-octanol and cyclohexanol, indicating the importance of the selection of solvent. Per-pass degradation model showed 3 to 4 times increase in the per pass degradation for polar solvents compared to cavitation alone. The results confirm no role of conventional solvent extraction and no specific contamination of wastewater due to the use of solvent as an additive in the process. Further, the cost was 2–3 times lower as compared to the conventional HC. The interesting observations in the proposed process can fuel further research to provide possible improvements in existing methodologies of wastewater treatment, in general, and for removal of ammoniacal nitrogen, in particular.

1. Introduction

Removal of ammoniacal nitrogen from wastewaters for environmental pollution control is an important problem in many industries such as dyes and textile, specialty chemicals and so on due to high ammoniacal nitrogen content. Industries such as fisheries that produce wastewaters with high biological oxygen demand (BOD), suitable for treating using conventional biological treatment methods, typically end up in treated wastewaters containing much higher ammoniacal nitrogen than the recommended norms of below 30–50 mg/L (Ranade and Bhandari, 2014a). Ammoniacal nitrogen (NH_4–N), nitrogenous organic matter which can be converted to ammonia, is a measure of the amount of ammonia, a toxic pollutant. Conventional wastewater treatment methodologies generally focus on the removal of chemical oxygen demand (COD)/total organic carbon (TOC) and biological oxygen demand (BOD) to meet the desired pollution control norms. The removal of ammoniacal nitrogen has received comparatively less attention. The conventional methods for the removal of ammoniacal nitrogen include biological, physical, and chemical methods, in isolation or in combination. Available technologies include adsorption, chemical precipitation, membrane filtration, reverse osmosis, ion exchange, air stripping, breakpoint chlorination and biological nitrification and denitrification (Metcalf & Eddy, 1991). Many treatment methods such as coagulation and adsorption focus on physical removal of pollutants, consequently generating secondary waste. A number of adsorbents were reported with varying success, such as zeolite (Çelik et al., 2001; Demir et al., 2002; Rozic, 2000; Sarioglu, 2005), minerals (Wang et al., 2014), limestone (Aziz et al., 2004), natural and waste materials such as shell, refuse concrete and cement (Ahsan, 2001), nanomaterials (Moradi and Zare, 2013) and ion exchange resins (Kotoulas et al., 2019). Precipitation of ammoniacal nitrogen as magnesium ammonium phosphate was reported for the treatment of tannery wastewaters (Tünay et al., 1997). The biological methodologies for ammoniacal nitrogen removal include conventional nitrification/denitrification, partial nitritation,

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ANAMMOX (anaerobic ammonium oxidation) (Kamp et al., 2019; Lackner et al., 2014), and its combined system CANON (completely autotrophic nitrogen removal over nitrite) for use at industrial scale. Biological methods typically require high residence time and are sensitive to temperature fluctuations and may require additional carbon sources for their smooth operation at large scale operation (Ahn, 2006). Advanced oxidation processes (AOPs) and their combinations such as Fenton, Photo Fenton, Photocatalysis, UV/H_2O_2, and ozone are also reported for ammoniacal nitrogen removal from wastewaters. Advanced oxidation processes typically have a high cost of treatment compared to cavitation, in general (mainly due to catalyst and processing) (Ranade and Bhandari, 2014b) and can also produce undesirable intermediates (Miklos et al., 2018; Oturan and Aaron, 2014). Pravin et al. (Patil et al., 2021a) successfully demonstrated effective removal of ammoniacal nitrogen using process intensification with treatment costs as low as 0.01 to 0.1 $/$m^3$. Membrane based processes have limitations in wastewater treatment, generate secondary waste apart from high cost. Methodologies such as cavitation can degrade the organic pollutants to achieve degradation of organics to the extent of mineralization and that the secondary waste generation can be partly/completely eliminated. In view of the constraints of most of the existing methodologies, high costs of treatment apart from limitations on the extent of pollutants removal with ease of operation, it is instructive to develop newer methodologies for removal of organic pollutants, specifically for ammoniacal nitrogen removal.

Hydrodynamic cavitation, is the most practical form of cavitation processes in general for industrial applications compared to acoustic, optic or particle cavitation processes (Gogate and Pandit, 2004). Cavitation involves *in situ* generation of oxidising species, by homolytically cleaving water molecules and consequently oxidising the organic pollutants for complete mineralization. In view of the ease of operation and scale-up, hydrodynamic cavitation is an attractive alternative compared to other conventional advanced oxidation processes in wastewater treatment.

Cavitation is a physico-chemical process where the physical component requires formation, growth and violent collapse (implosion) of cavities in microseconds. Consequent to cavities collapse, extreme temperature and pressures are experienced at the point of implosion; pressure about ~1000 atm and temperatures ~10000 k. Under these extreme conditions, water splits, a homolytic cleavage, generating hydroxyl radicals required for the oxidation of organics-chemical process (Gogate and Pandit, 2004). Hydrodynamic cavitation processes make use of different cavitating devices such as linear flow based devices e.g. orifice, venturi and rotational flow/vortex flow based devices such as vortex diode (non-moving element type) or high speed rotor stator assembly (moving element type). In recent years, vortex diode that employs vortex flow and without any moving elements has been shown to be useful in many wastewater treatment applications (Pandare and Ranade, 2015; Patil et al., 2021a, 2021b; Ranade et al., 2013). It was found to be superior to conventional cavitation devices such as orifice, venturi in applications such as dye removal (Hiremath et al., 2013), apart from many other applications such as solvent degradation (Patil et al., 2021b; Sarvothaman et al., 2018; Suryawanshi et al., 2018), microbial disinfection (Jain et al., 2019; Mane et al., 2020a, 2020b), ammoniacal nitrogen removal (Bhandari et al., 2016; Patil et al., 2021a; Ranade et al., 2016), biomass valorisation (Konde et al., 2021; Nagarajan and Ranade, 2019), desulphurization of transportation fuels (Suryawanshi et al., 2016) etc. The hydrodynamic cavitation process has been well discussed in many literature reports apart from the design details for various forms of devices.

The application of cavitation processes for wastewater treatment has not been largely successful in real life operations in spite of large number of studies on various types of cavitation processes, cavitating devices and process intensifications. It is essential that newer ways and process modifications be investigated to increase the efficiency in the removal of different types of organic pollutants and for reducing the cost of operation apart from ease of operation and scalability. In this context, the present study reports, for the first time, a new approach of solvent-assisted cavitation for the enhanced degradation of organic pollutants, using suitable solvent as an additive (1–5%v/V). The degradation of 4-aminophenol as a model nitrogen compound was discussed in detail. The nature of solvent was investigated using relatively polar solvents such as octanol and cyclohexanol and non-polar solvents such as octane and toluene. The removal kinetics was evaluated using the per-pass degradation model. The solvent can be easily separated, recycled, and reused. The findings of this work would provide a newer approach of solvent-assisted cavitation for the industrial wastewater treatment, in general and for removal of ammoniacal nitrogen, in particular.

2. Conceptual development of the process

A solvent-assisted cavitation process for the removal of pollutants from waste water envisages treating wastewater and a suitable immiscible solvent as an additive, in a small volume percent of 1–5%, using a cavitation process for the degradation of pollutants. The process involves the following steps:

1. Addition of suitable solvent as an additive in a wastewater tank.
2. Allowing the wastewater to be treated using the cavitation device for the required time to obtain the wastewater with reduced levels of COD and/or ammoniacal nitrogen.
3. Separating the solvent from water and possible recycle and reuse.
4. To obtain treated water with the desired COD and/or ammoniacal nitrogen removal.

The entire operation can be essentially carried out at ambient conditions. The proposed methodology envisages use of any suitable solvent, alone or in combinations, which is immiscible with water. While, in principle, any type of cavitation process can be applied, hydrodynamic cavitation can be a better option in view of the reported literature on wastewater treatment. Also, in hydrodynamic cavitation, the cavitating device can be selected from any type e.g. orifice, venturi, vortex diode etc. The process can be carried out in a batch or continuous mode or in combination with other wastewater treatment methods like adsorption, coagulation and oxidation for meeting the prescribed norms of pollution control and/or for cost-effectiveness.

A schematic flow diagram of the proposed process, based on the steps outlined as above, is given in Fig. 1A, depicting mixing suitable solvent with the wastewater stream in the desired proportions and carrying out the cavitation process in an usual manner for the oxidation of organic pollutants by generating oxidising species such as hydroxyl radicals or hydrogen peroxide. The objective is to enhance the performance of the conventional cavitation process using solvent additive-solvent expected to assist through generation of additional cavities for improved cavitation and possibly by providing conducive environment, by increased localized organic pollutant concentration at the interface due to the solvent-pollutant affinity.

Advanced Oxidation Processes (AOP) are well known for the degradation of pollutants and for the treatment of wastewaters. However, it is evident from the discussion above and Fig. 1, no AOP has any resemblance with the solvent-assisted cavitation process for the treatment of wastewaters. The commonly used Fenton oxidation requires use of iron catalyst and hydrogen peroxide in acidic medium which is entirely different from this new process that requires no catalyst or such conditions. Further, no AOP refers to the use of solvent in degradation of wastewaters using cavitation. The conventional solvent extraction process refers to the removal of species in its original physical form in a different phase (e.g. solvent extraction) or removal of its modified form (e.g. reactive extraction, dissociation extraction). The present work refers to destruction of the species using a solvent additive in cavitation (1–5%), completely different from extraction process. This can be viewed as “Transformed advanced oxidation process using solvent for

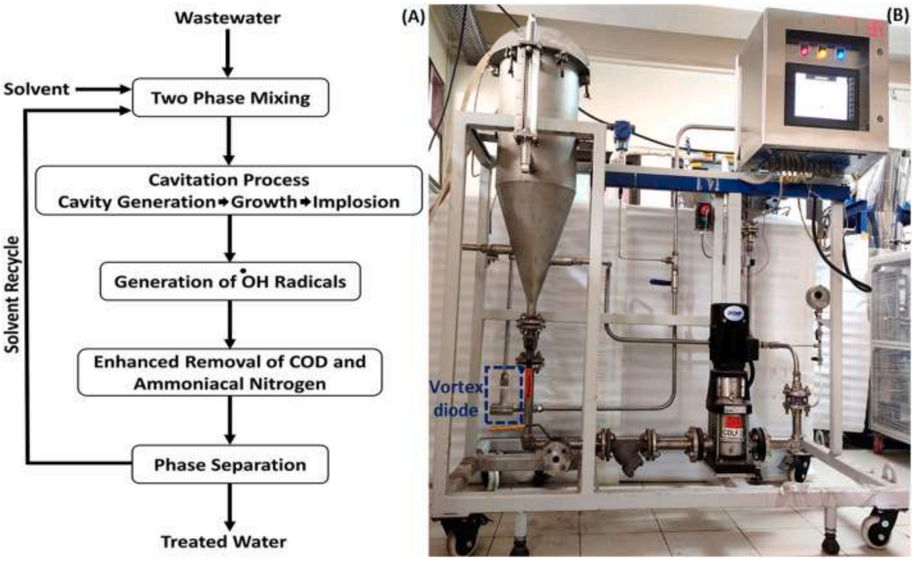

Fig. 1. Solvent-assisted hydrodynamic cavitation process (A) Flow diagram (B) Experimental set-up.

degradation of pollutants".

3. Experimental

Four different solvents, 1-octanol, cyclohexanol, 1-octane and toluene (HPLC grade, >99%, Loba Chemie) were used. Reagent grade 4-Aminophenol ($H_2NC_6H_4OH$; 99%) was obtained from Sigma Aldrich. The analysis of ammoniacal nitrogen, removal as NH_4–N, was carried out using Spectroquant® Pharo 100 spectrophotometer (MERCK, India), wavelength range 320–1100 nm while for total organic carbon, SHIMADZU TOC-L series of TOC analyzer was used. The degradation by way of mineralization is thus reflected in the TOC removal.

The essential parts of the experimental set up (Fig. 1B) include a vertical cylindrical feed cum recirculation tank (SS316) with working capacity of ~25 L, pumping arrangement for the wastewater, cavitating device and controls/measurements of process parameters. A vertical multistage centrifugal pump (Model CNP make CDLF2-6, SS316, 2 m^3/h at 45 MWC), rating 0.75 kW (1 hp), 2900 RPM, discharge pressure 0–5 bar was used and flow was controlled by ¾" NB valves (Wesmec Engineering Pvt ltd). SS316 seamless tubes of 0.75 inch diameter with appropriate fitting were part of the flow system. Flow transmitter (KRONE, H250), range 150–1500 LPH with integral analog indicator was used to measure mainline flow rate while the temperature was measured using RTD (EUREKA Eng. Enterprises India; 0–200 °C) inserted into the feed tank. A cooling coil (SS316) was used in the feed tank for precise temperature control. Horner make HMI display was used for data logging with the provision of a sim card for data monitoring and transfer from any location. The whole assembly was mounted on carbon steel powder coated skid with wheels.

The removal of ammoniacal nitrogen was studied using 4-aminophenol as a model nitrogen containing compound. An initial concentration of 100 mg/L was used for all the experiments, unless specified. A volume of 12 L of synthetic wastewater was typically used with predetermined solvent volume fraction (2 and 5%) as an additive. Vortex diode was used as a cavitating device (SS316, Chamber diameter 66 mm) and experiments were carried out using predetermined pressure drop. The solvent was separated after each cavitation experiment by simple layer separation using separating funnel. The removal of ammoniacal nitrogen and reduction in total organic carbon was monitored by sampling at periodic time intervals. For observing the extent of degradation and the rate behaviour, the experiments were carried out for 180 min and samples were withdrawn at 30 min intervals of time. In view of cavitation inception, based on earlier studies, at 0.48 bar for the vortex diode (Suryawanshi et al., 2016), the pressure drop condition of 0.5 bar or above was selected for all the experiments to ensure the operation in the cavitation regime.

The samples of both aqueous phase and solvent phase before and after the cavitation were analysed for para amino phenol in the two phases and also for any formation of intermediates using HPLC technique (Agilent, 1260 infinity series, equipped with UV visible detector and wavelength, $\lambda = 210$ nm, C-18 column (4.6×250 mm)). The mobile phase was in the ratio of 95:5 with aqueous buffer and acetonitrile with a flow rate of 0.8 ml/min. Aqueous buffer was prepared by addition of 4 ml of phosphoric acid, 50 ml of methanol in 1 lit HPLC grade water (He et al., 2007).

4. Results and discussion

4.1. *Effect of nature of solvent and solvent volume fraction*

The effects of pressure drop and initial concentration of the pollutants have been well reported in hydrodynamic cavitation (Suryawanshi et al., 2016) and also for the removal of ammoniacal nitrogen (Patil et al., 2021a). Accordingly, pressure drop, ΔP of 0.5 bar was used for evaluating the efficacy of solvent-assisted hydrodynamic cavitation process.

The solvent-assisted cavitation process invariably depends on the selection of the solvent, similar to solvent extraction. The nature of the solvent, the polarity of the solvent are expected to play important role in the new process. In the case of removal of ammoniacal nitrogen, for the representative pollutant, p-amino phenol, four different solvents were evaluated from slightly polar to non-polar solvent classes. The four solvents included n-octanol, cyclohexanol, toluene and octane.

The extent of removal of ammoniacal nitrogen using only hydrodynamic cavitation was ~55%. It was observed that the solvents, octanol and cyclohexanol have a significant effect in increasing the efficiency of degradation whereas, the solvents toluene and octane have an adverse impact on the removal efficiency.

The positive effect of solvent volume fraction was validated using 2% and 5% volume fraction of octanol, since it gave increased efficiency (Fig. 2A). A very high removal of 92% was obtained with 5% v/V of octanol (k, 15×10^{-3},min^{-1}) while in the case of 2% v/V of octanol 89% ammoniacal nitrogen removal was obtained (k, 12.4×10^{-3}, min^{-1}). Similarly, a high extent of removal of 86% was obtained for cyclohexanol (2%), in 180 min (Fig. 2B). Another interesting observation that can be made from Fig. 2 is that there is a significant increase in the rate

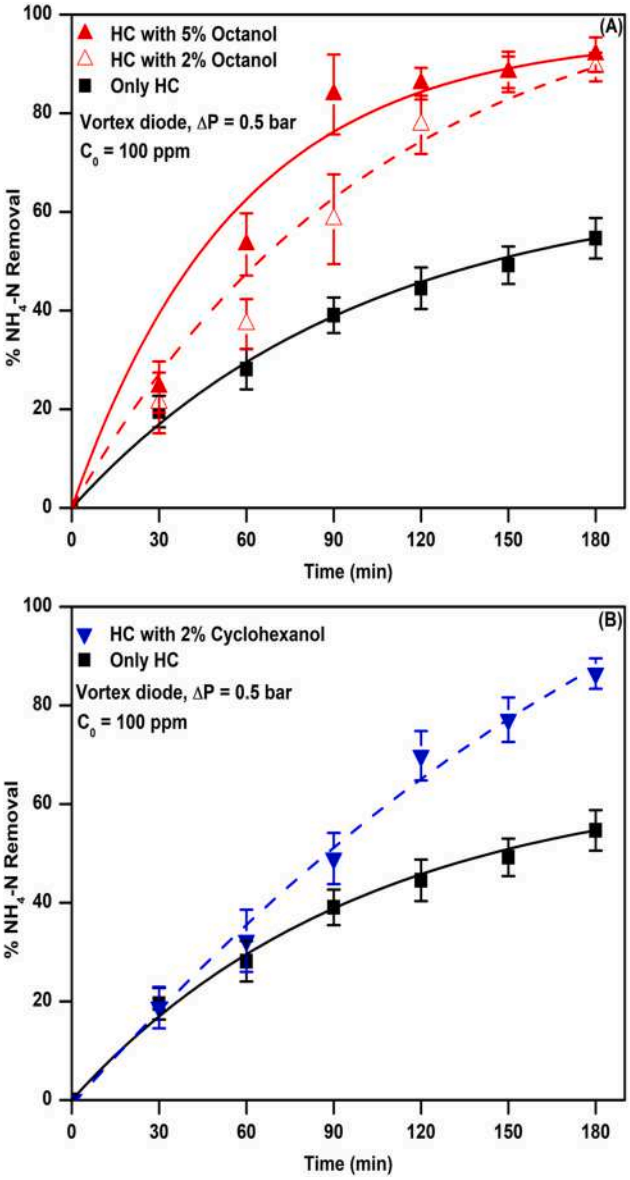

Fig. 2. Removal of ammoniacal nitrogen using solvents (A) Octanol (B) Cyclohexanol.

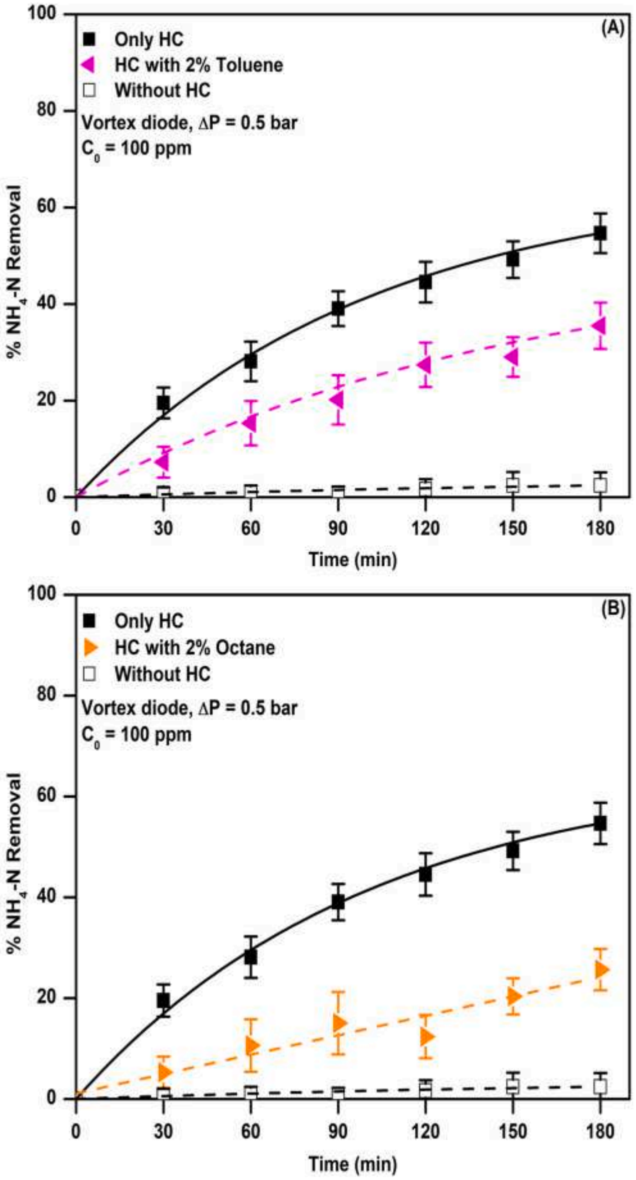

Fig. 3. Removal of ammoniacal nitrogen using solvents (A) Toluene (B) Octane.

of degradation process when the solvent volume fraction is increased and the difference in this regard is highlighted in Fig. 2A and B. Thus, in the solvent-assisted cavitation process, the degradation of pollutants can be accomplished by manipulating the process parameters such as solvent nature/polarity, solvent volume fraction etc. Similar to the conventional cavitation processes, the other parameters such as nature of the cavitation process (acoustic/hydrodynamic), pressure drop, nature of the cavitating device in the hydrodynamic cavitation etc. May also influence the performance. In view of the reported literature on the effects of pressure drop, the nature of cavitating device and cavitation process type, only the pertinent parameters are highlighted in this work and effects of other parameters are believed to be similar to those reported in the literature, though need to be separately investigated for quantitative analysis and comparison. Overall, the solvent-assisted cavitation process can provide significantly increased efficiency and substantially increased rates of degradation. The nonpolar solvents, octane and toluene (2% v/V) gave ammoniacal nitrogen removal only about 26% and 35% respectively, far lower than that obtained using only cavitation (Fig. 3A and Fig. 3B).

The results clearly highlight not just the effect of nature of the solvent, but also the importance of solvent volume fraction in the solvent-assisted cavitation process for improved removal of ammoniacal nitrogen. These aspects need detailed investigations for appropriate selection of the solvent.

4.2. *Kinetics of degradation*

The kinetics of the degradation was studied for the initial concentration of 100 mg/L of 4-aminophenol and for different volume fractions of solvents in water. A pseudo first order model was considered, where,

$$C = C_0\ e^{-kt} \tag{1}$$

C_0 and C denote the initial ammoniacal nitrogen concentration and concentration at any time, t, “t” is time (min), and k is an apparent rate constant (min^{-1}) of the reaction. The fit of the model was found good with $R^2 > 0.98$ for all the k value estimates. The values of the rate constant are given in Table 1. For only hydrodynamic cavitation using vortex diode, pressure drop of 0.5 bar, the k value was $4.7 \times 10^{-3}\ min^{-1}$

Table 1
Rate constant for different solvents (4-aminophenol (100 mg/L); vortex diode; ΔP, 0.5 bar).

Methodology	% NH_4–N Removal after 180 min	1st Order Rate Constant k × 10^3 (min^{-1})
HC only	55	4.7
Without HC	2.4	0.1
HC with 2% n-Octanol	89	12.4
HC with 5% n-Octanol	92	15
HC with 2% Cyclohexanol	86	9.9
HC with 2% n-Octane	26	1.5
HC with 2% Toluene	35	2.5

while for cavitation with 2% and 5% octanol it was 12.4 × 10^{-3} min^{-1} and 15 × 10^{-3} min^{-1} respectively. The k values in the case of 2% cyclohexanol, octane and toluene were 9.9 × 10^{-3} min^{-1}, 1.5 × 10^{-3} min^{-1} and 2.5 × 10^{-3} min^{-1} respectively. It was observed that the increase in the removal rate was significant when cavitation was carried out with relatively polar solvents such as octanol and cyclohexanol while in the case of non-polar solvents, such as octane and toluene, the removal rate was lower as compared to the cavitation alone.

In the case of octanol, with a volume fraction of 2%, the removal rate was significantly increased by 2.5 times than cavitation alone while increasing volume fraction to 5% gave more than 3 times increase in the rate of ammoniacal nitrogen removal. For cyclohexanol, 2% volume fraction gave ~2 times enhancement in the removal rate compared to the cavitation alone. Thus, the developed methodology can be viewed as a transformed advanced oxidation process using solvent for degradation of the pollutants.

4.3. *Per-pass degradation and cavitational yield*

In recent years, the use of per-pass degradation model in describing the hydrodynamic cavitation behaviour for different reactors has gained significance due to the physical understanding and for its ability to represent close to real life operation (Jain et al., 2019; Mane et al., 2020a, 2020b; Sarvothaman et al., 2018). The per-pass degradation factor is described as,

$$\text{Per} - \text{pass degradation factor } (\varphi) = k\,\tau \tag{2}$$

where, τ is residence time which is defined as the ratio of volume in holding tank and flowrate through cavitation reactor.

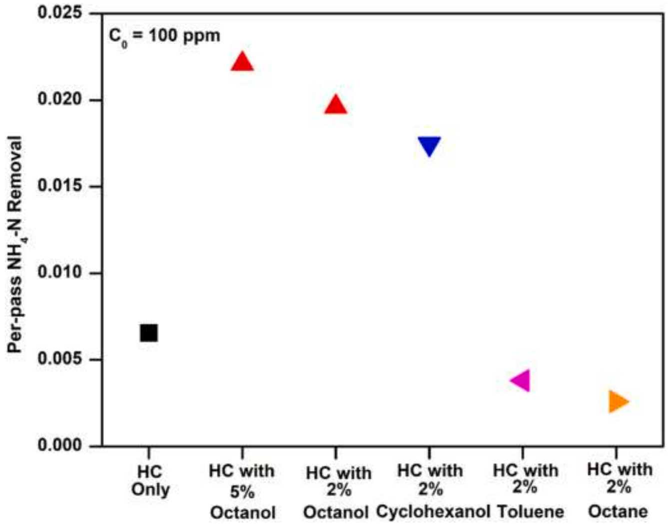

Fig. 4. Per-pass NH_4–N removal, C_0 = 100 ppm.

Fig. 4 shows a comparative analysis of per-pass degradation for the cavitation device, vortex diode at ΔP = 0.5 bar for cavitation alone and with the addition of different polar and nonpolar solvents and also for different solvent ratios. Cavitation with relatively polar solvents such as octanol and cyclohexanol shows almost doubling of the per-pass removal while there was no improvement for cavitation with the addition of non-polar solvents such as octane and toluene compared to cavitation alone, as discussed in the earlier section.

The energy dissipation rate is calculated as,

$$W = \Delta P \times Q \tag{3}$$

The overall cavitational yield (amount of ammoniacal nitrogen degraded per unit energy dissipation) can be obtained as,

$$Y = \frac{V(C_0 - C)}{\Delta PQt}\ \text{mg}\Big/\text{J} \tag{4}$$

The value of the cavitational yield in the case of hydrodynamic cavitation without solvent was 11.4 × 10^{-4} mg/J while in the case of octanol it was 14.5 × 10^{-4} mg/J and 16 × 10^{-4} mg/J for 2% and 5% volume fraction respectively. The values in the case of 2% volume fraction of cyclohexanol, octane and toluene were 14.3 × 10^{-4} mg/J, 5 × 10^{-4} mg/J and 7.5 × 10^{-4} mg/J respectively. The model, therefore, correlates increase in the cavitational yield for the relatively polar solvents.

The cavitation device will certainly have an important role in the process. However, the objective of this work is to provide the proof of concept for the solvent-assisted hydrodynamic cavitation for the degradation of the organic pollutants/removal of ammoniacal nitrogen using any cavitation process, in general and hydrodynamic cavitation, in particular. Hence, though the selection of cavitating device will impact the overall performance of the process, the enhancement due to the novel process to obtain solvent-assisted cavitation for wastewater treatment will maintain, irrespective of the type of the cavitating device. It is however, required that further investigations be carried out for different cavitation reactors to further assess the practical relevance of the process in wastewater treatment.

4.4. *Differentiating solvent assisted cavitation and solvent extraction processes*

The reported work in the literature pertaining to the solvent and wastewater can be broadly classified into two parts:

1. Solvent use in the solvent extraction process.
2. Different processes for degradation of solvents

The use of solvent extraction process for treating large volumes of wastewaters is not common due to correspondingly large quantities of solvent requirements and operational difficulties. Further, small concentrations of pollutants make it less suitable and economically not viable. A combination of solvent extraction and freeze thaw for oil recovery from petroleum refinery wastewater was recently reported by (Hu et al., 2015). The requirement of a high volume ratio of toluene/-wastewater was suggested for the recovery of nitrotoluenes from wastewater by solvent extraction (Chen et al., 2007). Recently, extraction and fractional distillation was reported for the removal of organic compounds from wastewater of the oil industry (Vegas Mendoza et al., 2019).

A number of studies have been reported for the degradation of solvents by advanced oxidation processes in wastewater treatment-solvents of the type acetone, toluene and so on, typically by employing O_3/UV process (Chen and Liang, 2009; Muruganandham et al., 2007; Wu et al., 2007), by Fenton process (Haseneder et al., 2007), by sonochemical and photochemical oxidation (Naffrechoux et al., 2000) or such multiple combinations using different oxidising agents such as hydrogen peroxide (Chitra et al., 2004; Daifullah and Mohamed, 2004; Wu et al., 2008). Degradation of solvents using cavitation processes was sparsely reported in the literature (Patil et al., 2021b; Sarvothaman et al., 2018; Suryawanshi et al., 2018).

The solvent extraction process, typically employs physical separation of the targeted species or its reacted form from wastewater to the solvent phase. Dissociation extraction is one such example, although such approaches have limited practical utility.

The degradation of solvents using advanced oxidation processes typically have Fenton process type catalyst and other reagent requirements apart from low concentrations of solvents, largely in ppm range. Cavitation methodologies reported for the degradation of solvents also involve low concentrations of different solvents.

The novelty in the developed solvent-assisted cavitation process can be visualized in the form of solvent additive being used for enhanced degradation of organic pollutants. Water is a continuous phase while the solvent is a dispersed phase. During the cavitation, cavities can form from both water as well as from solvent and the oxidation reactions can take place at the interface in accordance with the availability of the pollutant species. The vapour filled cavities of solvent and water exist only for a small duration of time (microseconds); essentially a transition state. Physical extraction of the organic pollutant may occur in the solvent, though equilibrium distribution is less likely due to transient nature and existence. Degradation of the pollutant and subsequent mineralization by the oxidation process makes the solvent-assisted cavitation completely different from the conventional extraction process as well as from the conventional cavitation process. The use of solvent for assisting the degradation of the pollutants is not reported so far in any form of cavitation processes and obtaining significant enhancement in the degradation of pollutants using the solvent-assisted cavitation process can be construed as a novelty in the process that can have practical utility and applications in wastewater treatment, especially when no additional pollution due to the use of solvent additives is observed or can be achieved.

4.5. *Mechanism of the solvent-assisted cavitation process*

Cavitation is known to generate cavities that grow in size and eventually implode to enable the formation of hydroxyl radicals through water cleaving at extreme conditions of temperature and pressure at the point of implosion. In the conventional process, therefore, the number of cavities and productive implosions of the cavities are most crucial for the generation of the oxidising radicals and consequently degradation of organic pollutants via oxidation. With the 3 zone theory in cavitation, it is also possible that when the pollutant is near the bubble implosion interface, there are high chances of pyrolytic break down (Gogate and Pandit, 2004). It was recently reported that any process intensification that can increase the number of cavities can aid/enhance the degradation performance, e.g. aeration, and also that the degradation mechanism of p-aminophenol involves oxidation with final oxidation products as benzoquinone, water and NOx (Patil et al., 2021a). In this work, therefore, elucidation of the mechanism of the solvent-assisted cavitation is specifically attempted.

It is believed that the addition of solvent as an additive in the solvent-assisted cavitation incorporates the third component in the system in both liquid and vapour phases-water containing organic pollutants, vapour filled cavities/vapours of both aqueous as well as organic, and third component in the form of the additional solvent as the organic liquid phase and solvent vapour phase. In the conventional cavitation process, the cavities inherently get formed in the aqueous phase and bring the organic moiety into the cavities or at the point of implosion for the degradation to take place. It is postulated that the addition of appropriate solvent as an additive results in the generation of additional cavities due to solvent flashing into vapour and also the subsequent collapse of these cavities, though the complete mechanism is rather not clear at this point of time. It is possible that the organic moiety may easily migrate into the solvent and therefore more chances of it to degrade due to the increased implosions of different cavities. Since all types of solvents are not suitable to enhance the degradation behaviour, it is believed that the affinity to solvent is crucial. The advantage, over and above the conventional hydrodynamic cavitation, in enhancing the degradation of pollutants and also the disadvantage or adverse impact due to some solvents in this regard, both the effects are clearly depicted in Fig. 5A where the positive effect is observed in terms of enhancing the rate as well as overall degradation for the two solvents, octanol and cyclohexanol, and the negative or adverse impact in terms of reduced degradation is obtained for the two solvents, toluene and octane.

Fig. 5B depicts the variation in the relative polarity for the four solvents. The enhancement in degradation with relatively polar solvents such as octanol and cyclohexanol can be attributed to the increased localized concentration of the pollutant at the solvent interface compared to the pollutant concentration in the aqueous phase. Consequently, the increased concentration at the point of implosion increases the rates of degradation and also increases overall degradation efficiency. Compared to the effect of relatively polar solvents, the pollutant species going into non-polar solvent is likely to get insulated from

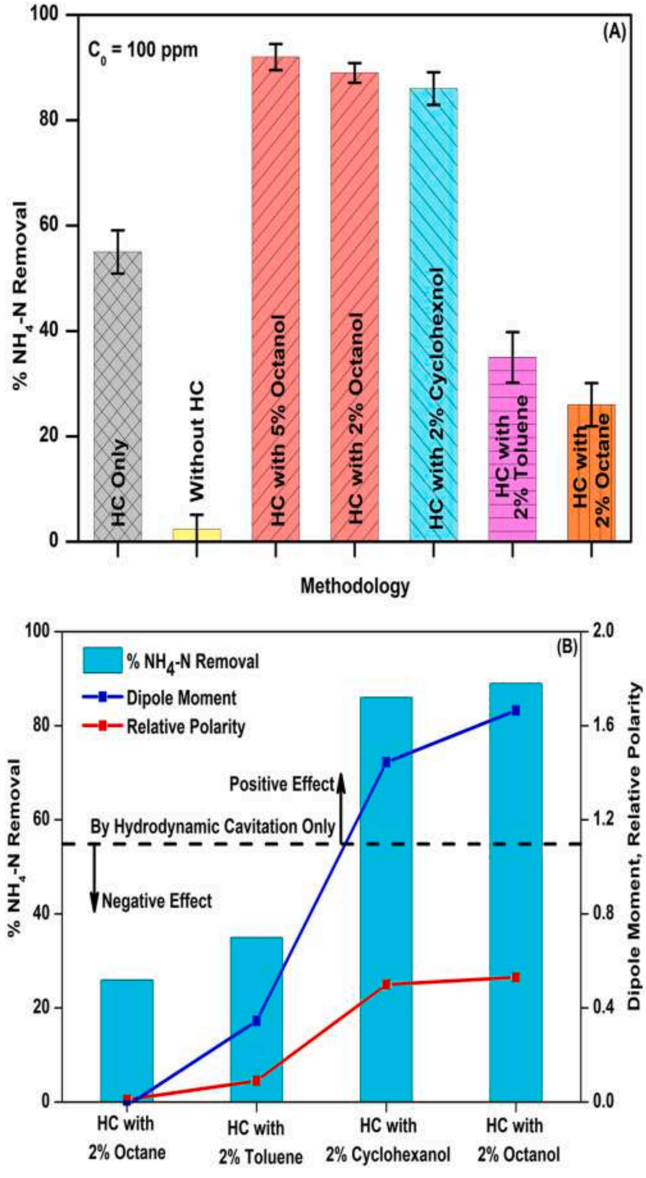

Fig. 5. Correlating solvent polarity with degradation efficiency.

hydroxyl radicals, subsequently reducing the local concentration of pollutant for oxidation which consequently results in lower rates of degradation and lowered efficiency compared to not only relatively polar solvents, but also that for only hydrodynamic cavitation. Thus, it can explain the increased degradation for the relatively polar solvents and reduced degradation efficiency for the non-polar solvents as compared to the conventional cavitation (~62% increase for 2% octanol, 56% for cyclohexanol in contrast to lowered degradation for toluene, (−36%) and for octane (−53%)).

The solvent physical properties such as viscosity and surface tension will also impact the cavity formation and therefore, the cavitation process. These aspects need to be investigated in detail for complete elucidation of the mechanism of the solvent-assisted cavitation process.

The developed process is distinctly different from the conventional solvent extraction. In the solvent extraction, there is a physical distribution of the species in two phases, aqueous and organic; extraction in the solvent takes place thereby depleting the concentration from the aqueous phase. Further, in the solvent extraction process, there is no degradation of the species or more specifically mineralization. In the present work, the analysis of both the solvent and aqueous phases before and after the cavitation confirmed that the removal is not through the extraction of the organic pollutant in the solvent. Fig. 6 shows the HPLC analysis of the solvent and the aqueous phase prior to and after the cavitation (180 min), for the experiment with 2% octanol. A sharp peak of 4-aminophenol can be seen in the aqueous phase before and after cavitation indicating its predominant concentration in the aqueous phase and only a minor distribution of 4-aminophenol (~2%) in the solvent phase was observed. Further, no major by-products formation was seen after the cavitation. There was no pollutant increase due to the use of the solvent. The solvent-assisted cavitation process is essentially carried out at ambient conditions and considering the higher boiling points of the solvents (Toluene, 111 °C; n-Octane, 125 °C; Cyclohexanol, 161 °C and Octanol, 195 °C), the loss of solvent due to vaporization is expected to be negligible. Preliminary analysis by physical separation showed the highest recovery for n-octane in the range of 96–98% (2% v/V) and lowest recovery for cyclohexanol, 75–78%; lower recovery can be attributed to the difficulty in the separation as a separate layer. The ease of separation of solvent depends on the miscibility and characteristics of the solvent and solvent selection is important similar to that in the case of solvent extraction. Also, no pollution due to the use of solvent additive was confirmed from the TOC analysis; reduced TOC after the treatment. The results clearly substantiate the suggested mechanism of the solvent assisted cavitation.

4.6. *Cost analysis for solvent assisted ammoniacal nitrogen removal*

The cost of treatment per unit volume of effluent by hydrodynamic cavitation can be calculated as (Ranade and Bhandari, 2014a),

$$\text{Cost of treatment per m}^3\text{ of effluent} = \frac{Nc \ \times \Delta P \times P_E}{36\eta} \tag{5}$$

where, Nc is the number of passes, ΔP is the pressure drop across the cavitation device, P_E is the cost of electricity and η is the pump efficiency.

In view of the negligible solvent usage/loss, the cost of the solvent was neglected in the present analysis. However, the solvent cost may have to be accounted, if required, for the solvent/recovery. Assuming the cost of electricity for typical Indian scenario as Rs. 10/kWh (1$ = 70 Rs) and pump efficiency at 66% (commercial high flowrates, above 10 m^3/h), the cost of treatment by the hydrodynamic cavitation alone using the vortex diode at ΔP = 0.5 bar was found to be 24 R/m^3 (0.34$/$m^3$), while for the solvent assisted cavitation using 2 and 5% octanol it was 11 R/m^3 (0.15$/$m^3$) and 8 R/$m^3$ (0.11$/$m^3$) respectively. The cost in the case of 2% cyclohexanol was 13 R/m^3 (0.18$/$m^3$). It is clear that the solvent assisted hydrodynamic cavitation using vortex diode as the cavitating device for ammoniacal nitrogen removal reduces cost by approximately 2–3 times compared to the hydrodynamic cavitation alone.

Thus, the solvent-assisted cavitation process for the wastewater treatment appears to be quite attractive alternative compared to the cavitation alone, both in terms of efficiency and cost of operation.

5. Conclusions

A newer approach of solvent-assisted cavitation process is proposed for the degradation of organic pollutants and use of suitable solvent, as an additive (1–5% v/V), is reported for the first time specifically for the enhanced removal of organic pollutants, in general and ammoniacal nitrogen, in particular. The proposed process was found to have higher efficiency in the removal of ammoniacal nitrogen compared to the conventional cavitation. The important findings are.

1. Vortex flow-based cavitation reactor was found to be highly effective for the removal of ammoniacal nitrogen.
2. Solvent-assisted cavitation process retains the advantages of conventional cavitation processes by employing mild operating conditions such as low pressure drop of 0.5 bar while accomplishing higher levels of degradation of organic pollutants.
3. Solvent characteristics are important for obtaining enhancement in the removal of pollutants and relatively polar solvents such as octanol and cyclohexanol were found to be highly effective compared to non-polar solvents e.g. toluene and octane.
4. A very high ammoniacal nitrogen removal to the extent of 90% could be obtained for relatively polar solvents-octanol and cyclohexanol; an enhancement of 65% over and above the conventional hydrodynamic cavitation under similar conditions.
5. Removal rate was also significantly enhanced by 2–3 times than individual operation of hydrodynamic cavitation depicting high efficacy of the new process.
6. Non-polar solvents, as additives, were found to diminish the effect of hydrodynamic cavitation, possibly due to the insulating effect for the pollutant moiety.
7. The developed process appears to have a significantly low cost compared to conventional hydrodynamic cavitation and more than 200% cost reduction was achieved.

The results can provide impetus to further research for possible improvements in the existing cavitation technologies and process intensification methodologies in the wastewater treatment, in general and for the removal of ammoniacal nitrogen, in particular.

Author contributions

V.M.B. and P. B. P conceived and developed the idea along with experimental methodology/result analysis. P.B.P. conducted all the experiments and analyzed the data. Both the authors were involved in the preparation of the manuscript.

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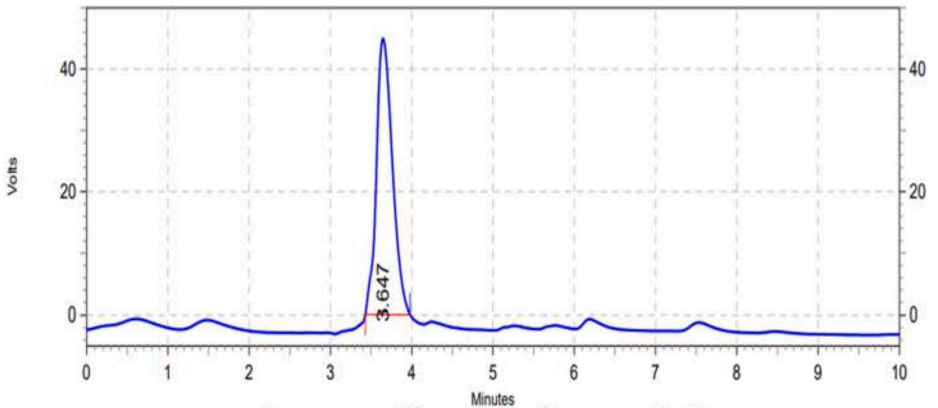
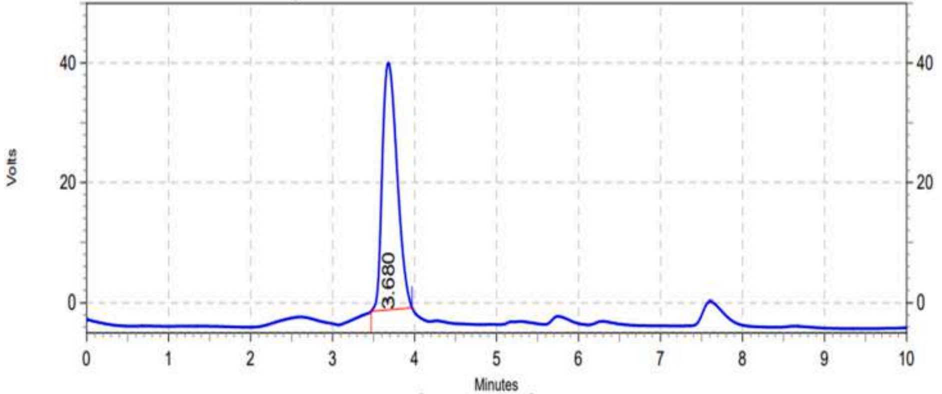
Data availability

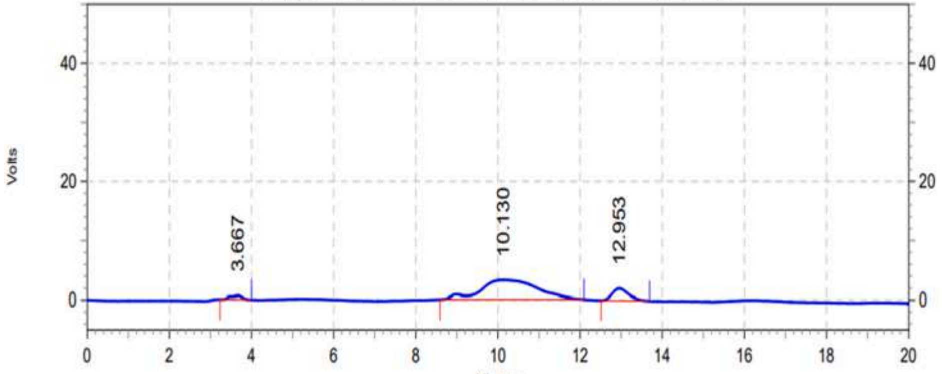
Data generated or analysed during this study are included in this



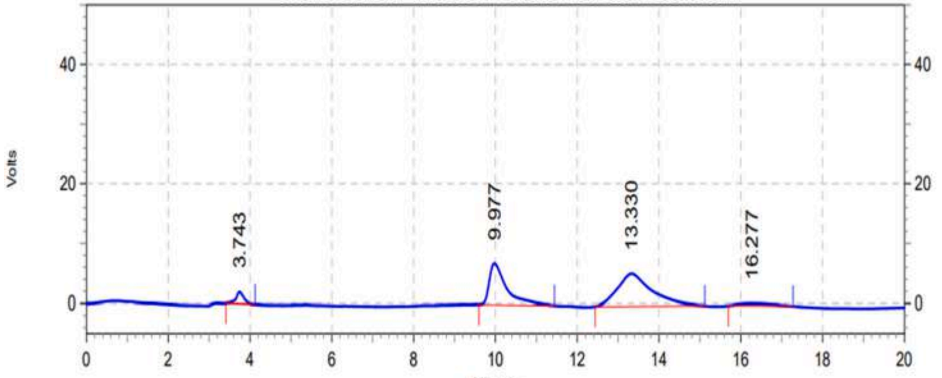
Aqueous Phase: Before cavitation



Aqueous Phase: After cavitation



Solvent Phase: Before cavitation



Solvent Phase: After cavitation

Fig. 6. HPLC results indicating degradation of para-aminophenol.

published article.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Nomenclature

C_0	Initial concentration, (mg/L or ppm)
C	Final concentration, (mg/L or ppm)
k	Rate constant, min^{-1}
N_C	Number of passes required for treatment
P	Pressure, bar
P_E	Cost of electricity per kWh, Rs
Q	Flow Rate, L/h
t	Time, min
V	Volume, L
W	Energy dissipation rate, W
Y	Cavitational yield, mg/J
φ	Per-pass degradation factor
ΔP	Pressure drop, bar
η	Efficiency of the pump

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