



Comparison of *o*-toluidine degradation by Fenton, electro-Fenton and photoelectro-Fenton processes

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ABSTRACT

A Box–Behnken design (BBD) statistical experimental design was used to investigate the degradation of *o*-toluidine by the electro-Fenton process. This method can be used to determine the optimal conditions in multivariable systems. Fe²⁺ concentration (0.2–1.0 mM), H₂O₂ concentration (1–5 mM), pH (2–4), and current (1–4 A) were selected as independent variables. The removal efficiencies for *o*-toluidine and chemical oxygen demand (COD) were represented by the response function. Result by 2-level factorial design show that the pH and the Fe²⁺ and H₂O₂ concentrations were the principal parameters. Among the main parameters, the removal efficiencies for *o*-toluidine and COD were significantly affected by pH and Fe²⁺ concentration. From the Box–Behnken design predictions, the optimal conditions in the electro-Fenton process for removing 90.8% of *o*-toluidine and 40.9% of COD were found to be 1 mM of Fe²⁺ and 4.85 mM of H₂O₂ at pH 2. Under these optimal conditions, the experimental data showed that the removal efficiencies for *o*-toluidine and COD in the electro-Fenton process and the photoelectro-Fenton process were more than 91% and 43%, respectively, after 60 min of reaction. The removal efficiencies for *o*-toluidine and COD in the Fenton process are 56% and 27%, respectively.

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1. Introduction

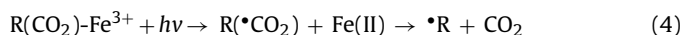
o-Toluidine is an important aromatic amine that is used in the dyestuffs and rubber industry. However, short-term exposure to *o*-toluidine may induce methaemoglobinaemia, whereas long-term or repeated exposure to *o*-toluidine could be possibly carcinogenic to humans [1]; it may cause bladder cancer [2]. It is difficult to completely treat wastewater containing *o*-toluidine because of its resistance to biodegradation. Presently, advanced oxidation processes (AOPs) have been used for wastewater treatment, particularly in cases where the contaminant species are difficult to remove by biological or physicochemical processes [3–7]. AOPs are based on the generation of a powerful oxidant, the hydroxyl radical ($\bullet\text{OH}$), which can react with most organic pollutants and then degrade them [8,9]. The Fenton process is one of the most widely used AOPs because of its low investment cost [10]. The Fenton reaction is shown below:



However, the iron sludge produced from the Fenton process requires further treatment and disposal, and this is a major disadvantage of this process. This major drawback can be resolved by coupling the Fenton process with electric discharge, the so-called “electro-Fenton (EF) process”. The advantage of the electrochemical Fenton process is that it produces much less iron sludge than the traditional Fenton process. In this process, ferric ions (Fe³⁺) are effectively electro-regenerated to ferrous ions (Fe²⁺), as shown in Eq. (2); this can be expressed in terms of current efficiency.



The capability of the electro-Fenton process has been confirmed by Harrington and Pletcher [11], with more than 90% chemical oxygen demand (COD) removal with current efficiencies higher than 50% and acceptable energy consumptions. The efficiency of the electro-Fenton process can be improved by using UV or visible light illumination in a process known as the photoelectro-Fenton (PEF) process. This improvement is due to the higher production rate of $\bullet\text{OH}$ from the photoreduction of Fe(OH)²⁺ (Eq. (3)) and the photodecomposition of complexes from Fe³⁺ reactions (Eq. (4)) [12–15]



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Normally, Fenton-type processes [16–18] are affected by the pH and initial Fe^{2+} and H_2O_2 concentrations. To determine the optimal conditions for *o*-toluidine degradation and the effect of variables on the electro-Fenton process, the Box–Behnken design (BBD) was used in this investigation. The BBD can be used to find the optimal conditions in multivariable systems [19]. The statistical design of an experiment reduces the number of experiments that must be performed and corresponding time spent and can be used to optimize the operating parameters in multivariable systems. Few studies have used BBD for the degradation of azo-dyes and organic contaminants by the photo-Fenton process [19,20]. However, there have been no studies published on the use of BBD for the degradation of *o*-toluidine by the electro-Fenton process. In this study, the optimal conditions for *o*-toluidine degradation and the effect of four variables (pH, Fe^{2+} concentration, H_2O_2 concentration and current) on the electro-Fenton process were investigated using BBD. As only several significant factors were involved in optimization, response surface methodology (RSM) was applied. Additionally, the *o*-toluidine degradation performances of ordinary Fenton, electro-Fenton and photoelectro-Fenton processes were also compared.

2. Materials and methods

2.1. Material and reactor

o-Toluidine (99.5%, Merck), hydrogen peroxide (H_2O_2 , 35%, Merck), and ferrous sulfate hepta-hydrated ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, Merck) were reagent grade and used without further purification. Fig. 1 shows the three kinds of reactors. The Fenton reactor was cylindrical stainless steel (diameter: 13 cm; height: 35 cm). The total volume of the reactor was 3.5 L. The electro-Fenton reactor, a cylindrical reactor, was operated in constant current mode. The anode was titanium net coated with $\text{RuO}_2/\text{IrO}_2$ (DSA), and the cathode was stainless steel. The DSA anode with an inside diameter of 7 cm and height of 35 cm, and the cathode had an inside diameter of 2 cm and height of 35 cm. The electrodes were connected with direct current (DC) power. In the photoelectro-Fenton reactor, a set of 6 UV lamps fixed inside a cylindrical Pyrex tube (allowing wavelengths $\lambda > 320$ nm to penetrate) were used as the irradiation source. The UV lamps were connected to the power supply E-safe, 2003, Switching Power Supply (Max. 300 W), Model: LC-B300AT.

2.2. Analysis method

In the photoelectro-Fenton experiment, synthetic wastewater containing 1 mM *o*-toluidine was prepared and then initial pH was adjusted with perchloric acid (HClO_4). After pH adjustment, a predetermined amount of catalytic ferrous sulfate was added into the solution and then the UV lights were turned on. H_2O_2 was also added in the same time to start the reaction. Additionally, in the electro-Fenton experiment, solution with 1 mM *o*-toluidine was prepared and then ferrous ions were added after the pH was adjusted to the desired value. In the meantime, the power supply was turned on, and hydrogen peroxide was added to initiate the reaction. Samples (1 mL) were taken at predetermined time intervals and were immediately injected into a tube containing sodium hydroxide solution to quench the Fenton reaction by increasing the pH to 11. The sample was then filtered (0.45 μm filter) to remove precipitates and kept for 12 h before COD analysis. This process was used to avoid quantifying the effect of the H_2O_2 concentration on the COD value. COD was analyzed by a closed reflux titrimetric method based on the standard methods [21]. The Fe^{2+} concentration was determined using the 1,10-phenanthroline method [22]. Total organic carbon was measured with an Elementar liquid TOC analyzer. The concentration of *o*-toluidine

was determined using high performance liquid chromatography (HPLC) with a Spectra system model SN4000 pump and Asahipak ODP-506D column (150 mm \times 6 mm \times 5 μm). The detection limit of *o*-toluidine was 0.005 mM or 0.535 ppm. Organic acids were analyzed using a Dionex DX-120 ion chromatograph with an Ion Pac AS11 anion column at 30 °C.

2.3. Experimental design

BBD are a class of rotatable or nearly rotatable second-order designs based on three-level incomplete factorial designs. Among all the RSM designs, BBD requires fewer runs [23]. The Design-Expert software version 7.0 (Stat-Ease, Inc., Minneapolis, USA) was used to find the optimal conditions of *o*-toluidine degradation by the electro-Fenton process. The effects of the significant factors were determined by BBD. The significant factors and the appropriate studied ranges were pH: 2–4, Fe^{2+} concentration: 0.2–1.0 mM, and H_2O_2 concentration: 1–5 mM. The concentration of *o*-toluidine was fixed at 1 mM for all experiments.

3. Results and discussion

3.1. Effect of various parameters on *o*-toluidine removal efficiency

The Fe^{2+} concentration, H_2O_2 concentration, pH and current were selected as experimental conditions for the BBD. The removal efficiencies for *o*-toluidine and COD were represented by a response function. Table 1 shows the two levels of the four factors on BBD. The values of variables, the experimental data and the results are presented in Table 2. The maximum removal rate of *o*-toluidine was 100% and the minimum was 23% (Table 2). When 1.0 mM of Fe^{2+} , 5.0 mM of H_2O_2 and 1.0 A of current at pH 2 were applied, the *o*-toluidine removal was 94.4% (run 2). However, as current increased from 1.0 A to 4.0 A, the removal of *o*-toluidine slightly increased to 100% (run 6). It was found that the amount of current was not sensitive in the applied range and therefore could be neglected. The correlation of *o*-toluidine and COD removal efficiencies obtained from BBD is shown in Table 1, where a higher correlation means that the parameter has a higher effect on *o*-toluidine and COD. The correlation can be as high as 1 or low as -1 . The result indicates that the current has a slight effect on *o*-toluidine, with a correlation of only 0.098 (Table 1). The degradation of *o*-toluidine depended on the initial concentration of Fe^{2+} and H_2O_2 , showing a high correlation in *o*-toluidine removal efficiency about 0.617 and 0.278 for Fe^{2+} and H_2O_2 concentration, respectively. The same trend was also observed in COD removal efficiency. This correlation indicates that the Fe^{2+} and H_2O_2 concentrations have a positive effect on the removal efficiencies for *o*-toluidine and COD, indicating that increasing Fe^{2+} and H_2O_2 concentrations increased the removal efficiencies for *o*-toluidine and COD. The pH has a negative effect on *o*-toluidine and COD removal, and so the removal efficiencies for *o*-toluidine and COD decreased with increasing pH of solution. From the correlation values, initial pH and the Fe^{2+} and H_2O_2 concentrations were the most significant factors that affected *o*-toluidine and COD removal. Table 3 shows the levels of significant factors of *o*-toluidine and COD removal efficiencies. Results from the experiment revealed that the maximum removal of *o*-toluidine was 91.4% and that of COD was 42% (run 1) (Table 4). The correlation values indicate that pH had the most pronounced effect on *o*-toluidine and COD removal (-0.725 for *o*-toluidine and -0.593 for COD) (Table 3). The Fe^{2+} concentration had a comparable effect on these responses, and H_2O_2 concentration had a greater effect on COD removal than the degradation of *o*-toluidine.

Fig. 2 shows the response surface plot of the effect of pH and Fe^{2+} concentration on the *o*-toluidine and COD removal efficiencies. This

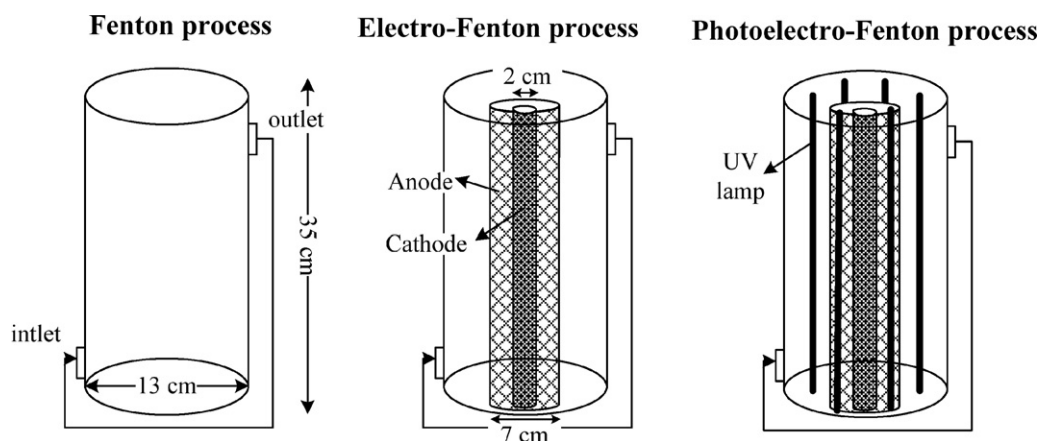


Fig. 1. The experimental reactors.

Table 1

The two levels of variables and the value of correlation on *o*-toluidine and COD removal efficiency from Box–Behnken statistical design.

Variables	Symbol	Variable level		Correlation	
		Low	High	<i>o</i> -Toluidine	COD
pH	A	2	4	−0.628	−0.517
Fe ²⁺ (mM)	B	0.2	1	0.617	0.633
H ₂ O ₂ (mM)	C	1	5	0.278	0.274
Current (A)	D	1	4	0.098	0.259

Table 2

o-Toluidine and COD removal from the two levels of variables in electro-Fenton process with 1 mM of *o*-toluidine designed by the BBD.

Run number	pH	Fe ²⁺ (mM)	H ₂ O ₂ (mM)	Current (A)	<i>o</i> -Toluidine removal (%)	COD removal (%)
1	4.0	0.2	5.0	4.0	17.0	23.0
2	2.0	1.0	5.0	1.0	94.4	57.0
3	4.0	0.2	5.0	1.0	32.0	22.0
4	4.0	1.0	5.0	4.0	56.0	33.02
5	2.0	0.2	5.0	1.0	42.0	8.0
6	2.0	1.0	5.0	4.0	100	59.5
7	2.0	1.0	1.0	1.0	66.4	33.0
8	2.0	1.0	1.0	4.0	68.5	46.0
9	4.0	1.0	1.0	4.0	45.0	34.0
10	4.0	0.2	1.0	1.0	23.0	19.0
11	2.0	0.2	5.0	4.0	74.0	38.4
12	2.0	0.2	1.0	1.0	40.0	22.5
13	4.0	0.2	1.0	4.0	26.5	27.0
14	4.0	1.0	5.0	1.0	61.4	36.0
15	2.0	0.2	1.0	4.0	56.4	34.6
16	4.0	1.0	1.0	1.0	48.0	31.0

plot shows the negative effect of pH on the removal efficiencies. The *o*-toluidine and COD removals decreased as the initial pH of the solution increased from 2.0 to 4.0 because the oxidation potential of hydroxyl radicals ($\cdot\text{OH}$) and the dissolved fraction of iron species decreased [24,25]. The results also show that increasing the Fe²⁺ concentration can enhance *o*-toluidine and COD removal efficiencies because more Fe²⁺ reacts H₂O₂ producing more $\cdot\text{OH}$.

Analysis of variance (ANOVA) tests for *o*-toluidine and COD removal were conducted to determine the suitability of the

response function and the significance of the effects of independent variables on the response function (Table 5). ANOVA indicates that the predictability of the model is at the 95% confidence level. Values of “Prob > F” less than 0.05 indicates a significant effect of the corresponding variable on the response. The result shows that the *F*-values of *o*-toluidine and COD removal were 11.10 and 8.06, respectively; imply that the model is significant. There are only 0.15% and 0.43% chances for *o*-toluidine and COD removal, respectively; that the model’s *F*-values this large could occur due to noise.

Table 3

The levels of significant factors and the value of correlation on *o*-toluidine and COD removal efficiency from BBD.

Significant factor	Symbol	Variable level			Correlation	
		Low	Center	High	<i>o</i> -Toluidine	COD
pH	A	2	3	4	−0.725	−0.593
Fe ²⁺ (mM)	B	0.2	0.6	1	0.484	0.455
H ₂ O ₂ (mM)	C	1	3	5	0.294	0.408

Table 4
o-Toluidine and COD removal from the levels of significant factors in electro-Fenton process with 1 mM of o-toluidine and 1 A designed by the BBD.

Run number	pH	Fe ²⁺ (mM)	H ₂ O ₂ (mM)	o-Toluidine removal (%)	COD removal (%)
1	2.0	0.6	5.0	91.4	42.0
2	4.0	0.6	5.0	31.2	17.6
3	2.0	1.0	3.0	75.0	36.0
4	2.0	0.2	3.0	47.4	16.4
5	2.0	0.6	1.0	63.4	30.0
6	4.0	0.6	1.0	34.0	16.0
7	3.0	0.2	5.0	51.0	24.0
8	4.0	0.2	3.0	15.0	17.0
9	3.0	0.6	3.0	60.0	32.0
10	3.0	1.0	1.0	52.0	21.0
11	3.0	0.2	1.0	42.4	16.4
12	4.0	1.0	3.0	49.4	21.2
13	3.0	1.0	5.0	78.0	36.0

In this case, pH and Fe²⁺ were significant model terms affecting percent o-toluidine and COD removal.

3.2. The prediction of optimal conditions of o-toluidine degradation by BBD

The goal of this part was to establish the optimal conditions for maximum removal of o-toluidine and COD by the electro-Fenton process. The BBD can provide an empirical relationship between the response function and the variables. The mathematical relationship between the removal of o-toluidine and the three significant variables can be approximated by quadratic polynomial equation, and the equations for the removal of o-toluidine and COD by the electro-Fenton process are shown below:

$$o\text{-toluidine removal (\%)} = 64.22 - 11.02A + 12.36B + 3.25C + 2.73AB - 1.02AC + 8.58BC - 1.17ABC \quad (5)$$

$$\text{COD removal (\%)} = 30.16 - 2.31A + 7.47B + 0.84C + 0.91AB - 2.81AC + 8.03BC - 1.81ABC \quad (6)$$

where A, B and C are pH, Fe²⁺ concentration and H₂O₂ concentration, respectively. The equations are used to calculate the removal

of o-toluidine and COD at each value of pH, Fe²⁺ concentration and H₂O₂ concentration. On the basis of the coefficients in Eqs. (5) and (6), it indicates that pH (A) and Fe²⁺ (B) concentration have negative and positive effects on o-toluidine and COD removal efficiencies, respectively. In other words, removal of o-toluidine and COD decreased with the pH (A) while increasing with Fe²⁺ (B) and H₂O₂ (C) doses. Fe²⁺ dose had a more profound effect on o-toluidine and COD removal as compared to H₂O₂. The electro-Fenton process utilizes electrochemical generation of ferrous ions from ferric ions and ferric complexes. Ferrous ions were continuously recycled electrochemically, and therefore they were not depleted during the degradation of o-toluidine. Fe²⁺ concentration has the greatest effect on removal of o-toluidine with the largest coefficient (12.36).

In this study, the removal of o-toluidine and COD were selected as “maximize” and then, Fe²⁺ and H₂O₂ concentrations and pH were used as “within the range.” Consequently, these individual goals were combined into an overall desirability function by the software to find the best optimal conditions. The final equation relationship between the response function (o-toluidine and COD removal) and the key parameters can be determined by Eqs. (7) and (8).

$$o\text{-toluidine removal (\%)} = 78.74 - 18.45 \times \text{pH} + 30.81 \times [\text{Fe}^{2+}] + 3.74 \times [\text{H}_2\text{O}_2] \quad (7)$$

Table 5
ANOVA tests for o-toluidine and COD removal by BBD.

Source	Sum of squares	df	Mean squares	F-value	p-value Prob > F	
o-Toluidine removal						
Model	7790.65	7	112.95	11.10	0.0015	Significant
A (pH)	3387.24	1	3387.24	33.78	0.0004	Significant
B (Fe ²⁺)	3271.84	1	3271.84	32.63	0.0004	Significant
C (H ₂ O ₂)	663.06	1	663.06	6.61	0.0330	
AB	1.56	1	1.56	0.016	0.9037	
AC	190.44	1	190.44	1.90	0.2055	
BC	262.44	1	262.44	2.62	0.1443	
ABC	14.06	1	14.06	0.14	0.7178	
Residual	802.07	8	100.26			
Cor Total	8592.72	15				
COD removal						
Model	1808.81	7	258.40	8.06	0.0043	Significant
A (pH)	552.25	1	552.25	17.23	0.0032	Significant
B (Fe ²⁺)	826.56	1	816.56	25.79	0.0010	Significant
C (H ₂ O ₂)	155.00	1	155.00	4.84	0.0591	
AB	52.56	1	52.56	1.64	0.2362	
AC	119.90	1	119.90	3.74	0.0891	
BC	68.89	1	68.89	2.15	0.1808	
ABC	33.64	1	33.64	1.05	0.3356	
Residual	256.41	8	32.05			
Cor Total	2065.22	15				

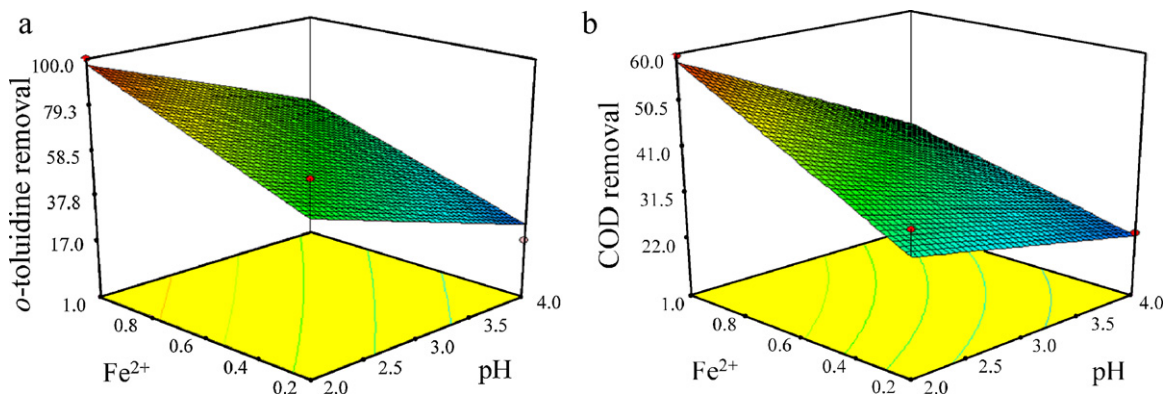


Fig. 2. Three-dimensional representation of the response surface plot of the effect of pH and Fe^{2+} concentration on (a) *o*-toluidine and (b) COD removal efficiency.

$$\text{COD removal (\%)} = 30.41 - 6.58 \times \text{pH} + 12.63 \times [\text{Fe}^{2+}] + 2.27 \times [\text{H}_2\text{O}_2] \quad (8)$$

According to Eqs. (7) and (8), at the optimal conditions of pH 2, 1 mM of Fe^{2+} and 4.85 mM of H_2O_2 , the maximum removals of *o*-toluidine and COD were 90.8% and 40.9%, respectively.

3.3. Comparison between various processes

The optimal conditions were used to investigate the removal efficiencies for *o*-toluidine and COD in the Fenton process, electro-Fenton process and photoelectro-Fenton process. The results are shown in Fig. 3. Fig. 3(a) shows that the removal efficiency for *o*-toluidine in the three processes was almost the same in the first 2 min. After 2 min, the removal of *o*-toluidine in the Fenton process was slightly increased. The removal efficiency for *o*-toluidine was approximately 56% after 60 min of reaction. However, the removal efficiencies for *o*-toluidine in the electro-Fenton process and the photoelectro-Fenton process were 91% and 99%, respectively, after 60 min of reaction. The removal of *o*-toluidine was due to the formation of $\cdot\text{OH}$ via Eq. (1). Moreover, Fe^{3+} in the solution was able to regenerate inside the reactor when electric discharge and UV irradiation were used, allowing numerous Fe^{2+} react with H_2O_2 to generate $\cdot\text{OH}$. Ferrous ions are not depleted during the oxidation reaction, as shown in Eqs. (2)–(4). Therefore, the electro-Fenton process and the photoelectro-Fenton process can enhance the oxidation rate of *o*-toluidine. The same result was found for COD removal efficiency, as shown in Fig. 3(b). The removal efficiencies for COD in the three processes were similar in the first 2 min. However, the removal efficiency of COD was significantly different between the various processes after two min of reaction. The removal efficiencies for COD were 27% for the Fenton process, 45% for the electro-Fenton process and 43% for the photoelectro-Fenton process after 60 min of reaction.

Fig. 4 shows that maleic and oxalic acids were identified as the intermediates from the oxidation of *o*-toluidine. Maleic and oxalic acid were found in the electro-Fenton and the photoelectro-Fenton processes after 1 min of reaction and the concentrations increased with time. The decrease in maleic acid occurred in the electro-Fenton and the photoelectro-Fenton processes after 45 and 10 min, respectively (Fig. 4(a)). The decrease in oxalic acid occurred in the electro-Fenton and the photoelectro-Fenton processes after 30 and 45 min, respectively (Fig. 4(b)). However, maleic and oxalic acids were found after 10 min of reaction in the Fenton process and their concentrations increased with time until the end of the reaction. The concentration of maleic and oxalic acid were generated

quickly because of the increased concentration of $\cdot\text{OH}$ and degradation of *o*-toluidine. This result indicates that the electro-Fenton and the photoelectro-Fenton processes have higher efficiencies to degrade *o*-toluidine than the traditional Fenton process. The accumulation of intermediates in the photoelectro-Fenton process was lower than in the electro-Fenton process (Fig. 4(a) and (b)). Moreover, the removal efficiency for TOC in the electro-Fenton and the photoelectro-Fenton processes were 12% and 31%, respectively (Fig. 4(c)). These phenomena show that the intermediates were efficiently mineralized by the action of UV light in the photoelectro-Fenton process.

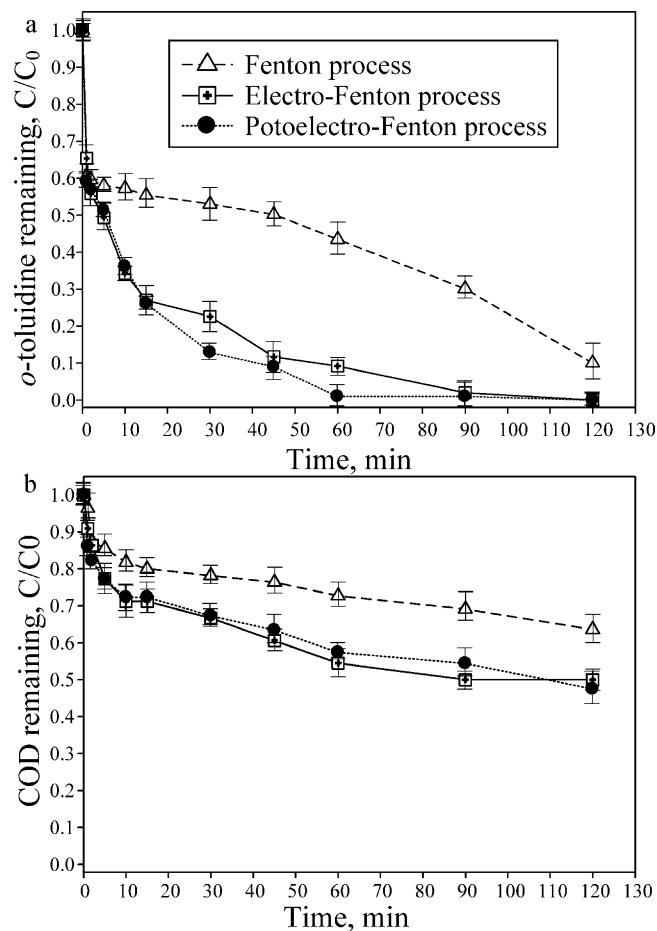


Fig. 3. Comparison between various processes on (a) *o*-toluidine removal and (b) COD removal efficiency. Experimental conditions: 1 mM of *o*-toluidine, 1 mM of Fe^{2+} and 4.85 mM of H_2O_2 at pH 2. Each data has twice samplings.

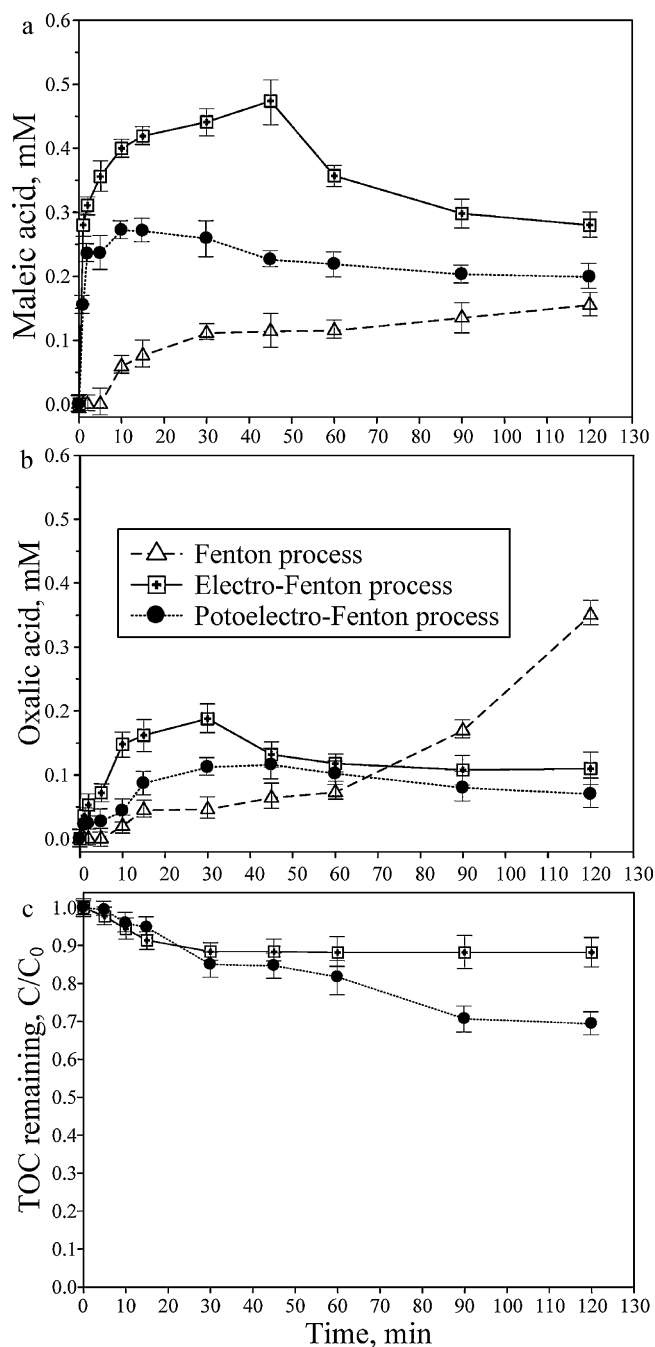


Fig. 4. The concentrations of (a) maleic acid, (b) oxalic acid and (c) TOC during the degradation of *o*-toluidine. Each data has twice samplings.

4. Conclusions

This study investigated the optimization of *o*-toluidine treatment by the electro-Fenton process applying the Box–Behnken experimental design methodology. The results showed that pH and Fe^{2+} concentrations were important factors in the removal efficiencies for both *o*-toluidine and COD. The removal efficiencies for *o*-toluidine and COD increase with decreasing pH and increasing Fe^{2+} concentration. The optimal conditions for the maximum removal of *o*-toluidine and COD (90.8% and 40.9%, respectively, from prediction) were 1 mM of Fe^{2+} and 4.85 mM of H_2O_2 at pH 2. Obviously, the calculating *o*-toluidine and COD removals applying the predicted conditions approaches the experimental

results with 91% of *o*-toluidine removal and of 45% COD removal in the electro-Fenton process, indicating the reliability of the methodology used. Both electric discharge and UV irradiation could significantly enhance the degradation of *o*-toluidine. Therefore, more intermediates, such as maleic and oxalic acids, were derived during the beginning of the electro-Fenton and the photoelectro-Fenton processes than in the traditional Fenton process.

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