



Research Article

FENTON OXIDATION OF CARBAMAZEPINE IN WASTEWATER WITH FEWER REAGENTS

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ABSTRACT

Pharmaceutical in natural waters could be an environmental problem because of their potential toxic risk on living organisms. Conventional wastewater treatment plant processes are not enough to remove pharmaceuticals therefore advanced oxidation process have become an attractive solution. Carbamazepine (CBZ), is an antiepileptic drug, is a most widely used medicine in almost every part of world. In present study, advance oxidation, using H₂O₂ and FeSO₄ (Fenton process) is used to degrade the concentrations of CBZ from water. Fenton process is known to be most effective and common methods for the treatment of such wastewaters. This study investigated the degradation of CBZ by H₂O₂ and FeSO₄ under changing pH and contact time of (3, 3.5, 4), (15, 20, 30 min) respectively. Results showed 75.86 % COD and 45.69 % TOC removal. But real degradation of CBZ were elucidated using liquid chromatography mass spectrometry (LCMS) coupled to tandem mass spectrometry (MS) indicating 53.73 % removal.

Keywords: Carbamazepine, pharmaceuticals, fenton process, water, wastewater.

1. INTRODUCTION

CBZ, 5H-dibenzo [b,f]azepine-5-carboxamide (Table 1), is an antiepileptic and mood-stabilizing drug and has received much attention worldwide due to its recalcitrant nature [1] along with this, its excessive use in mental problems like depression, stress disorders, drug and alcohol withdrawal, restless leg syndrome, diabetes insipidus and in certain pain syndromes [2] makes it a an emerging pollutants. CBZ has some serious health impacts including human growth complexities during placental and embryonic changes, even at environmental concentration of ng/L [3].

Mostly, attention has been focused on identification, fate and distribution of pharmaceutically active compounds (PhACs) in municipal wastewater treatment plants (WWTPs), and are found at very low concentrations (ppb level or low) [4]. Normal therapeutic use of the drug is the major source of discharge of these compounds to the environment [5,6]. CBZ is a persistent pharmaceutical of concern present in the range of 18 ng/l to 61 µg/l in water bodies [7]. Therefore, it is necessary to develop strategies to treat the effluents containing CBZ for careful

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release into ecosystem however many studies reported, only below 10% removal of CBZ with conventional wastewater treatment plant is possible [8].

Advanced oxidation processes (AOPs) have become the important treatment methods in various waters particularly Fenton process because Fenton or Fenton-like process is generally regarded as a rapid, efficient and simple water treatment technologies due to the generation of highly oxidizing hydroxyl radicals (OH) via the reaction of catalysts and H₂O₂ [9]. These processes are characterized by the generation of hydroxyl radicals, among other reactive oxygen species, which ensure high reactivity and low selectivity.

A variety of AOPs have been evaluated for removing trace organic contaminants in water treatment, including treatments which combine Fenton with different catalysts, UV and reagents as the AOPs strength relies on the promotion of the highly oxidative hydroxyl radical (HO) by various combinations such as UV/H₂O₂, UV/O₃, UV/TiO₂ and photo-Fenton technologies [10,11,12,13,14,15] but these processes simply increase the energy requirements and make the processes lengthy. Simple Fenton is widely used in different studies, oxidation with the Fenton reagent occurs in the presence of ferrous or ferric ions with hydrogen peroxide via a free radical chain reaction which produces hydroxyl radicals.

The organic substances are removed during two stages of oxidation and coagulation. Consequently, the aim of this work is to optimize the system by varying process parameters (pH, and contact time, concentrations of H₂O₂ and Fe⁺²) which is a relevant issue for application purposes. Later COD and TOC was compared with LCMS-MS results to check the percentage removal of CBZ.

Table 1. Physico-chemical and pharmacological properties of CBZ [16].

Chemical structure	
Molecular formula,	C ₁₅ H ₁₂ N ₂ O
Molecular weight	236.27 gmol ⁻¹
Water solubility	17.7 mg L ⁻¹ (20°C)
Octanol-water partitioning	2.45
pKa	13.9
Toxicity	Mild ingestion cause vomiting, drowsiness, ataxia, slurred speech, nystagmus, dystonic reactions, and hallucinations. Severe intoxications may produce coma, seizures, respiratory depression and hypotension
Affected Organisms	Human and aquatic organisms

2. MATERIAL AND METHODS

2.1. Chemicals

Chemicals used were CBZ >98% pure grade (Sigma-Aldrich); 35% pure grade Hydrogen Peroxide (Merck); 99.5% pure grade Iron Sulphate (Sigma Aldrich); 98% pure grade Sulfuric Acid (Merck); >99 % Sodium Hydroxide (Merck) for Fenton processes. Potassium Dichromate >99.9 (Merck); Iron Ammonium Sulphate (Carlo Erba) 99% pure grade; 1.10-phenanthroline and

monohydrate (Sigma Aldrich) >99.9%; Mercury Sulphate (Sigma Aldrich) >98%; Silver Sulphate (Sigma Aldrich) >99% for COD analysis. All chemicals were used as received without further purification. All aqueous solutions were prepared with distilled water except synthetic wastewater.

2.2. Preparation of synthetic wastewater

A solution of 7.11 mg L^{-1} was prepared in tap water by weighting 9.98 mg of powdered CBZ obtained from tablets used for medicinal purposes. Tap water is subject to many free cations and anions that can change chemistry of drug by simple reactions like in case of real wastewater which is a blend of different chemical species.

2.3. Analytical methods

Total organic carbon (TOC) was measured using Apollo 9000 combustion TOC analyzer. The COD tests were analyzed according to standard method (Methods: 5220 C. Closed Reflux Titrimetric Method) [17]. For chromatographic analysis, LCMS-MS, Shimadzu 8040 UPLC coupled with triple quadrupole Mass Spectrometer with electrospray ionization (ESI +) assisted with raptor C-18 analytical column (50mm x 30mm x 2.7 μm). The nebulizer gas temperature was set at 350 °C with a flow of 3L/min and a pressure of 660 bar. The sheath gas temperature was set at 250 °C at a flow rate of 15 L/min. The UPLC system was operated in gradient mode containing HPLC grade acetonitrile and ultrapure water (v:v=20:80) for Phase A and for phase B, HPLC grade acetonitrile and ultrapure water were in the ratio v:v=80:20 in the presence of 0.1 % ammonium acetate. The gradient elution program was changed between B phase 95 % to A phase 5% phase in 10 min following different time intervals as 0-3 min, 95-5% acetonitrile; 3-6 min 95-5% acetonitrile; 6-6.01 min 95-5% acetonitrile; 6.01 to 7 min 95-5% acetonitrile. Injection volume was 1.5ml [18].

2.4. Degradation experiments

Fenton's oxidation was carried out in stoppered glass batch flasks at ambient temperature for various contact times of 15, 20, 30 minutes using a stirrer, where stirring velocity was around 300 rpm. 7.11 mg L^{-1} CBZ synthetic solution was prepared from a tablet obtained from local market. Optimum experimental values of pH, reaction time and reagents were selected on the bases of literature review as presented in Table 2. It was observed in most of the research work conducted on CBZ optimum pH was in the range of (2-3.5), however, in present study, a pH 4 was tested along with pH 3, 3.5 to make sure the possible decrease of degradation efficiency by decreasing pH. In case of Fenton reagents, some pre-runs by changing quantities of reagents suggested satisfactory or unsatisfactory degradation. Therefore, only value with good percentage removal or values of impact were selected for the present study. To initiate Fenton's oxidation reaction, FeSO_4 and H_2O_2 solution were added to the wastewater samples with three different quantities: 0.17, 0.35, 0.53 mM and 2.90, 5.18, 11.63 mM respectively. Starting concentration of CBZ was 7.11 mg L^{-1} in all the experiments. This is much higher than the trace concentrations commonly found in water bodies and wastewaters but allows better detection of the reaction by-products. Before starting experiments, initial values of COD and TOC in untreated samples were also recorded. Each experiment was carried out by triplicate being the standard derivation less than 5% in all cases. Blanks with CBZ in absence of H_2O_2 and Fe^{2+} were also performed for all the tests. Biodegradability of the treated solutions (COD) and test with background constituents in the water matrix, like TOC will also observed. The pH of all the samples was measured using pH meter (Ohaus). The pH of the reaction mixture was maintained throughout the course of the Fenton experiment using 1N HCl and 1N NaOH.

Table 2. Studies reported in literature regarding CBZ and Fenton or Fenton-like processes

Serial No.	Method	Initial Value	pH	Fe ⁺²	H ₂ O ₂	Time	Removal Rate (%)	References
1	Fenton	50 µg L ⁻¹	<3.5	6 mg L ⁻¹	0.6 mg L ⁻¹	30 min.	99.66	[19]
2	Fenton	2.11*10 ⁻⁵ mol/L ⁻¹	3.52	1.25*10 ⁻⁵ mol/L ⁻¹	1.39*10 ⁻⁴ mol/L ⁻¹	48 h.	40	[20]
3	Fenton	442 mg L ⁻¹	3.5	8.5 g L ⁻¹	8.5 g L ⁻¹	6 h.	49.39	[21]
4	Photo-Fenton With Reagents	15 mg L ⁻¹	5	2.5 mg L ⁻¹	150 mg L ⁻¹	60 min.	80 TOC removal	[22]
5	Fenton	281 ng L ⁻¹	3	0.16mM	0.8mM	80 min.	84	[23]
6	Solar Photo-Fenton	422 ng L ⁻¹	2.8	5.5 mg L ⁻¹	30 mg L ⁻¹	6 h.	96	[24]
7	Fenton Process	4.2µm	3.5	2mM	5mM	7 min.	67.8	[25]
8	Fenton	9 ng L ⁻¹	6	5 mg L ⁻¹	50 mg L ⁻¹	30 min.	37	[26]
9	Photo Fenton	285 ng L ⁻¹	6-7	0-4	20-50	30 min.	94	[26]
10	Fenton Like Oxidation	0.236 g	7.0	-	20 mmol L ⁻¹	60 min	31	[27]
11	Fenton-Like Oxidation	10 mg L ⁻¹	3	2 mg L ⁻¹ of Fe ³⁺	5.6 mg L ⁻¹	3 h.	Conversion of CBZ reported	[28]
12	Photo Assisted Fenton Like System	0.1 mM	3	-	10.2 M	-	45	[29]
13	Solar Photo Fenton	50 µM	3	0.1 M	-	30	60	[30]
14	Fenton	7.2 mg L ⁻¹	3.5	0.35 mM	11.63 mM	30 min.	53.73	Present Study

3. RESULTS AND DISCUSSION

Before starting the analysis, initial physicochemical properties of synthetic wastewater prepared from tap water were recorded as pH 7.03; TDS 4.02µS/cm; Turbidity 1.5 NTU; Temperature 22.4 °C, dissolved oxygen 6.99 mg/L. All the Fenton experiments were carried out using jar apparatus for continuous and constant mixing of the reactants. FeSO₄.7H₂O was added in synthetic wastewater prior to the addition of H₂O₂ in a specified ratio according to the experimental design. The CBZ molecule's 10,11-double bond is very reactive and easily attacked by HO⁰ and other oxidizing reagents [31,32,33]. To test this property a series of reactions were conducted explained as below. Previously, more intensified and enhanced Fenton system are used to enhance degradation of CBZ with different more reactive reagents [26,27,28], but byproducts high cost and energy are their disadvantages, though they give more than 90% removal.

3.1. Effect of pH

The success of Fenton's treatment depends on the formation of hydroxyl radicals. CBZ can be efficiently degraded in the Fenton system in the pH 3, 3.5 and 4, performed with concentrations: 0.35 mM, FeSO₄; 5.18 mM, H₂O₂ and contact time, 20 minutes. For example, under weakly acidic condition such as 4 or above CBZ cannot be decomposed in less time. In the present study at 4 pH LCMS analysis showed only 9.41 % CBZ degradation. When the pH value was elevated to 3.5, CBZ efficiently degraded 67.24 % with COD removal of 47.12 %. LCMS removal obtained in 20 min. It is to be noted all the experiment were conducted at room temperature with a constant residence time of 120 minutes. After measuring COD and TOC pH 3.5 was decided as optimum like in some other studies [19, 34]. However different studies discussed 3 as optimum pH for CBZ [35] as shown in Table 2. But in case of present study upon pH 3 degradation

efficiency was started to decline. Likewise, TOC removal was 38.37, 32.13, 42.96 mg/L and at 3.5 pH 32.13 mg/L was optimum which shows 41.49 % removal. Finally, results were cross checked with LCMS results that showed 3.82, 3.76, 6.44 mg/L CBZ degradation at 3, 3.5, 4 pH respectively with 47.12 % degradation. That is an indicator that optimum selection of pH 3.5 was correct. Difference between results are show in Figure 1. These results suggest that optimum pH for every drug is different therefore every time before performing Fenton-like systems, finding optimum pH to continue reactions is important.

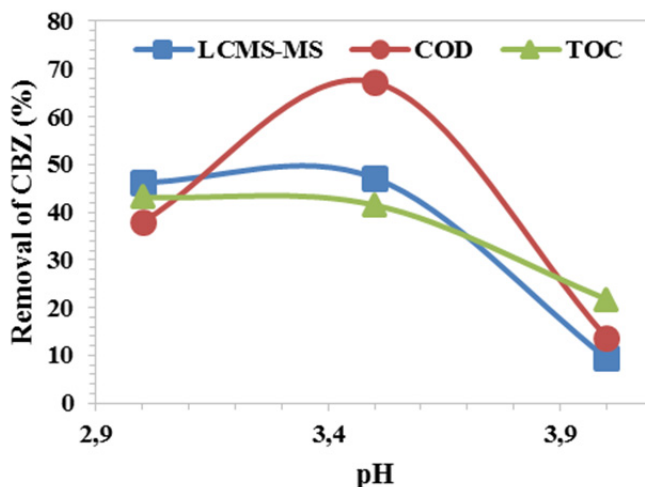


Figure 1. CBZ removal with Fenton process (pH 3,5 effect)

3.2. Effect of Fe^{2+} dosage

Different concentrations of Fe^{2+} like, 0.17, 0.35, 0.53 mM were applied to select optimum amount to carry out further series of steps at optimum pH of <3.5; 5.18mM, H_2O_2 ; contact time, 20 minute. Optimum Fe^{2+} was selected as 0.35 mM. As per the observed results of COD and TOC best value of FeSO_4 was 0.35 mM. COD removal was observed as 102.4, 59.7, 80 mg/L out of which 59.7 mg/L was at optimum Fe^{2+} dosage 0.35 mM. Likewise, TOC removal was 41.87, 31.58, 39.58 mg/L and at Fe^{2+} dosage 0.35 mM 31.58 mg/L was optimum. Finally, results were cross checked with LCMS results that showed 5.77, 3.35, 4.28 mg/L CBZ at 0.17, 0.35, 0.53 mM respectively. That is an indicator that selection of Fe^{2+} 0.35 mM dosage was optimum that is far less than many of studies mentioned in Table 2. Difference between results are show in Figure 2.

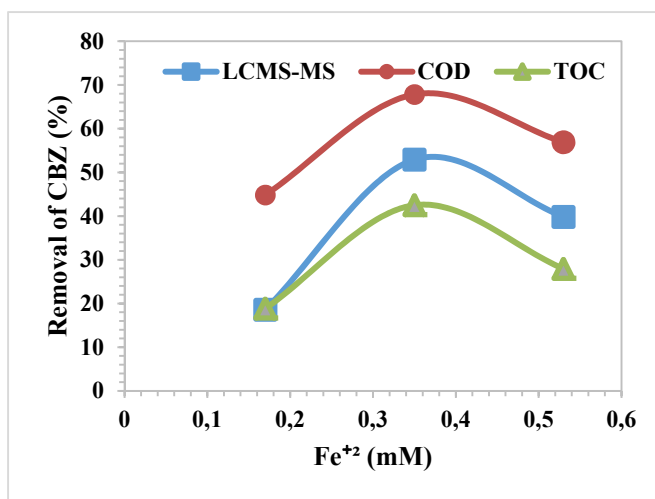


Figure 2. CBZ removal with Fenton process (Fe²⁺ Effect)

3.3. Effect of H₂O₂ dosage

The effects of H₂O₂ concentration and reaction with Fe²⁺ (optimum concentration 0.35 mM) at pH <3.5 value was investigated on the degradation of CBZ at 25°C. Increasing the concentration of H₂O₂ obviously prompted the degradation of CBZ [36]. When the dose of H₂O₂ was 2.90, 5.18, 11.63 mM the TOC degradation rate of CBZ was 51.54, 31.58, 30.17 mg/L out of which 30.17 mg/L was at optimum that is 45.06 % degradation in 20 min, and the value was decreased to 42.49 % and 6.15 % when the concentration of H₂O₂ was decreased to 31.58 and 30.17 at same contact time of 20 min. Same trend was observed in COD, where removal was observed as 131.12, 59.7, 57.6 where 57.6 was optimum at 68.96 % removal because COD removal by both the oxidation and coagulation was decreased with increasing pH. Finally, results were cross checked with LCMS results that showed 5.79, 3.35, 3.29 mg/L degradation of CBZ at 2.90, 5.18, 11.63 mM concentration of H₂O₂ respectively. Hence, 53.73 % at high concentration of H₂O₂. That is an indicator that optimum selection of H₂O₂ dosage 11.63 mM was correct and higher concentrations of H₂O₂ are proved to be beneficial in degradation. Difference between results are show in Figure 3.

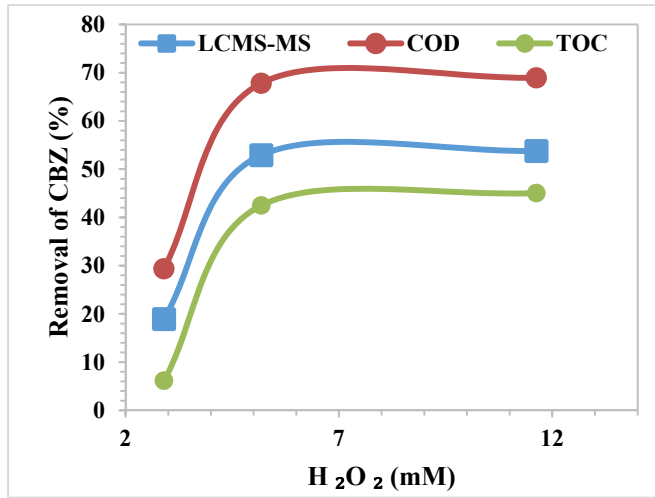


Figure 3. CBZ removal with Fenton process (H₂O₂ Effect)

3.4. Effect of Contact Time

Contact time was figured out by applying different stirring times of 15-20-30 minutes to the solution under optimized parameters: pH<3.5; 0.35 Mm, FeSO₄; 11.63 mM, H₂O₂. COD and TOC results showed that 30 minute is the best optimum contact time. COD removal was observed as 128.0, 57.6, 44.8 mg/L out of which 44.8 mg/L was at optimum Contact time 30 min. likewise TOC removal was 36.02, 30.17, 29.82 mg/L and at contact time 30 min 29.82 mg/L was optimum. Finally, results were cross checked with LCMS results that showed 5.79, 3.35, 3.29 mg/L CBZ at 15, 20, 30 min respectively. That is an indicator that optimum selection of contact time 30 min was correct. Difference between results are show in Figure 4.

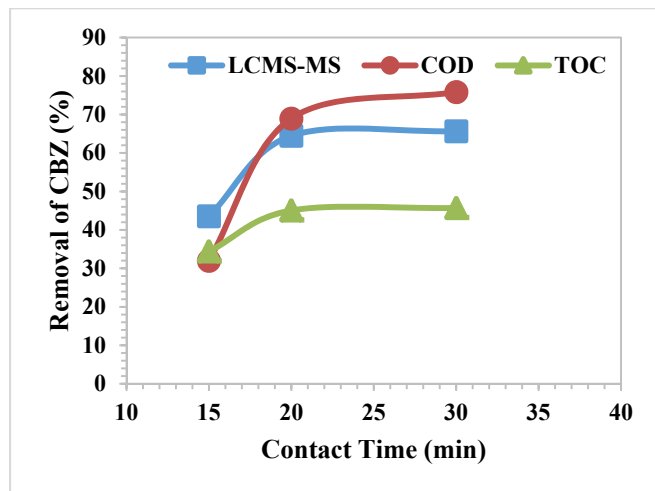


Figure 4. CBZ removal with Fenton process (Contec Effect)

4. CONCLUSION

CBZ is widely present in wastewaters and ultimately in water bodies. Therefore, it is necessary to evaluate and address its impact on the ecosystems by applying degradation techniques. In the present study, all the results and best working conditions for the degradation of CBZ are precisely described as: pH<3.5, FeSO₄, 0.35mM; H₂O₂, 11.63 mM, contact time, 30 minutes. According to these results highest removal efficiencies for COD, TOC and LCMS-MS analysis are 75.86, 45.69 and 53.73 % respectively at constant residence time of 120 minutes at room temperature. Results suggested that CBZ degradation enhanced as the H₂O₂ dosage increased. Although, CBZ degradation is difficult with conventional and biological treatment systems but still Fenton process is a compromising technique. We suggest further experiments at different conditions, for instance treatment efficiency may be enhanced in the presence of UV irradiation as more hydroxyl radicals are produced in the so-called photo Fenton reaction compared to classic Fenton process. In this study, we developed a Fenton system for efficient degradation of CBZ by relatively very less concentrations of H₂O₂ as compared to other studies and dramatically it provided good degradation at pH 3.5. It was found that the addition of H₂O₂ in mM concentrations instead of mg/L or M/L, improved the degradation merely in 30 minutes. The dramatic CBZ degradation enhancement could be attributed to the Hydroxyl radicals that were the primary radical species responsible for the CBZ degradation.

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