

# Enhanced electro-Fenton processes by persulfate radical for atenolol oxidation from aqueous solution

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## Abstract

**Background:** Pharmaceuticals and personal care products (PPCPs) are a group of emerging environmental pollutants that have attracted the attention of many researchers due to their harmful effects on aquatic environment, animals, and humans. Thus, it is necessary to remove these contaminants from water resources. This study aimed to assess the efficiency of enhanced electro-Fenton (EF) process by persulfate (PS) radical for removal of atenolol (ATL) from aqueous solutions.

**Methods:** The bench scale experimental setup was used to examine the factors affecting the ATL removal efficiency from synthetic wastewater; supporting electrolyte type, pH, contact time, PS concentration, Fe concentration, and ATL initial concentration.

**Results:** Based on the results, ATL removal efficiency of 78.6% was reached under the optimum conditions of enhanced EF process by PS radical. The optimum conditions included NaCl (as a supporting electrolyte) dose of 0.5 g/L, pH 5, contact time of 60 minutes, PS dose of 0.15 g/L, Fe dose of 0.15 g/L, current density (CD) of 1.5 A/m<sup>2</sup>, and ATL concentration of 40 mg/L. Kinetic model was following the second-order kinetics.

**Conclusion:** The studied advanced oxidation process (AOP) can effectively remove ATL from aqueous solutions. Therefore, it can be used as an effective technique for removing other organic matter from the wastewater.

**Keywords:** Atenolol, Environmental pollutants, Pharmaceuticals and cosmetics, Wastewater

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## Introduction

In recent decades, the development of industry and the growth of human societies have arisen many synthetic organic compounds and persistent organic pollutants (POPs) in aquatic environments (1, 2). Pharmaceuticals and personal care products (PPCPs) are two types of harmful micro-pollutants for human health, animals, and aquatic environment that are increasingly produced by pharmaceutical industries. Among them, beta-blockers ( $\beta$ -blockers) are an important subclass of PPCPs. Atenolol (ATL) is a  $\beta$ -blocker mostly used to treat hypertension, angina, and arrhythmia (3, 4). Conventional treatment techniques are unable to effectively remove the PPCPs (5). Some of these removal techniques have disadvantages, such as high costs, long operating time, and production of toxic by-products (6, 7). In order to solve the problems associated with these conventional purification methods, various advanced oxidation processes (AOPs) have been considered. These treatment processes can be divided into two classes: (a) conventional chemical treatments, and (b) AOPs (8). AOPs can be considered as potentially powerful approaches. These processes are consisted of photochemical, chemical, or

electrochemical techniques and capable of removing recalcitrant compounds (9, 10).

In-situ production of hydroxyl radicals ( $\cdot\text{OH}$ ) is the basis of AOPs for the degradation of organic contaminants. The  $\cdot\text{OH}$  is a highly reactive, non-selective, and powerful radical in the oxidation of various compounds that has strong oxidation potential ( $E_0=2.80\text{ V}$ ) (8, 11-13). Electro-Fenton (EF) advanced oxidation process (EAOP) is a developed electrochemical oxidation process based on the constant source of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) (14-16). Development of EAOP represents high efficacy of these processes in the degradation of aquatic solution polluted with toxic compounds and stable pesticides, synthetic organic dyes, pharmaceuticals, personal care products, and many industrial pollutants (17, 18). In the Fenton process,  $\text{Fe}^{+2}$  ions and  $\text{H}_2\text{O}_2$  are used simultaneously to decompose and remove contaminants. The EF process is the name given to the production of  $\text{Fe}^{+2}$  ions by iron electrodes with the help of an electrolytic system (5, 19). Studies have been performed to combine EF with chemicals to promote treatment efficacy. Persulfate ( $\text{S}_2\text{O}_8^{2-}$ ) has been considered as a possibly practicable



chemical oxidant for the oxidation of aquatic solution organic pollutants (1). Iranian researchers have not yet done any study on removal of ATL by this method. The present study evaluated the EF process which was improved by PS radical for degradation of ATL from aqueous solution. The effect of diverse operating conditions, such as pH, current density (CD) (I), ferrous ion ( $\text{Fe}^{2+}$ ) concentration, PS concentration, different reaction time, and ATL initial concentration were also investigated.

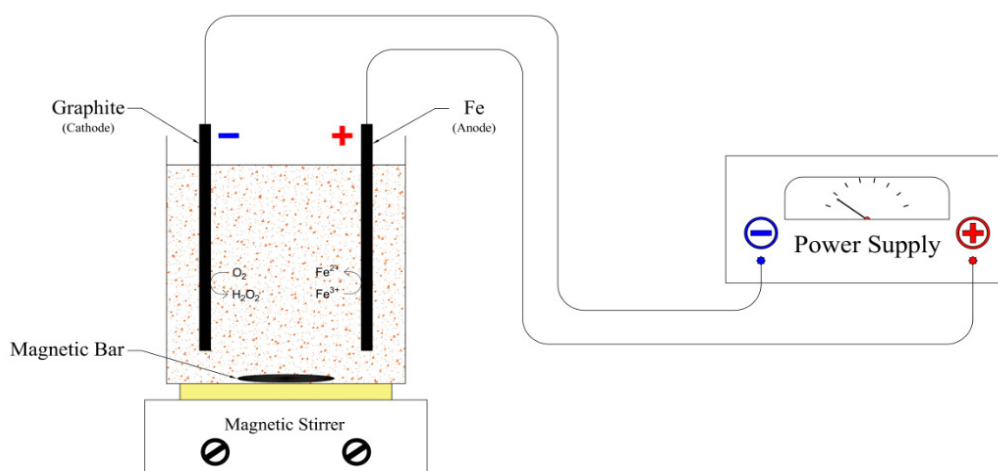
## Materials and Methods

### Materials

All the studied reagents and chemical compounds were analytical grade and without any additional purification. ATL (99%), high-performance liquid chromatography (HPLC) grade acetonitrile ( $\text{CH}_3\text{CN}$ ) and methanol, potassium dihydrogen phosphate ( $\text{KH}_2\text{PO}_4$ ), potassium persulfate ( $\text{K}_2\text{S}_2\text{O}_8$ ), ferrous sulfate heptahydrate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ), acid hydrochloric (HCl, 0.1 M), sodium hydroxide (NaOH, 0.1 M), sodium chloride (NaCl), sodium nitrate ( $\text{NaNO}_3$ ), sodium sulfate ( $\text{Na}_2\text{SO}_4$ ), and phosphoric acid ( $\text{H}_3\text{PO}_4$ ) were purchased from Merck Co. (Germany).

### Experimental procedure

This experimental laboratory study was conducted at a 1000-mL glass beaker as a batch-processing reactor. Four iron electrodes and four graphite probes, each  $200 \times 20 \times 2$  mm (length, width, thickness), with a distance of 1 cm were hanged inside the reactor. A direct current (DC) power supply with alternate cathode and anode replacement connected to the electrodes was used to power them. A magnetic stirrer (Labor Technik) was applied to accomplish uniform mixing of the solution. Figure 1 shows a schematic diagram of the experimental set-up used for the degradation of ATL solutions using enhanced EF by persulfate radicals ( $\text{PS}^\bullet$ ). A stock solution of ATL at a concentration of 1000 mg/L was ready, and the aliquots were taken from it and diluted in the reaction cell to attain the initial concentration of 40 mg/L in the reacting solution. The required amounts of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , NaCl, and PS were then added to the solution. The reaction pH, which was determined by a pH-meter (HQ-11d HACH instruments), was adjusted to a range of 3 to  $9 \pm 0.01$  by adding HCl and/or NaOH 0.1 M. Then, a centrifuge was used at 4000 rpm for 5 minutes to separate the samples, and their remaining ATL was measured using HPLC instrument.



**Figure 1.** Schematic diagram of the experimental set-up used for the degradation of ATL solutions (The anodes were Fe and cathodes were graphite electrodes).

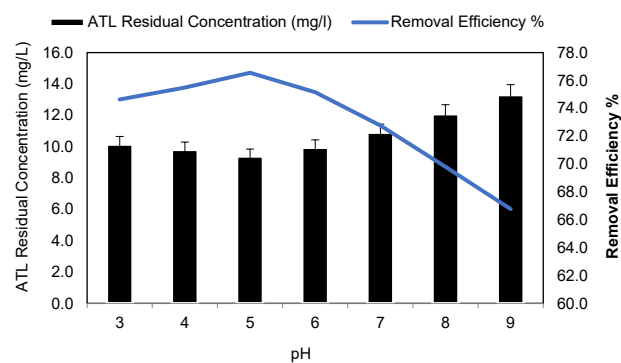
### Analysis methods

A HPLC system (WATERS, USA) equipped with an UV-VIS detector was used to determine the concentration of ATL in the samples. A  $\text{C}_{18}$  column was used for this analysis. The sample volume injection was 20 mL. The mobile phase comprised of acetonitrile and distilled water (60:40 v/v). To prepare buffer solution, 1.36 g/L potassium dihydrogen phosphate ( $\text{KH}_2\text{PO}_4$ ) was added to distilled water, and then, the solution pH was adjusted to 3 at a flow rate of  $1 \text{ mL} \cdot \text{min}^{-1}$ . The wavelength used was 235 nm, and the ATL retention time was 10 minutes.

### Results

In this study, the result of pH changes was examined in the range of 3 to 9 on enhanced EF processes through PS radicals for oxidation of ATL from aqueous solution. In this regard, the experiments were conducted with 40 mg/L of ATL solution, 0.025 g/L of PS, 0.025 g/L of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , 0.5 g/L of NaCl, and  $\text{CD} = 0.7 \text{ A/m}^2$ . Figure 2 reveals that the ATL removal efficiencies after 60 minutes for pH 3, 4, 5, 6, 7, 8, and 9 were 74.6, 75.5, 76.6, 75.2, 72.8, 69.8, and 66.8, respectively, indicating that the ATL removal efficiency is significantly influenced by the solution pH.

The supportive electrolyte affects the produced current and energy consumption of the process by increasing the solution conductivity. The effect of the type of electrolyte (NaCl,  $\text{NaNO}_3$ , and  $\text{Na}_2\text{SO}_4$ ) on the effectiveness of the EF process was investigated. Figures 3 and 4 show that the removal efficiency



**Figure 2.** The effect of pH on removal of ATL from aqueous solution (ATL= 40 mg/L,  $\text{CD} = 0.7 \text{ A/m}^2$ , NaCl= 0.5 g/L, PS= 0.025 g/L, time= 60 min,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O} = 0.025 \text{ g/L}$ ).

of ATL was higher after using NaCl as electrolytic supports compared to other salts. In addition, Figure 4 shows the effect of NaCl concentration on oxidation of ATL from aqueous solution.

According to Figure 5, the removal efficiency of ATL increased linearly with reaction time. This performance could be due to the occurrence of the adequate ATL molecules in the solution, which can contact with the electrodes surface and react with electro-generate  $\cdot\text{OH}$ .

To adjust PS concentration, the effect of several concentrations of PS (0.025-0.150 g/L) were analyzed at ATL= 40 mg/L, pH= 5, contact time= 60 min, CD= 0.7 A/m<sup>2</sup>, FeSO<sub>4</sub>·7H<sub>2</sub>O= 0.025

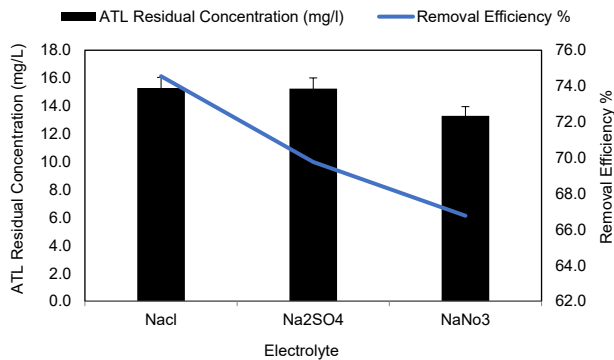


Figure 3. The effect of supporting electrolyte type on removal of ATL from aqueous solution.

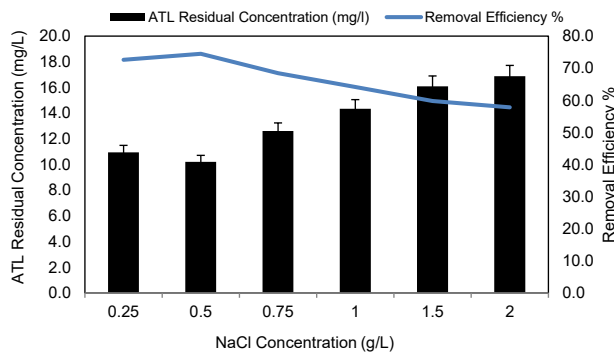


Figure 4. The effect of NaCl concentration on removal of ATL from aqueous solution (ATL= 40 mg/L, pH= 5, CD=0.7 A/m<sup>2</sup>, PS= 0.025 g/L, time= 60 min, FeSO<sub>4</sub>·7H<sub>2</sub>O= 0.025 g/L).

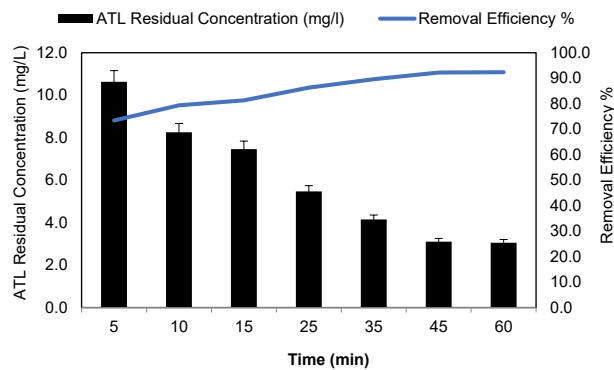


Figure 5. The effect of contact time on removal of ATL from aqueous solution (ATL= 40 mg/L, pH= 5, CD= 0.7 A/m<sup>2</sup>, NaCl= 0.5 g/L, PS= 0.025 g/L, FeSO<sub>4</sub>·7H<sub>2</sub>O= 0.025 g/L).

g/L, and NaCl= 0.5 g/L. The results showed that ATL removal efficiency improved by increasing PS concentration. Figure 6 shows that the removal efficiency of ATL in the EF process by  $\cdot\text{PS}$  improved from 61.8 to 78.0% by increasing PS concentration from 0.025 to 0.150 g/L.

The effect of different CD (0.25, 0.5, 0.7, 1, 1.25, and 1.5 A/m<sup>2</sup>) was analyzed at ATL= 40 mg/L, pH= 5, reaction time= 60 min, FeSO<sub>4</sub>·7H<sub>2</sub>O= 0.025 g/L, and NaCl= 0.5 g/L. Figure 7 revealed that ATL removal efficiency increased in the EF process by  $\cdot\text{PS}$  by increasing CD.

To optimize the Fe concentrations for removing ATL by the EF process, the required amount of FeSO<sub>4</sub>·7H<sub>2</sub>O was added to the solution. The effect of diverse concentrations of Fe<sup>+2</sup> (0.025-0.15 g/L) was investigated at ATL= 40 mg/L, pH= 5, CD= 0.7 A/m<sup>2</sup>, NaCl= 0.5 g/L, and PS= 0.15 g/L. Figure 8 indicates that ATL removal efficiency in the process increased from 75.8 to 86.3 by increasing the Fe<sup>+2</sup> concentration from 0.025 to 0.15 g/L.

Figure 9 shows the effect of the initial ATL concentrations (20–120 mg/L) on the enhanced EF by PS radicals process. As shown in this figure, by increasing ATL concentration from 20 to 120 mg/L, the removal efficiency decreased.

### Discussion

#### Effect of pH

pH generally plays a significant role in AOPs; since it affects specific organic matter and the production of a variety of important radicals. It also affects the creation of the species of transition metals and their availability to react with the

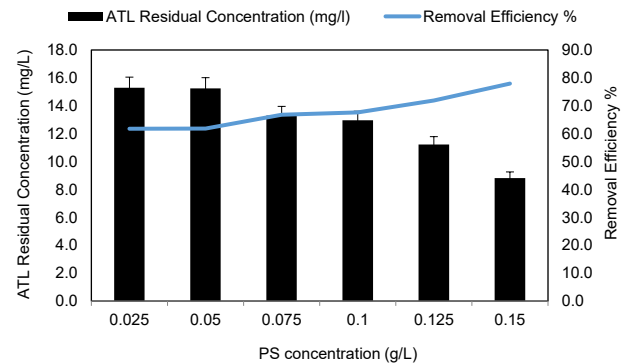


Figure 6. The effect of PS on removal of ATL from aqueous solution (ATL= 40 mg/L, pH= 5, CD= 0.7 A/m<sup>2</sup>, NaCl= 0.5 g/L, FeSO<sub>4</sub>·7H<sub>2</sub>O= 0.025 g/L).

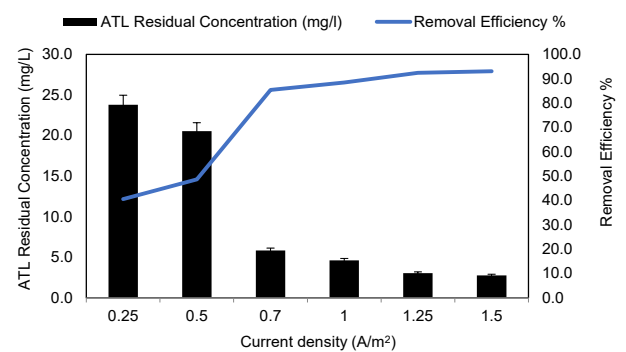
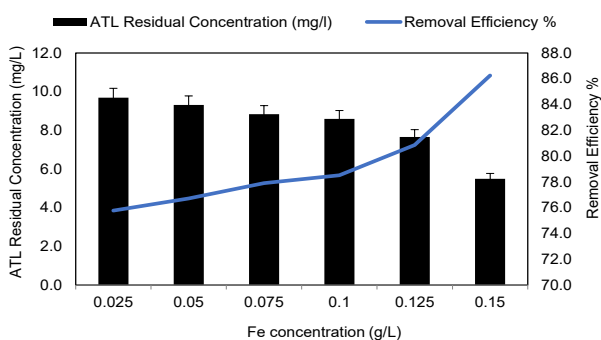
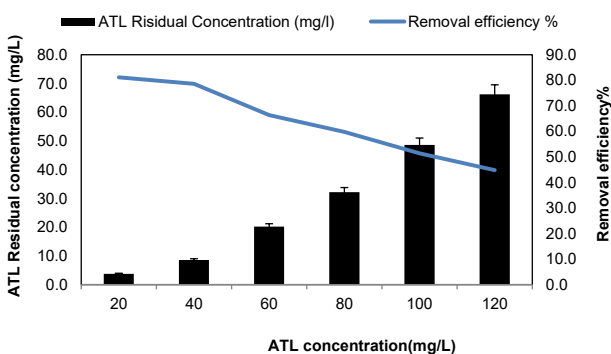


Figure 7. The effect of CD on ATL removal from aqueous solution (ATL= 40 mg/L, pH=5, NaCl= 0.5 g/L, FeSO<sub>4</sub>·7H<sub>2</sub>O= 0.025 g/L, and PS= 0.15 g/L).



**Figure 8.** The effect of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  concentration on ATL removal efficiency (ATL= 40 mg/L, pH= 5, CD= 0.7A/m<sup>2</sup>, NaCl= 0.5 g/L, and PS= 0.15 g/L).



**Figure 9.** The effect of concentration on removal of ALT from aqueous solution (pH= 5, CD= 1.5 A/m<sup>2</sup>, NaCl= 0.5 g/L, PS= 0.15g/L, contact time= 60 min,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ = 0.15 g/L).

oxidant (20, 21). The EF process is very sensitive to pH changes, indicating that pH can affect the solubility of iron, complexation, and the oxidation and reduction cycle between 2+ and 3+ states of iron, consequently, the stability of the ferrous ion depends on the pH of the solution (22, 23), as in this study, the optimum pH was at 5. Liu et al showed that increasing the solution pH from 3 to 9 enhanced the ATL removal due to the pH dependence of the photo-decomposition process of peroxymonosulfate (PMS,  $\text{HSO}_5^-$ ) (3). Shi et al reported that  $\text{O}_2^{\cdot-}$  was simply converted into  $\text{HO}_2^{\cdot}$  in acidic environments, and the ATL degradation rate was lower at pH 2.4 than pH 3.3 (4). According to Figure 2, pH changes in the range of 3 to 9 were surveyed on the enhanced EF processes through PS radicals for ATL oxidation from aqueous solution. Figure 2 shows that the ATL removal efficiencies after 60 min at pH 3-9 decreased from 74.6% to 66.8%, indicating that the ATL removal efficiency was significantly affected by the solution pH. At pH greater than 5,  $\text{Fe}^{3+}$  species began to precipitate as  $\text{Fe}(\text{OH})_3$ , so by decreasing the catalyst amount in the solution and converting the  $\text{H}_2\text{O}_2$  into  $\text{O}_2$  and  $\text{H}_2\text{O}$ , a drop in the  $\cdot\text{OH}$  generation rate occurred (Eq. 1), and also, the process efficiency decreased (21, 24-27).

$$\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow [\text{Fe}(\text{OH})_2]^{2+} \rightarrow \text{Fe}^{3+} + \cdot\text{OH} + \text{OH} \quad (1)$$

**Effect of electrolyte type**

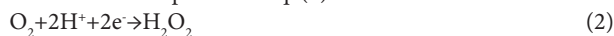
As can be seen in Figure 3, the removal efficiency of ATL was higher using NaCl than the other supportive electrolytes ( $\text{Na}_2\text{SO}_4$  and  $\text{NaNO}_3$ ). In other words, the order of these three salts in terms of the effect on the removal efficiency of ATL is  $\text{NaCl} >$

$\text{Na}_2\text{SO}_4 > \text{NaNO}_3$ , respectively.

Figure 4 also shows the effect of NaCl concentration on ATL oxidation from aqueous solution. By increasing the NaCl concentrations in the range of 0.25-2 g/L in the solution, the ATL removal efficiency decreased from about 70% to less than 60%. Many studies have found NaCl as the best auxiliary electrolyte (28, 29). The NaCl usage has benefits, so the chloride ions could considerably diminish the contrary results of other anions, like  $\text{HCO}_3^-$  and  $\text{SO}_4^{2-}$ . The existence of carbonate ions results in  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$  ions precipitation that form a protecting layer on the electrodes surface. This insulating layer rapidly increases the ohmic resistance of the electrochemical cell and causes a significant reduction in the efficiency of CD and decomposition of the compound. The existence of chlorine ions ( $\text{Cl}^-$ ) and free OH concurrently (synergic) improves and increases the degradation of the organic compound. Finally, the high efficiency and comparative inexpensiveness of NaCl have led to its use as an optimal electrolyte. Another study evaluated the impact of electrolyte concentration on the degradation profile with varying the electrolyte in the range of 250 to 2000 mg/L (including NaCl,  $\text{Na}_2\text{CO}_3$ ,  $\text{NaHCO}_3$ ,  $\text{Na}_2\text{SO}_4$ , and  $\text{NaNO}_3$ ). According to their results, by increasing the NaCl concentration due to increasing the number of  $\text{Cl}^-$  accelerating the pitting corrosion and escalating the degradation efficiency, the efficiency for EF process increased, and among them, NaCl has the most effect on the ATL degradation (24).

**Effect of contact time and kinetics**

Figure 5 shows the effect of contact time on ATL oxidation from aqueous solution. In this figure, by increasing the contact time of reaction, the ATL removal efficiency increased. The reaction occurred as interpreted in Eq. (2):



Based on Eq. (2),  $\text{H}_2\text{O}_2$  is formed and the ferrous ion is released from the sacrificial anode and reacts with  $\text{H}_2\text{O}_2$  (Eq. 3), which initiates the Fenton reaction and produces homogeneous  $\cdot\text{OH}$ . The generated oxidants can react with ATL molecules and convert them to  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , and intermediates. Longer reaction times make the aforementioned mechanism more effective and increase the ATL removal efficiency. Wu et al conducted a study on the iron-mediated activation of PS using catechin for removal of ATL from water samples. In their study, an optimal CAT concentration (5  $\mu\text{M}$ ) was utilized for systems containing 50  $\mu\text{M}$  of  $\text{Fe}^{3+}$  and 100  $\mu\text{M}$  of PS to limit the competitive reaction with generated radicals and ATL. The high degradation extent of 10  $\mu\text{M}$  ATL could be achieved in the dark after 60 min (approximately 50%) (25), also, the kinetic model of reaction was following the second-order kinetics, which is similar to the present study.



The purpose of the reaction kinetics study is to evaluate the efficiency of the EF process during the reaction time to remove the desired contaminant (30). Reaction kinetics basically show how the contaminant was removed, which can be used to better modeling and design the process to remove contaminants at a practical scale (31).

A reaction in which the concentration power of all substances in the velocity equation is zero and the reaction rate is independent of the concentration of the reactants is called the zero-order kinetic. This causes the zero-order kinetic to progress at a constant rate over time as the reactant is consumed and

its concentration decreases. In zero-order kinetic, the slope of the “concentration-time” curve is constant, because the rate of reaction is constant. But the slope of the “speed-time” curve is zero.

A reaction in which the sum of the capacitance of the concentration expressions in the velocity equation is 1, is called the first-order kinetic. That is, the reaction rate varies with the power of one relative to the concentration. It is a line that can be calculated. A reaction in which the sum of the powers of the concentration expressions in the velocity equation is 2, is called the second-order kinetic. In formulas,  $K_0$ ,  $K_1$ , and  $K_2$ , are the constant order of reaction speed of zero, one, and two-order kinetics, respectively. Also, “ $t$ ” is the reaction time in minutes and  $C$  (mg/L) is the final concentration of the reaction after the elapsed time and  $C_0$  (mg/L) is the initial concentration of ATL in the solution. The equations used for calculating zero-, first-, and second-order kinetics are as below (5 to 7):

Linear shape of zero-order kinetics:

$$C - C_0 = -K_0 t \tag{5}$$

Linear shape of first-order kinetics:

$$\ln C/C_0 = -K_1 t \tag{6}$$

Linear shape of second-order kinetics:

$$1/C - 1/C_0 = -K_2 t \tag{7}$$

According to the calculations performed to investigate the kinetic models during the reaction, the results showed that the ATL removal reactions using the EF process follow the second-order kinetic model with linear regression  $R^2 = 0.9572$ . This means that the reaction rate is related to the capacitance of 2 concentrations for ATL. Also, in the study of Liu et al, ATL degradation similar to this study, was following the second-order kinetics (3).

In a study by Gao et al, the effect of kinetics models on the

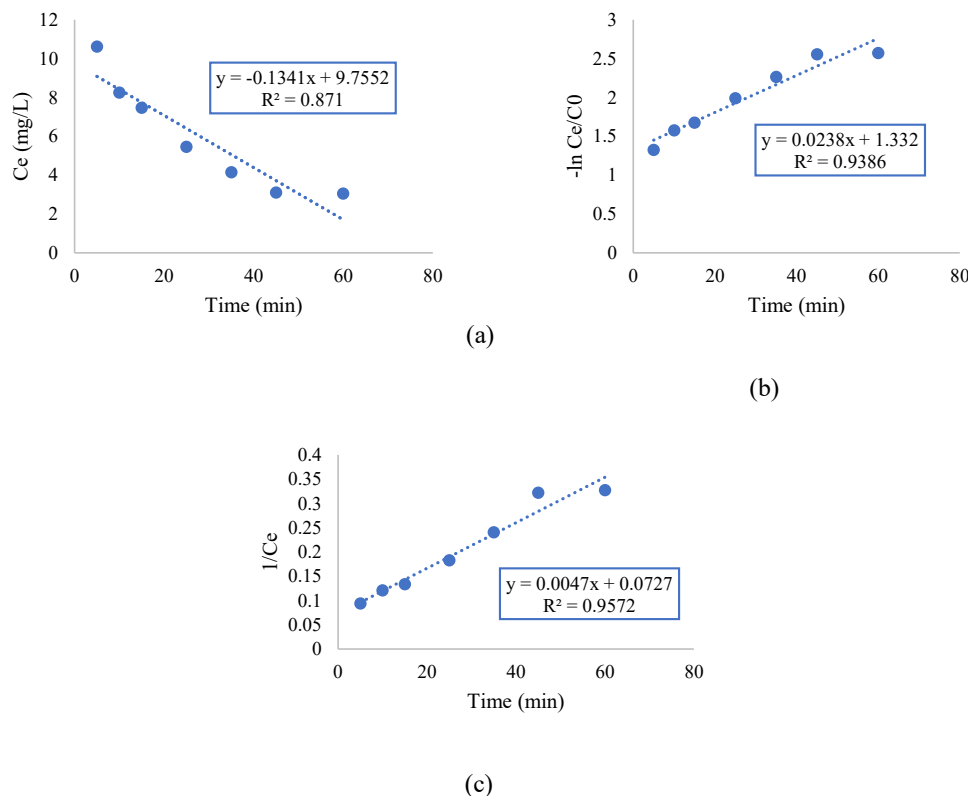
removal efficiency of sulfamethazine was examined. In this study, the PS/UV process followed zero-order kinetics (32). The results of the study of Acosta-Rangel et al show that reaction kinetics for removal of bisphenol A using UV/H<sub>2</sub>O<sub>2</sub> and UV/K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> processes followed the first-order reaction (33), which is not consistent with the results of the present study. Figure 10 shows the kinetic models for zero-, first-, and second-order kinetics of the present study.

**Effect of PS concentration**

As shown in Figure 6, by increasing the PS concentration from 0.025 to 0.15 g/L, the ATL removal efficiency enhanced from about 62% to 78%. It is noted that the concentration of oxidizing agents in the environment is the most important factor in the formation of SO<sub>4</sub><sup>•-</sup> radicals. As the concentration of oxidizing compounds increases, the production of sulfate radicals enhances, and consequently, the rate of decomposition reaction of ATL increases. New AOPs based on the activation methods by SO<sub>4</sub><sup>•-</sup> radical have higher redox potential (2.5-3.1 V), higher selectivity, and longer half-life compared to the traditional AOPs based on •OH. Usually, these radical properties of SO<sub>4</sub><sup>•-</sup> are obtained by activating PS or PMS in various methods, such as thermal, alkaline, ultraviolet light, activated carbon, ultrasound, transition metal oxides, and metal ions, such as Fe<sup>2+</sup> (1, 21). Therefore, they can quickly convert PS into SO<sub>4</sub><sup>•-</sup> radicals, and eventually, continuous generation of ferrous species assisted the EF-PS (1).

**Effect of applied current density**

Figure 7 represents the effect of CD on removal of ATL from aqueous solution. The CD is a key factor in the EF process; meanwhile it governs a large number of reactions. It affected the Fenton’s substance production rate and homogeneous •OH



**Figure 10.** Kinetics for ATL degradation: a) Zero-order; b) First-order; and c) Second-order. (ATL= 40 mg/L, pH= 5, CD= 0.7 A/m<sup>2</sup>, NaCl= 0.5 g/L, PS= 0.025 g/L, FeSO<sub>4</sub>·7H<sub>2</sub>O= 0.025 g/L).

generation rate in the bulk solution through the Fenton reaction (34). The present study investigated the CD effect on the ATL removal efficiency. The results showed that the rate of ATL mineralization was greater by increasing the CD (Figure 7). Growing CD causes a rapid ferrous production and reproduction of ferric, and improvement in the PS breakdown, and the  $\text{SO}_4^{\cdot-}$  radicals generation, and accordingly, increases the removal efficiency of ATL (35, 36). The enhanced CD can quicken the transfer of electron among the reactive solutions and progress the oxygen reduction reaction. In addition, at a higher CD, the anodic oxidation would increase, and produce more dissolved oxygen (DO). These two factors produce more  $\text{H}_2\text{O}_2$  at higher CDs (37). Yu et al reported that by increasing the CD from 10 to 50  $\text{A}/\text{m}^2$ , the amount of  $\text{H}_2\text{O}_2$  production developed significantly from 152.5 to 472.9  $\text{mg}/\text{L}$ . However, with further increase in CD to 60  $\text{A}/\text{m}^2$ ,  $\text{H}_2\text{O}_2$  production efficiency decreased to about 66% (37). ATL degradation was completely removed in both electrodes and reactors, except for the lowest CD (33  $\text{mA}/\text{cm}^2$ ), in the study of Mora-Gómez et al (38).

### Effect of Fe concentration

As revealed in Figure 8, removal efficiency of ATL in the process increased from 75.8 to 86.3 by increasing the  $\text{Fe}^{+2}$  concentration from 0.025 to 0.15  $\text{g}/\text{L}$ . The ferrous ions act as catalysts for the decomposition of  $\text{H}_2\text{O}_2$  and convert it into reactive forms ( $\cdot\text{OH}$ ) for the oxidation of the ATL molecules. The ferrous ion plays a considerable role in the initial decomposition of  $\text{H}_2\text{O}_2$ , and  $\text{Fe}^{2+}$  ion concentration was shown to have a remarkable impact on total organic carbon (TOC) removal in the EF process (39, 40). This process is one of the electrochemical methods in which  $\text{H}_2\text{O}_2$  and electro-generated ferrous ions, which are produced by oxidation of iron in the sacrificial anode, and can be explained according to Eq. (8):



The ferrous ion acts as a catalyst in the Fenton process. As a whole,  $\text{Fe}^{2+}$  ions are rapidly depleted and the production of  $\cdot\text{OH}$  is primarily dependent on the  $\text{H}_2\text{O}_2/\text{Fe}^{3+}$  ratio (7, 41, 42). Increasing the concentration of  $\text{Fe}^{2+}$  ions as a supplement accelerates the production of  $\cdot\text{OH}$ , and ultimately, increases the oxidation rate of aniline (35, 43-45). The  $\text{Fe}^{+2}$  concentrations have an important effect on the trimethoprim degradation.  $\text{H}_2\text{O}_2$  decomposition cannot be effectively occurred into  $\cdot\text{OH}$  with inadequate quantities of  $\text{Fe}^{+2}$ . Additional amounts of  $\text{Fe}^{+2}$  can act as a scavenger for  $\cdot\text{OH}$  and  $\text{SO}_4^{\cdot-}$  radicals, and this excess  $\text{Fe}^{+2}$  can form complexes with organic pollutants. Therefore, it is useful to

determine the optimal concentration of  $\text{Fe}^{+2}$  after determining the concentration of the oxidizing agent. In a study, when the molar ratio of  $\text{H}_2\text{O}_2/\text{Fe}^{+2}$  was 10:1, the highest removal efficiency for the trimethoprim compound was obtained in the Fenton process (9). EF process was used to assess the ATL degradation in aqueous solutions. Optimal conditions including 250 mL of ATL solution (0.17 mM), at initial pH 3, applied current (100-500 mA), ferrous ions concentration (1-10 mM), and sulfate dosage (0.01-0.5 M) were studied. Also, kinetic analysis indicated that ATL mineralization followed a pseudo-first-order model and the rate constant increased by increasing the concentration of ferrous ions (up to 5 mM), electrolyte amount, and rising CD. More than 87% of COD was removed under optimal contact time of 240 min and ferrous ions concentration higher than 5 mM (46).

### Effect of initial ATL concentration

Figure 9 represents the effect of initial concentration of ATL on its EF oxidation from aqueous solution. It is known that increasing the pollutants initial concentration requires higher oxidation potential, and a constant oxidant quantity, decreases the process efficiency. In reactions based on sulfate and  $\cdot\text{OH}$  where the initial concentration of the contaminant is high, it is important to determine the intermediates. This means that high initial contaminant concentrations can lead to competition between contaminant molecules and intermediates in reaction with  $\text{OH}$  or  $\text{SO}_4^{\cdot-}$  radicals. As a result, the degradation rate may decrease at higher initial concentrations of the contaminant (24, 25). Table 1 shows the results for the present study in comparison with the previous studies.

### Conclusion

The present study confirmed that enhanced EF by PS radicals is the most effective oxidizing process for ATL oxidation from aqueous solution. The effect of several parameters like pH, electrolyte type, PS dose,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  dose, reaction time, CD, and ATL concentration was studied. Based on the obtained results, the optimum conditions of enhanced EF process by PS radicals for ATL oxidation were determined. Accordingly, NaCl (as a supporting electrolyte) with a dose of 0.5  $\text{mg}/\text{L}$ , pH 5, reaction time of 60 min, PS dose of 0.15  $\text{g}/\text{L}$ , Fe dose of 0.15  $\text{g}/\text{L}$ , CD of 1.5  $\text{A}/\text{m}^2$ , and ATL concentration of 40  $\text{mg}/\text{L}$  with removal efficiency of 78.6% was determined. Also, kinetic model was in accordance with second-order kinetics. One of the limitations of this study is that it did not measure the residual

**Table 1.** Comparative evaluation of the results for this study with previous studies

Pollutant/removal method	pH	Contact time (min)	Initial concentration of pollutant	Fe concentration	Current density	PS concentration	Electrolyte type	References
ATL, combination of electrolysis and UV photolysis	7	40 min when MMO is an anode	8 $\mu\text{M}$	-	10 $\text{mA}/\text{cm}^2$	-	NaCl:30 mM	(47)
ATL, sunlight/ $\text{Fe}^{3+}$ /persulfate	6.5	60 min	2.5 $\text{mg}/\text{L}$	Fe (III)-DFOB complex: 15 $\mu\text{M}$	-	500 $\mu\text{M}$	Cl <sup>-</sup> :100 $\text{mg}/\text{L}$	(48)
Kketoprofen, persulfate activation Fe-APS	8.2	-	39.33 $\mu\text{M}$	0.05 mM	-	2.5 mM	-	(49)
ATL in water, UV/ peroxymonosulfate	7	30 min	20 $\mu\text{M}$	-	-	-	Humic acid:8 $\text{mg}/\text{L}$ 8 mM $\text{HCO}_3^-$	(3)
ATL in water, electro-Fenton (EC- $\text{H}_2\text{O}_2$ and PS)	7	-	2.5 $\text{mg}/\text{L}$	-	7.8 $\text{mA}/\text{cm}^2$	0.15 mM	$\text{C}_{\text{NaCl}}=1000$ $\text{mg L}^{-1}$	(24)
ATL, wastewater	5	60	40 $\text{mg}/\text{L}$	0.15 $\text{g}/\text{L}$	1.5 $\text{A}/\text{m}^2$	0.15 $\text{g}/\text{L}$	NaCl:0.5 $\text{mg}/\text{L}$	Present study

concentration of iron in the solution, and also, did not determine the concentration or type of intermediate compounds produced for financial reasons. Finally, the enhanced EF process by PS radicals can effectively remove ATL from aquatic solutions; therefore, this process can be used as an effective method for removing other organic matter from the wastewater.

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### Ethical issues

This research project was also approved by the Ethics Committee of Isfahan University of Medical Sciences (Ethical code: IR.MUI.RESEARCH.REC.1397.397).

### Competing interests

The authors declare that there is no conflict of interests.

### Authors' contributions

MC: Conceptualizing, methodology, writing original draft, review and editing, validation, data curation, and formal analysis. AE: Supervision, project administration, methodology, review and editing. AF: Data curation, review and editing.

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