



## Pharmaceutical Wastewater Chemical Oxygen Demand Reduction: Electro-Fenton, UV-enhanced Electro-Fenton and Activated Sludge

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### ABSTRACT

In this study, Chemical Oxygen Demand (COD) from a pharmaceutical wastewater (PhW) was reduced by several techniques such as electro-Fenton (EF), photo electro-Fenton (PEF) and activated sludge (AS) processes and the obtained data were compared with each other. The effects of several parameters such as pH, current density,  $H_2O_2/Fe^{2+}$  molar ratio, volume ratio of  $H_2O_2/PhW$ , reaction time and UVA light were studied on the COD reduction through the EF and PEF processes. The Box-Behnken Design (BBD) under Response Surface Methodology (RSM) was applied to design and then optimize these processes. The optimal conditions for 87% of COD removal through the EF process were at pH of 3.27, current density of 57 mA/cm<sup>2</sup>,  $H_2O_2/Fe^{2+}$  molar ratio of 3.5, volume ratio of  $H_2O_2/PhW$  of 1.34 ml/l and reaction time of 56.32 min while the optimal conditions for 91.6% of COD removal through PEF process were at pH of 3.5, current density of 57.5 mA/cm<sup>2</sup>,  $H_2O_2/Fe^{2+}$  molar ratio of 3.81, volume ratio of  $H_2O_2/PhW$  of 1.5 ml/l, reaction time of 10.12 min and 6 W UVA light while 77.70% of COD removal was obtained by the AS process with residence time of 1020 min. According to the kinetic study, the second order reaction (with high  $R^2$  data) could properly model the EF and PEF processes.

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## 1. INTRODUCTION

Organic pollutants such as pharmaceutical wastes can pollute water and result in negative consequences even at a low concentration (0.001 ppm) [1]. Pharmaceutical industries often generate high loads of wastewater containing toxic organic chemicals. These chemicals not only contaminate the drinking water but also affect the endocrine function in fishes and sea creatures which adversely affect humans and animals [2, 3].

There are some conventional techniques for treating the pharmaceutical wastewaters [4]. They usually have several disadvantages such as high cost, low efficiency and high energy requirements. Since the medicines consumption is increasing, the wastewaters produced by them are widely increasing. They will pollute water resources and adversely affect the aquatic and human life [5]. Furthermore, some analytical techniques have been

developed to detect the pharmaceutical pollutants in ultra-trace level [6].

Most of pharmaceutical wastes which can pollute the water sources are containing steroids, disinfectants, caffeine or similar compounds [7]. According to literature, there were some techniques based on the flocculation, sedimentation, filtration, chlorination and activated sludge on these compounds elimination from ecosystem. Some of them are treatment by activated sludge [8, 9], submerged membrane bioreactor [10, 11], pure cultures [12], mixed cultures [13], constructed wetland [14], coagulation [15], membrane technology [16], adsorption [17] and advanced oxidation processes.

In recent years, Advanced Oxidation Processes (AOPs) such as Fenton, electro-Fenton, photo-Fenton and photo electro-Fenton have been used to reduce the organic pollutants [18].

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The produced hydroxyl radicals attack to organic compounds and change them to CO<sub>2</sub> and H<sub>2</sub>O. Iron salt can catalyze this process as shown in Table 1 (Equations (1-10)) [19].

In the present study, EF and PEF processes were applied to treat an industrial pharmaceutical wastewater in terms of COD. These two processes were statistically designed and experimentally carried out. The optimized operating conditions data for maximum COD removal were investigated and compared with the data obtained from the activated sludge process.

## 2. EXPERIMENTAL

### 2.1. Materials and Method

**2.1.1. Wastewater Sampling and Characterization** The current study was conducted on a pharmaceutical wastewater obtained from Exir Pharmaceutical Company (Boroujerd, Iran). It was stored in a 20 l plastic container and immediately transported to Arak University, Chemical Engineering Faculty, Chemical Engineering Research Lab. The applied pharmaceutical wastewater was carefully analyzed. Its COD, BOD<sub>5</sub> and pH were at 750 ppm, 375 ppm and 7.5, respectively. The samples pH was adjusted by 0.1 M H<sub>2</sub>SO<sub>4</sub> and 0.1 M NaOH. A native activated sludge was prepared from Shazand Petrochemical Co. (Arak, Iran) and used for activated sludge process. The activated sludge was daily fed by a nutritional feed [C<sub>11</sub>H<sub>22</sub>O<sub>11</sub>, CO(NH<sub>2</sub>)<sub>2</sub> and KH<sub>2</sub>PO<sub>4</sub> (COD:N:P=100:5:1)]. All chemicals were purchased from a Merck supplier.

**2.1.2. Experimental Design** In the current research, Design Expert software (version: 10) was applied to minimize the number of runs. Then, Box-Behnken Design (BBD) under Response Surface Methodology (RSM) with a low-order polynomial equation was used to optimize the operating conditions [20–22]. Forty six and fifty four experiments were respectively designed for EF and PEF processes and the goal was to maximize COD removal. The independent variables were pH (X<sub>1</sub>), current

density (X<sub>2</sub>), H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup> molar ratio (X<sub>3</sub>), volume ratio of H<sub>2</sub>O<sub>2</sub>/PhW (X<sub>4</sub>), reaction time (X<sub>5</sub>) and UVA light (X<sub>6</sub>) (UVA light only is for PEF process). COD removal was chosen as a dependent variable. All of the variables were coded and were illustrated as low level number of -1, medium level number of 0 and high level number of 1 as shown in Table 2.

### 2.1.3. Experiments

The EF experiments were carried out on laboratory scale using 400 ml beaker (as reactor) at constant temperature (25±2 °C), stirring rate (400 rpm) and iron electrodes distance (3 cm) [18, 20–22]. pH of each sample was adjusted and measured by a pH-meter (METTLER-TOLEDO 320). In each run, 250 ml of wastewater was placed in the reactor and desired amounts of iron salt (Fe<sup>2+</sup>) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) (based on the design illustrated in Table 2) were added before turning on the electrical current. The current density (CD) was adjusted by a digital DC power supply (fabricated by Kala Gostaran-e-Farda supplier, 30 V and 3 A) operated at the galvanostatic mode. UVA lamps 3, 6, 9 W (LED lump, 365 nm, 3.2-3.4 V, 350-500 mA) were used in PEF process. The UVA light is simultaneously used to assist the oxidation of EF process. Then, the COD of pharmaceutical wastewater was reduced by AS at pH of 6.5 and the obtained results were compared with the data from EF and PEF processes. Efficiency of electrochemical oxidation process was controlled by COD values determination. The COD was measured by a general technique [with potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>)] as described in the standard method [23]. COD removal percentage was calculated by the following equation:

$$COD\ removal\% = \frac{C_i - C_o}{C_i} \quad (11)$$

where, C<sub>i</sub> and C<sub>o</sub> are initial and final concentrations of COD, respectively.

## 3. RESULT AND DISCUSSION

### 3.1. Regression Model and Analysis of Variance

The quadratic models parameters (obtained from the

**TABLE 1.** Chain reactions for EF and PEF processes

$Fe^{+2} + H_2O_2 \rightarrow Fe^{+3} + OH^- + OH^\circ$	(1)
$H_2O \rightarrow OH^\circ + H^+ + e^-$	(2)
$H_2O_2 + Fe^{3+} \rightarrow Fe^{2+} + HO_2 + H^+$	(3)
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	(4)
$Fe^{2+} + OH^\circ \rightarrow Fe^{3+} + OH^-$	(5)
$H_2O_2 + H^+ \rightarrow H_3O^{+2}$	(6)
$H_2O_2 \rightarrow O_2 + H_2$	(7)
$H_2O_2 + 2Fe(OH)_2 \rightarrow Fe_2O_3 + 3H_2O + 2OH^\cdot$	(8)
$Fe(OH)_2 + h\nu \rightarrow Fe^{+2} + OH^\cdot$	(9)
$Fe(OOCR)_2 + h\nu \rightarrow Fe^{+2} + CO_2 + R^\cdot$	(10)

**TABLE 2.** Independent variables and their levels obtained from the BBD

Symbol	Factor	Coded levels of variables		
		-1	0	1
X <sub>1</sub>	pH	2	3.5	5
X <sub>2</sub>	Current density (mA/cm <sup>2</sup> )	20	50	80
X <sub>3</sub>	Molar ratio H <sub>2</sub> O <sub>2</sub> /Fe <sup>2+</sup>	0.5	2.75	5
X <sub>4</sub>	H <sub>2</sub> O <sub>2</sub> /PhW (ml/l)	0.3	1.4	2.5
X <sub>5</sub>	Reaction time (min)	10	40	70
X <sub>6</sub>	UVA light (W)	3	6	9

software) for EF and PEF processes were shown in Table 3. According to this table,  $R^2$ ,  $R^2$  adjusted (Adj) and  $R^2$  predicted (Pred) were close to one. All of the data confirmed that the quadratic model properly works in this research.

In fact, radical hydroxyl production and then oxidation of organic compounds increases EF and PEF processes efficiency [24]. Furthermore, the efficiency of EF and PEF can normally be increased with increasing the  $Fe^{2+}$  concentration. Its reason is due to reacting  $Fe^{2+}$  with  $H_2O_2$  produced on the cathode and radical hydroxyl production [25]. An increase in amount of  $H_2O_2$  generally imposes a positive effect on both processes. This also is due to hydroxyl radical production [26].  $H_2O_2/Fe^{2+}$  molar ratio increment leads to an increase in  $H_2O_2$  amount in the wastewater and its reduction leads to an increase in iron salt in the wastewater [27]. The current density directly affects the production of hydroxyl radical on the anode surface. This reacts with  $Fe^{3+}$  ions on the cathode and produces  $Fe^{2+}$  ions. So, current density increment assists both processes although excess current density enhancement causes non-oxidizing reactions [28]. Moreover, time controls these processes. Since these processes use electricity as a source of energy, it is important to find an optimal reaction time. The results showed that both processes efficiency increase with increasing the reaction time although its large increment can decrease the COD removal. That is probably due to decreasing the reactive substances with respect to time. Furthermore, collision enhancement of substances in the cell may increase undesirable parasitic reactions [29, 30]. The photocatalytic reaction by UVA can dramatically assist the process with photolysis of  $Fe(OH)^{2+}$ , regenerating of  $Fe^{2+}$  ions and excess production of hydroxyl radicals.

**3. 2. Optimization Procedure** Numerical optimization is applied to determine the optimum parameters for maximum COD removal. All variables are purposed in the operating ranges and established in the software. Table 4 shows the optimized operating conditions for COD removal through EF and PEF processes obtained from the software (predicted) and then validated by experiment (observed).

The optimized operating conditions for COD removal of 91.6% through PEF process statistically were at pH of 3.8, current density of 57.5 mA/cm<sup>2</sup>, reaction time of 10.12 min,  $H_2O_2/Fe^{2+}$  molar ratio of 3.8, UVA light of 6 W and volume

ratio of  $H_2O_2/PhW$  of 1.5 ml/l while it experimentally was at 90.5% at the same operating conditions.

The optimized operating conditions for COD removal of 87% through EF process statistically were at pH of 3.27, current density of 57 mA/cm<sup>2</sup>, reaction time of 56.3 min,  $H_2O_2/Fe^{2+}$  molar ratio of 3.5 and volume ratio of  $H_2O_2/PhW$  of 1.34 ml/l while it experimentally was around 83.78% at the same operating conditions. The activated sludge was used in the cell and maximum COD removal (77.7%) was found at 1020 min and pH of 6.5 (as compared in Table 4).

According to the literature the other techniques such as ultrasonic, solar photo-catalysis, solar photo-Fenton could remove drugs from pharmaceutical wastewaters above 90%. Klamerth et al. [31] treated a municipal wastewater with modified photo-Fenton as a tertiary treatment for the degradation and disinfection of micro pollutants. They removed them around 90%. Dolar et al. [32] removed 87.1 % of emerging contaminants wastewater with an integrated membrane system and MBR-RO. As Davarnejad et al. [33] reported 84% of ibuprofen was removed from a pharmaceutical wastewater by adsorption process with nano clay for duration of 75 min.

**3. 3. Kinetic Study** The COD removal increased with the reaction time and reached to equilibrium at 50 min. In order to determine the order of reaction, the experimental

**TABLE 3.** Quadratic model parameters for EF and PEF processes

Variable	COD removal for EF	COD removal for PEF
Standard deviation	9.45	8.69
Mean	55.82	59.23
Coefficient of variance (CV%)	6.92	4.68
Press	8926.40	10264.93
R-Squared	0.9276	0.9557
Adj R- Squared	0.8696	0.9097
Pred R-Squared	0.7103	0.7686
Adequate precision	16.436	16.333
F-value	16.01	20.78
P-value	< 0.0001	< 0.0001

**TABLE 4.** Optimum conditions obtained by software and experiment for COD removal through EF and PEF processes. Comparison of the optimum data with the AS process results

process	pH	Current density (mA/cm <sup>2</sup> )	Molar ratio ( $H_2O_2/Fe^{2+}$ )	$H_2O_2/PhW$ (ml/l)	Reaction time (min)	UVA light (W)	COD removal%	
							Predicted	Observed
PEF	3.54	57.5	3.81	1.5	10.12	6	91.6	90.52
EF	3.27	57.06	3.51	1.34	56.32	-	87.0	83.78
AS	6.5	-	-	-	1020	-		77.7

data was plotted. The following expression represents the n<sup>th</sup> order reaction performed in a batch reactor:

$$\frac{dCOD}{dt} = -kCOD^n \tag{12}$$

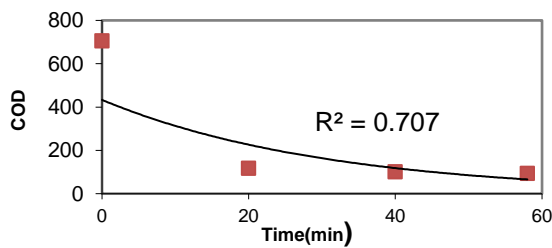
where, n and k are the order of reaction and rate constant of reaction, respectively. The following equations are obtained by integration of Equation (13):

$$COD - COD_0 = -k_0t \tag{13}$$

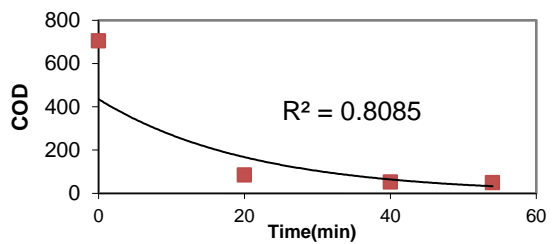
$$\ln \frac{COD}{COD_0} = -k_1t \tag{14}$$

$$\frac{1}{COD} - \frac{1}{COD_0} = k_2t \tag{15}$$

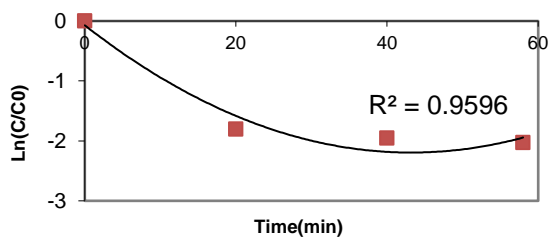
where, COD and COD<sub>0</sub> are COD amounts at any time of t and zero (initial COD), respectively. k<sub>0</sub>, k<sub>1</sub> and k<sub>2</sub> are the rate constants for zero, first and second order reactions, respectively [34]. Figures 1-6 show the plots for zero, first and second order reactions. The linear regression analysis shows that the second order reaction model (Figures 5 and 6) with R<sup>2</sup> of 0.9773 for EF process and 0.9988 for PEF process can properly legitimize both processes kinetics.



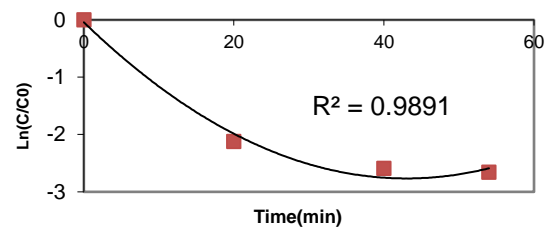
**Figure 1.** Graphical analysis for the determination of kinetic data Zero order reaction of EF



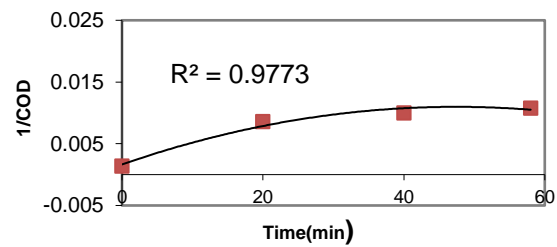
**Figure 2.** Graphical analysis for the determination of kinetic data Zero order reaction of PEF



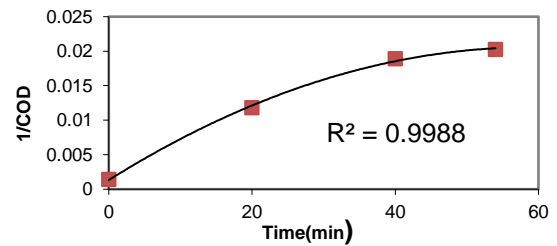
**Figure 3.** Graphical analysis for the determination of kinetic data First order reaction of EF



**Figure 4.** Graphical analysis for the determination of kinetic data First order reaction of PEF



**Figure 5.** Graphical analysis for the determination of kinetic data, second order reaction for EP



**Figure 6.** Graphical analysis for the determination of kinetic data, second order reaction for PEP

#### 4. CONCLUSIONS

The main goal of this study was to optimize the operating conditions for the COD removal from a pharmaceutical wastewater through EF and PEF processes. These are the most effective processes in removing the organic compounds. It is concluded that time and current density have the greatest impact on the COD removal although a higher COD removal and lower reaction time was found through PEF process compared to the EF one. The results confirm that BBD (under RSM) is a powerful tool for investigating the optimized operating conditions for COD removal through both processes. Furthermore, the UVA light through PEF process can increase the COD removal more than that of the EF process at the optimum conditions. The UVA lamp dramatically increased COD removal more than that of the EF and AS processes (high percentage of COD removal with low reaction time). According to the kinetic study, the second order reaction (with high R<sup>2</sup> data) can properly model both EF and PEF processes.

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Photo Electro-Fenton

Response Surface Methodology

در این مطالعه حذف COD پساب دارویی توسط روش‌های الکتروفتون و فوتوالکتروفتون و مقایسه با لجن فعال بررسی شد. اثرات متغیرهای مستقل که بر پاسخ عملکرد تاثیر دارند شامل pH، چگالی جریان، نسبت مولی پراکسید هیدروژن بر یون آهن، نسبت حجمی پراکسید هیدروژن بر حجم پساب (میلی لیتر بر لیتر)، زمان واکنش و نور هستند. این پارامترها از طراحی باکس بنکن تحت روش سطح پاسخ بهینه‌سازی شدند. شرایط بهینه برای حذف ۸۷ درصد COD در روش الکتروفتون شامل pH برابر ۳/۲۷، چگالی جریان ۵۷ میلی آمپر بر سانتیمتر مربع، نسبت مولی پراکسید هیدروژن بر یون آهن برابر ۳/۵، نسبت حجمی پراکسید هیدروژن بر حجم پساب برابر با ۱/۳۴ میلی گرم بر لیتر و زمان واکنش ۵۶/۳۲ دقیقه می‌باشد. شرایط بهینه برای حذف ۹۱/۶ درصد COD در روش فوتوالکتروفتون با بهبود درصد حذف نسبت به الکتروفتون شامل pH برابر ۳/۵، چگالی جریان ۵۷/۵ میلی آمپر بر سانتیمتر مربع، نسبت مولی پراکسید هیدروژن بر یون آهن برابر ۳/۸۱، نسبت حجمی پراکسید هیدروژن بر حجم پساب برابر با ۱/۵ میلی گرم بر لیتر، زمان واکنش ۱۰/۱۲ دقیقه و شدت نور یو-وی ۶ وات می‌باشد. برای حذف ۷۷/۷ درصد COD در روش لجن فعال نیاز به صرف زمان ۱۰۲۹ دقیقه می‌باشد و در نهایت با استفاده از مطالعه سنتتیک واکنش، واکنش درجه دوم فرایند الکتروفتون و فوتوالکتروفتون را برآورده می‌کند.

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