Process Intensification for Removal of API Cetirizine HCl from Simulated Wastewater using Advance Oxidation Processes

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By

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Certificate

This is to certify that the work incorporated in this **M. Tech Major-Project Report** entitled **"Process Intensification for Removal of API Cetirizine HCl from Simulated Wastewater using Advance Oxidation Processes"** submitted by **Mr. Aashay Brahme** to **Academy of Scientific and Innovative Research (AcSIR)** for the fulfilment of the requirements for the award of the Degree of M. Tech, embodies original research work under my supervision. We further certify that this work has not been submitted to any other University or Institution in part or full for the award of any degree or diploma. Research material obtained from other sources has been duly acknowledged in the report. Any text, illustration, table etc. used in the report have been duly cited and acknowledged.

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Abstract

Various Active Pharmaceuticals Ingredients are consumed all over the world for the treatment of several ailments and disorders. The presence of these ingredients in water poses a serious threat to the environment and public health. The inefficiency of sewage treatment plants for removal of these APIs has raised alarms for the invention of efficient, sustainable and cost-effective technologies. Cetirizine HCl which is a 2nd generation anti-histamine drug used for the treatment of various allergic infections is commonly found in wastewater due to its low biodegradability and high solubility. Advance Oxidation Process such as hydrodynamic Cavitation (HC), Ozonation, UV, catalysts such as Titanium dioxide (TiO_2), Hydrogen Peroxide (H_2O_2) and their hybrid processes have shown a great potential for the removal of persistent pharmaceuticals from wastewater. The current study involves the removal of Cetirizine HCl from simulated wastewater using the above-mentioned techniques, mainly a combination of UV /ozone, which gave maximum removal of TOC of 91.3 %. The effect of the various operational parameters viz. initial concentration of cetirizine HCl, pH of the solution, variation in ozone flowrate, effect of salts, effect of sources of water has been studied and optimum condition have been established. Thus, from the experimental study it was observed that UV/O_3 is a promising AOP for the treatment of cetirizine containing wastewater.

Keywords: Active Pharmaceutical Ingredients (APIs), Cetirizine HCl, Advance Oxidation Processes (AOPs), UV/O_3, Total Organic Carbon (TOC)

Scientific Publications

- Rinka Pramanik, Narendra Bodawar, Aashay Brahme, Sanjay Kamble, Mahesh Dharne, "Comparative evaluation of advanced oxidation processes (AOPs) for reducing SARS-CoV-2 viral load from campus sewage water". Journal of Environmental Chemical Engineering. https://doi.org/10.1016/j.jece.2023.109673

- Aashay Brahme, Narendra Bodawar, Sanjay Kamble, Process Intensification for Removal of API Cetirizine HCl from Simulated Wastewater using Advance Oxidation Processes, to be communicated to Journal of Water Process Engineering (2023).

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Chapter 1: Introduction

1. Introduction

Effluent wastewater treatment is crucial for safeguarding the environment and protecting public health. Improperly treated effluent wastewater can contain various pollutants, including harmful chemicals and pathogens, which can pose significant risks to aquatic ecosystems and human health. By removing these pollutants through proper treatment, effluent wastewater can be made safe for discharge into water bodies, minimizing the risk of contamination and protecting the environment. Additionally, effective effluent wastewater treatment can help conserve water resources by allowing for the safe and responsible reuse of treated wastewater for non-potable applications, such as irrigation or industrial use.

Water is crucial component required in the pharmaceutical industry serving as a raw material for drug manufacturing, washing after filtration and cleaning of equipment among other unit operations such as extraction, blending, heating, in cooling towers etc. Unfortunately, this industry generates a significant amount of waste water with a market worth of 50 billion USD and is projected to grow at a CAGR of 11.2 %. To mitigate the impact of pharmaceutical wastewater on the environment, the government has established certain national standards for the release of pharmaceutical effluent, which are detailed in Table 1.

Various Active Pharmaceutical Ingredients such as analgesics, antibiotics, blood lipid regulators, antihistamines, antidepressants, contraceptive drugs, chemotherapy drugs are regularly consumed worldwide. However, these compounds are not fully metabolized in the body and are excreted through urine and faeces, eventually entering sewage treatment plants. Due to their low biodegradability, these APIs persist in the environment for extended periods, posing significant concerns for public health and the aquatic ecosystem. Even in trace amounts, these compounds can have adverse effects, including disruption of endocrine systems in biological organisms, pathogenic bacteria resistance, and genotoxicity. As a result, wastewater containing APIs is a major cause for concern and requires proper management to mitigate its impact.[1]

Extensive research has been carried out for studying the occurrence of various pharmaceuticals in the environment. Henning et. al performed the study for presence of various Active Pharmaceutical Ingredients (APIs) in surface and sea waters. It was found that surface waters contained APIs whose concentration varied in the range of 0.0018- 0.12 μg/L. Several APIs with concentrations such as norethisterone (1.1- 2.1 ng/L), clarithromycin (3.9 – 42 ng/L), carbamazepine (2 – 440 ng/L), telmisartan (7.4 – 2800 ng/L), atorvastatin (44 – 1000 ng/L), metformin (230 – 1350 ng/L), diclofenac (33 – 85 ng/L) were found in rivers and coastal regions. Among the various pharmaceuticals detected, cetirizine was one of the most common occurring API in the samples collected from various regions surrounding the Baltic Sea and the water bodies near the adjoining cities, which is used for treatment of asthmatic and allergic infections. Its concentration in the water varied in the range of 0.27 – 630 ng/L. [2]

Conventional wastewater treatment techniques, such as biological treatment and physical-chemical processes, were primarily designed to remove conventional pollutants, such as organic matter and nutrients, from wastewater. However, these techniques have limited effectiveness in removing active pharmaceutical ingredients (APIs) from wastewater due to their complex and persistent nature. APIs have unique physicochemical properties and are present in low concentrations, making their removal challenging. Additionally, the conventional wastewater treatment processes may not target specific APIs and may even generate transformation products that may have toxicological implications. Therefore, conventional wastewater treatment techniques alone may not be sufficient for the removal of APIs from wastewater and alternative, more advanced treatment processes, such as advanced oxidation processes, membrane filtration, or adsorption, may be required to effectively treat wastewater containing APIs. To remove these refractory compounds modern techniques like advance oxidation processes, adsorption using advanced membranes etc need to be employed.

Advanced oxidation processes (AOPs) have demonstrated high efficiency in removing pharmaceutical compounds from wastewater due to their ability to generate highly reactive and non-selective hydroxyl (OH·) radicals, which can effectively degrade a wide range of organic compounds. AOPs can significantly reduce the organic load in wastewater and increase the biodegradability of effluent. Various AOPs and their combinations, such as ozone, hydrogen peroxide (H2O2)/ozone, UV/ozone, and Fenton process, have been extensively used for the degradation of pharmaceutical pollutants. These advanced treatment processes can provide an effective means for the removal of complex and persistent pollutants from wastewater, thereby reducing their potential impact on human health and the environment. [3]

A detail study has been carried out in the major report for complete removal of API cetirizine from simulated water using advance oxidation processes namely Hydrodynamic cavitation, ozonation (O_3), UV, Hydrogen peroxide (H_2O_2). Titanium dioxide (TiO_2), and their hybrid processes. Particularly combination of UV/O_3 process has been used for the degradation of cetirizine. The study examined the effect of various parameters including the initial concentration of cetirizine, solution pH, ozone flowrate, different types of salts, different types of water. The mineralization study is carried out by measuring the Total Organic Carbon (TOC) load. The results of this study can help in developing effective wastewater treatment strategies for the removal of pharmaceutical pollutants, which can significantly reduce their impact on human health and the environment.

Table 1: National Environmental quality standards for pharmaceutical effluents according to CPCB norms

	Parameter	**Permissible limit (ppm)**
Compulsory	pH	6.5 -8.5
	COD	250
	Oil & grease	10
	BOD (3 days at 27°C)	100
	Total suspended solids	100
Additional	Mercury	0.01
	Arsenic	0.20
	Lead	0.1
	Cyanide	0.1
	Phosphates (as P)	5.0
	Phenolic compounds (C_6H_5OH)	1.0
	Chromium	0.1
	Sulfide groups (as S)	2.0

Chapter 2: Literature Review on Removal of Cetirizine HCL

2. Literature review

2.1 Removal of Cetirizine HCl using adsorption technique

Adsorption method for removal of pollutants is highly efficient, cost effective, viable for various concentration levels of contaminants. Another advantage of adsorption process is that the adsorbent can be used for multiple cycles of adsorption by washing and regenerating using various techniques. Removal of cetirizine hydrochloride is carried out by adsorption techniques using certain adsorbents.

Stanisz et. al investigated the adsorptive removal of cetirizine by lignin based spherical particles derived from Saponaria officianilis L and the soap nuts of the Sapindus Mukorossi tree using green surfactants. The adsorption study was carried out at room temperature and pH from 6-8 with initial concentration of cetirizine in the range of 1- 20 ppm. Maximum adsorption efficiency of 90 % was observed when the reaction was carried out for 240 mins. The analysis of the samples was carried out using High performance liquid chromatography and UV-vis spectroscopy. [4]

Howell et. al performed the adsorption study of enterosorbent enterosgel for the removal of pharmaceutical drugs cetirizine and amitriptyline hydrochloride. The initial concentration for the drugs was taken 40 ppm and the maximum adsorption for cetirizine was observed 53 % when the study was carried out for 120 min. The adsorptive study was performed at a temperature of 37 °C and kept for stirring at 120 RPM. UV- vis spectroscopy was used for analyzing the samples.[5]

Although adsorption process is used for treatment of wastewater, it has certain shortcomings

- High initial cost for investment is required.
- Regeneration of the adsorbent generates more waste.
- The pollutant is only transferred and concentrated from one phase to another phase.

2.2 Removal of Cetirizine HCl using AOPs technique

AOP techniques are widely used in industries for abatement of harmful pollutants from wastewater. Degradation causes the disintegration of pollutants into simpler compounds which have less toxicity as compared to the parent compound and subsequently get converted to CO_2

and water. The removal of cetirizine hydrochloride in wastewater is carried out by using advance oxidation processes.

Gadepalli et. al investigated the degradation of cetirizine hydrochloride by using UV and persulfate ($S_2O_8^{2-}$). The initial concentration of cetirizine was taken 100 ppm for the degradation. The study was carried out in a cylindrical quartz double jacketed photoreactor and enhanced biodegradability of cetirizine was observed. Maximum degradation of 95 % was achieved in 90 minutes of exposure to UV light. [6]

Mohamed et. al studied the photodegradation of cetirizine by using titanium dioxide nanoparticles grafted onto polyacrylonitrile (PAN)/ Multiwalled Carbon Nanotubes (MWCNT) composite nanofibers. The initial concentration for cetirizine was taken in the range of 5-50 ppm and the reaction was carried out in a pH range of 2-9. 99% of cetirizine was degraded within 40 minutes of exposure to UV irradiation. The MWCNT analysis was performed using Fourier Transform Infrared Spectroscopy (FTIR), Scanning electron Microscopy (SEM) and the Cetirizine degradation study was carried out using initial and final concentration study. [7]

Cheng et. al investigated the removal of cetirizine hydrochloride by UV and chlorine treatment. The initial concentration for cetirizine was taken in the range of 2-50 micro-molar and the degradation study was carried out in a photochemical reactor at room temperature of 25 °C. The degradation efficiency for cetirizine was achieved 85- 90 % in 15 minutes. [8]

Nasrallah et. al studied the degradation of cetirizine by using UV and TiO_2 supported on luminous textile. The initial concentration was taken in the range of 2.5- 20 ppm and the reaction was performed in a cylindrical glass photochemical reactor with different pH values 3, 6.5 and 10. Maximum degradation of cetirizine was observed 96 % for 2.5 ppm concentration in 330 minutes of reaction time. [9]

Sutar et. al investigated the removal of antihistamine cetirizine by using ultrasound and enzyme laccase. The initial concentration for the degradation study was taken 5 ppm and the degradation was performed in a flat bottom baffle glass reactor having 3 blade turbine glass impellers. The reaction was carried out at different pH values ranging from 4 to 8 and maximum degradation of 91 % of cetirizine was achieved in 420 minutes at optimum experimental conditions of 50 °C temperature, power input of 100 W, 25 kHz frequency. 50 % duty cycle and 200 RPM agitation speed. [10]

Mead et. al studied the photodegradation of cetirizine in natural waters. The initial concentration for cetirizine was taken 250 nano molar and the exposure study was carried out in spectrophotometric quartz cells of 10 cm length and by using LH 153 lamp which mimicked the wavelength distribution at the surface of the natural water bodies. 50 % degradation of cetirizine was achieved in 1440 minutes of exposure to the light. [11]

Iqbal et. al investigated the degradation of cetirizine dihydrochloride by using zinc vanadate flower and UV light. The degradation study was performed for initial concentration of cetirizine in the range of 10 – 30 ppm and at different pH values ranging from 3 – 9. Maximum degradation efficiency of 87 % was observed for initial cetirizine concentration of 10 ppm at optimum conditions of catalyst dose 500 ppm, pH 6 and 120 minutes of exposure to UV light. Zinc vanadate catalyst was characterized with respect to X-ray diffraction (XRD), UV-vis Spectroscopy to measure its physiochemical properties. [12]

Agnihotri et. al studied the degradation of cetirizine by using electro-oxidation and electro-fenton process using RuO_2 coated Ti electrodes (Ti/RuO_2). The initial concentration of 50 ppm was used for the study. Stainless steel was use as anode and RuO_2 coated Ti electrode was used as cathode for both the processes. For electro-oxidation process maximum degradation of 57.61 % was observed at optimum operating parameters pH 7, 0.54 A current and 89 minutes of electrolysis time, whereas for electro-fenton process maximum degradation of 78.37 % for cetirizine was observed at optimum parameters 0.84 A current, Fe^{+2} dose of 1 mmol and 52.86 minutes of reaction time. The sensitivity of the reaction parameters was analyzed using Response Surface Methodology (RSM). [13]

Ceglie et. al investigated the removal of antihistamine cetirizine by using UV and mesoporous Titanium di-oxide (TiO_2) coated on glass fibers. The initial concentration for cetirizine was taken 0.2 ppm and the reaction was carried out in an up-flow reactor of volume 0.5 L which was equipped with mercury lamp emitting UV light of wavelength 254 nm. Complete degradation of cetirizine was noted in 60 minutes of exposure to UV light. Mesoporous TiO_2 was characterized by X-ray Diffraction (XRD), Brunauer, Emmett and Teller (BET) surface area measurements, Field Emission Scanning Electron Microscopy (FESEM). [14]

The above literature survey gives a brief idea for the removal of cetirizine removal by adsorption and by using advance oxidation processes (AOPs).

Chapter 3: Materials and Experimental Setup for Degradation of Cetirizine HCl

3. Materials

Cetirizine HCl is a piperazine class of second-generation antihistamine drug which is used for treatment of allergic infections. Its IUPAC name is 2-(2-(4-(4-chlorophenyl) phenylmethyl) piperazin-1-yl) ethoxy) acetic acid. It has structure which is depicted in the Figure 1. The physicochemical properties of cetirizine are given in Table 2.

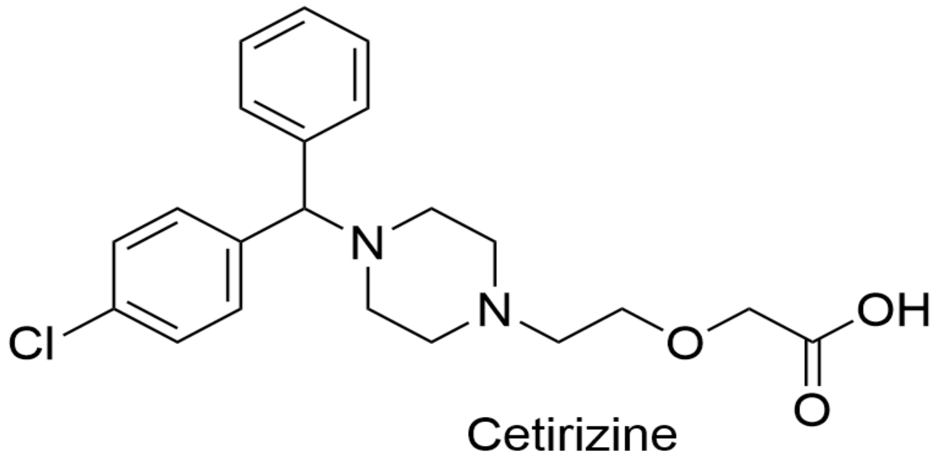

Figure 1: Cetirizine HCl structure

Table 2: Physicochemical properties of cetirizine

Property	Value
Appearance	Crystalline powder
Colour	White
Odour	Odourless
Molecular weight (g/mol)	388.9
Melting point (°C)	110-115
Boiling point (°C)	542.1
Water solubility (ppm)	101

3.1 Experimental setup for removal of cetirizine from wastewater using AOPs

3.1.1 Experimental setup for cavitation base hybrid AOPs:

The experimental setup used for cavitation-based hybrid AOPs: is shown in the Figure 2. It comprises of an Effluent Holding Tank (EHT), centrifugal pump for recirculation and devices venturi-meter and orifice-meter and vortex diode which were used for cavitation study. Pressure gauges were installed across the devices to monitor the inlet and outlet pressure.

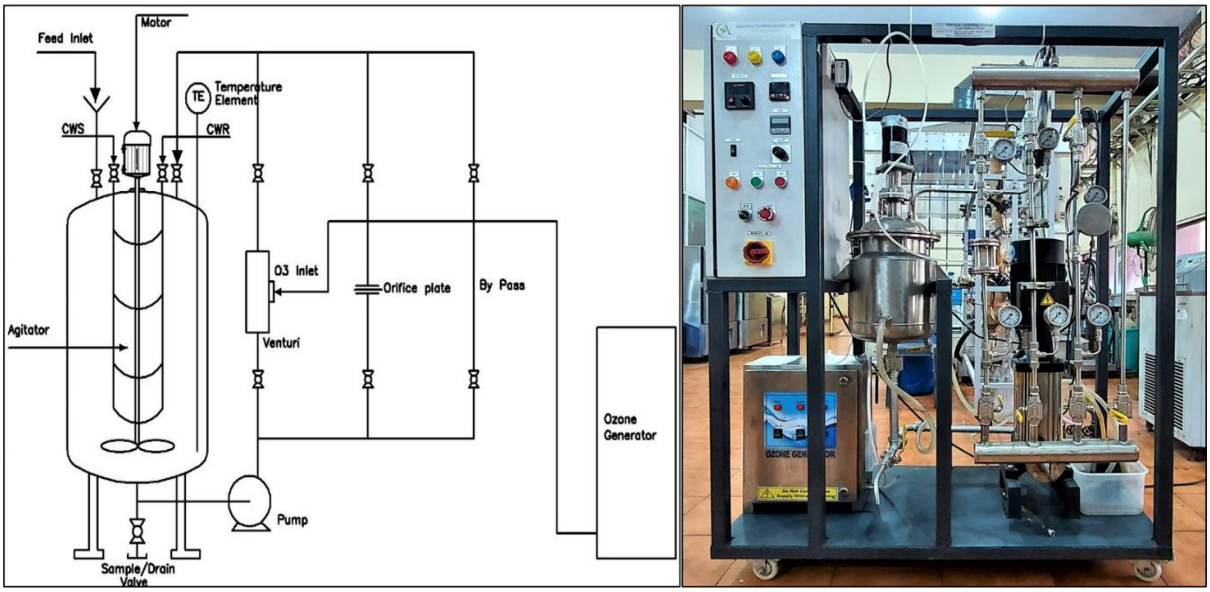

Figure 2: Setup for cavitation and hybrid processes

3.1.2 Experimental setup for hybrid AOPs:

The experiment setup used for experimentation of photocatalytic and its photolytic (UV), photochemical (UV/H_2O_2) and hybrid AOPs viz. UV/ozonation, UV/photocatalyst, Photocatalyst/ozonation, H_2O_2/ozonation, processes along with ozonation is shown in the Figure 3. The setup comprises of annular quartz glass reactor which has a quartz candle in it. The capacity of the annular reactor was 1 litre. Ozone flow rates in the range of 5 g/h to15 g/h were produced by operating the ozone generator within a range of 0.05 A and 0.15 A. The UV lamp used for degradation study was placed in the quartz candle through which cooling water was circulated for maintaining the temperature.

Figure 3: Setup for hybrid AOPs

3.2 Experimental procedure for cavitation-based hybrid AOPs

- Cavitation along with its hybrid techniques viz cavitation / ozonation, UV / cavitation, H_2O_2 / cavitation / ozone has been studied for removal of cetirizine using venturi meter, orifice meter and vortex diode-based cavitation devices.
- Known quantity of simulated waste water containing cetirizine (2 L) was fed to the EHT having a capacity of 5 L.
- Centrifugal pump was used to circulate the wastewater through the lines consisting of venturi meter, orifice meter, vortex diode and back into the EHT.
- The cavitation study was performed for three different pressure values 2, 4, 6 bar for all the devices.
- A submersible pump was used to circulate cooling water to the EHT for maintaining the temperature during cavitation.
- Samples were removed periodically for their TOC analysis.

3.3 Experimental procedure for hybrid AOPs

- Photolytic (UV), photochemical (UV/ H_2O_2) and hybrid AOPs viz. UV/ozonation, UV/photocatalyst, Photocatalyst/ozonation, H_2O_2 /ozonation, Photocatalytic and its hybrid process were performed using catalysts TiO_2 / H_2O_2 AOPs were studied using in annular glass reactor having a capacity of 1 L.
- Known quantity of simulated wastewater containing cetirizine (500 ml) was fed to the glass reactor.
- Ozone gas with desired flow was bubbled through the bottom of the reactor with the help of a ring sparger.
- UV lamp with characteristics 80 W, and wavelength of 254 nm was placed in the quartz candle.
- Cooling tap water was continuously circulated through the annular space between the lamp for maintaining the reaction temperature.
- Wastewater samples were removed periodically from the reactor for their TOC analysis.

Chapter 4: Results and Discussion

4 Results and discussion for experiments performed for the degradation of Cetirizine HCl using hybrid AOPs

4.1 Removal of Cetirizine HCl from wastewater using cavitation-based hybrid AOPs

The removal of cetirizine from wastewater has been studied using Hydrodynamic cavitation devices such as venturi meter (Contraction dia: 15 mm, Expansion dia: 12 mm Throat dia: 5 mm), orifice meter (dia: 3 mm) and vortex diode at 3 different pressure values of 2, 4 and 6 bar. The required Hydrogen peroxide (H_2O_2) concentration was kept constant throughout the study (100 ppm) and ozone flowrate was 10 g/h for all the experiments. UV lamp having 11W input wavelength 254 nm was used. The comparative results of removal of cetirizine from wastewater using cavitation-based hybrid AOPs are shown in the Table 3.

Table 3: Results for cavitation-based hybrid AOPs performed for Cetirizine HCl degradation

Technique	Device	Pressure (bar)	Initial TOC (ppm)	Final TOC (ppm)	Time (min)	% Reduction in TOC
Cavitation	Venturi meter	2	48.2	36.3	150	24.6
		4	43.1	37.	420	12.2
		6	49.6	47.52	120	0.04
Cavitation	Orifice meter	2	50.5	44.9	120	10.9
		4	48	37.9	420	21.1
		6	44.9	44.3	120	1.3
Cavitation	Vortex diode	2	45.3	45.2	120	0.04
		4	44.6	42.4	120	4.8
		6	45.6	45.3	120	1.2
Cavitation / H_2O_2 (100 ppm) / ozone (10 g/h)	Venturi meter	4	48	43.9	90	8.4
UV / cavitation	Vortex diode	4	39.1	31.1	120	20.4

4.2 Results for degradation of Cetirizine HCl using hybrid AOPs

The degradation of cetirizine HCl were studied by using Photolytic (UV), photochemical (UV/ H_2O_2) and hybrid AOPs viz. UV/ozonation, UV/photocatalyst, Photocatalyst/ozonation, H_2O_2 /ozonation. The comparative degradation of cetirizine HCl using photolytic (UV), photochemical (UV/ H_2O_2) and hybrid AOPs viz. UV/ozonation, UV/photocatalyst, Photocatalyst/ozonation, H_2O_2 /ozonation are shown in Table 4.

Table 4: Comparative degradation of cetirizine HCl using photolytic (UV), photochemical (UV/ H_2O_2) and hybrid AOPs viz. UV/ozonation, UV/photocatalyst, Photocatalyst/ozonation, H_2O_2 /ozonation

AOP methods	Initial TOC (ppm)	Catalyst dose (ppm)	Time (min)	TOC (ppm)	UV (nm)	% Reduction
UV / O_3 (10 g/h) / H_2O_2	48	200	120	32.9	256	31.6
UV / O_3 (15 g/h) / H_2O_2	50.7	200	120	6.7	256	86.7
UV / O_3 (10 g/h)	48	-	120	23.8	256	50.4
UV / O_3 (15 g/h)	54.9	-	120	4.8	256	91.3
UV / air / TiO_2	46.6	500	120	21.9	256	52.8
UV / O_3 (10 g/h) / TiO_2	55.8	500	120	7.7	256	86.1
UV / O_3 (15 g/h) / TiO_2	53.7	500	120	6.3	256	88.2
UV / H_2O_2	48	200	120	45.6	256	5.01
O_3 (15 g/h)	43.5	-	120	29.6	-	31.5
O_3 (15 g/h) / H_2O_2	55.4	500	120	29.2	-	47.2

4.3 Screening and selection of AOPs for degradation of Cetirizine HCl

Experiments involving different AOPs namely hydrodynamic cavitation, ozone, H_2O_2, TiO_2, UV and their combination were performed for cetirizine degradation. From the experimental data it was observed that combination of UV (80 W, 254 nm) and ozone for flowrate of 15 g/h gave the best results for removal of TOC for cetirizine of 91.3 % in 120 minutes. Therefore, UV/ozonation process was selected to study the effect of various operational parameters on degradation of Cetirizine HCl. The graphical representation for screening of different AOPs for cetirizine degradation is depicted in the Figure 4.

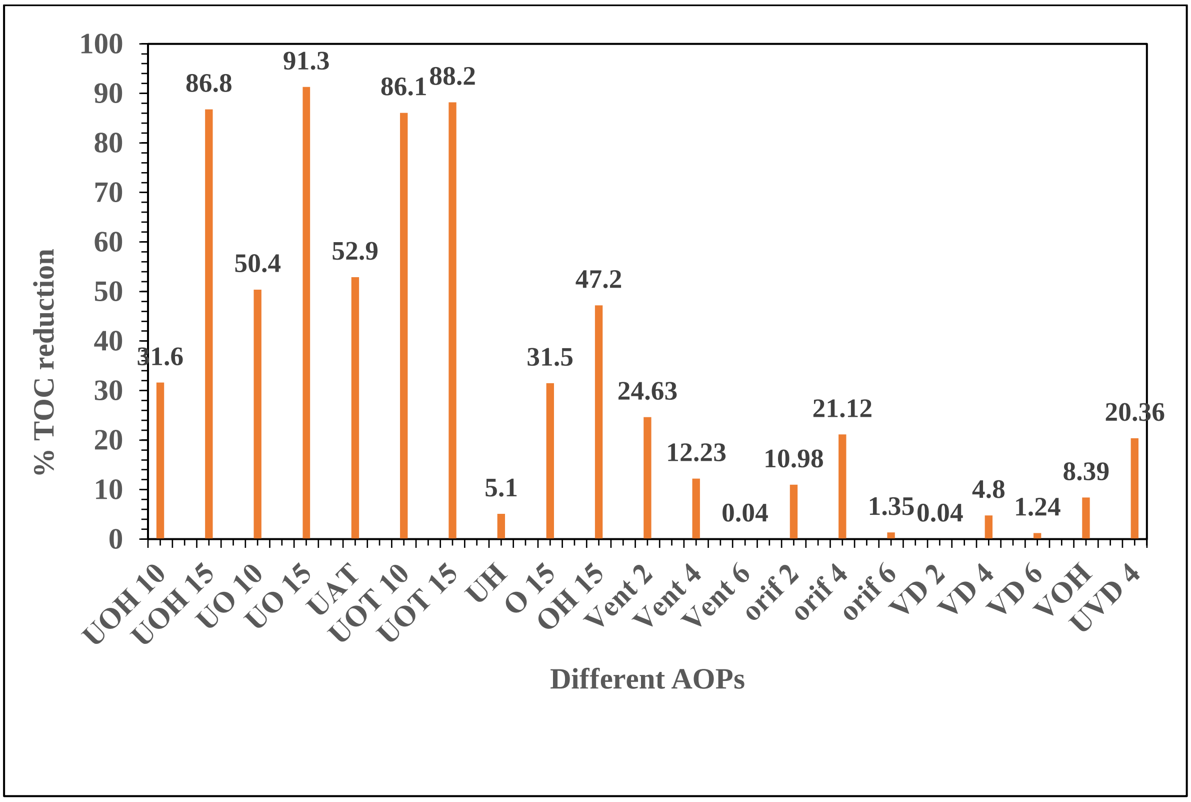

Figure 2: Screening and selection of AOPs for degradation of Cetirizine HCl

4.4 Effect of operational parameters on the removal of Cetirizine HCl using UV/O_3 process

Several parameters like initial concentration of cetirizine, solution pH, variation in ozone flowrate, effect of salt, effect of type of water, were studied for the selected process UV/O_3 (15 g/h) for cetirizine degradation.

4.4.1 Effect of variation in initial concentration of Cetirizine HCl

Initial concentration study for cetirizine removal by degradation was performed for different concentrations 25, 50, 75 and 100 ppm. Best removal efficiency (94.5 %) of TOC for cetirizine was achieved at 25 ppm initial concentration. This may be attributed to the fact that at higher concentration of cetirizine lower number of hydroxyl radicals are available for degradation therefore the TOC removal efficiency is reduced as the cetirizine concentration is increased. For kinetic study, plot of ln (C/C0) against time was plotted in which C0 represents the initial TOC before reaction and C is TOC of sample removed at that instant of time during the degradation study. The results for % reduction in Total Organic Carbon (TOC) and kinetic parameters are shown in the Figures 5 & 6 respectively.

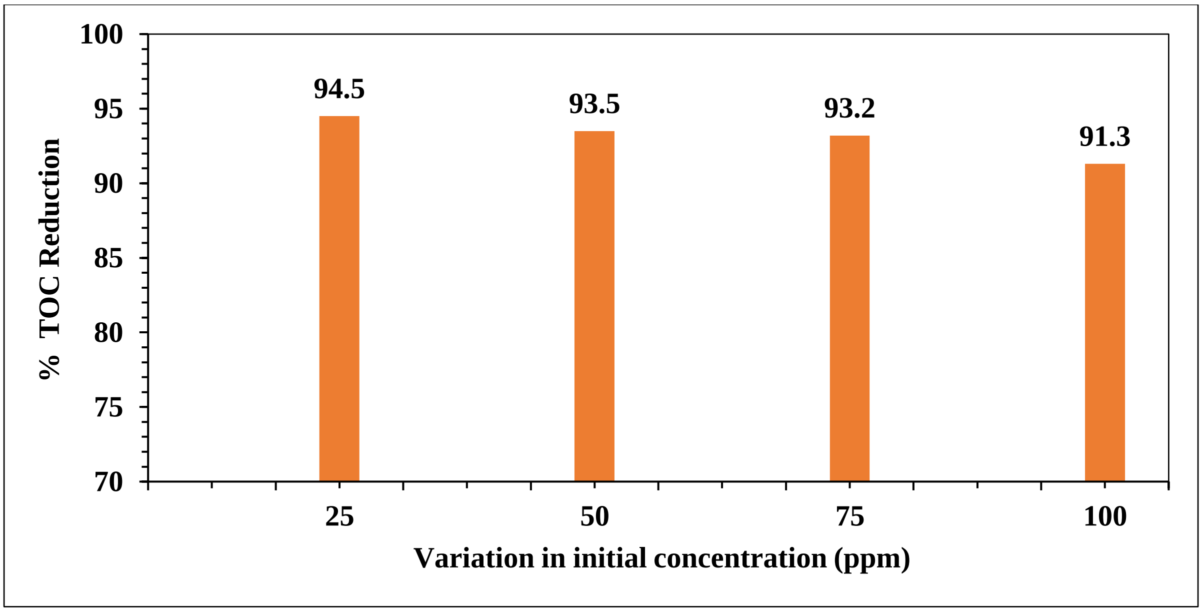

Figure 3: Variation in initial concentration of Cetirizine HCl

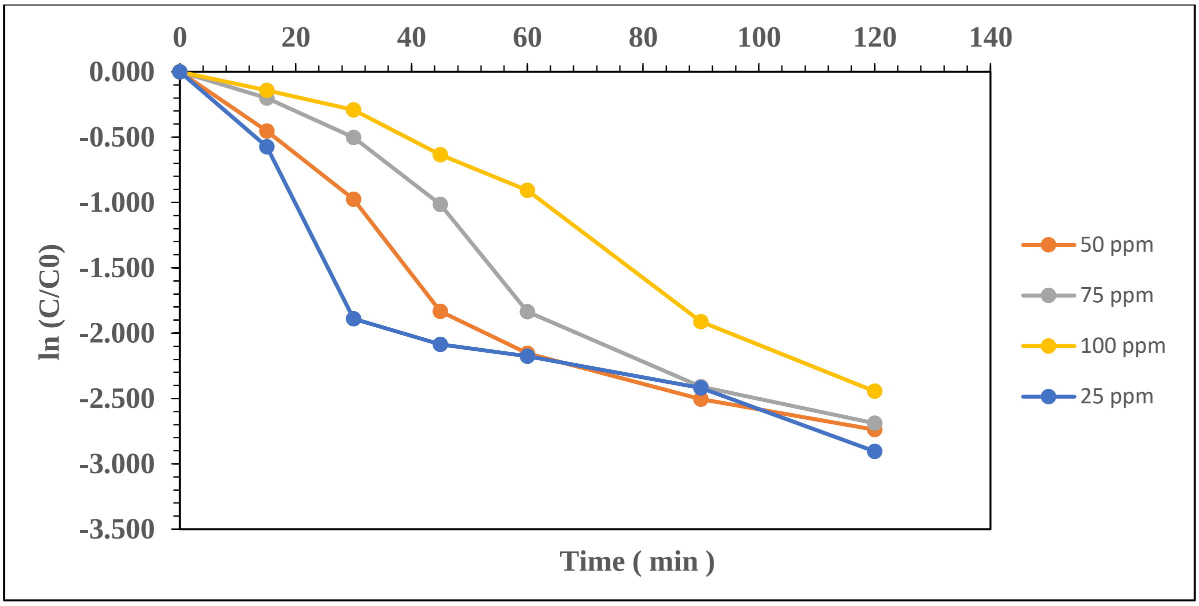

Figure 4: Kinetic study for variation in initial concentration of Cetirizine HCl

4.4.2 Effect of variation in pH of the solution on Cetirizine HCl degradation

Cetirizine removal by degradation was carried out for different pH values 3, 5, 7, 9, and 11. Solution pH was regulated using 1 M sulfuric acid (H_2SO_4) and 1 M sodium hydroxide (NaOH). At 11 pH maximum removal efficiency for TOC of 94.3 % was observed for cetirizine. At higher pH cetirizine reacts readily with ozone due to presence of N_2 - amine group which is predicted to be the most reactive site for cetirizine, resulting in more reduction in TOC, as against lower pH where the activity of cetirizine is reduced, which is clearly observed from the lowering of TOC removal efficiency. [15] For kinetic study plot of ln (C/C0) against time was plotted in which C0 represents the initial TOC before reaction and C is TOC of sample removed at that instant of time during the degradation study. The results for % TOC reduction and kinetic parameters are depicted in the Figures 7 & 8 respectively.

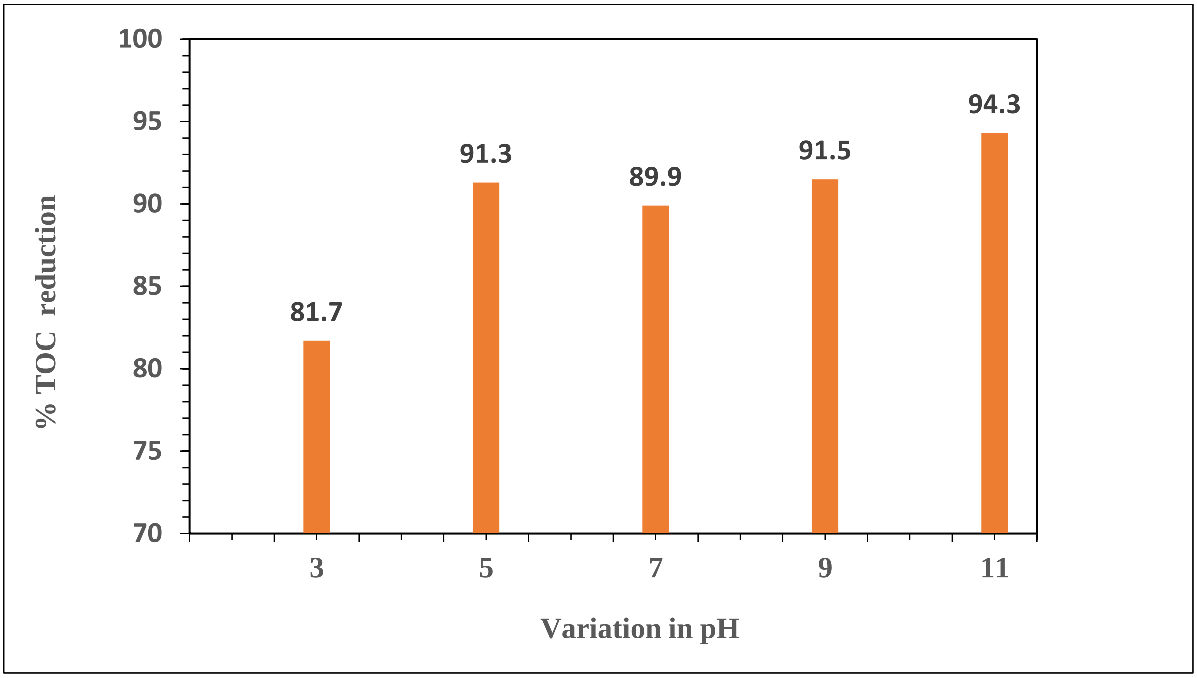

Figure 5: Study for variation in pH of the solution for Cetirizine HCl degradation

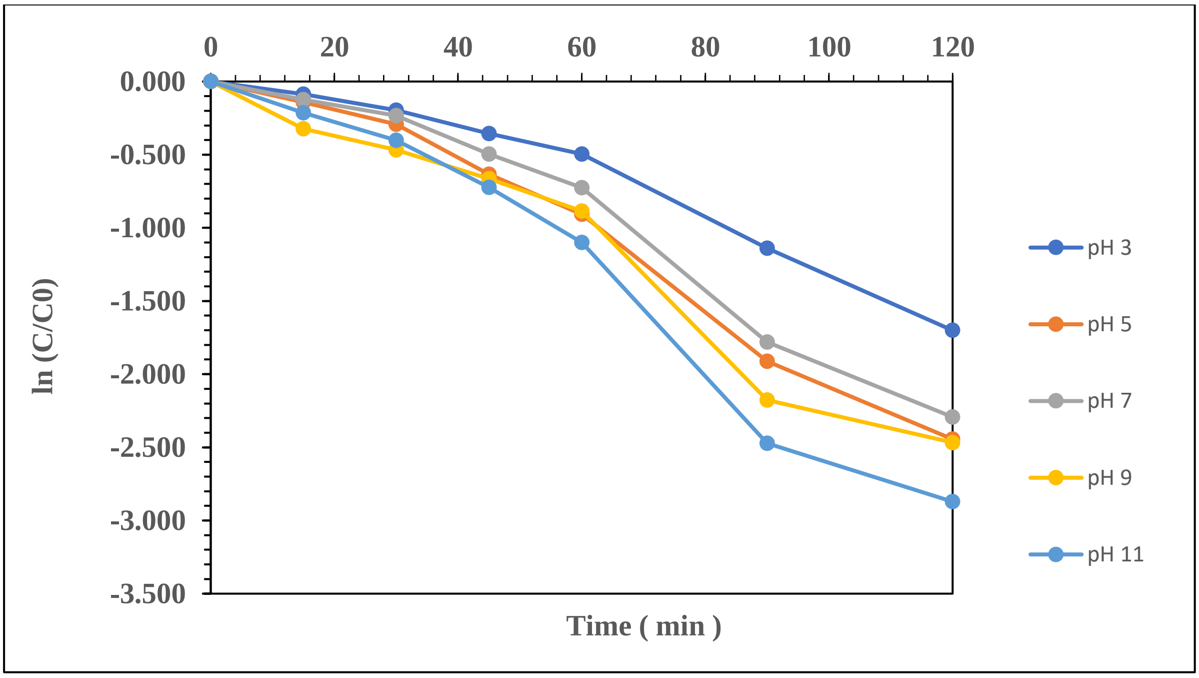

Figure 6: Kinetic study for pH variation of the solution for Cetirizine HCl degradation

4.4.3 Effect of variation in ozone flowrate for degradation of Cetirizine HCl

The removal of cetirizine by degradation was carried out at different ozone flowrate 5, 8, 10, and 15 g/h. It was observed that maximum removal efficiency for TOC of 91.3 % was achieved at ozone flow rate of 15 g/h. There is direct corelation between ozone exposure and ozone flowrate. As the ozone flow rate increase a greater number of hydroxyl radicals are generated, which are responsible for the degradation of cetirizine, resulting in enhanced TOC reduction. At lower ozone flowrates hydroxyl radicals generated are not sufficient for the degradation of cetirizine which is evident from the TOC reduction rate. For kinetic study plot of ln (C/C0) against time was plotted in which C0 represents the initial TOC before reaction and C is TOC of sample removed at that instant of time during the degradation study. The % reduction in TOC and the kinetic parameters are depicted in the Figures 9 & 10 respectively.

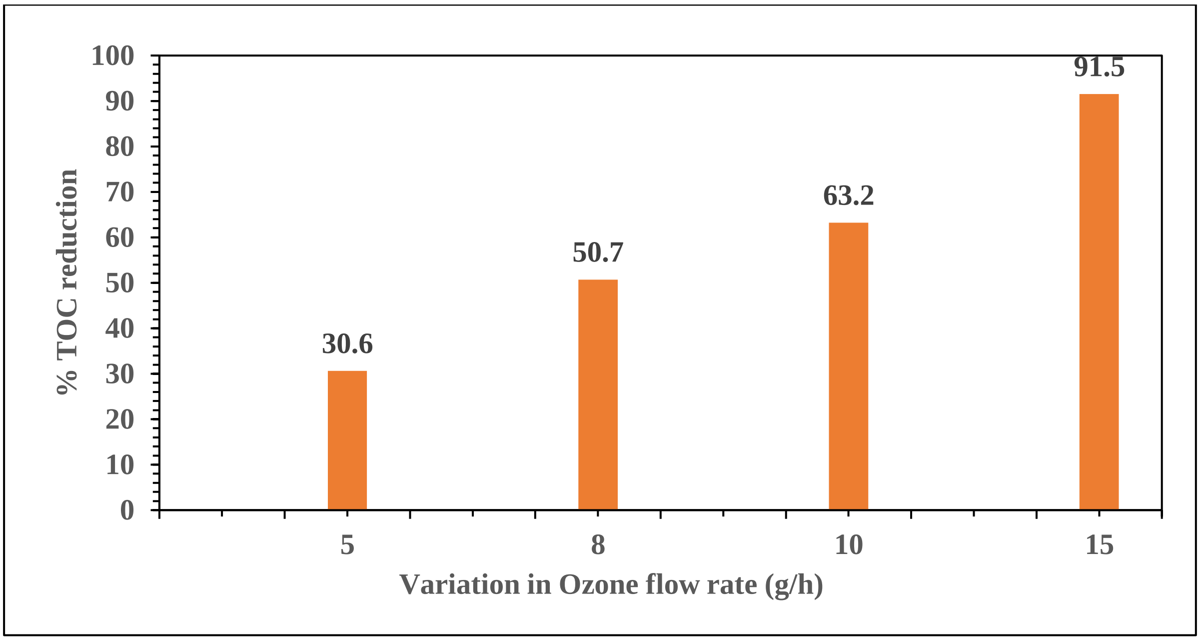

Figure 7: Study for variation in ozone flowrate for degradation of Cetirizine HCl

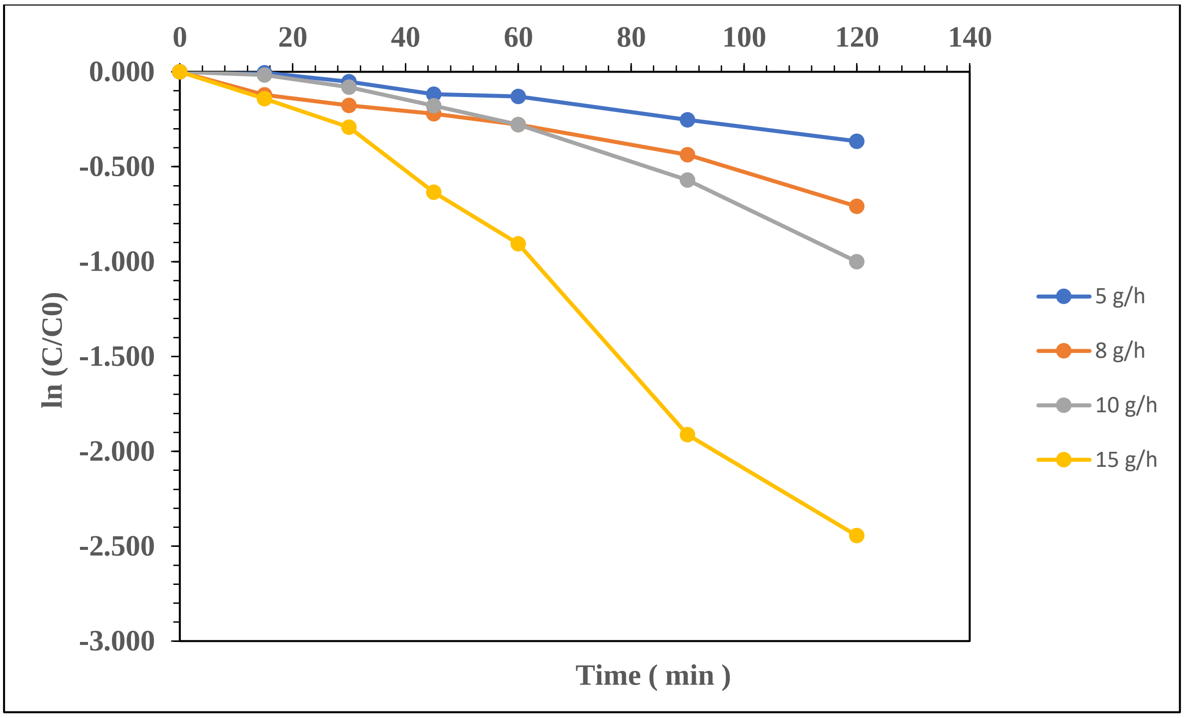

Figure 8: Kinetic study for ozone flowrate variation for degradation of Cetirizine HCl

4.4.4 Effect of different salts on degradation of Cetirizine HCl

The effect of different salts on the removal of cetirizine by degradation was investigated. Commonly used salts such as Sodium carbonate (Na_2CO_3), Sodium chloride (NaCl) and Ammonium sulphate $(NH_4)_2SO_4$ were taken for the study. Maximum removal efficiency for TOC of 94.7 % for cetirizine was achieved in the presence of Na_2CO_3 which led to the increase in the pH of the solution thereby enhancing efficiency for TOC removal. For NaCl the solution pH is almost neutral, hence there is decrease in TOC removal rate as it is evident from the study performed at neutral pH. For $(NH_4)_2SO_4$ the pH of the solution is mild acidic so there is slight decrease in the TOC removal rate. [15] For kinetic study plot of ln (C/C0) against time was plotted in which C0 represents the initial TOC before reaction and C is TOC of sample removed at that instant of time during the degradation study. The % reduction in TOC and kinetic parameters are depicted in the Figures 11 & 12 respectively.

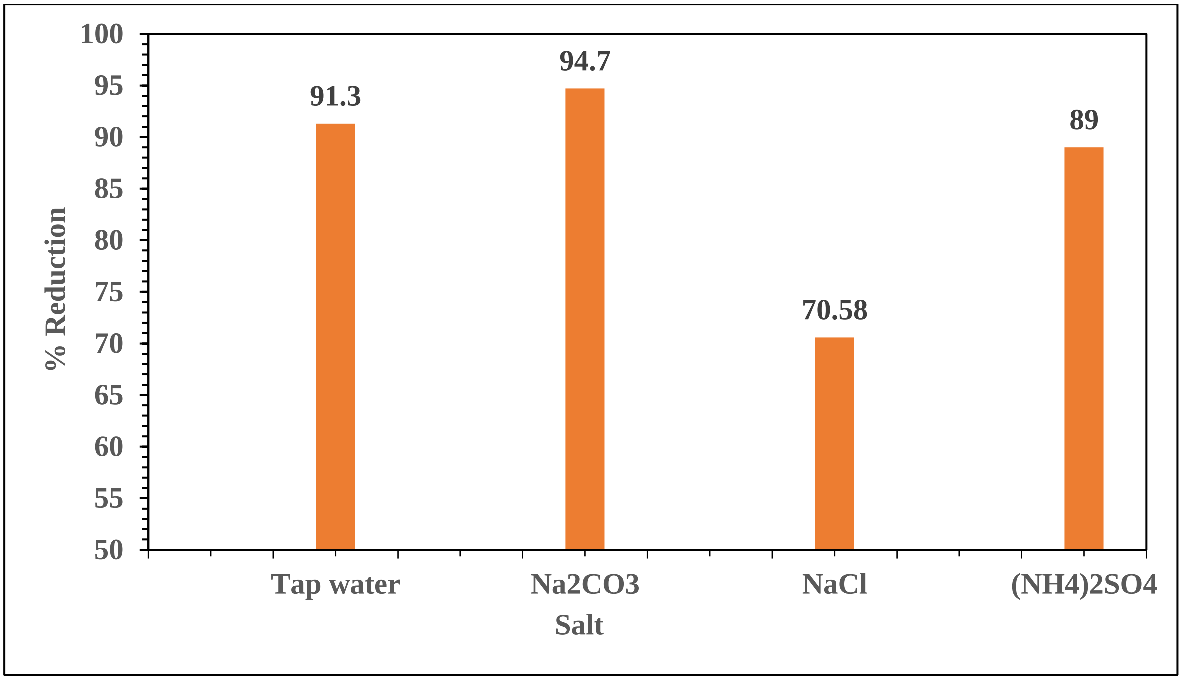

Figure 9: Effect of different salts on degradation of Cetirizine HCl

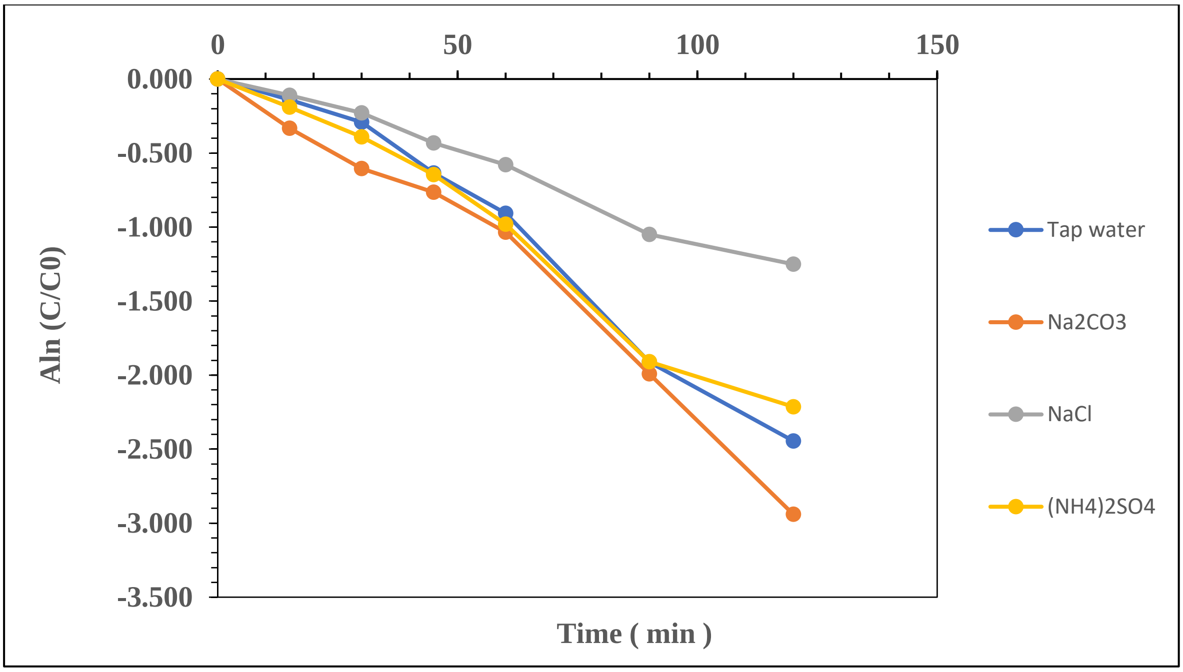

Figure 10: Kinetic study for effect of different types of salts on degradation of Cetirizine HCl

4.4.5 Effect of different types of water on removal of Cetirizine HCl

The effect of multiple water sources on removal of cetirizine by degradation was studied using different types of water. Sewage water was collected from campus sewage treatment plant. The cetirizine solution was prepared in actual sea water. The reduction in TOC removal rate in case of sea water is mainly because pH of sea water is almost neutral and as mentioned earlier cetirizine degradation is less at neutral pH. In sewage water, the efficiency of TOC removal is affected mainly due to the presence of other organic matter, suspended solids, which may act as scavenger for hydroxyl radicals. Maximum removal efficiency for TOC of 91.3 % for cetirizine was observed in case of tap water since it has almost negligible suspended solids and organic content. For kinetic study plot of ln (C/C0) against time was plotted in which C0 represents the initial TOC before reaction and C is TOC of sample removed at that instant of time during the degradation study. The % reduction in TOC and kinetic parameters for the study are depicted in the Figures 13 & 14 respectively.

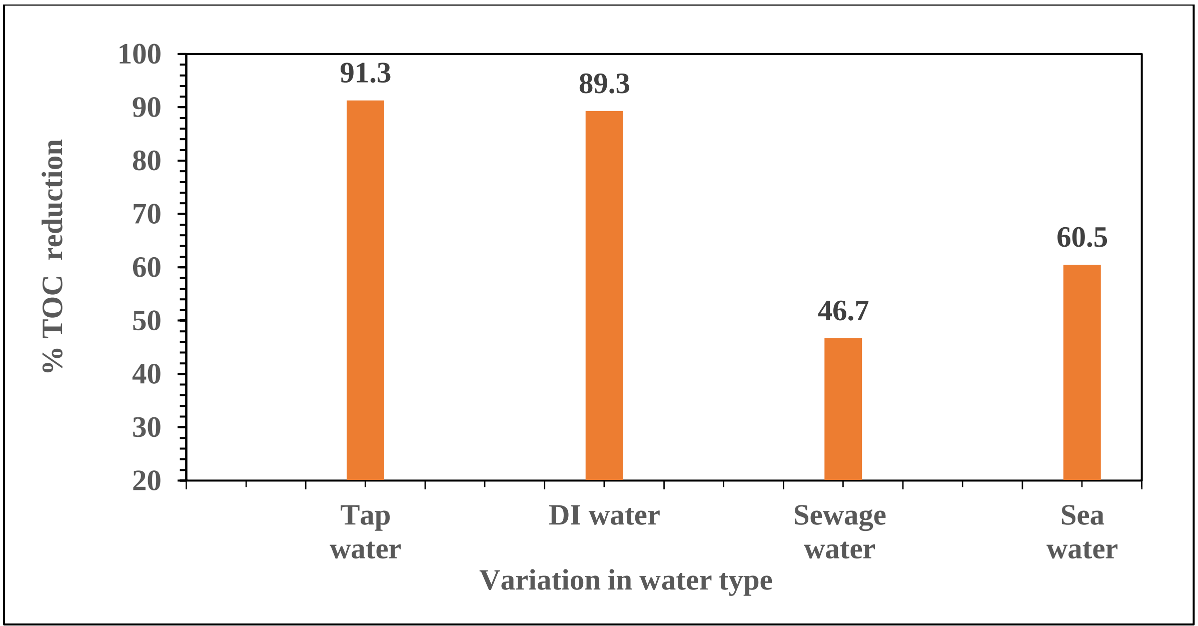

Figure 11: Effect of different sources of water on degradation of Cetirizine HCl

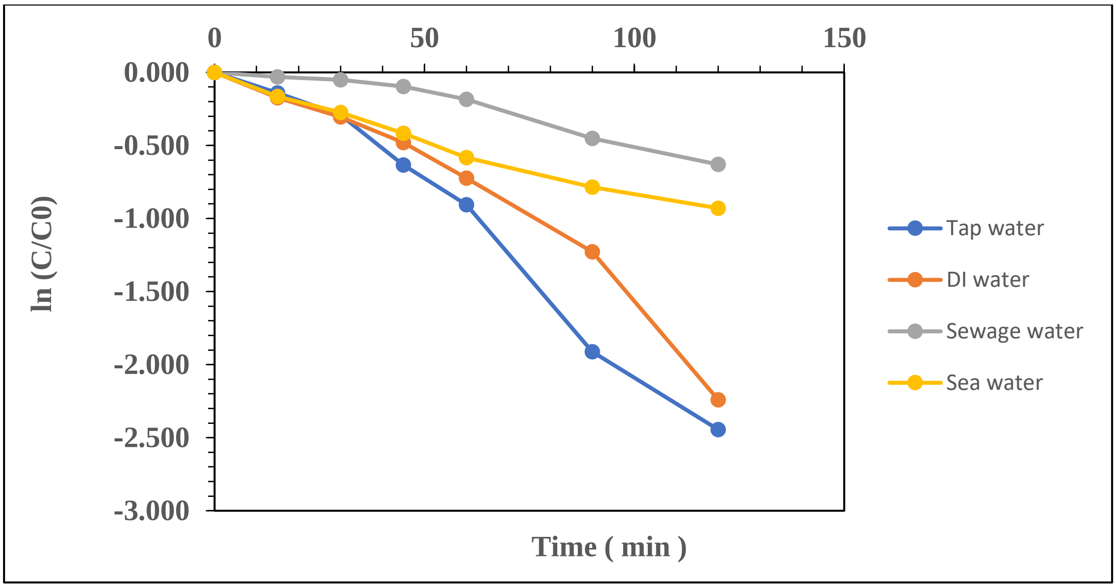

Figure 12: Kinetic study for effect of different sources of water on degradation of Cetirizine HCl

5. Conclusions

In the major project a detailed study has been carried out for the complete removal of API cetirizine di-hydrochloride, which is a piperazine class 2nd generation antihistamine drug, used for treatment of allergies, from simulated waste water, using various Advanced Oxidation Process (AOPs) such as UV, ozone, Hydrogen Peroxide (H_2O_2), Hydrodynamic Cavitation (HC), Titanium dioxide (TiO_2) and their hybrid techniques.

Among the above selected processes combination of UV (80 W, 254 nm) and ozone at flowrate of 15 g/h gave the maximum removal efficiency of 91 % for Total Organic Carbon (TOC). For this shortlisted process, various parameters such as initial concentration of cetirizine (25, 50, 75, 100 ppm), pH of the solution (3, 5, 7, 9, 11), variation in ozone flowrate (5, 8, 10, 15 g/h), effect of different salts (NaCl, Na_2CO_3, $(NH_4)_2SO_4$), effect of different types of water (DI water, sewage water, sea water) were studied. Actual sea water and sewage water were used for carrying out the experimental study.

For the initial concentration study, the maximum TOC reduction of was reached at 25 ppm, and the maximum cetirizine degradation efficiency was attained with an ozone flowrate of 15 g/h. In case of pH study maximum degradation of cetirizine was achieved at pH value of 11. In the salt study, the presence of Na_2CO_3 accelerated the degradation of cetirizine, while the presence of NaCl slowed down TOC removal. In the water study, tap water provided the greatest results for TOC removal, however sewage water and sea water drastically affected the effectiveness of TOC removal.

The mineralization of cetirizine was investigated using TOC measurement.

In summary, the study demonstrated that cetirizine which is second generation anti histamine drug can be degraded in waste water samples using combination of UV and ozone. These results are notable in development of effective processes for removal of various Active Pharmaceutical Ingredients (APIs) from wastewater. [

Future Recommendations

- Kinetics of the degradation needs to be studied in detail for the possible commercialization of the UV/O_3 process.
- Use of AOPs for degradation of pollutants from pharmaceutical wastewater need to be investigated.
- The effect of scavenger on the generation of hydroxyl radicals needs to be studied
- The study for toxicology of the transformation products after the degradation of Cetirizine HCl needs to be performed

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