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Comparison of electrochemical advanced oxidation processes for removal of ciprofloxacin from aqueous solutions

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ABSTRACT

The aim of this study was to compare the efficiency of two dimensional electrochemical (2DE), electro-Fenton (EF), three dimensional electrochemical (3DE) and three dimensional electro-Fenton (3DEF) processes in removal ciprofloxacin (CIP) from aqueous solutions. The central composite design (CCD) with response surface methodology (RSM) was used to study the effect of experimental parameters on the removal efficiency of CIP by various electrochemical processes. The results showed that obtained quadratic model had a high R-squared coefficient based on the analysis of variance (ANOVA). The optimum condition for the removal of CIP by the studied processes was pH of 3, current of 0.45 A, and electrolysis time of 60 min. The results of the comparison between the processes showed that the removal efficiency of CIP after 60 min of electrolysis time is reduced as follows: 3DEF>3DE>EF>2DE. The removal efficiency enhancement was attributed to much more hydroxyl radicals generated in the three dimensional (3D) processes because single-walled carbon nanotubes (SWCNTs) could activate molecular oxygen to produce more H_2O_2. These results showed that 3D systems, especially 3DEF, could be considered as an appropriate method for the treatment of persistent pollutants such as antibiotics due to good electro-catalytic activity, high efficiency, no secondary pollution.

Keywords: EAOPs; Ciprofloxacin removal; Single-walled carbon nanotubes; Response surface methodology

1. Introduction

In recent years, the presence of large amounts of antibiotics in aquatic environments has become a major environmental concern [1]. Due to low biodegradation, most of these antibiotics are not removed by conventional wastewater treatment processes [2]. Ciprofloxacin (CIP), as a second generation of fluoroquinolone antibiotics, is extensively used to treat the bacterial infectious diseases in humans and animals [3,4]. Due to the strong chemical stability of the carbostyril nucleus, this antibiotic is not completely metabolized in the body and more than 70% of this compound enters into natural environments without metabolizing [3]. Due to the inadequate removal of CIP by conventional

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wastewater treatment processes, these drugs have been identified at concentrations ranging from ng/L to mg/L in hospital sewage, pharmaceutical industries effluents, and surface water [5,6]. In the long term, the presence of this pollutant in the environment leads to increasing the antibiotic-resistant bacteria, harmful effects on the quality of water and formation of toxic side effects in humans [7]. Therefore, the removal of CIP from aqueous solutions is essential before discharging into the environment. In recent years, physico-chemical techniques such as membrane separation [8], adsorption [9], and activated sludge treatment [10] have been used for removal CIP. Nevertheless, these technologies enable only the separation of antibiotics without degrading them, as a result producing large amounts of sludge and secondary pollution [11].

In recent decades, advanced oxidation processes (AOPs) have been considered as one of the most promising methods for the treatment of wastewaters containing resistant organic materials [12]. In this process, based on the production of radical hydroxyl the recalcitrant organic compounds could be quickly and efficiently converted into harmless compounds, CO_2 and H_2O [13]. Among different AOPs, electrochemical advanced oxidation (EAO) processes could be a good option to treat pharmaceutical wastewater due to their high versatility, efficiency and environmental compatibility [14–16]. These methods degrade the persistent contaminants by radical hydroxyl production through water oxidation on the anode surface (direct oxidation) and the reaction of Fenton with electro-generated H_2O_2 (indirect oxidation) [16]. The efficiency and flexibility of EAO processes have been proven by studies conducted to treatment of various pollutants [14].

The two-dimensional electrochemical (2DE) process was the first method which could be considered as an EAO processes due to the production and active role of OH radical on the oxidation of organic compounds. During this process, organic pollutants found in industrial and hospital wastewaters can be degraded by direct or indirect oxidation [17]. In the direct oxidation process, the pollutant is initially adsorbed onto the anode surface and then it is degraded by the anodic transfer reaction. In the indirect oxidation process, the strong oxidants such as hypochlorite or oxidized metal ions can be generated by the electrochemical reactions during electrolysis and, then, they can participate in partial and complete degradation of pollutants [18,19]. The electrochemical processes have been considered as a promising technique to treatment the industrial wastewater due to the rapid degradation of persistent pollutants without formation of new toxic species, the complete mineralization of toxic pollutants and the simplicity of the method [20,21]. In some studies, the disadvantages such as short life of electrodes, limitations of mass transfer and application in acid pH have been reported for this process [22].

Electro-Fenton process (EF) is another EAOPs where the hydroxyl radical is produced through reaction electrogeneration of H_2O_2 with iron ions [Eq. (1)] [23]. This process, in comparison with the Fenton process, has advantages such as high efficiency, continuous electrogeneration of H_2O_2 on the surface of the cathode [Eq. (2)], lack of /or insignificant production of sludge, Fe^{2+} regeneration by direct reduction of Fe^{3+} on the cathode surface [Eq. (3)] and etc. [24,25]. The effectiveness of this method has been well proven in recent investigates on the degradation of antibiotics of CIP [6], amoxicillin [26], levofloxacin [27], enoxacin [28], moxifloxacin [29] and sulfanilamide [30].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\circ}OH + OH^{-} \tag{1}$$

$$O_2 + 2H^{+} + 2e^{-} \rightarrow H_2O_2 \tag{2}$$

$$\mathrm{Fe}^{2+} + \mathrm{e}^{-} \rightarrow \mathrm{Fe}^{3+} \tag{3}$$

$$\mathrm{H_2O_2} + \mathrm{e}^{-} \rightarrow \mathrm{OH}^{-} + {}^{\circ}\mathrm{OH} \tag{4}$$

In addition to the previously described EAO processes, another interesting alternative to treatment the pollutants in the wastewaters is the three-dimensional electro-oxidation processes [22]. These systems include a two-dimensional electrode with electrode particles loaded between the two anode and cathode electrodes [31]. In three-dimensional (3D) processes, the particle electrode can be easily polarized to form of charged microelectrodes by the suitable current density, which it not only increases the distribution of ion charge and mass transfer, but also increases the production of OH radical in the 3D system [22,32–35]. In addition, the particle electrode, as a catalyst, can directly accelerate the production of electrochemical H_2O_2 and reduces it to OH hydroxyl [Eq. (4)] [36]. Also, the polarization and the high specific surface of these particles not only provide more active sites than the 2D electrodes for adsorption of pollutants, but also can help to formation of another anode and cathode surface in the 3D process [22]. In most of the previous studies, 3D systems have been successfully used to treatment the various types of pollutants. Xiao and Zhang [37] used a three-dimensional electrochemical process catalyzed with Fe_2O_3/y-Al_2O_3 for phenacetin oxidation and found that the COD removal efficiency using 3D reactor was 2.39 times greater compared to 2D process. Li et al. [38] studied the role of TiO_2-SiO_2/GAC particles in increasing the electro-catalytic removal of color in the 3D reactor. They found that the adding of the particles into the 2D reactor would improve the removal efficiency of acid orange 7. Li et al. [39], by evaluating the electrochemical degradation of 2-diethylamino-6-methyl-4-hydroxypyrimidine using 3D reactors, concluded that the presence of the particle electrode is led to reduce the energy consumption and to increase the production of reactive oxygen species such as OH radical in the electrochemical process.

Despite the high efficacy reported for the above-mentioned processes and the significant risk of ciprofloxacin in natural environments, there are few studies towards the use of EAO processes, in particular 3D electrochemical and 3D electro-Fenton processes, in removal of CIP from aqueous solutions. Therefore, the purpose of this study is to compare the efficiency of 2DE, 3DE, EF and 3DEF processes in removal of CIP from aqueous solutions by taking into account the factors of pH, current density and electrolysis time. In this study, the synthesized Ti/PbO_2 was applied as an anode electrode and SWCNTs were used as a novel particle electrode in 3D processes. The response surface methodology was used to reduce the number of experiments and to optimize the operational parameters of the EAO processes.

2. Materials and methods

2.1. Materials

The Ciprofloxacin (CIP; CAS Number 85721-33-1; $C_{17}H_{18}FN_3O_3$; 331.34 g/mol; see the structure in Fig. 1) was supplied by Sigma Aldrich (USA) at ≥ 98% purity. Stock solution of CIP (50 mg/L) was prepared by dissolving 50 mg CIP in 1 L of distilled water. Compounds iron (II) sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) and sodium sulfate anhydrous (Na_2SO_4) were obtained from Merk company (Germany). The single-walled carbon nanotubes (SWCNTs) with a specific surface area of >110 m^2/g and an average pore diameter of 5–10 nm was purchased from US research nano materials, Inc., (Houston, USA) and used as the particle electrodes in the study. Fig. 2 shows XRD pattern and the scanning electron microscope (SEM) for the SWCNTs.

2.2. Preparation of Ti/PbO$_2$ electrode

Pre-treatment of the titanium surface was performed following the procedures suggested by Bonyadinejad et al. [40]. The sheet of titanium was polished on 320-grit paper strips for removal the oxide layers and increase surface roughness. Then, the sheet was degreased in an ultrasonic bath of distilled water for 15 min and then acetone for 30 min. The sheet was then degreased for 2 h in 10% boiling of oxalic acid and washed with distilled water. Coating by active metal oxide was carried out immediately to minimize formation of oxide layers. Finally, the cleaned sheet was transferred to an electrochemical deposition cell, which contained 12% (w/v)$Pb(NO_3)_2$, 5% (w/v) $CuSO_4 \cdot 5H_2O$ and 3% (w/v) surfactant (Triton X-100).The electrodeposition of PbO_2 was carried out in a constant anodic current of 20 mA/cm^2 for 120 min at 60°C with continuous stirring. The morphology and crystalline structure of the Ti/PbO_2 electrode was studied by Philips XI30 scanning electron microscope (SEM) and X-ray diffraction (XRD, Bruker).

2.3. Experimental Setup

The 2DE, EF, 3DE and 3DEFprocesses were performed in an open reactor 500 mL under vigorous stirring with a magnetic bar at 200 rpm. Ti/PbO_2 and graphite felt electrodes (50 cm^2 area) were selected as the anode and the cathode. The distance between anode and cathode electrodes was fixed at 1 cm. Electrolysis were operated at various current (as value listed in Table 1) using a DC power supply (Model MP-6003) from MEGATEK Taiwan. In order to increase H_2O_2 production and mass transfer, the reactor was aerated using an air compressor with a flow rate of 1 L/min. In this the study, maximum Na_2SO_4 (as electrolyte) concentration was selected as 3 g/L, because of in pharmaceutical wastewater 2–3 g/L TDS exist [41]. The initial pH adjustment was performed with 0.1M HCl and 0.1 M NaOH, and the constant amount of iron ions (1 mM) and SWCNTs (40 mg/L)

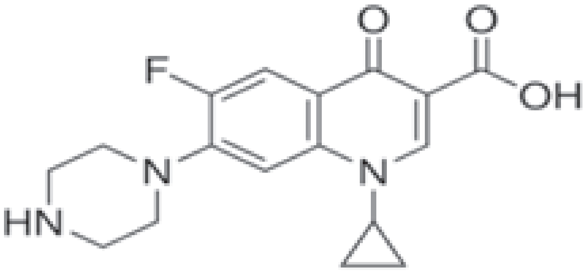

Fig. 1. Chemical structure of ciprofloxacin (CIP).

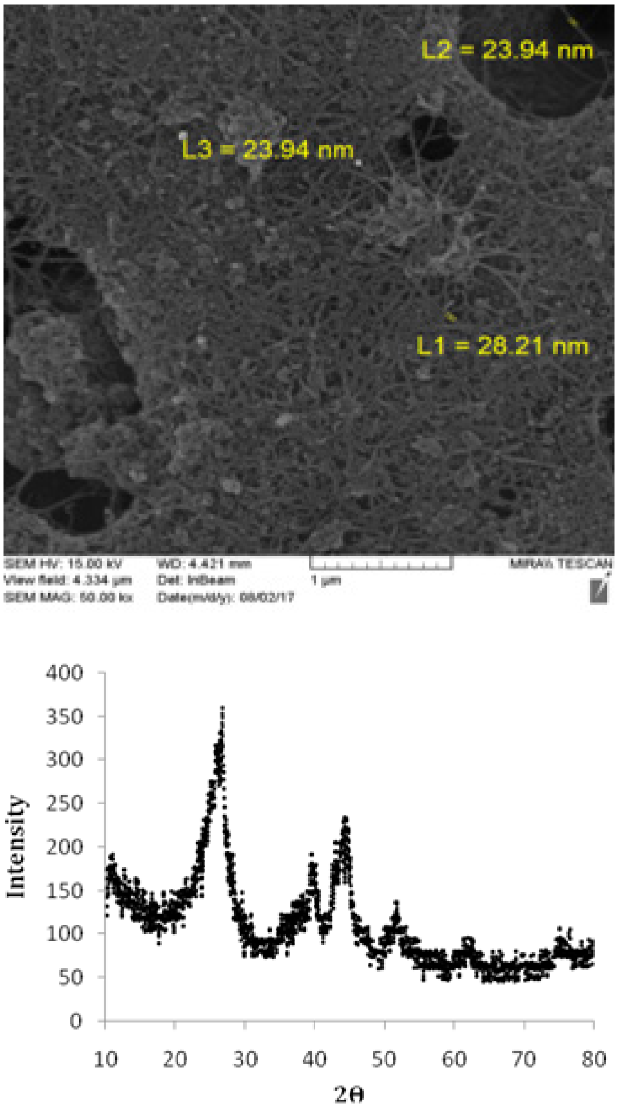

Fig. 2. SEM image and XRD pattern of SWCNTs.

Table 1
Experimental ranges and levels of the independent test variables

Factors	Ranges and levels	
	–1	1
pH (X_1)	3	6
Current (X_2)	0.15	0.45
Electrolysis time (X_3)	15	60

was added for EF, 3DE and 3DEF processes. The electrochemical degradation of 500 mL CIP solution with a concentration of 50 mg/L (This concentration was constant in all tests) was studied at various pH levels, current, and electrolysis times according to design of experiments. Samples for analyses were withdrawn at various times during the electrolysis time and centrifuged to remove particles immediately before analysis.

2.4. Experimental design

The Design Expert Software (10.0 trial) was utilized for the statistical design of tests and data analysis. The central composite design (CCD) in RSM was used to study the interaction between three factors: pH, current, electrolysis time. These parameters range was divided into two levels (–1,1), as shown in Table 1.

2.5. Analytical methods

The initial and final CIP concentration was determined by UV-spectrophotometer with maximum wavelength (λ_{max}) of 275 nm. Chemical oxygen demand (COD) was determined using a UV/VIS spectrophotometer (HACH, DR 5000, USA) according to standard method. Hydrogen peroxide concentration was determined using the $KMnO_4$ titration. The CIP degradation efficiency and energy consumption (EC, kWh/m^3) was determined following the equations:

$$\%\ Degradation = \frac{Initial\ CIP\ concentration - Final\ CIP\ concentration}{Initial\ CIP\ concentration} \times 100 \quad (5)$$

$$\mathrm{EC}\left(\frac{\mathrm{kWh}}{\mathrm{m}^3}\right) = \frac{IVt}{V_s} \quad (6)$$

where I is the average applied current (A), V is the cell voltage (V), t is the treatment time (h) and V_s is the treated volume.

3. Results and discussion

3.1. Characterization of the Ti/PbO_2 electrode

Fig. 3 indicates a SEM image of the Ti/PbO_2 sheet synthesized by electrodeposition. It is observed that a dense layer of lead is deposited on the titanium sheet. The energy dispersive X-ray spectroscopy (EDS) analysis confirmed the presence of lead and oxygen atoms on the surface of the sheet of titanium. Fig. 4 shows the XRD pattern for lead oxide coating on the Ti substrate. According to this figure, the main peaks for various phases of PbO_2 (α-PbO_2 and β-PbO_2) and the corresponding peak for the titanium surface are observed. It can be confirmed that PbO_2 phases are formed by an electrodeposition process. These results are in good agreement with the Zhang et al. [42] and Saratale et al. [43] results.

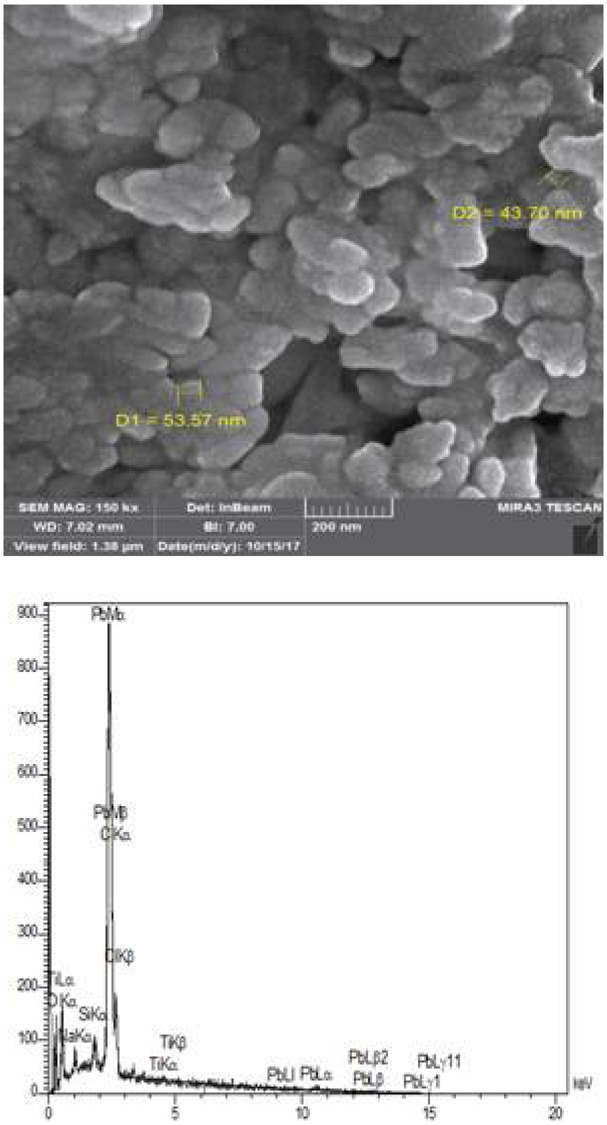

Fig. 3. SEM-EDX micro graphs of Ti/PbO_2.

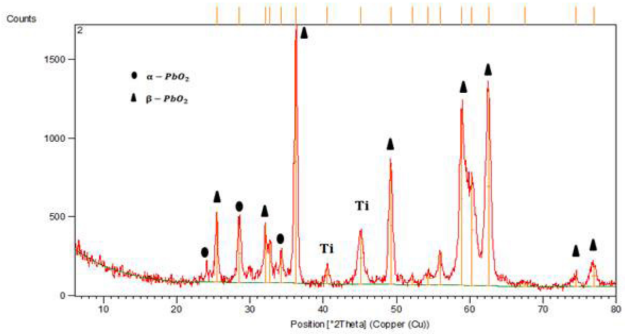

Fig. 4. XRD patterns of Ti/PbO_2.

3.2. Statistical analysis and modeling

The statistical combinations of the main parameters, such as initial pH, current, and electrolysis time, with the maximum actual and predicted degradation efficiency are listed in Table 2. Polynomial regression modeling was carried out between the dependent and independent

Table 2
Experimental design and results obtained for CIP removal efficiency by studied processes

Run	X_1 pH	X_2 current (A)	X_3 Time (min)	Response 1 2DE		Response 2 EF		Response 3 3DE		Response 4 3DEF	
				Actual	Predicted	Actual	Predicted	Actual	Predicted	Actual	Predicted
1	4.5	0.3	45	45.67	46.57	48.98	48.87	56.57	57.46	71.19	71.88
2	3	0.45	30	79.93	78.26	80.36	80.19	90.91	88.99	92.98	91.56
3	4.5	0.3	45	46.78	46.57	47.98	48.87	55.67	57.46	71.42	71.88
4	6	0.15	60	40.11	42.19	44.34	43.94	53.67	55.32	64.6	65.84
5	4.5	0.3	45	48.11	46.57	49.19	48.87	57.21	57.46	73.42	71.88
6	6	0.45	30	36.11	36.78	38.11	38.52	46.84	49.12	65.88	66.29
7	3	0.45	60	86.43	87.01	88.65	88.78	94.87	96.52	96.98	98.02
8	3	0.15	30	56.98	55.33	59.96	58.79	70.1	69.58	81.83	81.58
9	4.5	0.071	45	38.98	39.16	37.89	39.77	49.9	51.96	69.32	69.78
10	2.21	0.3	45	76.67	78.83	79.87	81.06	83.23	85.29	88.67	89.39
11	4.5	0.3	22.13	47.12	49.16	50.48	51.29	64.87	66.11	74.71	76.26
12	4.5	0.3	45	47.1	46.57	49.03	48.87	59.12	57.46	73.12	71.88
13	4.5	0.3	67.86	70.45	67.71	71.98	72.14	81.34	80.56	86.91	85.67
14	3	0.15	60	70.67	70.41	73.98	73	80.23	77.69	86.72	86.13
15	6	0.15	30	26.76	26.6	25.87	25.18	45.8	43.89	61.17	59.95
16	4.5	0.528	45	60.45	59.57	62.87	61.97	71.9	70.3	83.83	83.68
17	4.5	0.3	45	46.1	46.57	48.9	48.87	57.7	57.46	68.9	71.88
18	4.5	0.3	45	45.18	46.57	49.8	48.87	58.8	57.46	73.44	71.88
19	6.78	0.3	45	28.56	25.7	27.35	27.14	39.45	37.84	55.06	54.65
20	6	0.45	60	43.98	46.04	51.05	51.66	59.71	59.96	74.03	74.1

variables, and finally, the best fitted model equation was obtained for all four oxidation processes in the form of following equations:

$$\text{The degradation of CIP by 2DE (Y)} = 46.49 - 17.79X_1 + 6.69X_2 + 6.09X_3 - 3.19X_1X_2 + 0.13X_1X_3 - 1.58X_2X_3 + 1.98X_1^2 + 1.38X_2^2 + 5.28X_3^2 \quad (7)$$

$$\text{The degradation of CIP by EF (Y)} = 48.92 - 17.68X_1 + 7.04X_2 + 6.84X_3 - 2.01X_1X_2 + 1.14X_1X_3 - 1.41X_2X_3 + 2.13X_1^2 + 1.17X_2^2 + 5.41X_3^2 \quad (8)$$

$$\text{The degradation of CIP by 3DE (Y)} = 57.46 - 15.56X_1 + 6.01X_2 + 4.74X_3 - 3.55X_1X_2 + 0.83X_1X_3 - 0.15X_2X_3 + 1.77X_1^2 + 1.58X_2^2 + 6.83X_3^2 \quad (9)$$

$$\text{The degradation of CIP by 3DEF (Y)} = 71.88 - 11.39X_1 + 4.56X_2 + 3.09X_3 - 0.91X_1X_2 + 0.34X_1X_3 + 0.48X_2X_3 + 0.06X_1^2 + 2.09X_2^2 + 3.91X_3^2 \quad (10)$$

The analysis of variance (ANOVA) for the response variables (2DE, EF, 3DE, and 3DEF processes) are shown in Table 3. According to this table, the F-value and p-value <0.0001 imply that the model is significant for all four oxidation processes. For Eqs. (7), (8), (9), and (10), Lack of Fit F-values of 27.01, 4.34, 40.55, and 11.55 implies the significance for CIP removal by 2DE, EF, 3DE, and 3DEF systems, respectively. The R-squared value shows that more than 98% of the variability for CIP removal by studied oxidation processes can be explained by the regression model, while less than 2% of the response variability cannot be explained through the obtained model. Moreover, the predicted R-squared of model is in reasonable agreement with the adjusted R-squared as another evidence for desirable of the model fit. The relatively lower value of the coefficient of variance (CV = 1.43–3.48 % for all responses) shows high precision and reliability of the experiments performed. The fifth column of Table 3 indicates the percent contribution (PC%) of each of the parameters in the model. It is clear from Table 3 that the most important variable for degradation of CIP by studied processes was initial pH. The percent contribution results are confirmed by perturbation plot results (Fig. 5).

Fig. 6 indicates the relationship between the actual and predicted values of removal efficiency of CIP by 2DE, EF, 3DE, and 3DEF processes. As can be seen from the figure, experimental values are in good agreement with the predicted values. Therefore, the model could be used to calculate the CIP removal by studied processes in the investigational range of parameters.

3.3. Contour plotting for estimation of operating variables

3.3.1. Influence of initial solution pH

The effect of the initial pH on the CIP removal is shown in Figs. 7–10, at a current of 0.3 A, and initial CIP concentration 50 mg/L. As shown in plots, with increase of initial pH from 3–6 the CIP removal efficiency decreased. The decay of the oxidation ability with increasing pH is usually ascribed

Table 3
ANOVA results for the quadratic model of CIP removal using studied processes

Source	DF	F Value				p-value Prob > F				PC (%)			
		2DE	EF	3DE	3DEF	2DE	EF	3DE	3DEF	2DE	EF	3DE	3DEF
Model	9	187.40	1028.4	101.08	90.91	< 0.0001	< 0.0001	< 0.0001	< 0.0001				
A-pH	1	1226.5	6522.7	622.60	597.74	< 0.0001	< 0.0001	< 0.0001	< 0.0001	72.7	70.5	68.4	73.1
B- DC	1	173.73	1033.9	92.99	95.78	< 0.0001	< 0.0001	< 0.0001	< 0.0001	10.3	11.2	10.2	11.7
C-time	1	143.56	975.38	57.73	43.96	< 0.0001	< 0.0001	< 0.0001	< 0.0001	8.51	10.5	6.3	5.4
AB	1	24.92	53.53	20.45	2.41	0.0005	< 0.0001	0.0011	0.1519	1.48	0.6	2.2	0.3
AC	1	0.041	17.10	1.12	0.33	0.8435	0.0020	0.3141	0.5787	0.00	0.2	0.1	0.0
BC	1	6.15	26.09	0.035	0.67	0.0325	0.0005	0.8558	0.4328	0.36	0.3	0.0	0.1
A^2	1	12.99	81.06	6.86	0.014	0.0048	< 0.0001	0.0256	0.9078	0.77	0.9	0.8	0.0
B^2	1	6.29	24.54	5.47	17.13	0.0310	0.0006	0.0414	0.0020	0.37	0.3	0.6	2.1
C^2	1	92.35	521.79	102.42	60.12	< 0.0001	< 0.0001	< 0.0001	< 0.0001	5.48	5.6	11.3	7.3
Residual	10												
Lack of Fit	5	4.80	2.51	4.96	0.73	0.055	0.1672	0.0576	0.6329				
Pure Error	5												
C.V (%)		3.48	1.43	3.47	2.19								
R^2		0.9941	0.9989	0.9891	0.9879								
R^2_{adj}		0.9888	0.9979	0.9793	0.9771								
R^2_{pre}		0.9615	0.9938	0.9175	0.9457								

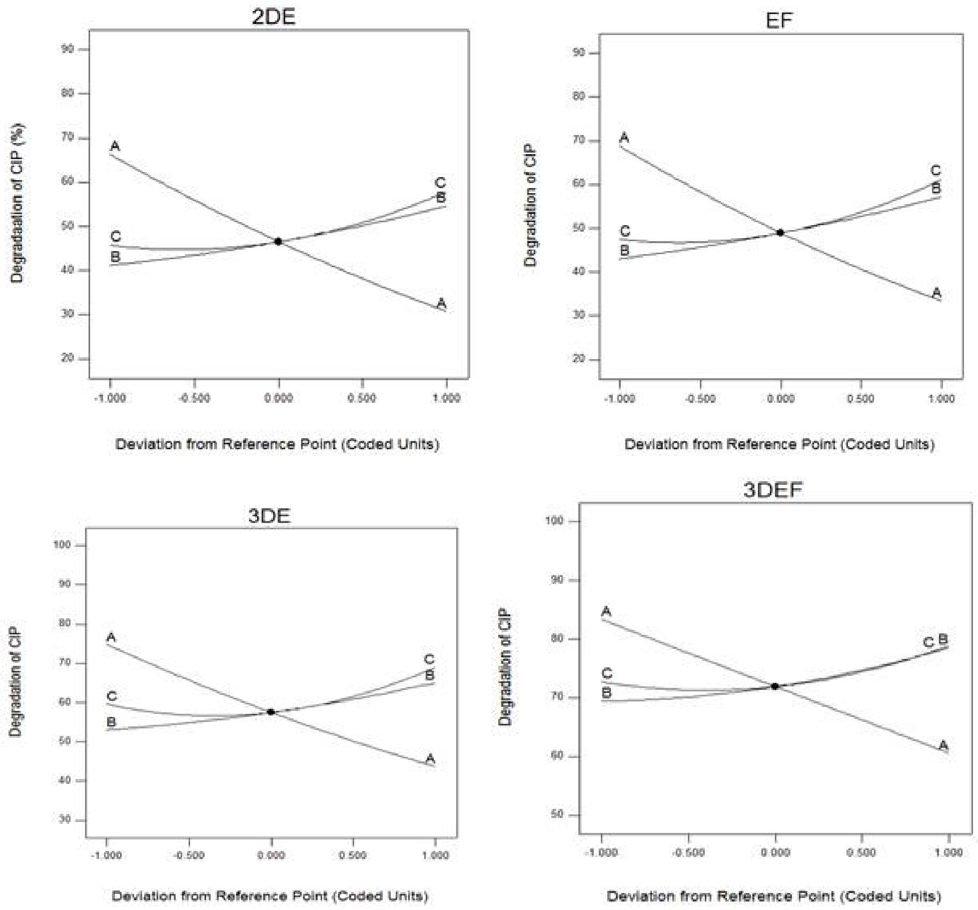

Fig. 5. Perturbation plots showing the effect of all factors on CIP removal during various oxidation processes.

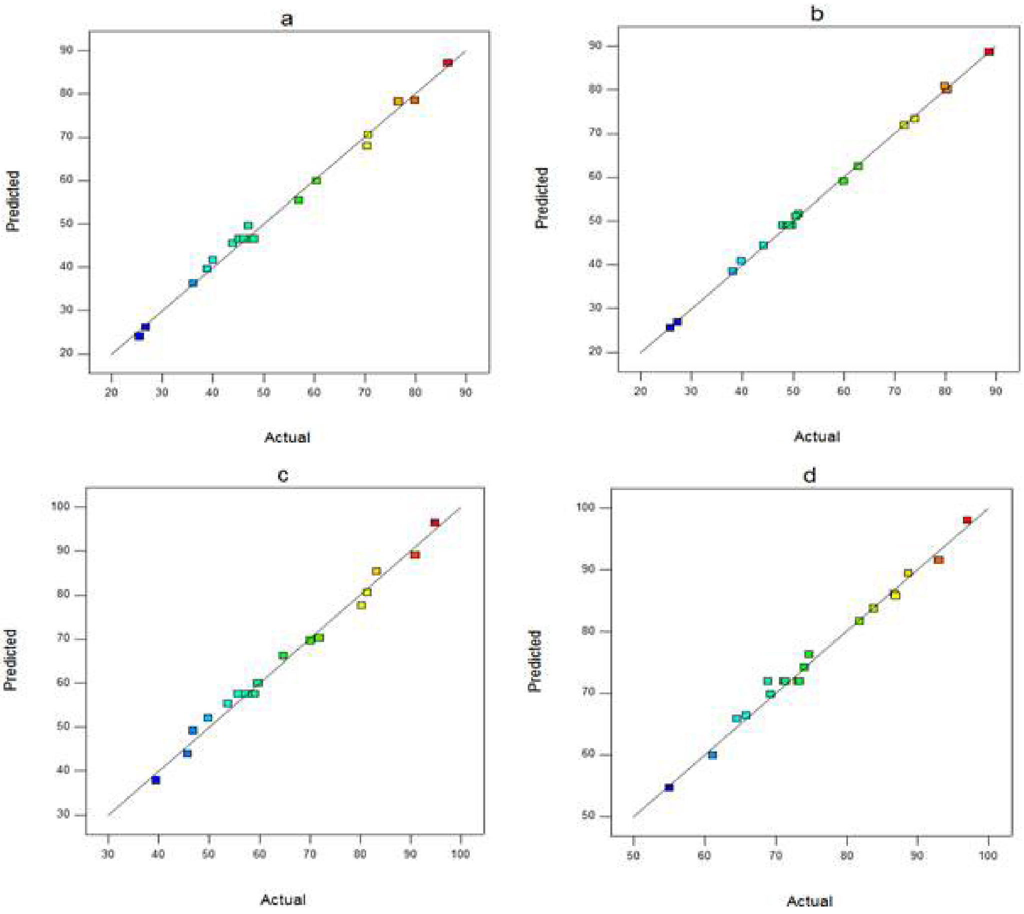

Fig. 6. Predicted values versus experimental removal efficiencies of CIP by 2DE (a), EF (b), 3DE (c), and 3DEF (d) processes.

to the lower $^{\bullet}$OH production due to the inhibition of reactions 1 and 4. At pH of 3, CIP removal efficiency observed were much higher in 3DEF process than other processes, which is due to the presence of SWCNTs and Fe^{2+} ions. At pH 6, the rate of removal of ciprofloxacin by the 3DEF process was equal to the rate of CIP removal by the 2DE and EF processes at acidic pH. These results indicated that 3DEF system can work well within a wide pH range compared with 2DE and EF processes. At acidic pH, the performance of 3DE and 3DEF processes was found to be same. This is due to the increased production of reactive oxygen species (ROSs) such as hydroxyl radicals by electrode particle. The SWCNTs reduces O_2 to H_2O_2 and acts as the catalyst for the decomposition of H_2O_2 to $^{\bullet}$OH [Eqs. (2) and (4)]. Hou et al. [44] obtained same results and showed the amount of TOC removed by 3DEF process decreased from 67.13% to 60.23% as the initial pH increased from 3 to 7.5. Liu et al. [45] showed that the removal efficiency of the 3DEF process at near neutral pH is greater than of EF and 3DE processes.

3.3.2. Effect of electrolysis time

Figs. 7–10 show the variation of CIP removal with electrolysis time at current of 0.3, CIP concentration of 50 mg/L for the studied processes. According to these plots, the removal efficiency of CIP by 3DEF process increases from 84.27% to 89.61% with an increase in the reaction time from 30 to 60 min. Similar results were observed for the other studied processes, indicating that the removal efficiency increases with increasing reaction time within the operation conditions in this study. The results of these plots also showed that the removal efficiency of the 3DEF process in a period of 30 min was much higher than the efficiency of 2D and EF processes in 60 min of reaction time. This enhancement in the removal of CIP by 3DEF can be attributed to synergistic effect between 3DE and EF processes in the novel 3DEF system. Moreover, the result indicated that CIP removal rate in 3DEF process in various time was higher than 3DE process and this may be due to the rapid production of hydroxyl radicals by Fe^{2+} ions as shown in Eq. (1).

3.3.3. Effect of current

The current density is one of the most important parameter in electrochemical systems since it influence on the reaction rate of electrochemical processes, the amounts of $^{\bullet}$OH formed in the non-active PbO_2 anode and polarization behavior of particle electrodes in 3D systems. The effect of current on removal efficiency of CIP is shown in the contour plots of Figs. 7–10, at an initial pH of 4.5 and a CIP concentration of 50 mg/L. The according these of plots, the removal efficiency increased with increasing current. This increase

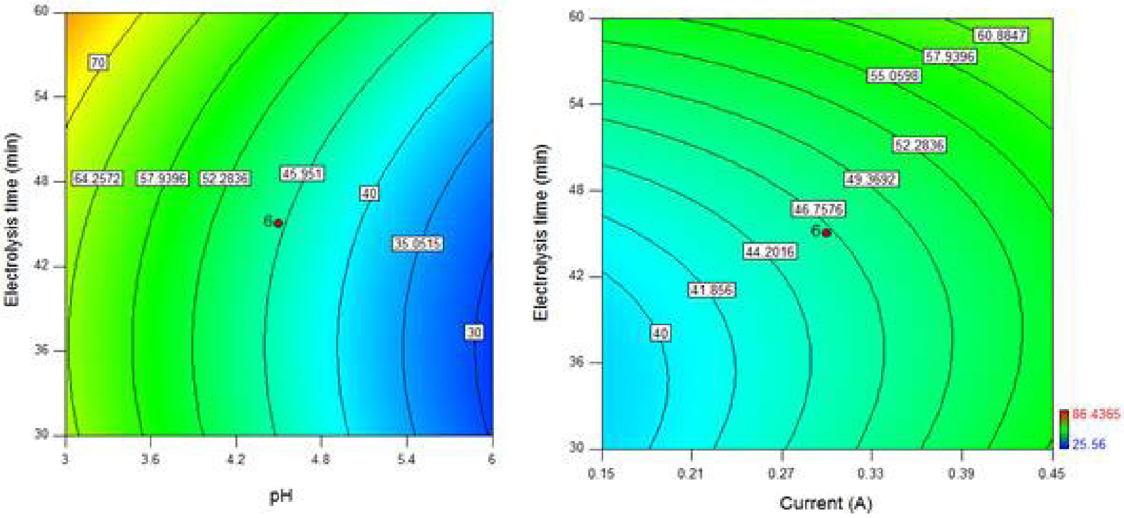

Fig. 7. Effects of pH, current, and electrolysis time on CIP removal by 2DE process.

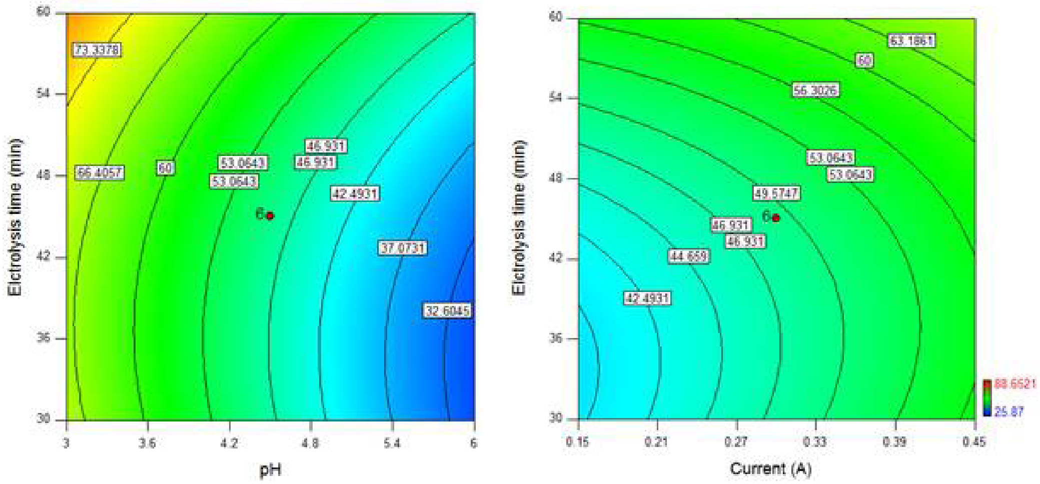

Fig. 8. Effects of pH, current, and electrolysis time on CIP removal by EF process.

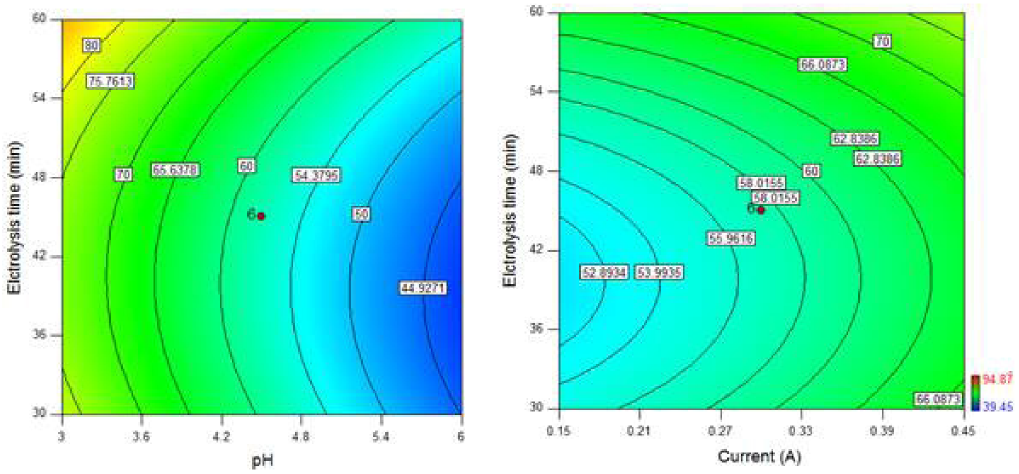

Fig. 9. Effects of pH, current, and electrolysis time on CIP removal by 3DE process.

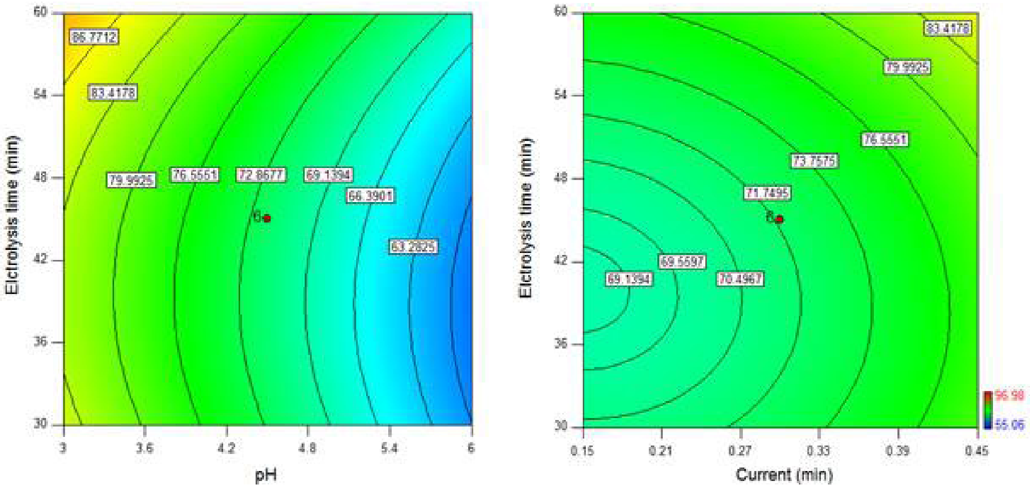

Fig. 10. Effects of pH, current, and electrolysis time on CIP removal by 3DEF process.

Table 4
Results of validation experiments conducted at optimum conditions as obtained from RSM

Processes	pH	Current (A)	Time (min)	Fe^{2+} (mM)	SWCNTs (mg/L)	Predicted value (%)	Actual value (%)	Desirability
2DE	3	0.45	60	–	–	87.17	83.45	1
EF	3	0.45	60	1	–	88.66	85.91	1
3DE	3	0.45	60	–	40	96.51	92.82	1
3DEF	3	0.45	60	1	40	98.02	95.18	1

in removal efficiency of antibiotic by 2DE process may be due to the production of high amount of oxidant species such as H_2O_2 and $^{\bullet}OH$ radical. For EF process,the enhancement in removal efficiency with current can be related with greater production of H_2O_2 and $^{\bullet}OH$ radical through reaction (2) and (1), respectively. Also, for 3D systems could be because of the enhanced polarization of particle electrodes at high current. The increase of the current can improve the production of electro generated H_2O_2 by electrode particle, and the generated H_2O_2 subsequently lead to more production of $^{\bullet}OH$ in the solution according to Eqs. (2) and (4). The results plots also showed 63.53, 67.44, and 76.01 % CIP removal for 2DE, EF, and 3DE processes at 0.45 A in 60 min while 85.78% removal was observed with 3DEF at 0.45 A in 60 min. Moreover the results of these plots show that the removal efficiency of the 3DEF process in a current of 0.15 A was much higher than the efficiency of 2D, EF, 3DE processes in a current of 0.45 A. This high removal rate in the 3DEF process may be due to the presence of SWCNTs and Fe^{2+} ions in solution [46]. In other words, this great removal enhancement can be due to the existence of synergistic effect between 3DE and EF processes in the novel 3DEFsystem with SWCNTs as the particle electrodes [46].

3.4. Optimization of process

The main purpose of this investigate is to confirm the adequacy of the CCD model for predicting the maximum removal efficiency of CIP and find the optimum conditions of parameters. Based on this, a series of experiments were performed according to the optimal conditions predicted for studied processes by the CCD model. As shown in Table 4, the experimental results are in good agreement with the predicted conditions.

3.5. Kinetics of CIP Removal by studied processes

At the optimized condition of operational parameters (pH = 3, current = 0.45 A, and CIP concentration = 50 mg/L), a kinetic study for CIP removal by various electrochemical processes was carried out at room temperature. The kinetic data of the treatment CIP by 2DE, EF, 3DE and 3DEF processes were analyzed by using the first-order kinetic equation, which its equation could be expressed as:

$$\ln\left(\frac{CIP_0}{CIP_t}\right) = kt \tag{11}$$

where k is the reaction rate coefficient for the electrochemical process of CIP removal and t is the electrolysis time. The results are shown in Fig. 11 and Table 5. These results show that the rate constant increases with developing electrochemical processes through their combination. These results are in good agreement with the other studies results [47].

3.6. Comparison between EAO processes

A series of comparative experiments for ciprofloxacin degradation in 2D, 3D, EF, and 3DEF electrochemical reac-

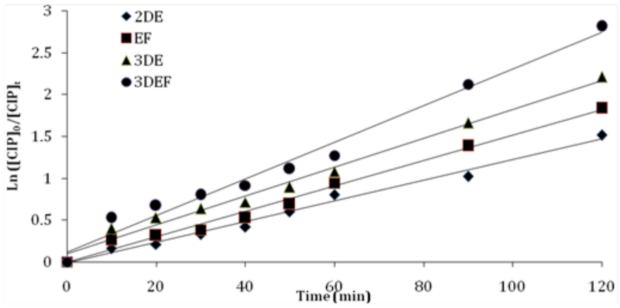

Fig. 11. Plot of the first-order equation for the removal kinetics of CIP by studied processes.

Table 5
Calculation of kinetic constant in the studied processes

Processes	Kinetic constant, k (min^{-1})	Coefficient
2DE	0.0123	0.9884
EF	0.0151	0.9895
3DE	0.0173	0.9865
3DEF	0.0213	0.9808

tors was performed in the same optimum condition. The degradation efficiency and energy consumption were used as indicators for the evaluation of reactors. As shown in Fig. 12a, the efficiency of CIP degradation was increased with increasing reaction time in all processes studied. This increase in degradation efficiency is due to the increasing of the direct and indirect oxidation process in EAO reactors. Fig. 12a also shows that the degradation efficiency of 3D processes is much higher than the 2D processes. This increase in the degradation efficiency in 3D processes may be due to the formation of numerous microelectrodes at an appropriate current density, which results in the generation of an additional OH radical and increasing the efficiency of the direct and indirect oxidation process [34]. These results are consistent with the results of Qin et al. [48], Luo et al. [49]. In addition, the results of Fig. 12a show that the 3DEF process efficiency in the removal of COD is 4.7–11.5% higher than the 3DE process at the reaction time studied. This high efficiency is related to the production of more hydroxyl radicals in the 3DEF process due to the presence of Fe^{2+} and particle electrodes of SWCNTs. Liu et al. [45] used the 3DEF system for wastewater treatment, and reported that increasing the 3DEF process efficiency compared to the 3DE process may be due to more OH radical production in this process.

Fig. 12b shows the value of the energy consumption (kWh/m^3) in various electrochemical processes. According this figure the energy consumption in 3DEF system is much lower than that in 3DE, EF, and 2DE systems. Yan et al. [32], and Liu et al. [45] investigated the energy consumption of different electro-oxidation processes, and they reported that the energy consumption of the 3D systems are much lower than the 2D systems.

Along with the degradation of CIP and calculation of energy consumption, various tests were carried out to evaluate the rate of H_2O_2 electrochemically generated by 2DE, EF, 3DE, and 3DEF processes. Fig. 12c indicates the variation of the H_2O_2 value as a function of the electrolysis time as well as studied electro-oxidation processes. As can be seen in Fig. 12c, in all processes, by increasing the reaction time, the electrochemical production of H_2O_2 occurred more rapidly; and then, with a further increase, its production will gradually increase. This behavior can be explained

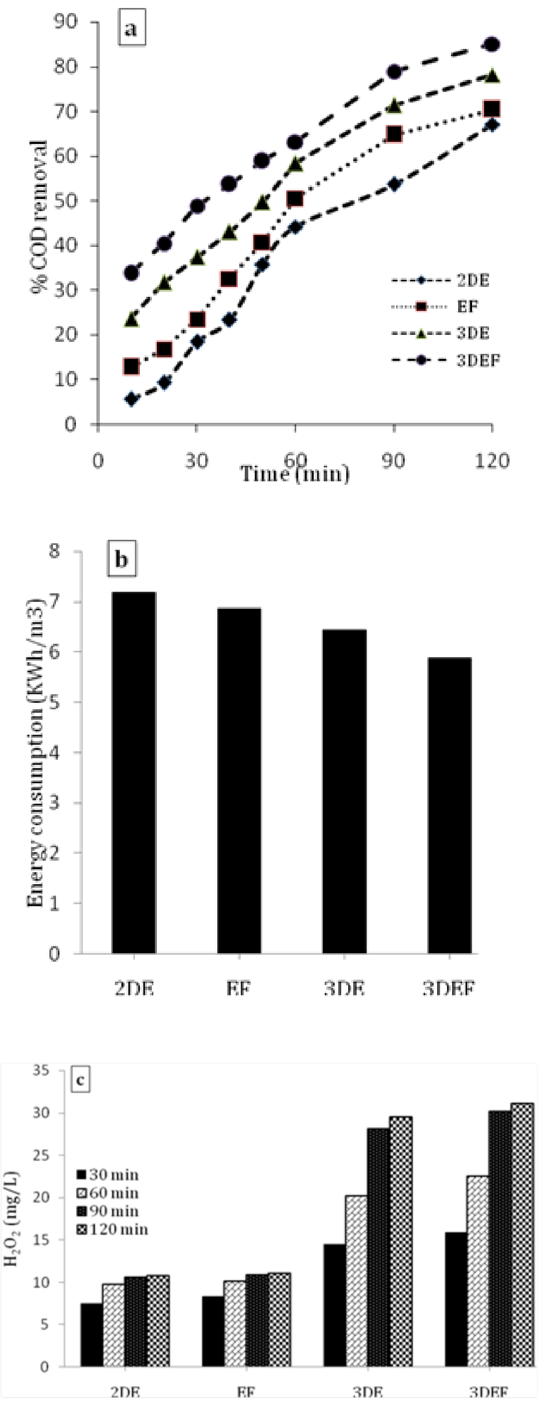

Fig. 12. Comparison between EAO processes on (a) COD removal, (b) energy consumption and (b) electrochemical production of H_2O_2 in optimum conditions obtained by RSM.

by the fact that H_2O_2 produced by reducing oxygen at the cathode surface [Eq. (2)] is simultaneously consumed by parasitic reactions in the same cathode [Eqs. (12) and (13)] and oxidation in Ti/PbO$_2$ anode [Eq. (14)]. In other words, by increasing the electrolysis time, the production of H_2O_2 as well as its consumption will increase and the rate of accumulation of H_2O_2 decreases.

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \tag{12}$$

$$2H_2O_2 \rightarrow O_2 + 2H_2O \tag{13}$$

$$\mathrm{H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-} \tag{14}$$

Moreover, from Fig. 12c it is apparent that the quantification of H_2O_2 generated in 3D systems was much more than 2D systems. This enhanced H_2O_2 generation in 3D systems is mainly due to the formation of numerous microelectrodes in the electric field, which produces the additional H_2O_2 by reduces oxygen to H_2O_2 [Eq. (2)]. These findings are in accordance with those reported by Qin et al. [48], who observed the concentration of H_2O_2 generated in the 3D systems was several times higher than the 2D systems.

4. Conclusion

In the present study the efficiency of 2DE, EF, 3DE and 3DEF processes for the removal of CIP using the response surface methodology under the central composite design was studied. Based on the results, it can be seen that the removal of ciprofloxacin strongly depends on the initial pH, current and electrolysis time. The results of the percent contribution showed that initial pH plays an important role in increasing the efficiency of electrochemical processes and has a direct correlation with the reduction of ciprofloxacin in aqueous solutions. The maximum removal efficiency of ciprofloxacin by the studied processes was found at initial pH of 3, current 0.45 A, and electrolysis time of 60 min. A quadratic equation in this study indicates the existence a high correlation between the predicted value and the experimental value obtained. The results of the comparison between the efficiency of the studied processes showed that the removal of CIP and COD by the 3DEF process is much higher than the 3DE, EF and 2DE systems. This increase in removal rate is related to the higher production of H_2O_2 and OH radical in the 3DEF system. In addition, the results showed that energy consumption in 3DEF system was lower than other systems. Finally, the results confirmed that CCD is an effective method to optimization various electrochemical systems. Also, the combination of the three-dimensional electrochemical process and the electro-Fenton can be used as an alternative method to increase removal of antibiotics due to high electro-catalytic activity, high efficiency at different pHs and low energy consumption.

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