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RESEARCH ARTICLE

Integrated Advanced Oxidation Process for the Treatment of Pharmaceutical Effluent

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ABSTRACT

Increased exploitation of water resources by the industries has attained a level of saturation denoting the complete exploitation of water in the near future. The organic contaminants in the pharmaceutical effluent remain partially degraded at the end of conventional wastewater treatment technologies thereby posing a challenge. Electrochemical Oxidation and UV Oxidation processes have proven to be effective in treating these type of contaminants in the pharmaceutical effluents. This study focuses on the integration of Electrochemical and UV Oxidation in the presence of Fenton's reagent for the effective treatment of pharmaceutical contaminants. It has been observed that the maximum reduction (>90%) of Chemical Oxygen Demand (COD) and Total Organic Carbon (TOC) was achieved during the combination of Electrochemical and UV Oxidation in the presence of 500 mg L^{-1} Fenton's reagent.

Keywords: *Electrochemical oxidation; Photo-chemical oxidation; Pharmaceutical effluent; Chemical oxygen demand*

INTRODUCTION

In the era of the modern industrial revolution, there has been an intensive deterioration of natural resources that include air, water, and soil. In rivers and lakes that receive wastewater, pharmaceuticals are often found in concentrations of 0.1 µg L^{-1} to 1.0 µg L^{-1} (Frank-Andreas Weber, 2014). The effluent from pharmaceutical industries has shown an increased concern because of the contaminants that prevail even after conventional wastewater treatments (Domínguez *et al*., 2011). Water has been polluted from both point source and non-point source of pollutants. These pollutants may be of organic or inorganic form (Gadipelly *et al*., 2014). Pharmaceutical effluent primarily consists of disposed antibiotics, analgesics, and other chemical substances that can persist in the environment over some time. As a result, these compounds enter humans through the food chain, thereby producing antibiotic resistance with the higher vulnerability of disease incidence (Moreira *et al*., 2017).

Despite implementing conventional treatment technologies, there is always a portion of pollutants that remains undisturbed without degradation, prevailing as a critical factor in deciding the quality of water (Garcia-Segura *et al*., 2018). Various stimulated research activities have resulted in introducing a process named as advanced oxidation process. Advanced oxidation process has derived as an efficient technology in treating wastewater wherein both the organic and inorganic forms of pollutants have been removed to an extent possible (Nidheesh *et al*., 2018). The advanced oxidation process involves the production of highly reactive hydroxyl radicals as intermediates that help in the destruction of target pollutants (Moreira *et al*., 2017). As a result of which, the organic form of pollutants will be oxidized and finally gets converted to carbon dioxide, water, and inorganic forms, wherein, the latter is removed by electrochemical methods.

$$\text{AOPs .OH} + \text{Pollutants} \longrightarrow CO_2 + H_2O + \text{Inorganic Compounds}$$

Various advanced oxidation process includes photo catalysis, Ozone Oxidation, UV Oxidation, Fenton and Photo-Fenton Oxidation. The removal efficiency of 86% COD and 90% turbidity by using UV/H_2O_2 works best for wastewater with a high concentration of refractory chemicals (Boroski *et al*., 2009). Similar trends were obtained in the utilization of photo-Fenton oxidation with a retention time above 120 minutes (Kulik *et al*., 2008). The process was capable of achieving satisfactory levels of TOC removal at short treatment times (Domínguez *et al*., 2011). Every day, about 500 m^3 of wastewater with high COD and BOD due to organic vapor contaminations have been

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released as effluent. This water is also used as a coolant due to low inorganic salt concentration but it is inhibited by organic contamination. So, this denotes the necessity for removing the latter contaminants from the wastewater. This study ends up in checking the effectiveness of Electro-oxidation and UV oxidation, particularly focused on removing COD and TOC from the pharmaceutical effluent. The treated effluent contains mineralized forms of nutrients that were released due to the degradation of organic contaminants, which can be recovered using nutrient recovery technologies (Huang *et al.*, 2020). Recently, nutrient recovery technologies using adsorbent materials have gained attention; specifically, waste-derived carbon materials like hydrochar are used as a potential nutrient recovery option and the nutrient-laden hydrochar can be disposed of as a slow release nutrient fertilizer (Oumabady *et al.*, 2021). With this prelude, this study focuses on the integration of Electrochemical and UV Oxidation processes in the presence of Fenton's reagent with an aim to reduce the Chemical Oxygen Demand (COD), Total Organic Carbon (TOC) and Total Dissolved Solids (TDS) contents of the pharmaceutical effluent.

MATERIAL AND METHODS

Sample collection

The effluent was collected from the solvent extraction plant of M/s Orchid Chemicals and Pharmaceuticals Ltd., Alathur, Chennai, Tamil Nadu, India. The effluent was collected in air tight PPFE containers and stored at 4 °C for further characterization.

Jar test

A preliminary Jar test (Table 1) has been conducted for solid-liquid separation using polymeric coagulants and flocculants and the efficient one has been selected for further analysis. Lime, Alum, and Poly aluminum chloride (PAC) are used as coagulants and CHEMPURE 9150 is used as Flocculants. The test jar-3 was selected and further used for the study.

Experimental Setup

The experiment was carried out in a laboratory equipped with an electrochemical cell, UV reactor and filters for the EO and UV oxidation. The effluent was circulated through a dual media filter (DMF), UV Reactor, and EO Reactor for 60 minutes. The final treated effluent was passed through an activated carbon filter (ACF). The samples were taken for analysis in the regular interval (15, 30, 45 & 60 minutes).

Electrochemical oxidation reactor

Electrochemical oxidation was carried out in a batch recirculation setup of 5L capacity with constant agitation and temperature control (Fig. 1). The cells were powered by a manually controlled 0.3 kW (12V/25A) DC power supplier (rectifier) with proper electrical connections. The anode and cathode used for the study were titanium coated plate and SS316 plate, respectively, with dimensions of 125 mm × 100 mm and a current density of 1000 Am^{-2} at an electrode gap of 8 mm.

Fig 1. Electrochemical oxidation reactor

UV reactor

Design tests were performed to measure the UV dosage required to achieve the desired effluent concentration. The dosage to be applied to a particular stream is determined iteratively by examining the effect on the treatment of selected process variables such as pH, oxidant concentration, and choice of catalyst. A 13W powered OSRAM/ mercury UV lamp was used with a wastewater flow rate of 1 to 2L h^{-1} at a wavelength of 254nm (Fig. 2).

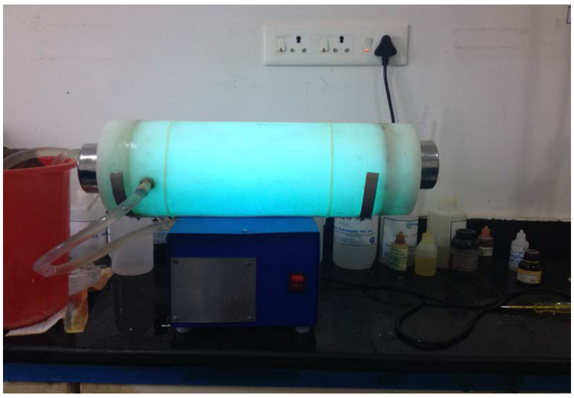

Fig 2. UV reactor

Fenton's reagent

The reagent was prepared by dissolving 2.48g of Fe_2SO_4 in 200mL distilled water and adjusting the pH between 4 and 5 using 0.01N H_2SO_4, followed by adding 6 mL of H_2O_2 into the solution.

Experimental trials

The batch experiments of the advanced oxidation process were conducted by integrating electrochemical oxidation (EO), UV oxidation (UV), and Fenton's reagent at different pHs. The pH adjustments were performed by 1M HCl and 1M NaOH solutions. The trials conducted for the current study are presented in Table 2.

RESULTS AND DISCUSSION

Characteristics of raw effluent

The chemical characterization of raw effluent is listed in Table 3. The pH of the effluent was slightly alkaline with higher salinity. The total solids and COD of the effluent were also higherthat pave the way for the treatment through advanced oxidation process.

Jar test experiment

The selected jar test experiment results using the effluent are listed in Table 3. The color and turbidity of the sample were much reduced while the COD reduction was less than 12% which indicated the non-suitability of clarification with the coagulant.

Table 1. Details of preliminary jar test experiments

Description	Test Jar - 1	Test Jar - 2	Test Jar -3
Sample volume (ml)	1000	1000	1000
Lime Dosage (mg L^{-1})	300	500	600
Coagulant dosage (mg L^{-1})	Alum 200	Alum 300	PAC 300
Polymer solution (Chempure-9150) (g L^{-1})	1	1	1
Polymer dosage (mg L^{-1})	1	1	1
Initial agitation time @ 100rpm (minutes)	3	3	3
Floc size	Smaller	Larger	Larger
Settling rate	Slow	Slow	Fast
Settle sludge volume	2%	3 %	2%
Supernatant color	Pale yellowish	Colorless	Colorless
Supernatant clarity	Slightly turbid	Slightly turbid	Clear
TSS in supernatant (mgL^{-1})	11.2	8.4	1.2
Compactness of the settled sludge	Fine particles	Fine particles	Fine particles
Overall efficiency	Not considerable	Not considerable	Considerable
COD of the supernatant effluent (mgL^{-1})	2040	2018	1878

Batch experiments

The advanced oxidation process encompasses unique treatment technologies whose integration can lead to the efficient removal of the contaminants that remain persistent over a period of time. A combined EO & UV oxidation system can be installed prior to the biological system in the case of effluents contaminated with recalcitrant (Gadipelly *et al.*, 2014). It has been observed that there has been a high rate of oxidation within 15 minutes in all the trials. The rate of oxidation has gradually reduced for higher circulation time. However, more circulation time (60 minutes) has given better COD and TOC

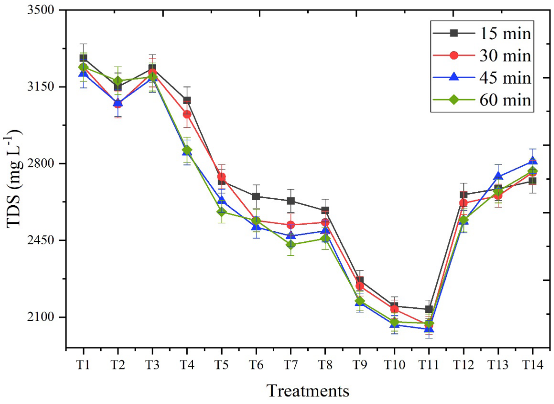

Fig 3. Effect of trials on TDS with respect to reaction time

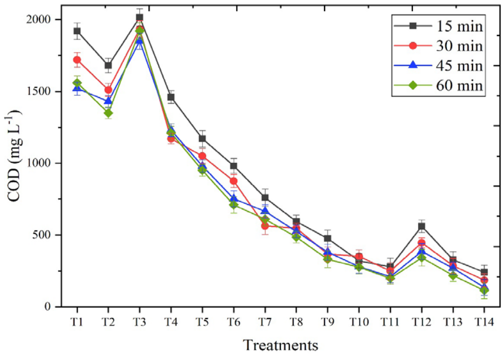

Fig 4. Effect of trials on COD with respect to reaction time

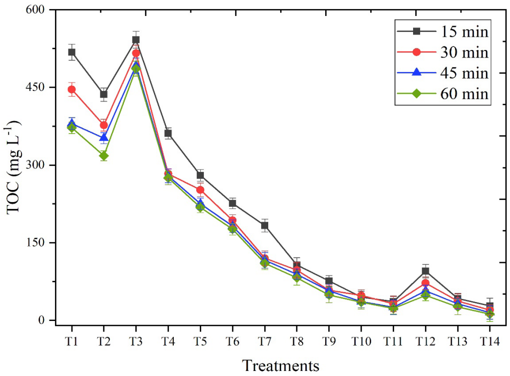

Fig 5. Effect of trials on TOC with respect to reaction time

removal performance. The pH of the substrate has played a significant role throughout the process. Increased substrate pH accounts for efficient removal of pollutants (Murugananthan *et al*., 2007).

Table 2. Trial details for the advanced oxidation process

Treatment	Details
T_1	EO at pH 8.65
T_2	EO + UV at pH 8.65
T_3	UV + Fenton's reagent (100 mg L^{-1}) at pH 8.65
T_4	EO + UV + Fenton's reagent (50 mg L^{-1}) at pH 8.65
T_5	EO + UV + Fenton's reagent (100 mg L^{-1}) at pH 8.65
T_6	EO + UV + Fenton's reagent (150 mg L^{-1}) at pH 8.65
T_7	EO + UV + Fenton's reagent (200 mg L^{-1}) at pH 8.65
T_8	EO + UV + Fenton's reagent (250 mg L^{-1}) at pH 8.65
T_9	EO + UV + Fenton's reagent (300 mg L^{-1}) at pH 8.65
T_{10}	EO + UV + Fenton's reagent (400 mg L^{-1}) at pH 8.65
T_{11}	EO + UV + Fenton's reagent (500 mg L^{-1}) at pH 8.65
T_{12}	EO + UV + Fenton's reagent (500 mg L^{-1}) at pH 7.5
T_{13}	EO + UV + Fenton's reagent (500 mg L^{-1}) at pH 6.5
T_{14}	EO + UV + Fenton's reagent (500 mg L^{-1}) at pH 5.5

This is confirmed in trial 11, wherein higher pH condition (8.65) has mediated towards the efficient removal of the contaminants from the pharmaceutical effluent. Moreover, higher circulation time has also contributed towards a cumulative removal of the contaminants with higher removal efficiency, as depicted in Fig. 3, 4, and 5.

Table 3. Characteristics of raw and treated effluent after Jar test

Parameters	Raw sample	Treated sample
Appearance	Slightly turbid	Clear
Color	Pale yellowish	Colorless
Odor	Characteristic	Odorless
Turbidity, NTU	18.4 ± 0.8	1.2 ± 0.05
pH	8.65 ± 0.25	7.50 ± 0.22
Electrical Conductivity, dSm^{-1}	5.77 ± 0.17	4.84 ± 0.14
Total Solids, mg L^{-1}	3506 ± 70.1	3437.4 ± 68.7
TSS, mg L^{-1}	46 ± 1.15	3.4 ± 0.085
TDS , mg L^{-1}	3460 ± 121.1	3432 ± 120.1
BOD as O_2, mg L^{-1}	354 ± 14.16	318.3 ± 12.72
TOC as C, mg L^{-1}	573 ± 21.74	488.3 ± 18.5
COD , mg L^{-1}	2120 ± 84.5	1878 ± 75.3

The desirable result was achieved in trial 11, reducing COD and TOC to 90% (Fig. 6). This was due to the combined influence of electrochemical oxidation and UV oxidation with the help of Fenton's reagent as a catalyst. The removal of TOC from ≥90% to ≤3% denoted the efficiency of a different combination of trials with EO and UV oxidation. Usage of Boron doped diamond has attained 97% TOC removal at 300 mA, in line with the experiment conducted (Brillas *et al*., 2010).

Table 5. Chemical Oxygen Demand for the treatments

	15 min	30 min	45 min	60 min
T_1	1920^{b}	1720^{b}	1520^{b}	1560^{b}
T_2	1680^{c}	1510^{c}	1430^{c}	1350^{c}
T_3	2016^{a}	1935^{a}	1850^{a}	1921^{a}
T_4	1460^{d}	1170^{d}	1230^{d}	1210^{d}
T_5	1170^{e}	1050^{e}	980^{e}	950^{e}
T_6	982^{f}	876^{f}	752^{f}	710^{f}
T_7	760^{g}	563^{g}	664^{g}	610^{g}
T_8	594^{h}	547^{g}	525^{h}	485^{h}
T_9	476^{i}	367^{i}	380^{i}	331^{i}
T_{10}	320^{jk}	351^{i}	280^{j}	276^{j}
T_{11}	278^{kl}	249^{j}	210^{k}	198^{k}
T_{12}	561^{h}	446^{h}	385^{i}	342^{i}
T_{13}	327^{j}	285^{j}	268^{j}	218^{k}
T_{14}	240^{l}	185^{k}	136^{l}	114^{l}

*$^{a,b,c \text{ and } d}$ are the significant levels at 5% for Duncan's Multiple Range Test

Optimum residence time of 77 minutes has mediated towards complete removal of TOC from pharmaceutical effluent (Domínguez *et al*., 2011) so that it was clear that residence time of more than 60 minutes favors complete removal of the contaminants from the effluent.

Table 6. Total Organic Carbon content for the treatments

	15 min	30 min	45 min	60 min
T_1	518^{b}	446^{b}	380^{b}	372^{b}
T_2	436^{c}	377^{c}	352^{c}	318^{c}
T_3	542^{a}	516^{a}	492^{a}	486^{a}
T_4	361^{d}	283^{d}	279^{d}	275^{d}
T_5	280^{e}	252^{e}	225^{e}	218^{e}
T_6	226^{f}	193^{f}	182^{f}	176^{f}
T_7	183^{g}	120^{g}	116^{g}	110^{g}
T_8	107^{h}	97^{h}	89^{h}	82^{h}
T_9	76^{j}	58^{j}	57^{i}	49^{i}
T_{10}	45^{k}	48^{jk}	36^{j}	35^{j}
T_{11}	36^{kl}	32^{lm}	25^{jk}	23^{k}
T_{12}	95^{i}	72^{i}	57^{i}	48^{i}
T_{13}	42^{k}	37^{kl}	32^{j}	26^{k}
T_{14}	28^{l}	20^{m}	15^{k}	12^{l}

*$^{a,b,c \text{ and } d}$ are the significant levels at 5% for Duncan's Multiple Range Test

CONCLUSION

Combination of EO & UV oxidation can be efficiently used for pharmaceutical effluent treatment in TOC and COD removal processes where biological treatment is not recommended. The use of hybrid technologies has been proved to be mandatory for the treatment of pharmaceutical compounds which are not completely eradicated by the single-stage treatment. The operation cost is Rs.33.75 m^{-3}, acceptable in current industrial treatment practice. The combined EO & UV oxidation treatment can be studied with various other industrial effluent and can be implemented. More risk assessment studies should be performed to investigate the ecological effects of pharmaceuticals and their metabolites. Future studies should consider developing AOP degradation protocols on mixtures of pharmaceuticals, given that they do not occur individually in water bodies.

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Ethics statement

No specific permits were required for the described field studies because no human or animal subjects were involved in this research.

Originality and plagiarism

Authors ensure that the manuscript has been written and submitted only entirely original works,

Consent for publication

All the authors agreed to publish the content.

Competing interests

The authors declare no competing interests.

Data availability

All the data of this manuscript are included in the MS. No separate external data source is required. If anything is required from the MS, certainly, this will be extended by communicating with the corresponding author through corresponding official mail; paulsebastian.s@tnau.ac.in

Author contributions

Idea conceptualization - PS, SB; Experiments – SB; Guidance – PS; Writing-original draft - SO, PS, SB; Writing- reviewing & editing - VD, PK.

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