

REMEDIATION TREATMENT

Mineralization of mefenamic acid from hospital wastewater using electro-Fenton degradation: Optimization and identification of removal mechanism issues

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Abstract

Mefenamic acid (MFA) is a nonsteroidal anti-inflammatory drug widely used for the short-term treatment of mild to moderate pain as well as treatment of primary dysmenorrhea and for decreasing the pain and blood loss during menstrual periods. Since MFA has been detected in raw and sewage water worldwide, the current work deals with the optimizing of removal of MFA from hospital wastewater using the electro-Fenton (E-Fenton) process. A cylindrical Pyrex reactor containing 250 ml of wastewater was employed for treatment investigation. The effects of main variables on the removal process were investigated and the optimum experimental condition was obtained with adequate desirability under the response surface methodology. The obtained results revealed that the removal efficiency of 95.3% was achieved under the optimal experimental condition, including MFA initial concentration of 7.0 mg L⁻¹, the H₂O₂ dosage of 700 µl/L, the current density of 6.6 mA cm⁻², and the reaction time of 12 min. The removal mechanism studies showed that •OH as the dominant radical species plays the main role in E-Fenton process. The MFA removal followed the pseudo-first-order kinetic model. Under the optimum condition of the E-Fenton process, the removal efficiency of MFA from synthetic wastewater was in satisfactory agreement with the real hospital wastewater treatment.

KEYWORDS

degradation, electro-Fenton process, hospital wastewater, Mefenamic acid

1 | INTRODUCTION

Recently some pharmaceuticals including various categories of antibiotics, steroidal hormones, blood-lipid regulators, and anti-inflammatory agents, which are known as emerging contaminants, received extraordinary attention due to their low biodegradability, and high stability in the environmental media.¹ The release of pharmaceuticals into the wastewater from domestic, industrial, and medical sources as well as aquaculture and livestock sources in the form of unused overtime drugs along with excretion in urine and animal excrement leads to a severe undesirable effect on the environmental ecosystems.^{2,3} The risks associated with the variable nature of emerging contaminants mixtures provided

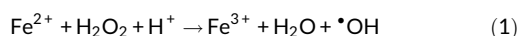
excessive challenges in environmental analysis for surface and ground waters in addition to global wastewaters.

Among the medicines applied for relief of mild to moderate pain, mefenamic acid (MFA) as a nonsteroidal anti-inflammatory drug has been extensively used all over the world. MFA detected in sewage effluents with the concentrations exceeding the predicted no-effect concentration of 0.43 µg L⁻¹ (References 4 and 5). Several processes have been developed for the treatment of wastewaters, among which advanced oxidation processes (AOPs) offer the advantage of high efficiency for removal of nonbiodegradable compounds, whereas other processes such as biological degradation, chlorination, adsorption, and flocculation have not provided the ultimate solution. In the mentioned

alternative processes, the contaminant accompanies with sludge or sorbent and is transferred into the solid phase. It means that the contaminant is only displaced and not decomposed.^{6,7} AOPs such as electro-Fenton (E-Fenton), UV/H₂O₂, ozonation, and photo-Fenton are considered as an economical and reasonable wastewater treatment processes for efficient removal of resistant synthetic emerging contaminants to improve the quality of effluents after conventional treatment.⁸⁻¹⁰

Throughout the ozonation process, due to the high consumption rate of ozone, the treatment process encountered mass transfer limitations. It resulted in diminishing the removal efficiency and increasing the treatment costs. Moreover, the high cost of employed equipment, considered as another disadvantage of the ozonation process. On the other hand, UV/H₂O₂ and photo-Fenton techniques are suitable for treating the photosensitive contaminants in the aqueous media such as drinking water and rivers with low COD concentrations.¹¹ Since the current work deals with treating the hospital wastewater, the E-Fenton treatment process was employed as a cost-effective and fast approach with high efficiency for removal of MFA contaminant.

In situ generation of nonselective radicals such as hydroxyl (*OH) through the AOPs provided an ecofriendly and effective approach for mineralization of emerging contaminants and degraded them into CO₂, H₂O, and inorganic ions (see Equation 1).



Current work deals with developing an efficient treatment process for eliminating the MFA as a typical nonsteroidal anti-inflammatory drug from hospital sewage. Response surface methodology (RSM) was employed to optimize the main operating parameters values, including the initial concentration of MFA, H₂O₂ dosage, the current density, the pH of the solution, and the reaction time. To the best of our knowledge, there no report on MFA removal from hospital wastewater using E-Fenton process. Unlike most of the reported studies on wastewater treatment are based on a one-factor-at-a-time method, in the current study, treatment process is designed by RSM, which provided significant advantages such as reducing the number of experimental runs and providing useful information on the specific contribution of each operational parameters as well as their simultaneous interactions and quadratic effect to achieve the optimum condition for the treatment process. Furthermore, to understand the exact mechanism of MFA removal from hospital wastewater, the kinetics of MFA degradation, molar ratio Fe²⁺/H₂O₂, and the effect of the presence of radical scavengers investigated. Due to the existence of MFA and its metabolites with high toxicity in the wastewater, its removal from aqueous medium considered in the current study.

2 | EXPERIMENTAL

2.1 | Chemicals and materials

Mefenamic acid was provided by RAZAK Laboratories. Co. (Tehran, Iran). HPLC-grade acetonitrile (LiChrosolv[®] Reag. Ph Eur, ≥ 99.9%),

hydrochloric acid (EMSURE[®] ACS, ISO, Reag. Ph Eur, fuming 37%), ortho-phosphoric acid (Suprapur[®], ≥ 85.0%), hydrogen peroxide (Calbiochem, 30% solution, stabilized), dichloromethane (EMSURE[®] ACS, ISO, Reag. Ph Eur, ≥ 99.8%), sulfuric acid (EMSURE[®], ≥ 98%), tert-butanol (EMSURE[®] ACS, Reag. Ph Eur, ≥ 99.5%), sodium chloride (Suprapur[®], ≥ 99.5%), manganese (IV) oxide (EMPLURA[®], ≥ 89.0%), sodium carbonate (EMSURE[®] ISO, ≥ 99.9%), sodium sulfate (EMSURE[®] ACS, ISO, Reag. Ph Eur, ≥ 99.0%), sodium hydroxide (EMPLURA[®], ≥ 97.0%), methanol (LiChrosolv[®] ≥ 99.8%), and ethylenedinitrilo tetraacetic acid (Titriplex[®] ACS, Reag. Ph Eur, ≥ 99.4) were purchased from Merck (Germany). Potassium titanium oxide oxalate dehydrate (≥ 98% Ti basis) and titanium (IV) oxide (anatase ≥ 99%) were purchased from Sigma Aldrich (United States). All reagents used without further purification as received. Distilled water was used throughout the experiments.

2.2 | Reactor setup and operation

A cylindrical Pyrex container with 9 cm height and 7 cm internal diameter was employed as lab-scale electrochemical treatment reactor containing 250 ml of wastewater. The pH changes do not affect the reactor and its contents. The reactor was placed on magnetic stirrer applying 100 rpm at the ambient temperature. Moreover, two iron electrodes with the immersed dimensions of 3.5 cm × 1 cm × 0.2 cm and interelectrode distance of 3 cm and 50 mM Na₂SO₄ as supporting electrolyte hired for all experiments. MEGATEK two-channel DC power supply (model MP-3005D, Taiwan) applied to supply the constant current (see Figure 1).

The Metrohm pH meter (model 827 pH lab, Switzerland) employed to adjust the solution pH using NaOH or H₂SO₄ solutions. Shimadzu atomic absorption spectrophotometer (model AA-670, Japan) set at 248 nm employed for determination of Fe²⁺ concentration in the treated solution. Optizen UV-Vis spectrophotometer (model 3220UV, Republic of Korea) set at 410 nm employed for the determination of H₂O₂ concentration using titanium oxalate method. KNAUER HPLC system (model Smartline, Germany) with C₈ column (150 mm × 4.6 mm i.d., 3 μm) and a UV detector set at 220 nm employed for the quantitative determination of MFA in initial and treated wastewater. The chromatography performed isocratically using mobile phase of acetonitrile: water (70:30) phosphate buffer solution pH 3 with the flow rate of 1 ml min⁻¹ under temperature 25°C. MFA degradation efficiency evaluated using the following equation¹²:

$$\text{Removal MFA (\%)} = \frac{C_0 - C_t}{C_0} \times 100 \quad (2)$$

where C₀ and C_t (mg L⁻¹) denote the concentration of MFA before the treatment process and time t, respectively. Electrical energy consumption (EEC) throughout the treatment process (kWh m⁻³) calculated using the equation expressed below¹³:

$$\text{EEC} = \left(\frac{Ult}{V} \right) \quad (3)$$

where U , I , t , and V denote the applied voltage (V), applied current (A), treatment time (h), and volume of wastewater (L), respectively.

2.3 | Response surface methodology

The Design-expert 7 software was employed for optimizing the experimental condition and modeling the process under the RSM. Four independent operational parameters, including initial MFA concentration (X_1), H_2O_2 dosage (X_2), current density (X_3), and reaction time (X_4) consecutively coded from low to high level ($-\alpha$, -1 , 0 , $+1$, $+\alpha$) to optimize the treatment process efficiency and the suggested runs with the details of experimental range and levels of independent variables summarized in Table 1.

The relation between the independent variables (main operational parameters) is expressed as¹⁴:

$$Y = \beta_0 + \sum_{i=1}^n \beta_i X_i + \sum_{i=1}^n \beta_{ii} X_i^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^n \beta_{ij} X_i X_j \quad (4)$$

where Y denotes the removal efficiency as the response of the developed model. $X_i X_j$, β_0 , β_i , and β_{ii} , β_{ij} denote the independent variables, constant of the model, linear coefficient, and the quadratic coefficients, respectively.

To eliminate the effects of the unexpected operating parameters on the removal efficiency, the experimental run randomized. Analysis of variance (ANOVA) was applied to evaluate the lack of fit, the coefficient of determination (R^2), and the adequacy of the developed model. To interpret the optimal operating condition, response surface contour plots demonstrated the regression analysis performed over the confidence level of 95.0%. The developed model was validated by comparing the obtained experimental results with the predicted results.

3 | RESULTS AND DISCUSSION

3.1 | Effect of initial pH

Iron is mainly present as Fe^{2+} under acidic condition ($pH < 3$), which changes to $Fe(OH)^+$ and $Fe(OH)_2$ by increasing the pH to 4. Hence, the Fenton reaction revealed high performance at the acidic condition, where the hydroxyl radical displayed moderately stronger oxidation ability. The pH value at the end of the degradation process was found to be in the range of 3.5 ± 0.5 , which does not interfere in the generation reaction of OH radicals. To investigate the influence of initial pH on the E-Fenton process, several runs with various solution pH conditions were conducted and the obtained results are shown in Figure 2. As seen, the satisfactory degradation efficiency of close to 90% was achieved for the initial solution pH of 2 and 3 after 10 min. However, the degradation efficiency diminished up to 12% in the alkaline condition, where the solution pH was equal to 12, which could be attributed to the superior decomposition of H_2O_2 as revealed in the following interactions¹⁵⁻¹⁷:

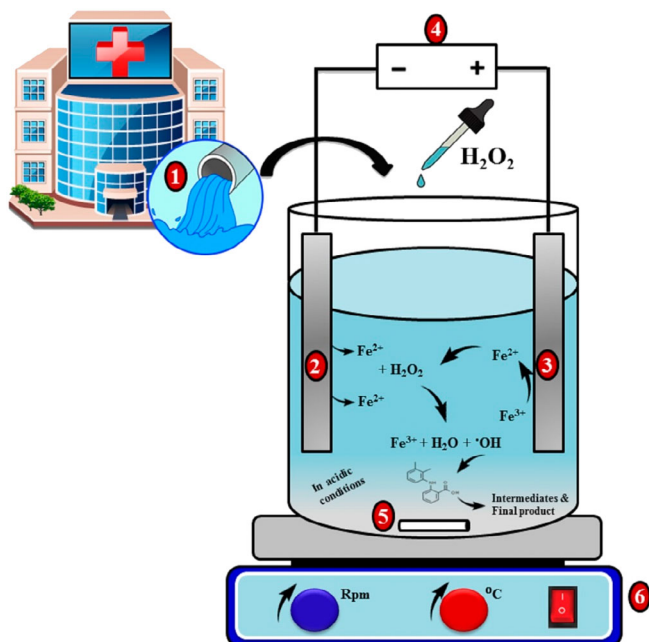
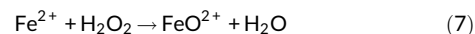
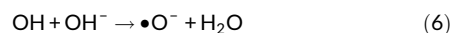


FIGURE 1 Schematic set up of employed treatment reactor, including 1: hospital wastewater, 2: anode electrode (iron), 3: cathode electrode (iron), 4: DC power supply, 5: magnet, 6: magnet stirrer [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 1 Experimental independent variables

Coded variables (X_i)	Factors (U_i)	Experimental field				
		$-\alpha$	-1 level	0	$+1$ level	$+\alpha$
X_1	A = initial MFA concentration ($mg\ L^{-1}$)	2	6.5	11	15.5	20
X_2	B = H_2O_2 dosage ($\mu l/L$)	200	400	600	800	1,000
X_3	C = current density ($mA\ cm^{-2}$)	3	4.5	6	7.5	9
X_4	D = reaction time (min)	2	5.25	8.5	11.75	15

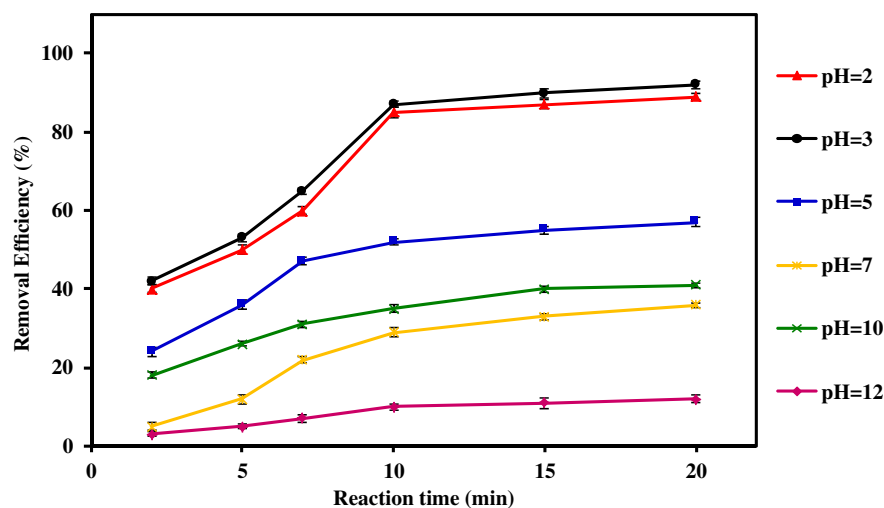


FIGURE 2 Effect of the pH on the degradation of MFA. (Experimental condition: initial MFA concentration of 5 mg L⁻¹, the H₂O₂ dosage of 600 µl/L, and the current density of 4 mA cm⁻²) [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 2 Experimental factors in coded units and the obtained responses

Run	Actual values				Coded values				Actual removal (%)	Predicted removal (%)
	A (mg L ⁻¹)	B (µl/L)	C (mA cm ⁻²)	D (min)	X ₁	X ₂	X ₃	X ₄		
1	11.0	200	6.0	9	0	-2	0	0	47.8	46.9
2	6.5	400	4.5	5	-1	-1	-1	-1	58.6	55.9
3	6.5	400	4.5	12	-1	-1	-1	1	63.7	65.3
4	6.5	400	7.5	5	-1	-1	1	-1	69.8	66.8
5	6.5	400	7.5	12	-1	-1	1	1	75.0	76.1
6	15.5	400	4.5	5	1	-1	-1	-1	48.5	45.9
7	15.5	400	4.5	12	1	-1	-1	1	55.9	55.2
8	15.5	400	7.5	12	1	-1	1	1	63.8	66.1
9	15.5	400	7.5	5	1	-1	1	-1	53.1	56.8
10	2.0	600	6.0	9	-2	0	0	0	86.7	91.5
11	11.0	600	3.0	9	0	0	-2	0	38.5	40.1
12	11.0	600	6.0	9	0	0	0	0	76.7	76.8
13	11.0	600	6.0	9	0	0	0	0	76.5	76.8
14	11.0	600	6.0	9	0	0	0	0	78.4	76.8
15	11.0	600	6.0	9	0	0	0	0	75.0	76.8
16	11.0	600	6.0	9	0	0	0	0	79.4	76.8
17	11.0	600	6.0	9	0	0	0	0	78.2	76.8
18	11.0	600	6.0	15	0	0	0	2	87.1	86.2
19	11.0	600	6.0	2	0	0	0	-2	63.0	67.5
20	11.0	600	9.0	9	0	0	2	0	61.3	61.9
21	20.0	600	6.0	9	2	0	0	0	63.1	62.2
22	6.5	800	4.5	5	-1	1	-1	-1	69.7	68.0
23	6.5	800	4.5	12	-1	1	-1	1	78.6	77.3
24	6.5	800	7.5	5	-1	1	1	-1	77.8	78.9
25	6.5	800	7.5	12	-1	1	1	1	93.4	88.2
26	15.5	800	4.5	5	1	1	-1	-1	49.9	48.7
27	15.5	800	4.5	12	1	1	-1	1	54.8	58.1
28	15.5	800	7.5	12	1	1	1	1	69.1	68.9
29	15.5	800	7.5	5	1	1	1	-1	62.8	59.6
30	11.0	1,000	6.0	9	0	2	0	0	58.7	61.8

The literature review revealed that the oxidation potential of hydroxyl radical reduced by increasing the solution pH. At the pH values greater than 7, the $\cdot\text{OH}$ promptly reformed into $\cdot\text{O}^-$ as its conjugate base with lower degradation activity.^{18,19} In addition, in the alkaline condition, generation of ferryl ions (FeO^{2+}) as an inactive species speeded up, which resulted in diminishing the Fenton reaction. On the other hand, the relatively better degradation of the contaminant at alkaline condition ($\text{pH} > 10$) was probably related to the generation of $\text{Fe}(\text{OH})_3$ with satisfactory precipitation and surface adsorption capacity.^{20,21} According to the obtained results the solution pH of 3 with the highest degradation efficiency set and kept constant for further studies. Since the solution pH was 3 with the highest degradation efficiency set and kept constant for the current treatment process, to eliminate the excess iron from the treated wastewater, the pH of the effluent was adjusted to the neutral range of 7–7.5 using sodium hydroxide. Subsequently, the excess iron settled at the bottom of the reactor as sediment and removed from the effluent as sludge.

3.2 | Response surface methodology and results analysis

RSM as a statistical approach was employed to optimize the treatment process variables along with reducing the number of experimental runs and the obtained actual and predicted removal efficiencies as the response values of the developed process summarized in Table 2. All experiments were carried out for three times and the average data presented.

Multiple linear regressions were conducted to obtain the best-fitted quadratic model and to eliminate the negligible operating parameters with p -values higher than .05. Table 3 presents the obtained ANOVA data. The p -value and F -value of the linear regression for the developed quadratic model were found to be lower than

.0001 and 876, respectively. Moreover, according to the obtained statistical data, the lack of fit of the model was nonsignificant, the coefficient of determination, and the adequate precision were found to be 0.9654 and 35.5, respectively. It concluded that the response of the model revealed a satisfactory statistical regression relationship with the main operating parameters as the independent variables.

To investigate the accuracy of the model, the values of the coefficients of determination including R^2 (0.9654) and adjusted R^2 (0.9544) for the removal efficiency of MFA as the response of the model calculated. The developed quadratic model based on response surface methodology revealed that the variability of the response could be validated up to 96.5% of the variation values.

Since a difference of less than 0.2 observed between the adjusted R^2 and predicted R^2 of the developed model and the value of lack of fit were found to be insignificant (p -value $> .05$) which is acceptable and the adequacy of the quadratic model validated to fit the experimental data for all the response variables. The following polynomial equation expressed the removal efficiency of MFA according to the regression analysis of the obtained experimental results:

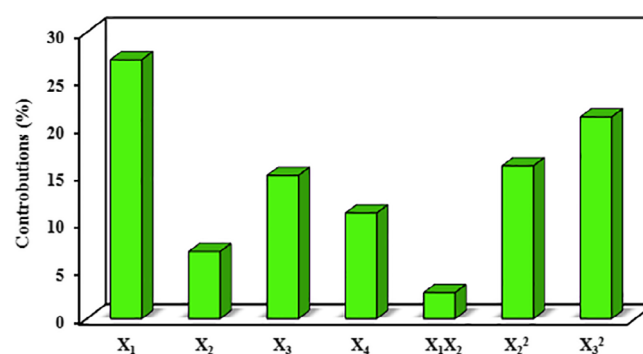


FIGURE 3 Pareto chart of main operating parameters effects on removal efficiency of MFA [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 3 ANOVA results for the response surface quadratic model

Source	Sum of squares	Degree of freedom (df)	Mean square	F-value	p-value prob > F
Model	4,830.0	7	690.0	87.6	<.0001
X_1	1,289.2	1	1,289.2	163.7	<.0001
X_2	333.8	1	333.8	42.4	<.0001
X_3	711.8	1	711.8	90.4	<.0001
X_4	525.5	1	525.5	66.7	<.0001
$X_1 X_2$	86.0	1	86.0	10.9	.0032
X_2^2	901.2	1	901.2	114.5	<.0001
X_3^2	1,189.4	1	1,189.4	151.1	<.0001
Residual	173.2	22	7.9	—	—
Lack of fit	160.5	17	9.4	3.7	.0761
Pure error	12.7	5	2.5	—	—
Cor Total	5,003.2	29	—	—	—

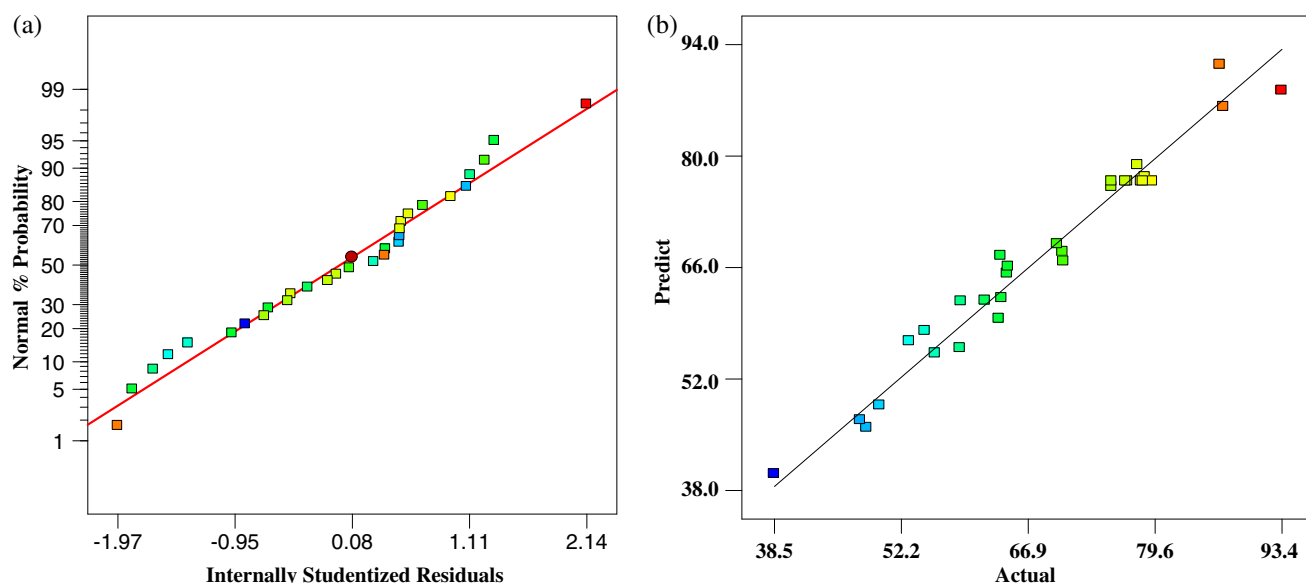


FIGURE 4 (a) Normal probability plot of studentized residuals for the suggested quadratic treatment model. (b) Predicted removal efficiency of MFA versus experimental removal efficiency [Color figure can be viewed at wileyonlinelibrary.com]

$$Y(\%) = 76.84 - 7.33X_1 + 3.73X_2 + 5.45X_3 + 4.68X_4 - 2.32X_1X_2 - 5.63X_2^2 - 6.47X_3^2 \quad (8)$$

where Y denotes the removal efficiency of MFA, and the coded variables of X_1 , X_2 , X_3 , and X_4 denote the initial MFA concentration, H_2O_2 dosage, current density, and reaction time, respectively. The Pareto analysis, which provides worthwhile evidence on the superiority effect of main operating parameters, was carried out and the obtained results are illustrated in Figure 3.

As seen, the main effect of initial MFA concentration (X_1), the quadratic effect of current density (X_3^2), the quadratic effect of H_2O_2 dosage (X_2^2), and the main effect of current density (X_3) significantly affected the removal efficiency of MFA.

3.3 | Adequacy check of the model

The normal plot of residuals which was presented as the normal probability versus studentized residuals revealed that a normal distribution for the response observed, which indicated that no transformation function needs to be applied (see Figure 4A).

Moreover, to confirm the normality of the data, the predicted values of removal efficiency versus the actual values were plotted (Figure 4B), which revealed that the predicted values for the response were in satisfactory agreement with the obtained experimental results.

3.4 | Effect of process variables on the response

The individual effects of main operating parameters on the removal efficiency of MFA demonstrated in Figure 5. Moreover, to investigate

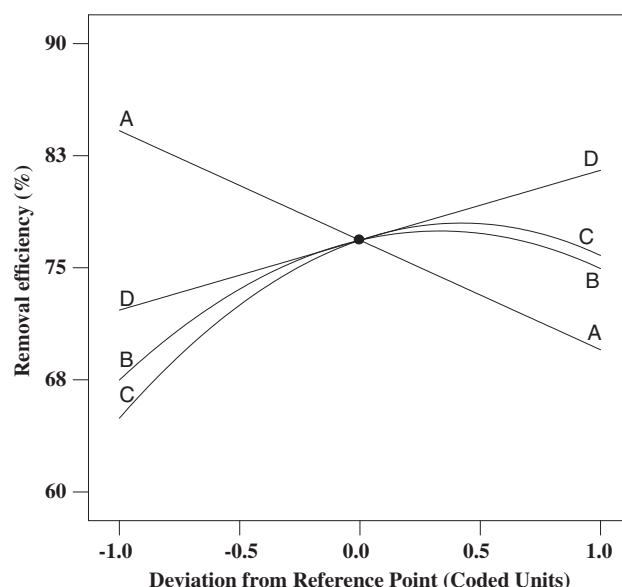


FIGURE 5 The individual effects of main operating parameters on the removal efficiency of MFA. Initial MFA concentration (a), H_2O_2 dosage (b), current density (c), reaction time (d)

the influence of main operating parameter interactions on the removal efficiency of MFA as the response of the developed quadratic model, regression equation was employed and 3-D surface plots was schemed.

Figure 6A reveals a 3-D surface plot, which demonstrates the response against the simultaneous function of initial MFA concentration and H_2O_2 dosage on the constant current density of 6 mA cm^{-2} and reaction time of 8.5 min. The obtained results revealed that the removal efficiency of MFA reduced from 91.5% to 62.2% by

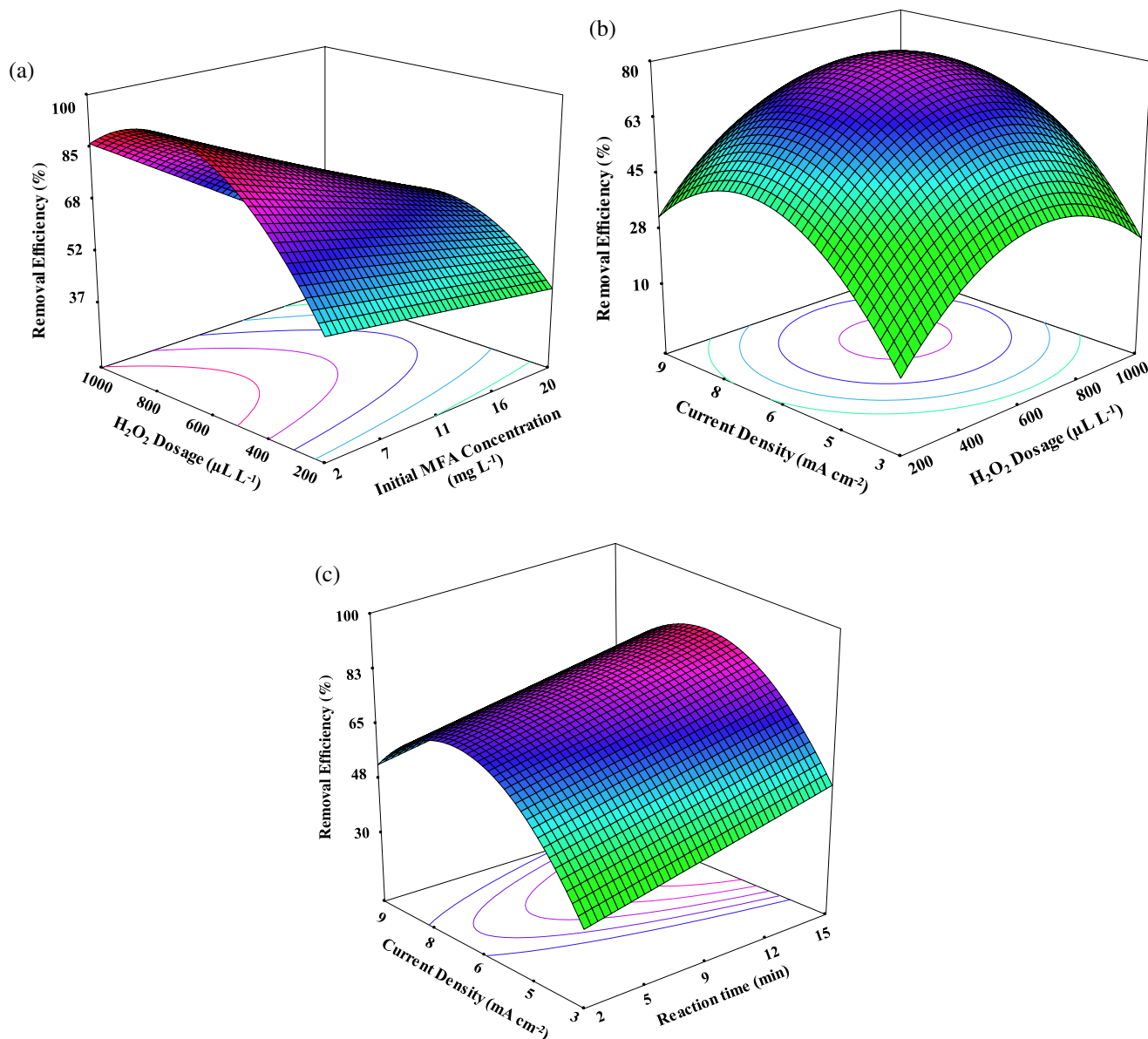
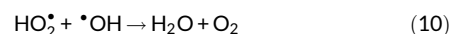
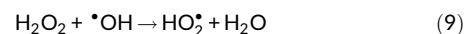


FIGURE 6 (a) Response surface graph as a function of H₂O₂ dosage and initial MFA concentration (Experimental conditions: current density of 6 mA cm⁻² and reaction time of 8.5 min). (b) Response surface graph as a function of current density and H₂O₂ dosage (Experimental conditions: initial MFA concentration of 11 mg L⁻¹ and reaction time of 8.5 min). (c) Response surface graph as a function of current density and reaction time (Experimental conditions: initial MFA concentration of 11 mg L⁻¹ and H₂O₂ dosage of 600 μL/L) [Color figure can be viewed at wileyonlinelibrary.com]

increasing the initial concentration of MFA from 2 mg L⁻¹ to 20 mg L⁻¹, which was probably due to the limited amount of hydroxyl radicals generated throughout the mention condition compared with the increasing amount of MFA. It concluded that for the defined condition, complete elimination of MFA as the contaminant was not observed, where the generated intermediate compounds were persistent even to the end of the treatment process.

On the other hand, increasing the H₂O₂ dosage from 200 to 700 μL/L led to improvement of removal efficiency from 46.8% to 77.3%. However, further addition of H₂O₂ resulted in the decrease of the removal efficiency due to quenching of hydroxyl radicals ([•]OH) with the additional H₂O₂ as expressed as follows²²:

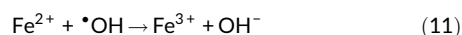


Since the standard reduction potential of generated hydroperoxyl radical (HO₂[•] E₀ = 1.7 V) was lower than the standard reduction potential of the consumed hydroxyl radical ([•]OH E₀ = 2.8 V), the removal efficiency of MFA diminished due to radical-radical recombination reaction, which resulted in H₂O and O₂ formation.

The combined effect of H₂O₂ dosage and current density on the removal efficiency of the MFA investigated and the obtained results were illustrated as a 3-D surface plot (see Figure 6B). As seen, the

gradual increase in the current density from 3 to 7 mA cm⁻² caused a significant increase of 38% in the removal efficiency, while the other variables remained constant at their center point, including initial MFA concentration of 11 mg L⁻¹, the H₂O₂ dosage of 600 µl/L, and reaction time of 8.5 min.

However, an additional increase in current density from 7 to 9 mA cm⁻² resulted in the undesirable decrease in the removal efficiency of E-Fenton process from 78.2 to 62.4%, which is due to increasing the rate of Fe²⁺ ion generation as a catalyst on the anode. The extra amount of Fe²⁺ consumed the •OH radicals and led to diminution the degradation rate of MFA.



According to the statement of Equation 1, if the amount of electro-generated H₂O₂ was adequate, the presence of Fe²⁺ increased the generation of •OH and accelerated the E-Fenton reaction. However, the excessive amount of Fe²⁺ probably resulted in flocculation of Fe(OH)₃, which limited the progress of E-Fenton reaction.²³

Moreover, the simultaneous effect of current density and reaction time was investigated (see Figure 6C). The obtained 3-D surface plot revealed that the removal rate of MFA at the initial steps of the electrolysis process was high due to the available large amount of H₂O₂, which reacts with the Fe²⁺ produced at the anode to generate hydroxyl radicals. With the passage of reaction time, the concentration of H₂O₂ gradually decreased which resulted in diminishing the removal efficiency of the treatment process. The observed behavior defines as “collision theory” which stated that the residual amount of MFA contaminant decreased with time, which led to reducing the collision frequency of •OH with MFA molecules.

3.5 | Process optimization using desirability functions

RSM applied to optimize the value of operating independent variables to the desired level to provide the most cost-effective and fast treatment process with high efficiency. According to the developed model, the value of desirability, which is described as an objective function that ranges from zero outside of the limits to one at the goal, was found to be 0.99, which presented the proximity of the desired condition with the developed experimental model. The level of all main parameters including initial concentration, H₂O₂ dosage, current density and reaction time within the range of investigation set for maximum desirability and the best optimal condition was found to be at initial MFA concentration of 7.0 mg L⁻¹, H₂O₂ dosage of 700 µl/L, current density of 6.6 mA cm⁻², and reaction time of 12 min, which resulted in 96.7% of the MFA removal efficiency. The predicted removal efficiency of 96.7% was in satisfactory agreement with the obtained experimental removal efficiency of 95.3%, which confirmed the desirability of the model.

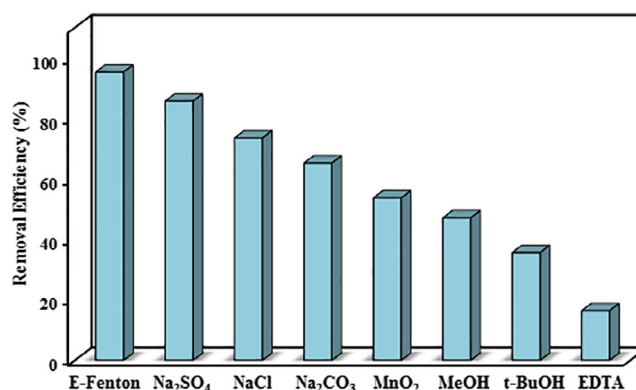
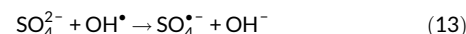
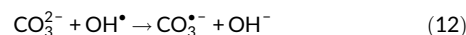


FIGURE 7 The effect of inorganic and organic scavengers on the removal of MFA throughout the E-Fenton process [Color figure can be viewed at wileyonlinelibrary.com]

3.6 | Effect of the addition of scavengers

The mechanism of the MFA degradation via the E-Fenton process investigated by applying the trapping experiments for primary active oxidant species employing 1 M inorganic scavengers such as Na₂CO₃, Na₂SO₄, NaCl, and MnO₂ or organic scavengers, including MeOH, t-BuOH, and EDTA, at the optimum condition of the treatment process.

As seen from Figure 7, addition of Na₂SO₄ and Na₂CO₃ as the •OH radical scavengers resulted in diminishing the removal efficiency of MFA to 85.7% (for Na₂SO₄) and 65.2% (for Na₂CO₃) in optimum condition, which is probably due to the formation of radical species CO₃•⁻ and SO₄•⁻ with the weaker oxidation ability as expressed below:



Furthermore, the addition of NaCl and MnO₂ as the stronger radical scavengers led to significant loss of removal efficiency to 73.5% and 53.7%, respectively, which confirmed the major role of •OH radical as the main active oxidizing species throughout the E-Fenton process. On the other hand, the presence of organic compounds such as MeOH and t-BuOH, and EDTA, which acts strongly as the radical scavengers for oxidizing species such as •OH, O₂•⁻, and HO₂• radicals resulted in dropping the removal efficiency to the level of 47.1%, 35.6%, and 16.4%, respectively. The observed behavior indicated that the generation of •OH radical as the main oxidative species controlled the treatment process throughout the E-Fenton reaction.^{24,25}

3.7 | Kinetic study for MFA degradation

The kinetics investigations were carried out to comprehend the exact mechanism and the reaction order of the removal process. The pseudo-first-order kinetics reaction expressed as^{26,27}:

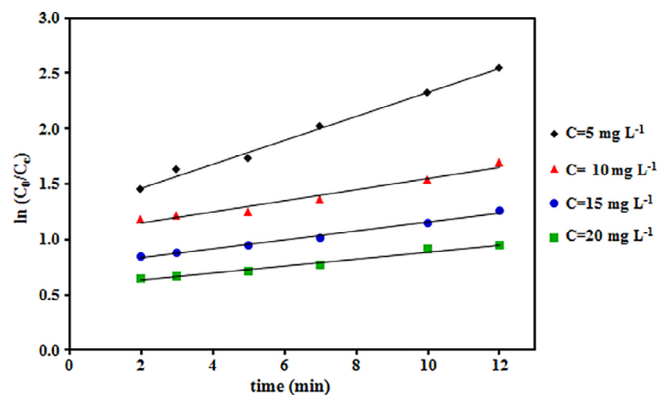


FIGURE 8 Kinetic model of MFA degradation [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com)]

TABLE 4 Kinetics data for MFA degradation process

Initial MFA concentration (mg L ⁻¹)	k_{app} (min ⁻¹)	R^2
5	0.107	0.993
10	0.052	0.987
15	0.040	0.990
20	0.031	0.980

$$\frac{dC}{dt} = -k_{app}C \quad (14)$$

$$-\ln\left(\frac{C_t}{C_0}\right) = k_{app}t \quad (15)$$

where C_t and C_0 denote the MFA initial concentration and MFA concentration at time (mg L⁻¹), respectively. k_{app} (min⁻¹) denotes the pseudo-first-order constant and t (min) is the applied degradation time. As seen from Figure 8, the kinetics of MFA degradation process best fitted the pseudo-first-order reaction by varying the initial concentrations of MFA. Moreover, according to the Table 4, The value of the kinetic constant (k_{app}) diminished by increasing the initial concentration of MFA from 5 mg L⁻¹ to 20 mg L⁻¹ which is probably due to the acceleration of competitive reactions between hydroxyl radicals and the oxidation intermediates of MFA.

3.8 | H₂O₂/Fe²⁺ molar ratio

As expressed through Equation 1, to generate the hydroxyl radicals as the main oxidizing species, the hydrogen peroxide should be decomposed in the presence of sufficient amounts of Fe²⁺. It is known that the insufficient or excess amount of Fe²⁺ led to diminishing the removal efficiency.

The excess amount of Fe²⁺ resulted in the formation of various complexes between iron and the emerging contaminants as well as acting as a hydroxyl radical scavenger which consumed the active

*OH oxidizing species and reduced the degradation rate of MFA. Under the optimal condition of the treatment process with the removal efficiency of 95.3%, the molar ratio of H₂O₂ to Fe²⁺ was found to be 2.2.

3.9 | Treatment of hospital wastewater

To prepare the hospital wastewater for analyzing by HPLC, the amount of 70 µl hospital wastewater, 100 µl of (internal standard) IS, and 100 µl of 1 M phosphoric acid mixed in a 1.5 ml Eppendorf polypropylene tube for 30 s. Afterward, 1 ml dichloromethane was added to the tube and the solution vortex mixed for 3 min and centrifuged at 10,000 rpm for 3 min. The separated organic phase with the proximately volume of 700 µl was transferred to a clean glass tube and evaporated to dryness under N₂ stream at 45°C. The obtained residue dissolved in 200 µl of 70:30 (acetonitrile: water) mobile phase and a small fraction of 50 µl injected into the HPLC system.²⁸ The hospital wastewater samples analyzed before and after E-Fenton treatment process by HPLC and the obtained results revealed that the initial concentration of 314 ± 37 µg.L⁻¹ in the real hospital wastewater samples reached to zero after the treatment process.

4 | CONCLUSION

Herein, the E-Fenton treatment process as a cost-effective and efficient approach was successfully applied for degradation of MFA as a nonsteroidal anti-inflammatory drug in hospital wastewater. Response surface methodology was employed to obtain the optimum condition of the process by developing a quadratic model. ANOVA was applied to evaluate the significance and adequacy of the model. The obtained results revealed the highest efficiency of 95.3% achieved under the acidic condition of pH solution of 3, where the hydroxyl radical displayed moderately strong oxidation ability under the optimum treatment condition of MFA initial concentration of 7.0 mg L⁻¹, H₂O₂ dosage of 700 µl/L, the current density of 6.6 mA cm⁻², and reaction time of 12 min. The comparison of the obtained experimental removal efficiency with the predicted one by the model confirmed the validation of the developed treatment process. The investigations of kinetics and the presence of radical scavenger revealed that the generation of *OH radical as the main mechanism controlled the treatment process and the kinetics of MFA degradation followed pseudo-first-order kinetics model. The energy consumption for degradation of MFA under the optimum condition was found to be 0.622 kWh m⁻³.

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