Photocatalytic degradation of cephalexin by UV activated persulfate and Fenton in synthetic wastewater: optimization, kinetic study, reaction pathway and intermediate products

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Abstract

We used Low pressure mercury vapor lamp activated of Sodium Persulfate (UV/SPS) and Fenton processes in two separate reactors to comparison of cephalexin (CPX) degradation in aqueous solution. The effect of pH, initial concentration of SPS, concentration of CPX, concentration of H₂O₂ and concentration of Fe²⁺ on the degradation of CPX were investigated. The residue of CPX and metabolites were determined by HPLC and GC/MS. The Total Organic Carbon (TOC) analysis was utilized for surveying the mineralization of CPX. Biodegradability of CPX in both advanced oxidation processes was evaluated by BOD₅/COD in optimum condition. The results indicated that the maximum CPX removal was obtained at pH 3, H₂O₂ 3 mM, concentration of initial CPX 10 mg/L and by increasing the doses of SPS from 0.1 to 0.2 mM, the degradation of CPX was enhanced. In this study, the most important factors for AOP efficiency was concentration of initial CPX; and then pH in UV/SPS and H₂O₂ in Fenton processes. The TOC measurements indicate that the UV/SPS and Fenton can efficiently mineralize CPX. CPX removed enough to achieve suitable biodegradability for a further biological process. Too, analysis of generated intermediates during the degradation of CPX was conducted by GC/MS method and a degradation pathway was proposed.

Keywords Cephalexin · Advanced oxidation process · Metabolite · HPLC · GC/MS

Introduction

Antibiotics are compounds that are widely used in medicine, veterinary medicine and agriculture. Medicines and pharmaceutical compounds are continuously grown and consumed in a large volume; and are added annually to the number of consumers and the variety of antibiotics [1].

Since a small amount of antibiotics are absorbed into the body, a significant portion of them are excreted through the urine and feces, and enter the aquatic environment. The concentration of antibiotic in hospitals and urban wastewaters is in the range of 0.3 to 100 mg/L and higher [2]. Unfortunately,

conventional wastewater treatment plants do not show suitable efficiency removal of these compounds. Concentrations ranging from ng/L to mg/L of antibiotics in surface and underground waters and other aquatic resources have been found [3, 4]. The presence of antibiotics is known as an environmental and health risk. Aquatic environments are steadily resistant to antibiotics in the environment and can transmit this behavior through cellular plasmids to other bacteria. This is while bacterial resistance causes deaths of at least 18,000 people in the United States and 25,000 people in Europe, every year, which represents the risk of this phenomenon [5]. Therefore, wastewater treatment containing antibiotics is required prior to discharge into the receiving waters, biological treatment and water recycling systems.

There are several options for the removal of antibiotics from aqueous solution that can be called adsorption, biofiltration and reverse osmosis processes, but these methods transfer pollutants from one phase to another [6]. While the advanced oxidation process successfully destroys organic pollutants [7].

The Fenton process is the simplest advanced oxidation process, which includes the famous reaction of hydrogen peroxide as an oxidizing agent and ferrous ion as a metal catalyst

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in acidic conditions [8]. The main product of this reaction is radical production ($\text{OH}^\bullet$) with an oxidation potential of 2.8 v. The benefits of this process include high performance, simple technology, low cost and low toxicity of the reactants [9, 10].

Anion persulfate with the chemical formula $\text{S}_2\text{O}_8^{2-}$ is used as an oxidant with oxidation reduction potential (ORP) 2.01 V. Various studies have emphasized the need for activation of persulfate to increase the oxidizing capacity of the process [11]. Although the activation of persulfate by metal ions increases the efficiency of these oxidants in reducing of contaminants in the water, its negative effects on human health are important. In contrast, ultraviolet radiation is used as an environmentally friendly and functional method for activating persulfate to produce oxidizing radicals [12].

Cephalexin (CPX) is an antibiotic that is widely used to care various types of infections due to its potent antimicrobial effect and its high dissolution in aqueous solution. This antibiotic results in the death of gram-positive and gram-negative bacteria by destroying the cell wall of the bacteria [13]. CPX causes the destruction of beneficial microorganisms in the treatment of wastewater and the resistance of pathogenic microbial agents.

Due to the solubility of this pharmaceutical compound in water and its non-degradability by conventional treatment methods, we are witnessing its accumulation in the wastewater. Hence, removal of these compounds from water and wastewater is considered an important consideration.

The present study was conducted to investigate the feasibility of using UV/SPS and Fenton processes for the degradation of CPX from aqueous solutions and its mineralization. Biodegradability of CPX were identified, while intermediates formed were analyzed through GC–MS. The tentative degradation pathway for CPX has also been proposed.

Materials

Chemicals and apparatus

CPX, ferrous sulfate, hydrogen peroxide and sodium persulfate were purchased from the Merck Co. Germany (Table 1).

The pH was adjusted with 0.1 N NaOH or H_2SO_4 . The water used was purified using the Milli-Q system. Mercury chlorine, potassium dichromate, silver sulfate and sulfuric acid, which were used to measure chemical oxygen demand (COD), were obtained from the Merck Co. Methanol, acetonitrile, formic acid and distilled water for a mobile phase were used in high performance liquid chromatography (HPLC) to determine the residual CPX. Phosphate buffer, magnesium sulfate, calcium chloride, ferric chloride, sodium hydroxide, sulfuric acid, sodium sulfite, potassium iodide solution, acetic acid solution, sulfuric acid, (2 chloro6 (trichloromethyl) pyridine) were used to measure biochemical oxygen demand (BOD). All materials had a purity of 99.9% with analytical grade.

Experimental procedure

In this study, a batch reactor of 1000 cc was used. The effect of pH, Conc. CPX, Conc. SPS in the UV/SPS process; and Conc. Fe^{2+} , H_2O_2 and CPX were studied in the Fenton process. A stock solution of CPX (100 mg/L), SPS (1 mM), H_2O_2 (10 mM) and Fe^{2+} (1 mM) with double-distilled water in a glass bottle was prepared.

To control the interveners, control group (without oxidants) was used in each run, the results showed very slight changes in CPX and COD degradation (<3%).

In the Fenton process, pH was adjusted to 3. In previous studies, this amount has been introduced as an optimum in the Fenton process [14].

The contact time in both processes was 60 min. All experiments were conducted at room temperature ($25 \pm 2^\circ\text{C}$). Methanol solution at a concentration of 100 mM was added to the quench of hydroxyl radicals and sulfate into the advanced oxidation reactor. The reactor was placed on a magnetic stirrer at 150 rpm.

In the SPS/UV, a low-pressure mercury lamp (UVC, Phillips, Netherland) with 16 watt and quartz coating was placed inside the reactor and covered with aluminum foil to prevent the penetration of ultraviolet radiation to the external environment.

Table 1 Physical and chemical properties of CPX, SPS and H_2O_2

Chemical Name	Molecular formula	Molecular weight, g/mol	Density, g/cm ³	Chemical structure
Cephalexin	$\text{C}_{16}\text{H}_{17}\text{N}_3\text{O}_4\text{S}$	347.39	1.304
Sodium Persulfate	$\text{Na}_2\text{S}_2\text{O}_8$	238.09	2.40
Hydrogen peroxide	H_2O_2	34.01	1.11 (30%) 1.45 (pure)

The kinetic study of CPX was also performed using first-order, the elovich and intraparticle diffusion models [15, 16].

Analytical methods

The CPX residual was determined by high-performance liquid chromatography (HPLC) (Agilent 1200 Series, Agilent, USA) at 254 nm. Mobile phase including 20 mM ammonium acetate ($\text{CH}_3\text{COONH}_4$): Acetonitrile (CH_3CN) (75:25 v/v) at a flow rate of 1.5 mL/min. To adjust the pH to 4.3, diluted acetic acid was used. With the aid of 0.45 μm pore nylon membranes, ammonium acetate solution filtered and mixed with acetonitrile HPLC grade. The sample size of 10 μL was injected. TOC values were determined using TOC analyzer (Multi N/C2100, Jena, Germany). Also, the concentration of H_2O_2 and SPS were determined by spectrophotometric method at 400 nm [17] and 352 nm wavelengths [18], respectively. COD and BOD_5 were measured by 5220D method (closed reflux colorimetric) and 5210D method (Winkler) [19].

Gas chromatograph (6890 N, Agilent, U.S.A) incorporated with mass detector (MS-SCION-45P, Bruker) and equipped with MS wax column (length 30 m and diameter 0.25 mm) was used for the identification of intermediates. The range of scanning mass m/z was set from 50 to 410. Helium, carrier gas was employed at a flow rate of 1.0 mL/min. The temperature for injector was set at 280 °C. The GC oven temperature program was adjusted from 40 to 260 °C. The injection volume of sample was 1 mL and split ratio of GC used was 1:10 [20].

Experimental design

Statistical design of the experiments and analysis of data was done with design expert software (version 7). The central composition design (CCD) is used alternately under the design of the response surface methodology (RSM). The design consists of a point 2^k with axial points and a central point that k is the number of variables.

It is very important to determine variable's range in designing experiments to save time and cost and reduce errors. Based on the pre-tests conducted, the range of the variables at

Table 2 Independent variables code and the range of actual values

Process	Variables	Code	Unit	Range		
				-1	0	+1
Fenton	Conc. CPX	A	mg/L	10	30	50
	Conc. H_2O_2	B	mM/L	2	3	4
	Conc. Fe^{2+}	C	mM/L	0.2	0.3	0.4
UV/SPS	Conc. CPX	A	mg/L	10	30	50
	Conc. SPS	B	mM/L	0.1	0.2	0.3
	pH	C	—	3	6	9

three levels of +1, 0 and − 1 was selected (Table 2). P value with 95% confidence level is used to evaluate the effect of model functions.

The process performance was evaluated based on 4 responses of CPX degradation, COD removal, TOC removal and BOD_5/COD ratio. According to three independent variables in each process, 20 runs (7 variable points, 7 axial points, 1 central point and 5 repetitive points in the center) were performed (Table 3).

The quality of the models is evaluated using the coefficient R^2 . The values of the Fisher (F-value) of the models represent the significance of the models. $\text{Prob} > F$ less than 0.05 represent the meaning of the terms in the model.

Results and discussion

RSM modeling

In this study, the central composite design (CCD) was used to design experiments. In the CCD, a large amount of information can be obtained from a small number of experiments [21]. The first step in analyzing the results is the select an appropriate model for the system that can accurately predict the results.

Table 3 Experimental design

Run	UV/SPS			Fenton		
	Conc. CPX mg/L	Conc. SPS mM/L	pH	Conc. CPX mg/L	Conc. H_2O_2 mM/L	Conc. Fe^{2+} mM/L
1	30	0.2	6	50	2	0.4
2	30	0.2	6	30	3	0.3
3	30	0.2	6	10	2	0.2
4	50	0.2	6	10	4	0.4
5	30	0.1	6	10	2	0.4
6	50	0.1	9	50	3	0.3
7	30	0.2	9	10	3	0.3
8	10	0.1	3	30	3	0.3
9	10	0.1	9	30	3	0.3
10	50	0.3	3	10	4	0.2
11	30	0.2	3	50	4	0.2
12	50	0.3	9	30	3	0.4
13	30	0.2	6	30	3	0.3
14	30	0.3	6	30	4	0.3
15	10	0.3	3	30	3	0.3
16	50	0.1	3	50	4	0.4
17	30	0.2	6	30	2	0.3
18	10	0.2	6	30	3	0.2
19	30	0.2	6	50	2	0.2
20	10	0.3	9	30	3	0.3

Table 4 ANOVA results for the efficiency of CPX and COD removal in advanced oxidation process

Process	Eq of CPX and COD removal	R ²	Adj.R ²	Fvalue	Adeq. precesion	SD	Prob > F	Probability for lack of fit
UV/SPS	CPX removal = +55.16–17.35 A + 4.85 B - 18.55 C + 16.22 A ² –25.28B ² + 11.19 AC	0.940	0.912	33.98	19.933	6.91	0.001	1.22
	COD removal = +41.09–17.50 A + 2.79B -15.89 C + 17.51 A ² –23.24 B ² + 10.94 AC	0.962	0.945	56.11	24.464	5	0.001	0.162
Fenton	CPX removal = +88.15–12.50A +4.40B +6.40C -17.75B ² –20.75 C ² + 9.12 AB +9.37 AC	0.951	0.923	33.91	23.228	6.32	0.001	0.160
	COD removal = +68.00–12.06 A + 4.71B +4.32 C -16.04B ² –17.39 C ² + 7.09 AB +9.41 AC	0.920	0.874	19.88	17.96	7.31	0.001	0.166

In this study, the quadratic model was used to analyze CPX (Table 4).

The equations in Table 4 are obtained after eliminating ineffective variables and interacting within them. Based on statistical analyzes, the models have low probability values and high reliability levels [4].

In Fenton process, the three terms of single- effects (A, B, C), two terms of quadratic effects (B², C²) and two terms of dual effect (AB, AC) for CPX and COD removal were significant.

In UV/SPS process, the three terms of single effects (A, B, C), two terms of quadratic effects (A², B²) and one terms of dual effect (AC) for CPX and COD removal were significant.

Also, the accuracy of the model indicates the signal-to-noise ratio, which the ratio greater than 4 is acceptable [22]. This value in current study was 23.228 and 17.96 for CPX and COD removal on Fenton process. Adeq. Precesion for UV/SPS was 19.933 (CPX removal) and 24.464 (COD removal).

In this study, R² for UV/SPS and Fenton processes is 0.940 and 0.962; and 0.951 and 0.920, respectively. Whatever the value of R² is closer to one, the selected model is more reliable, when R² is more than 0.8, the model can be safely used to optimize the responses [23]. Some researchers prefer to use adjusted-R² because R² always increases when the new variable enters the model, while adjusted-R² always counteracts adding unnecessary sentences. Adjusted-R² level for UV/SPS and Fenton processes was shown in Table 4.

Considering the coefficients of the factors in the above equations, one can determine the importance of each of the parameters on the removal efficiency. Hence, in UV/SPS, pH (in CPX removal) and CPX concentration (in COD removal) are most important on responses. In Fenton, CPX concentration is most important on responses, so that its direct and negative relation with efficiency is observed.

Effect of CPX

Determining the effect of the initial concentration of antibiotics on the effectiveness of the process and selecting the appropriate removal process based on the initial concentration is essential.

Selection of the most effective parameter on the efficiency of antibiotic degradation has a significant role in reducing operational costs, because knowing the most effective parameter can lead to research on this basis. If the coefficient factor was higher (Table. 4), its effect on the removal efficiency is higher. In this study, the effect of CPX concentration on CPX degradation is more than the effect of other parameters.

In current study, the effect of initial CPX on process efficiency was examined (Fig. 1). The decrease in the CPX concentration showed a significant effect on CPX and COD removal. As can be seen in Fig. 1, we obtained 100% removal efficiency at CPX of 10 mg/L in 60 min. In runs of 4 and 18, with decreasing CPX concentration from 50 to 10 mg/L, removal efficiency increasing from 35.2 to 84.7%.

Moreover, as shown in Fig. 2, the maximum removal of COD was in UV/SPS (85.6%) and Fenton (86.4%) was in CPX of 10 mg/L. In total, COD removal was at range of 11.3–85.6% in UV/SPS and 5.6–86.4% in Fenton process.

In some studies, the reason for the reduction in efficiency is that the level of contact with oxidants decreases due to the surface-contact rule, with an increase in the CPX concentration [24]. In some studies, the reduction in efficiency is attributed to the production of interventional, lateral and intermediate produced from contaminated composition. Thus, during the process, the materials from the decomposition are overextended to be able to be oxidant consumers [25]. On the other hand, by increasing the concentration of CPX, the penetration of radiation into the solution decreases [26]. Through decreasing the initial concentration of CPX from 50 to 10 mg/L, CPX and COD is removed with a high slope. Ajoudanian et al. reported that when the concentration of CPX was decreased, the degradation rate of CPX is slowed down, which in accordance with our findings [27]. Thus, increase of CPX through abstraction of radical can reduce the slope of CPX removal efficiency.

Effect of pH

pH is one of the most important factors affecting chemical reactions and the rate of chemical reactions depends on the

Fig. 1 3D surface plots for CPX removal efficiency with respect to concentration of CPX and SPS at time of 60 min; (a) pH = 3 (b) pH = 6 (c) pH = 9 (d) perturbation plot

pH of the environment. pH directly and indirectly affects the oxidation of organic matter [28]. According to previous studies, the best pH for Fenton is, which was applied in this study [29]. This seems to be due to the high persistence of hydrogen peroxide and iron sulfate at pH = 3. Studies by researches have shown that at pH > 3, the solubility of Fe^{2+} and all its species is reduced, resulting in less radical hydroxyl [14].

In UV/SPS, the pH of 3, 6 and 9 was studied. The results (Fig. 3) indicate that the removal efficiency of the process highly depends on pH. The removal efficiency of CPX at pH 3 was 100% (run 15 in UV/SPS and run 7 in Fenton), however, removal of CPX decreased at higher pH Levels.

The pH of the solution after the concentration of CPX was the most effective variable. The efficiency of UV/SPS at pH 3 and 9 was 80% (run 8) and 25% (run 9), respectively (Fig. 2). As a result, the pH = 3 in the present study was optimum level.

According to Table 3, the removal rate of COD at pH 3 (run 11), 6 (run 1) and 9 (run 7) were respectively obtained 53.6, 44.3 and 22% at a reaction time of 60 min, where the highest removal rate was observed at pH 3.

Acidic condition is important for maintaining sulfate ion. Due to the molecular structure of CPX, the tendency to absorb positive ion is high and therefore, when the pH is

reduced and the positive charge of the medium increases, CPX is modified by the positive charge absorption and removed. In acidic pH, sulfate is constantly reduction, and thus free electron production will continue [30]. Due to the CPX solubility factor, with decreasing pH, CPX solubility also increases [31].

Some researchers interpret the effect of pH based on antibiotic pKa [32]. CPX is a group of β -lactam antibiotic and has two proton binding sites, which has a low acidity constant with a carboxylic acid β -lactam group ($\text{pK}_a = 2.69\text{--}3.63$) [27]. In acidic pH, the nitrogen atom's protonation (especially amidic nitrogen due to its higher acidity than aminic nitrogen) decreases. Most of the structure of CPX is formed from the carboxylate group. For this reason, CPX molecules are more available in the positive charge of the environment and increase the removal of CPX. In pH values higher than 3, repulsive forces reduce the degradation between the negative charge of the solution and free electron pairs of amine, amid and carboxylate [33].

On the other hand, the product of the activation of $\text{S}_2\text{O}_8^{2-}$ with ultraviolet radiation, which leads to radical production of $\text{SO}_4^{\cdot -}$ can change with pH. Generated radical hydroxyl is reacted with radical persulfate and eventually resulted in the

Fig. 2 3D surface plots for COD removal efficiency with respect to concentration of pH and SPS at time of 60 min; **(a)** CPX = 10 mg/L **(b)** CPX = 30 mg/L **(c)** CPX = 50 mg/L **(d)** perturbation plot

production of SO_4^{2-} , which causes the cycle to continue alternately [34]. In the study of Adhami et al. (2018), CPX removal with the help of UV/ZnO was the best in acidic condition (pH = 3), which is in line with the current study results. Low

Fig. 3 3D surface plots for CPX removal efficiency with respect to concentration of SPS and pH at CPX of 10 mg/L

efficiency along with increased pH can be expressed in the form of the following reactions:

The results of our study are also consistent with the results of the study conducted by Norzaee et al. who revealed that decomposing of penicillin through heat activated persulphate is maximum at acidic pH [35].

Effect of SPS

Oxidizing concentrations are one of the important and influential factors in the efficiency of the advanced oxidation process. Anion SPS has two electrons as a strong oxidizer, which reacts in the presence of the activator to produce free radical sulfate with high oxidation and resuscitation power [36]. In this study, the effect of different concentrations of SPS (0.1–0.3 mM) was investigated. The results of this study show that

the removal of CPX is proportional to the increase of SPS concentration. In this way, increasing the SPS up to 0.2 mM, the removal efficiency increases and then decreases with increasing concentrations up to 0.3 mM. When the concentration of SPS ion increases from 0.1 to 0.2, more sulfate radicals are able to attack CPX, so the removal efficiency of COD and CPX is increased. The efficiency of CPX removal increases from 33% in the run 14 to 59% in the run 15 with decreasing SPS from 0.3 to 0.2 mM (Fig.1).

The average removal of COD at 0.1, 0.2 and 0.3 mM of initial concentration of SPS were obtained to be 18.2 (run 5), 44.3 (run 8) and 20.2 (run 14) percent, respectively; with the highest removal rate of COD observed at 0.2 mM.

Of course, in CPX concentration of 10 mg/L, removal rate and CPX concentration have a direct relation (Fig.2). In the process of UV/SPS, the radical $\text{SO}_4^{\bullet-}$ plays a role in electron capture at high pH.

Reducing hydroxyl radical in the environment leads to a reduction in the probability of oxidation, which decreased the removal efficiency [37]. At pH less than 7, radical sulfate is predominant in the reaction medium (Eq.6).

Increasing the concentration of over-optimal persulfates led to the conversion of sulfate to persulfate, which led to the loss of radical sulfate and lower COD and CPX removal [38].

By increasing the concentration of the oxidant to more than the optimal amount, it also acts as a radical scavenger and acts as an agent for the conversion of radical sulfate to persulfate and, in general, destroys sulfate radicals [39]. The results in this section correspond to a study by Lin et al. by assessing the effect of UV/ $\text{Na}_2\text{S}_2\text{O}_8$ oxidizing in aquatic environments. According to Lin et al. study, the cause of these changes is that by increasing the concentration of $\text{Na}_2\text{S}_2\text{O}_8$, the production of SO_4 radicals, which play a major role in the oxidation of polyvinyl alcohol, is consistent with the present study [40].

Effect of H_2O_2 and Fe^{+2}

The Fenton process depends on the concentration of hydrogen peroxide. One of the most important parameters affecting advanced oxidation processes is oxidizing radicals. The present study shows the effect of different concentrations of H_2O_2 in the range of 2–4 mM for CPX degradation. In the Fenton process, hydrogen peroxide is a source of radical hydroxyl production, which, by reacting with bivalent Fe^{2+} ions, produces radical hydroxyl [41]. The only source of $\text{OH}^\bullet$ in the process of Fenton is H_2O_2 . Increasing the amount of H_2O_2 to a certain extent will increase the concentration of $\text{OH}^\bullet$ and thus

increase the process efficiency [42]. As shown in Fig. 4, CPX removal increase to a certain extent by increasing hydrogen peroxide. So that a solution of CPX concentration of 10 mg/L in the presence of hydrogen peroxide 4 mM is eliminated about 62%.

It should be noted that the Fenton efficiency at the concentration of hydrogen peroxide 3 mM is maximum. This can be attributed to the reaction of excess peroxide with $\text{OH}^\bullet$ in response to the following reactions and the formation of $\text{HO}_2^\bullet$, which has less oxidizing power compared to free radical hydroxyl.

It can be argued that excess hydrogen peroxide plays an inhibitory role in the production of hydroxyl radicals and reduces the process efficiency. In fact, they are produced at higher values than the optimal radionuclide scavenger ($\text{HO}_2^\bullet$) ratios.

These results are consistent with the other studies reported on the decomposition of chloramphenicol [43], amoxicillin, ampicillin and coloxazine [44] with the advanced oxidation process.

Fan et al. Studied the sulfasalazine antibiotic degradation with the Fenton-like process, with an emphasis on Fe^{2+} concentration and hydrogen peroxide. They found that by increasing the concentration of hydrogen peroxide from 1 mM to 16 mM, the removal of antibiotics increased to 99.5%. Increasing the amount of ionic ferric and combining this ion with radical hydroxyl prevented the increase in ciprofloxacin elimination efficiency. They reported that the highest efficiency was achieved at a concentration of 0.2 mM [45].

According to Fig. 5, the removal rate of COD at concentration of H_2O_2 of 2, 3 and 4 mM were respectively obtained 37.5% (run 17), 68.2% (run 2) and 58.9% (run 14) at a reaction time of 60 min, where the highest removal rate was observed at concentration of H_2O_2 of 3 mM.

One more reason can be described that i) at high concentrations of hydrogen peroxide it acts as a radical hydroxyl scavengers and will affect the radical concentration of hydroxyl, ii) in high concentrations of hydrogen peroxide, two $\text{OH}^\bullet$ react together to produce hydrogen peroxide, iii) when excessive hydrogen peroxide is raised, HO_2 is produced. This intermediate has a reaction rate and lower oxidation power than $\text{OH}^\bullet$ [46].

Fe^{2+} have a significant effect on the efficiency of the Fenton process. Another important point is that Fe^{2+} plays a role in reacting with hydrogen peroxide, which leads to an increase in $\text{OH}^\bullet$ production; therefore, its concentration is very important. Without Fe^{+2} , $\text{OH}^\bullet$ do not form and do not occur at the concentration of CPX. Based on the results obtained in this study, increasing the concentration of Fe^{2+} increases the

Fig. 4 3D surface plots for CPX removal efficiency with respect to concentration of H_2O_2 and CPX at time of 60 min; (a) $\text{Fe}^{2+} = 0.2$ (b) $\text{Fe}^{2+} = 0.3$ (c) $\text{Fe}^{2+} = 0.4$ (d) perturbation plot

efficiency of process. With increasing ferrous from 0.1 to 0.2 mM, Fenton efficiency increased. In the hydrogen peroxide of 3 mM, the increase of ferrous from 0.2 (run 18) to 0.3 (run 20) and 0.4 mM (run 12), the removal efficiency of CPX was 50, 90, and 83%, respectively (Fig. 6).

In the above conditions, the COD removal efficiency was obtained 32.4, 69.7 and 61.3% respectively. No significant increase in process efficiency was observed with an increase of more than 0.3 mM. As a result, the concentration of 0.3 mM was chosen as the optimum concentration, with an elimination efficiency of 100%.

Ferrous ions act as catalyst in acidic conditions. On the other hand, when the amount of Fe^{2+} in the aqueous solution is high, ferrous ion is used as a reactant, not a catalyst, in the Fenton process. In fact, the increasing of ferrous ion can be combined with $\text{OH}^\bullet$ and remove them from the reaction (Eq. 9) [47].

In a study by Farokhi et al. on the removal of pentachlorophenol by Fenton, it has also been observed that increasing the concentration of Fe^{2+} of 0.05 mM increases the process efficiency but in higher concentrations, the process efficiency was

reduction [48]. By increasing the amount of Fe^{+2} , the color of solution becomes the brown. In this case, Fe^{2+} with hydroxyl radical to form a complex that reduces the hydroxyl radicals in the solution and process efficiency.

TOC removal efficiency

In this study, the CPX degradation in optimal conditions was 100% and no residues were observed in water. However, CPX may not have been completely mineralized and has become secondary organic metabolites. Therefore, the TOC removal in optimal conditions was investigated (CPX: 10 mg/L, SPS: 0.2 mM, pH:3, H_2O_2 : 3 mM, Fe^{+2} : 0.3 mM). It should be noted that in order to determine the mineralization of CPX, optimal conditions were conducted at 30–60 min. Mineralization of CPX at 30, 40, 50, 60 min in the UV/SPS was 35.4, 41.8, 48.7 and 52.3%, respectively. These values in the Fenton process were 46.3, 50, 56.1, and 59.4%, respectively. In Coledam et al. (2017) study, using the electrooxidation process for CPX removal, the TOC removal efficiency was obtained at 80% at contact time of 45 min. The results of present study showed that CPX and its metabolites

Fig. 5 3D surface plots for COD removal efficiency with respect to concentration of H_2O_2 and CPX at time of 60 min; (a) $\text{Fe}^{2+} = 0.2$ (b) $\text{Fe}^{2+} = 0.3$ (c) $\text{Fe}^{2+} = 0.4$ (d) perturbation plot

have been mineralized so that the TOC removal in Fenton and UV/SPS was 59.4% and 52.3%, respectively (Fig. 7).

Fig. 6 3D surface plots for a) CPX b) COD removal efficiency with respect to concentration of H_2O_2 and Fe^{2+} at time of 60 min and CPX 10 mg/L

Bio degradability (BOD_5/COD ratio)

Advanced oxidation processes are one of the most effective processes for the analysis of resistant compounds and enhancement of their biodegradability, which are highly regarded for high efficiency. By using advanced oxidation processes, the biodegradability of resistant compounds can be enhanced as a pre-treatment of biological processes [49]. CPX is oxidized with

Fig. 7 TOC removal during Fenton and UV/SPS process. Experimental conditions: [CPX] = 10 mg/L, [SPS] = 0.2 mM, pH = 3, $[\text{H}_2\text{O}_2]$ = 3 mM, $[\text{Fe}^{2+}]$ = 0.3 mM

hydroxyl radicals in a non-selective manner and is converted to intermediate products, sometimes intermediate products that are more toxic and less biodegradable [50]. In this study, COD and BOD₅ were evaluated to determine the bioavailability of CPX in UV/SPS (CPX 10 mg/L, time 60 min, SPS 0.2 mM) and Fenton (CPX 10 mg/L, time 60 min, H₂O₂ 3 mM and Fe²⁺ 0.3 mM). In this study, the BOD₅/COD ratio ranged from zero to 0.4 in UV/SPS and 0.45 in Fenton process after 60 min. This is probably due to the rapid breakdown of CPX into small interstitial products and their greater oxidation and increased biodegradability. In general, if the BOD₅/COD ratio is more than 0.3, it is considered to be biodegradable [51].

The result shows that the biodegradability of CPX has increased significantly after time of 60, and the effluent has become almost biodegradable. Therefore, it can be concluded that the effluent from the Fenton and UV/SPS processes can be in biological reactors, the secondary treatment will be. In other words, these processes can be used as a pre-treatment system in existing biological treatment that are unable to treat antibiotics.

RSM optimization

Graphical optimization is a multi-layered map to indicate the region in which the response values considered as criteria are obtained. Figure 8 illustrates graphical optimization, which represents the areas that provide the desired response values (yellow areas). The optimal area was identified based on CPX and COD removal upper 90 and 80%, respectively in UV/SPS and 90 and 70% in Fenton process. The optimal condition was estimated in Table 5. Then the results were compared with the experiment at the optimal conditions.

Comparison of the efficiency of UV/SPS AND Fenton with other advanced oxidation processes

Advanced oxidation processes that act as the first oxidizing agent based on the production of reactive radicals, especially OH[•], are effective in the degradation of antibiotics [24]. As shown in Table 6, some researchers investigated CPX removal in aquatic solution using advanced oxidation processes. Compared to other researches, the present study showed that

Fenton and UV/SPS are effective processes to CPX removal from aqueous solutions with appropriate cost effectiveness, high oxidation potential, good stability and increased biodegradability.

Intermediate compounds

The identification of the intermediate compounds due to cephalixin degradation during the Fenton-photo persulfate process helps identify toxic compounds and propose a pathway for decomposition during the process. In this study, GC/Mass have been used to identify intermediate compounds. Figure 6 shows the proposed route for the synthesis of cephalixin during the process. Due to the structure of cephalixin, the intermediate products formed are the result of hydroxylation (the addition of hydroxyl radical to the antibiotic molecule; pathways 2 and 3) and the oxidation of the cephem group (which consists of the beta-lactam ring containing thiazine) or the methyl group (pathway 1) replacement. The cephem group is an active antibiotic part of cephalixin, which has antibacterial properties and antibiotic breakdown begins in this section. According to Wu et al. used the Ag/Fe nanoparticles to remove cephalixin, antibiotic failure initially began with beta-lactam ring. In this study, one of the pathways of the failure reaction in the beta-lactam ring is released by the continuation of the process and hydroxylation of the amino groups of the beta-lactam nitrogen ring, NH₄⁺ and NO₃, and an open chain comprising the sulfonic group. [52]. In the study of Coledam et al., which used the electrochemical process for the synthesis of CPX, failure has been observed in cephem group. In this study, most of the intermediate compounds were introduced with the addition of radical hydroxyl to CPX, and no breakdown in the benzene ring was observed [1]. In current study, the reactions proceed with hydroxylation and decarboxylation and lead to failure in the benzene ring and the formation of the compound with m/z = 97 (Figs. 9 and 10).

Kinetic degradation

The kinetics of the reactions provides information on the reaction ratio and the mechanism of exchange of reactants into products. The plots of ln C₀/C_t versus time (first order), C_t versus ln t (elovich) and C_t versus t^{1/2} (intraparticle diffusion) is shown in

Table 5 Validation Test for optimal condition

Process	Optimal Condition		CPX removal, %	COD removal, %
Fenton	Conc. CPX, 10 mg/L	experimental	100%	86.4
	Conc. H ₂ O ₂ , 3 mM/L	Model, CI = %95	100%	80.05
	Conc. Fe ⁺² , 0.3 mM/L	SE Mean	2.91	3.37
UV/SPS	Conc. CPX, 10 mg/L	experimental	100	85.6
	Conc. SPS, 0.3 mM/L	Model, CI = %95	118.46	102.92
	pH, 3	Standard deviation	5.46	3.95

Fig. 8 Overlay plot for optimal conditions in a) UV/SPS and b) Fenton processes **Table 6** Summary of the degradation processes applied in treatment of CPX

Method	Operational condition	Analytical method	Results	Reference
Sonochemical	Time: 0–160 min CPX: 20 mg/L pH: 4, 6, 10 Ultrasonic power: 100–500 w frequency: 24 kHz	BOD COD	BOD/COD = 0–0.36	(Guo et al., 2010)
Electro-Fenton	Time: 0–480 min CPX: 50, 100, 200, 300 mg/L pH: 2, 3, 4, 5 Fe ²⁺ = 0.0, 0.5, 1, 2.5, 3.5 μ mol H ₂ O ₂ : 0–895 μ mol current density: 2.72, 4.44, 6.66, 8.88 mA/cm ²	CPX BOD ₅ COD TOC	BOD ₅ /COD: 0–0.26 CFX removal: 100% TOC removal: 50%	(Estrada et al., 2012)
catalytic ozonation	Time: 0–600 min CPX: 100, 300, 400 mg/L pH: 2, 4, 7, 10, 12 O ₃ : 4, 16, 21, 35, 38 mg/L	CPX COD BOD	CFX removal: 100% COD removal: 85.45% BOD/COD: 0.1–0.6	(Akhtar et al., 2012)
photodegradation	Solar NiO/nano-clinoptilolite Time: 0–400 min CPX: 20 mg/L pH: 3, 4.5, 7.5 and 9 NiO: 1.7, 1.8, 2.3, 3.4%	CPX COD	CFX removal: 76% COD removal: 73.5%, 89%	(Ajoudanian and Nezamzadeh-Ejliah, 2015)
Electrochemical (conductive diamond anode)	Time: 0–500 min CPX: 100 mg/L pH: 3, 7, 10 current density: 5, 10, 20 mAcm ⁻²	CPX	CFX removal: 80%	(Coledam et al., 2017)
Photo-Fenton Photocatalysis	Time: 300 min CPX: 50 mg/L pH = 3.5 H ₂ O ₂ : 300–1500 mg/L flow rate: 25, 50, 100, 200, 400 ml/min	CPX COD TOC	photocatalysis CFX removal: 56% photo-Fenton CFX removal: 41% COD removal: 70% TOC removal: 63%	(Bansal and Verma, 2018)
UV/SPS Fenton	UV/SPS Time: 60 min CPX: 10, 30, 50 mg/L SPS: 0.1, 0.2, 0.3 mmol pH = 3, 6, 9 Fenton Time: 60 min CPX: 10, 30, 50 mg/L H ₂ O ₂ : 2, 3, 4 mmol Fe ²⁺ : 0.2, 0.3, 0.4 mmol pH: 3	CPX COD BOD ₅ TOC	UV/SPS CFX removal: 100% COD removal: 85.6% TOC removal: 52.3% BOD ₅ /COD: 0.4 Fenton CFX removal: 100% COD removal: 86.4% TOC removal: 59.4% BOD ₅ /COD: 0.45	Present study

Fig. 9 GC/MS data for the intermediate compounds detected during oxidation of CPX

Fig. 8. Based on the R^2 , we identified a good fit to the first-order, the elovich and intra particle diffusion kinetic model for two processes. The constant rates in first-order kinetic model were 1.99 min^{-1} for UV/SPS and Fenton. Norzaee et al. reported a good fit to the first-order kinetic model for degradation of penicillin G by heat activated persulfate process [35]. In Xu et al. on azo dye orange G removal by persulfate with ferrous ion, K constant rate was obtained 0.040 min^{-1} [53]. As a result, an increase in the contact time for the both processes can lead to an increase in the rate constant.

In the elovich kinetic model, the kinetic constants α and β were calculated from the slope and intercept of plot qt versus $\ln t$. The different elovich kinetic values were $1.96 \text{ mg/L} \cdot \text{min}$ and 9.1 g/mg (in UV/SPS). In Fenton process, α and β level equal $1.71 \text{ mg/L} \cdot \text{min}$ and 8.01 g/mg .

Intraparticle diffusion model is used to identify the diffusion mechanism and the rate controlling steps that affect the adsorption process. The values of C represent the thickness of the boundary layer in the process of removal. The correlation rate changed from 0.729 (in UV/SPS) and 0.75 (in Fenton) using a first order model to 0.963 using elovich-type equation in both processes.

To choose the better fit, all correlation rates were considered globally, and the elovich-type equation and intraparticle diffusion model were selected due the high correlation rates (R^2 higher than 0.96). Pseudo first order model had a correlation rate 0.75 for Fenton and 0.729 for UV/SPS.

Regarding the geometrical sense of the different equation, pseudo-first order model can describe the CPX removal. Lopez-Lopez et al. (2015) [15] used a pseudo first-order kinetic model and elovich type equation for photo-Fenton process in a dye-containing wastewater and Arbabi et al. (2017) tested a pseudo first-order kinetic model for ciprofloxacin antibiotic using Fenton process. Bahrami Asl et al. (2015) used a Intraparticle diffusion model to describe the kinetic Removal of Metronidazole in an ozonation system. As a result, an increase in the activation time can lead to an increase in the rate constant.

Cost evaluation

The cost of the treatment process, especially in developing countries such as Iran, is the basis for selecting the treatment process. So that the solution has a priority to be economically

Fig. 10 The degradation kinetic of CPX using advanced oxidation process. **a)** first order model **b)** elovich equation, **c)** Intraparticle diffusion model

feasible. The cost of the advanced oxidation process involves the cost of chemicals, electricity, reactor operating, and so on. In this study, the overall cost of Fenton and UV/SPS processes was evaluated in a laboratory scale to generalize the results on a real scale (Table 7).

Considering that advanced oxidation process alone has high energy consumption costs, if hybrid advanced oxidation processes are used to remove resistant pollutants from water, some of the cost of these processes can be reduced [54]. Such studies in Iran provide a framework for the use of advanced

Table 7 Evaluation of cost of treatment process [55]

S.No.	Type of cost in UV/SPS and Fenton	UV/SPS	Fenton
A	Operation of reactor	Cost, USD	Cost, USD
B	Electricity price in Iran	0.0122 \$/kWh	0.0122 \$/kWh
	Oxidants:	0.0129\$	0.5343\$
	Total SPS (1.188 g) used (for 20 run) in UV/SPS		0.463\$
	Total H ₂ O ₂ (2.040 g) used (for 20 run) in Fenton		
	Total Fe ²⁺ (1.389 g) used (for 20 run) in Fenton		
C	Operating:		
	stirrer (35 w)	66.66 \$	66.66 \$
	ultra violet lamp (40 w)	18\$	
	No. runs	20	20
	Volume of water treated	1 L × 20 = 20 L (0.02 m ³)	1 L × 20 = 20 L (0.02 m ³)
	Cost per m ³	B/0.02 = 0.645\$/m ³	B/0.02 = 0.9973 \$/m ³
	With 100% degradation (C ₀ = 10 mg/L) Conc. Removed CFX	10 mg/L (0.01 kg/m ³)	10 mg/L (0.01 kg/m ³)
	Cost per kg/m ³ of concentration removal	B/0.01 = 1.29 \$	B/0.01 = 99.73 \$
	Energy consumption during operation of process	20 × 0.04kw = 0.8 kwh	0.035 × 20 = 7 kw/h
	(UV irradiation, stirrer)	0.035 × 20 = 7 kwh	
	Energy consumed per kg/m ³ of concentration removal	7.8/0.01 = 780 kwh	7 / 0.01 = 700 kwh
	Cost for energy consumption	780 × 0.0122 = 9.516 \$/kWh	700 × 0.0122 = 8.54 \$/kWh
D	cost of reactors	3.33 \$	3.33 \$
	Total cost of treatment process (for 20 runs)	18+ 0.645+ 1.29 + 9.516 + 66.66 + 3.33 = 99.44 \$	8.54 + 99.73 + 0.9973 + 0.5343 + 0.463 + 66.66 + 3.33 = 180.254 \$
	Total cost of treatment process for single run (1 L)	4.972 \$	9.012 \$

oxidation processes for the treatment of water and wastewater at an industrial scale in the country's water and wastewater industry, and further explains the ways in which the efficiency of these methods will be increased and the cost of treatment reduced.

In the present study, the overall cost of the treatment, including the cost of electricity, oxidant, reactor, operational equipment (low pressure mercury vapor lamp, stirrer), was studied at pilot scale. The overall cost has been evaluated for 20 runs which came out to be 99.44 \$ and 180.254\$ for Fenton and UV/SPS, respectively; and for one run was stimulated 9.012 \$ and 4.972 \$.

This is the first study to examine the exact cost of Fenton and UV/SPS in the CPX degradation. Overall cost for Fenton was higher than UV/SPS. In Fenton, cost per kg/m³ of concentration removal was 99.73 \$ while in UV/SPS was 1.29 \$.

The costs of treatment in current study are significantly lower than other reported studies related oxidation oxygenated compounds by Fenton Reagent by Kušić et al., (2016) and Sharma et al., (2015).

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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