



A statistical experimental design to determine *o*-toluidine degradation by the photo-Fenton process

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ABSTRACT

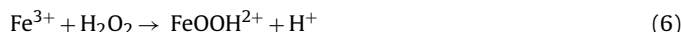
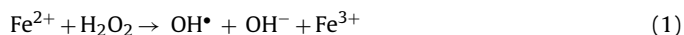
o-Toluidine is used primarily in the manufacture of dyestuffs, and also in the production of rubber, chemicals, and pesticides and as a curing agent for epoxy resin systems. It is considered to be toxic and carcinogenic. This study uses the Box–Behnken statistical experiment design to investigate the degradation of *o*-toluidine by the photo-Fenton process. The effects of ferrous ion dosage, hydrogen peroxide concentration and UVA irradiation were selected as factors in the Box–Behnken design experiment, while, *o*-toluidine and COD removal efficiency were considered as response functions. Results show that ferrous ion and hydrogen peroxide concentrations were the main parameters affecting the *o*-toluidine and COD removal, while the number of UVA lamps had a slight effect on the reaction. From the Box–Behnken statistical design prediction, the optimum condition for removing 100% of *o*-toluidine and 74% of COD was 1.2 mM of ferrous ion, 8 mM of hydrogen peroxide and UVA 85.7 W/m³ at pH 3.

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1. Introduction

o-Toluidine (OT) is a monosubstituted aniline used as an intermediate in the dyeing industry with a number of uses in other fields such as rubber processing, chemical production, pesticide manufacture and pharmaceutical production [1]. It has been in production for over 100 years [2]. It is a carcinogen in mice and rats and has been classified as a human carcinogen [3]. *o*-Toluidine can cause urinary bladder cancer and/or renal pelvis cancer [4]. These hazardous properties of *o*-toluidine necessitate the treatment of contaminated wastewater to prevent harm to life forms and the natural environment, generally by powerful oxidation methods.

The Fenton process is one of the most practical advanced oxidation technologies available due to its generation of hydroxyl radicals that can oxidize many kinds of chemicals. The Fenton reaction involves several reactions, which can be described by Eqs. (1)–(8) [5]:



These reactions show that hydrogen peroxide may be consumed when it reacts with Fe²⁺, as shown in Eq. (1), producing hydroxyl radicals that will degrade organic compounds through Eq. (3). Hydrogen peroxide can also react with Fe³⁺ via Eq. (6), but the major drawback of Fenton reaction is the production of Fe(OH)₃ sludge that requires further separation and disposal. One of the alternative processes to minimize this sludge and improve the degradation efficiency uses UV irradiation, the so-called “photo-Fenton process”. Applying UV irradiation to Fenton’s reaction can enhance the oxidation rate of organic compounds by the photoreduction of produced ferric ions (Fe³⁺) and ferric complexes. Ferrous ions are recycled continuously by irradiation, and so they are not depleted during the course of the oxidation reaction, as shown in Eq. (7). Moreover, the production of hydroxyl radicals is limited only by the availability of UV/vis radiation and H₂O₂. This route facilitates the formation of hydroxyl radicals and promotes the degradation rates of organic compounds (Eq. (8)) [6].



In order to determine the optimum conditions for *o*-toluidine degradation and the effect of three variables on the photo-Fenton process, the Box–Behnken statistical design was applied in this study. The classical approach of changing one variable at a time

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Table 1The 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 –1	Center 0	High +1	<i>o</i> -Toluidine	COD
UVA irradiation (W/m ³)	A	38.1	76.2	114.3	0.087	0.075
Fe ²⁺ (mM)	B	0.1	1	1.9	0.535	0.468
H ₂ O ₂ (mM)	C	1	5	9	0.529	0.603

to study the effect of variables on the response is a time consuming method, particularly, for multivariable systems and also when more than one response is considered. In contrast, statistical design of an experiment reduces the number of experiments to be performed and can be used to optimize the operating parameters in multivariable systems. Response surface methodology (RSM) is used when only several significant factors are involved in optimization. To our knowledge, there have been no studies published on the use of the Box–Behnken experimental design on the degradation of *o*-toluidine by photo-Fenton process. Moreover, this method can be used to find the optimum condition for operating parameters in multivariable systems [7]. The three variables here were UVA irradiation, ferrous ion concentration, and hydrogen peroxide concentration.

2. Materials and methods

2.1. Photo-Fenton reactor and chemicals

All the photo-Fenton experiments were carried out using batch mode with a total reaction time of 2 h using an acrylic reactor of 15 cm × 21 cm × 20 cm, and the working volume was 5 L. The reactor was equipped with two mixers to ensure proper agitation, and a pH meter. The UVA source of 0.06 W/UVA lamps (Sunbeamtech.com) fixed inside a cylindrical Pyrex tube (allowing wavelengths $\lambda > 320$ nm to penetrate) was turned on to initiate the reaction. In addition to all the experimental conditions mentioned above, UV light with maximum wavelength of 360 nm was irradiated inside the reactor, supplying a photoionization energy input to the solution at the maximum of 0.72 W/12 UVA lamps. The intensity of the incident light inside the solution was 8.3×10^{-7} Einstein dm⁻³ min⁻¹.

All chemicals were prepared using de-ionized water from a Millipore system with a resistivity of 18.2 M Ω cm. *o*-Toluidine (99.5%), perchloric acid (70–72%), ferrous sulfate (99.5–102%) and hydrogen peroxide (35–36.5%) were purchased from MERCK. Sodium hydroxide (99%) was purchased from Riedel-da Haën.

Synthetic wastewater containing 1 mM of *o*-toluidine was dissolved in de-ionized water and then initial pH was adjusted with perchloric acid. According to the literature review, the acidic pH level around 3 are usually optimum for Fenton oxidation, therefore in this study, pH 3 was used in all experiment [8,9]. After pH adjustment, a calculated amount of ferrous sulfate was added as the source of ferrous ions and then the UVA lights were turned on. After that, H₂O₂ was added to the reactor to start the reaction. At selected time intervals, 1 mL of reaction mixture was taken and immediately injected into a tube containing 9 mL of NaOH (0.1N) solution to stop the reaction. The samples were then filtered using membranes with 0.2 μ m pore size to remove the precipitates formed, and kept for 12 h before chemical oxygen demand (COD) analysis. This step was carried out to correctly quantify the effect of the concentration of hydrogen peroxide on the COD value. Samples were then analyzed for COD and *o*-toluidine remaining. COD was determined using the closed-reflux titrimetric method based on standard methods [10]. The removal of *o*-toluidine was determined using a high performance liquid chromatography (HPLC) with Spectra SYSTEM model SN4000 pump and Asahipak ODP-506D column (150 mm × 6 mm × 5 μ m) where the mobile phase was 60% acetonitrile with 40% DI water. The detection limit of HPLC instrument on *o*-toluidine is 0.005 mM or equal to 0.535 ppm. All experimental scenarios were duplicated.

2.2. Design experiment

Box–Behnken designs (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 [11]. The Design-Expert software version 7.0 (Stat-Ease, Inc., Minneapolis, USA) was used for determining the optimum condition of *o*-toluidine degradation by the photo-Fenton process. The effects of significant factors were determined by BBD. The optimization procedure involves studying the response of statistically designed combination, estimating the coefficients by fitting experimental data to the response functions and predicting the response

Table 2*o*-Toluidine and COD removal in photo-Fenton process designed by the Box–Behnken program.

Run number	UVA irradiation (W/m ³)	Fe ²⁺ (mM)	H ₂ O ₂ (mM)	Fe ²⁺ :H ₂ O ₂	OT removal (%)	COD removal (%)
1	38.1 (–1)	0.1 (–1)	5.0 (0)	0.1:5	27.26	25.00
2	114.3 (+1)	0.1 (–1)	5.0 (0)	0.1:5	57.27	31.37
3	38.1 (–1)	1.9 (+1)	5.0 (0)	1.9:5	100.00	46.43
4	114.3 (+1)	1.9 (+1)	5.0 (0)	1.9:5	100.00	51.67
5	38.1 (–1)	1.0 (0)	1.0 (–1)	1:1	43.88	30.00
6	114.3 (+1)	1.0 (0)	1.0 (–1)	1:1	43.31	30.36
7	38.1 (–1)	1.0 (0)	9.0 (+1)	1:9	100.00	70.49
8	114.3 (+1)	1.0 (0)	9.0 (+1)	1:9	100.00	73.02
9	76.2 (0)	0.1 (–1)	1.0 (–1)	0.1:1	32.40	23.40
10	76.2 (0)	1.9 (+1)	1.0 (–1)	1.9:1	43.34	39.29
11	76.2 (0)	0.1 (–1)	9.0 (+1)	0.1:9	43.07	32.00
12	76.2 (0)	1.9 (+1)	9.0 (+1)	1.9:9	100.00	66.67
13	76.2 (0)	1.0 (0)	5.0 (0)	1:5	100.00	62.07
14	76.2 (0)	1.0 (0)	5.0 (0)	1:5	100.00	62.75
15	76.2 (0)	1.0 (0)	5.0 (0)	1:5	100.00	62.26
16	76.2 (0)	1.0 (0)	5.0 (0)	1:5	100.00	62.00
17	76.2 (0)	1.0 (0)	5.0 (0)	1:5	100.00	62.50

of fit model [7]. The significant factors and the appropriate studied ranges were UVA light from 38.1 to 114.3 W/m³, concentration of Fe²⁺ from 0.1 to 1.9 mM and concentration of H₂O₂ from 1 to 9 mM. The concentration of *o*-toluidine was fixed as 1 mM for all experiments.

3. Results and discussions

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

In this study, the three important factors on photo-Fenton process, including UVA irradiation, ferrous ion concentration and hydrogen peroxide concentration were selected as factors in BBD. For a response function, *o*-toluidine and COD removal efficiencies were chosen.

Table 1 shows the levels of the three factors on BBD. The low, center and high levels for each variable are designated as –1, 0 and +1, respectively. The values of variables, the experimental data and the result are presented in Table 2 for all experiments. Seventeen experimental runs were performed, including five replications at the center point (0, 0, 0).

Results from the BBD experiments, as shown in Table 2, reveal that the maximum removal rate of *o*-toluidine was 100% and the minimum was 27%. It was found that increasing ferrous ion concentration increased *o*-toluidine removal efficiency. When 0.1 mM of ferrous ions and 5 mM of hydrogen peroxide were applied, the *o*-toluidine removal was only 27% (run number 1). However, by increasing Fe²⁺ concentration from 0.1 to 1.9 mM, the *o*-toluidine removal increased to 100%, showing that ferrous ions have a significant effect on *o*-toluidine degradation.

The results also show that increasing the UVA irradiation can improve degradation efficiency. When 0.1 mM of Fe²⁺, H₂O₂ 5 mM and UVA 38.1 W/m³ were applied, the *o*-toluidine removal was 27% (run number 1). Increasing the UVA irradiation from 38.1 to 114.3 W/m³ enhanced the *o*-toluidine removal efficiency (run number 2). Moreover, the results also reveal that increasing H₂O₂ concentration improved OT removal efficiency. When 1.9 mM of Fe²⁺ and 1 mM of H₂O₂ with UVA 76.2 W/m³ were used, the OT removal was 43% (run number 10). Furthermore, increasing H₂O₂ concentration from 1 to 9 mM increased the OT removal efficiency to 100% (run number 12). This was because more H₂O₂ can react with Fe²⁺ and then produce more hydroxyl radicals. The results also showed that Fe²⁺:H₂O₂ is one of the important parameter. The removal efficiency of *o*-toluidine was 100% when Fe²⁺:H₂O₂ was 1:5, 1:9, 1.9:5 and 1.9:9. However, when Fe²⁺:H₂O₂ was 0.1:1, 0.1:5, 0.1:9, 1:1 and 1.9:1 can remove only 27.26–57.27% of *o*-toluidine. This means that Fe²⁺:H₂O₂ is a significant variable. Ferrous ions seem to be the limited factor in Fe²⁺:H₂O₂ molar ratio. When fer-

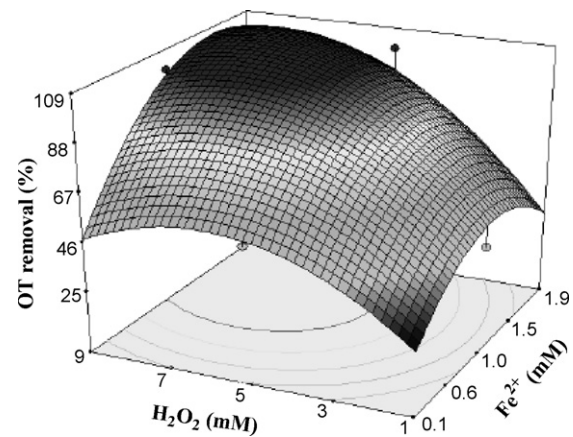


Fig. 1. Three-dimensional representation of the response surface plot of the effect of Fe²⁺ and H₂O₂ concentration on *o*-toluidine removal efficiency.

rous ions was only 0.1, the removal efficiency of *o*-toluidine was very low. However, when increasing ferrous ions to 1 and 1.9, the removal efficiency was higher than that of 0.1. Moreover, increasing hydrogen peroxide ratio also increased the removal efficiency as shown in Table 2.

The correlation of *o*-toluidine removal efficiency obtained from BBD is shown in Table 1, where a higher correlation means that the parameter has a higher effect on *o*-toluidine. The correlation can be as high as 1 or low as –1. The results indicate that the degradation of *o*-toluidine depended on the initial concentration of Fe²⁺ and H₂O₂, showing a high correlation in *o*-toluidine removal efficiency about 0.535 and 0.529 for Fe²⁺ and H₂O₂ concentration, respectively. The correlation indicates that concentrations of ferrous ion and hydrogen peroxide have a positive effect on *o*-toluidine removal efficiency, and so increasing ferrous ion and hydrogen peroxide concentration increased the *o*-toluidine removal efficiency. This is due to the large number of hydroxyl radical that can be produced from the reaction between ferrous ion and hydrogen peroxide. The UVA irradiation shows a slight effect on the *o*-toluidine removal, with a correlation of only 0.087. However, it also means that increasing the UVA irradiation can slightly increase the *o*-toluidine degradation efficiency.

Fig. 1 demonstrates the response surface plot of the effect of ferrous ion and hydrogen peroxide concentration on the *o*-toluidine removal efficiency at pH 3 when using UVA 114.3 W/m³. This shows the positive effect of ferrous ion and hydrogen peroxide concentration on the *o*-toluidine removal. Using 1 mM of H₂O₂ and 0.1 mM of Fe²⁺ can remove 32% of *o*-toluidine in 2 h. The results also show that increasing both ferrous ion and hydrogen peroxide concentra-

Table 3
ANOVA test for *o*-toluidine removal by Box–Behnken design.

Source	Sum of squares	df	Mean square	F-Value	p-Value	Prob > F
Model	14,148.06	9	1572.01	16.55	0.0006	
A (UVA)	112.50	1	112.50	1.18	0.3125	Significant
B (Fe ²⁺)	4232.00	1	4232.00	44.55	0.0003	Significant
C (H ₂ O ₂)	4140.50	1	4140.50	43.58	0.0003	Significant
AB	225.00	1	225.00	2.37	0.1677	
AC	0.000	1	0.000	0.000	1.0000	
BC	529.00	1	529.00	5.57	0.0504	
A2	151.58	1	151.58	1.60	0.2470	
B2	2227.37	1	2227.37	23.45	0.0019	Significant
C2	2131.58	1	2131.58	22.44	0.0021	Significant
Residual	665.00	7	95.00			
Lack of Fit	665.00	3	221.67			
Pure error	0.000	4	0.000			
Corr total	14,813.06	16				

tions can enhance the removal efficiency. The *o*-toluidine removal can increase to 100% when using 1 mM of ferrous ion and 5 mM of hydrogen peroxide.

As the concentration of H_2O_2 increased, the degradation of *o*-toluidine also increased because the amount of oxidant present in the reaction system is higher. However, the radical-scavenging reaction will occur at the higher hydrogen peroxide concentration, reducing treatment efficiency as describe in Eq. (4) [12].

For ferrous ion concentration, the removal efficiency of *o*-toluidine increased with increased ferrous ion concentration, because more ferrous ions can react with hydrogen peroxide and produce hydroxyl radicals. Moreover, in the presence of UVA irradiation, the ferrous ions will be regenerated during the photo-Fenton process in Eqs. (7) and (8). However, too many ferrous ions inhibit the degradation of *o*-toluidine via Eq. (2).

Analysis of variance (ANOVA) test were also conducted and the results are shown in Table 3, indicating that the predictability of the model is at 95% confidence level. The model predictions were in good correlation with the experimental data ($R^2 = 0.9551$). The Model *F*-value of 16.55 implies the model is significant, since there is only a 0.06% chance that a Model *F*-value this large could occur due to noise. Values of “Prob > *F*” less than 0.0500 indicate model terms are significant. In this case B, C, B^2 , C^2 are significant model terms. Values greater than 0.1000 indicate the model terms are not significant.

3.2. Effect of various parameters on COD removal efficiency

Table 2 shows the COD removal efficiency by various experimental conditions by BBD. The experiment show that the maximum COD removal was 73% using 1 mM of Fe^{2+} , 9 mM of H_2O_2 and UVA 114.3 W/m³ (run number 8); whereas the minimum COD removal was 23%, using 0.1 mM of Fe^{2+} , 1 mM of H_2O_2 and UVA 76.2 W/m³ (run number 9). The results reveal that increasing ferrous ion concentration improved COD removal efficiency. When 0.1 mM of ferrous ion and 9 mM of hydrogen peroxide were applied, the COD removal was only 32% (run number 11). However, increasing Fe^{2+} concentration from 0.1 to 1.9 mM increased COD removal to 67% (run number 12), indicating that ferrous ions have a significant effect on COD removal. The results also show that increasing UVA irradiation can improve degradation efficiency. Additionally, the results reveal that increasing H_2O_2 concentration significantly improved COD removal efficiency [13]. When 1 mM of Fe^{2+} and 1 mM of H_2O_2 with UVA 114.3 W/m³ were applied, the COD removal was 30% (run number 6). Increasing H_2O_2 concentration from 1 to 9 mM raised the COD removal efficiency to 73% (run number 8).

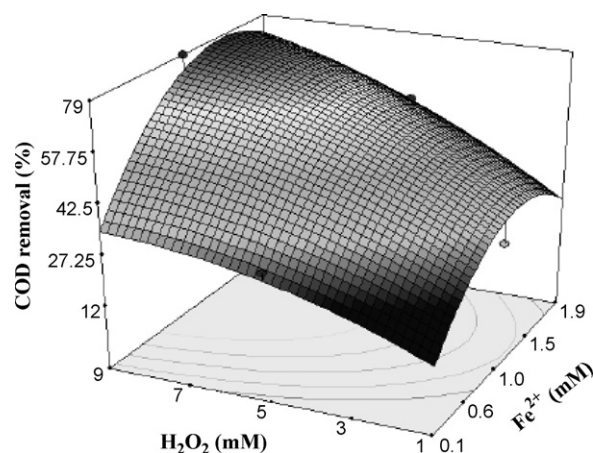


Fig. 2. Three-dimensional representation of the response surface plot of the effect of Fe^{2+} and H_2O_2 concentration on COD removal efficiency.

The correlation of COD removal efficiency obtained from BBD is shown in Table 1. The COD removal efficiency depended on the initial concentrations of H_2O_2 and of Fe^{2+} , which gave the high positive effect. It can be seen that an increased initial concentration of ferrous ion and hydrogen peroxide concentration can enhance the COD removal. Additionally, it can be concluded from the data that hydrogen peroxide have greater effect on the COD removal since the correlation number was 0.603, which is higher than the other factor. Effect of Fe^{2+} : H_2O_2 molar ratio was followed the same trend as *o*-toluidine removal efficiency. The results also showed that the removal efficiency of COD was 46–73% when Fe^{2+} : H_2O_2 molar ratio was 1:5, 1:9, 1.9:5 and 1.9:9. However, when Fe^{2+} : H_2O_2 molar ratio was 0.1:1, 0.1:5, 0.1:9, 1:1 and 1.9:1 can remove only 25–39% of COD.

Fig. 2 shows the response surface plot of ferrous ion and hydrogen peroxide concentration on COD removal efficiency at pH 3 and UVA 114.3 W/m³. It is clear that both factors have a significant effect on COD removal. As mentioned above, the COD removal increased as the ferrous ion and hydrogen peroxide concentration increased. However, using excess amounts of Fe^{2+} and H_2O_2 has a negative effect on COD removal since they could cause a scavenging effect on the hydroxyl radicals and reduce the removal efficiency. The COD removal efficiencies from BBD experiments were between 23 and 73%. The results show that Fenton's reagent (Fe^{2+} and H_2O_2) was the most important factor affecting on the COD removal. As the concentration of H_2O_2 increased, the degradation of COD also increased, because there was more oxidant present in the reaction system. However, the radical-scavenging reaction occurred at

Table 4
ANOVA test for COD removal by Box–Behnken design.

Source	Sum of squares	df	Mean square	<i>F</i> -Value	<i>p</i> -Value	Prob > <i>F</i>
Model	4658.52	9	517.61	12.67	0.0015	Significant
A (UVA)	28.13	1	28.13	0.69	0.4341	
B (Fe^{2+})	1081.13	1	1081.13	26.47	0.0013	Significant
C (H_2O_2)	1800.00	1	1800.00	44.06	0.0003	Significant
AB	0.000	1	0.000	0.000	1.0000	
AC	2.25	1	2.25	0.055	0.8212	
BC	90.25	1	90.25	2.21	0.1808	
A2	189.01	1	189.01	4.63	0.0685	
B2	1245.64	1	1245.64	30.49	0.0009	Significant
C2	103.17	1	103.17	2.53	0.1560	
Residual	285.95	7	40.85			
Lack of Fit	284.75	3	94.92	316.39	<0.0001	Significant
Pure error	1.20	4	0.30			
Total (corr)	4944.47	16				

Table 5
Predicted optimum condition for removing *o*-toluidine and COD by photo-Fenton process.

Experimental variables			Response functions			
UVA irradiation (W/m ³)	Fe ²⁺ (mM)	H ₂ O ₂ (mM)	<i>o</i> -Toluidine removal (%)		COD removal (%)	
			Predicted result	Actual result	Predicted result	Actual result
85.7	1.2	8.0	100.0	100.0	74.0	71.4

the higher hydrogen peroxide concentration, reducing treatment efficiency, as describe in Eq. (4) [5].

The analysis of variance (ANOVA) test for percent COD removal was conducted and results are presented in Table 4 to determine the suitability of the response function and the significance of the effects of independent variable on the response function. The *F*-value of 12.67 implies that the model is significant. ANOVA indicates that the predictability of the model is at the 95% confidence level. The model predictions are in good correlation with the experimental data ($R^2 = 0.9422$). There is only a 0.15% chance that a Model *F*-value this large could occur due to noise. Values of “Prob > *F*” less than 0.05 indicate a significant effect of the corresponding variable on the response. In this case B, C, B² were significant model terms affecting percent COD removal. Values greater than 0.10 indicate the model terms are not significant. The “Lack of Fit *F*-value” of 316.39 implies the Lack of Fit is significant. There is only a 0.01% chance that a “Lack of Fit *F*-value” this large could occur due to noise.

3.3. The prediction of optimum condition of *o*-toluidine degradation by BBD

The main objective of this part was to determine the optimum condition for maximum removal of *o*-toluidine and COD by the photo-Fenton process. The Box–Behnken experiment design 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 a quadratic polynomial equation, and the equations for the removal of *o*-toluidine and COD by photo-Fenton process are shown below:

$$\begin{aligned} \textit{o-Toluidine removal (\%)} = & +100.00 + 3.75A + 23.00B + 22.75C \\ & - 7.50AB + 0.000AC + 11.50BC \\ & - 6.00A^2 - 23.00B^2 - 22.50C^2 \end{aligned} \quad (9)$$

$$\begin{aligned} \text{COD removal (\%)} = & +62.40 + 1.88A + 11.63B + 15.00C + 0.000AB \\ & + 0.75AC + 4.75BC - 6.70A^2 - 17.20B^2 \\ & - 4.95C^2 \end{aligned} \quad (10)$$

where A, B and C are UVA irradiation (W/m³), Fe²⁺ (mM), and H₂O₂ (mM), respectively. The equations are used to calculate the *o*-toluidine and COD removal at each value of UVA irradiation, Fe²⁺ and H₂O₂ concentration. Each model contains one value, three linear (A, B, C), three quadratic (A², B², C²), and three interaction (AB, AC, BC) terms. The coefficients of the response functions for different response functions were determined by correlating the experimental data with the response functions using a Stat-Ease regression program. The response function coefficients (Eq. (9)) indicate that UVA irradiations, especially Fe²⁺ and H₂O₂ concentrations have positive effects on *o*-toluidine removal efficiency. In other words, *o*-toluidine removal efficiency increases with increasing ferrous ion and hydrogen peroxide concentrations. Ferrous ion concentration has the greatest effect on *o*-toluidine removal with the largest coefficient (23.00). The response function for COD

removal efficiency (Eq. (10)) indicates that UVA irradiation has a slightly positive effect, but Fe²⁺ and especially H₂O₂ concentrations have significant positive effects on COD removal efficiency. Thus COD removal efficiency increased with increasing the hydrogen peroxide and ferrous ion doses.

For the optimization process, the desired goals for each variable and response should be established first. In this study, *o*-toluidine and COD removal were chosen as “maximize”. At the same time, UVA irradiation, ferrous ion and hydrogen peroxide were selected as “within the range”. Then these individual goals were combined into an overall desirability function by the software for optimization to find the best optimum conditions.

At the optimum condition of UVA 85.7 W/m³, 1.2 mM of Fe²⁺ and 8 mM of H₂O₂, the maximum *o*-toluidine and COD removals were predicted to be 100 and 74%, respectively, as shown in Table 5. Additionally, the removal efficiency by using this predicted optimum condition was 100% for *o*-toluidine removal and 71.4% for COD removal. The difference between observed value and the predicted value was not significant in this study. This predicted optimum condition is suggested when the UVA irradiation

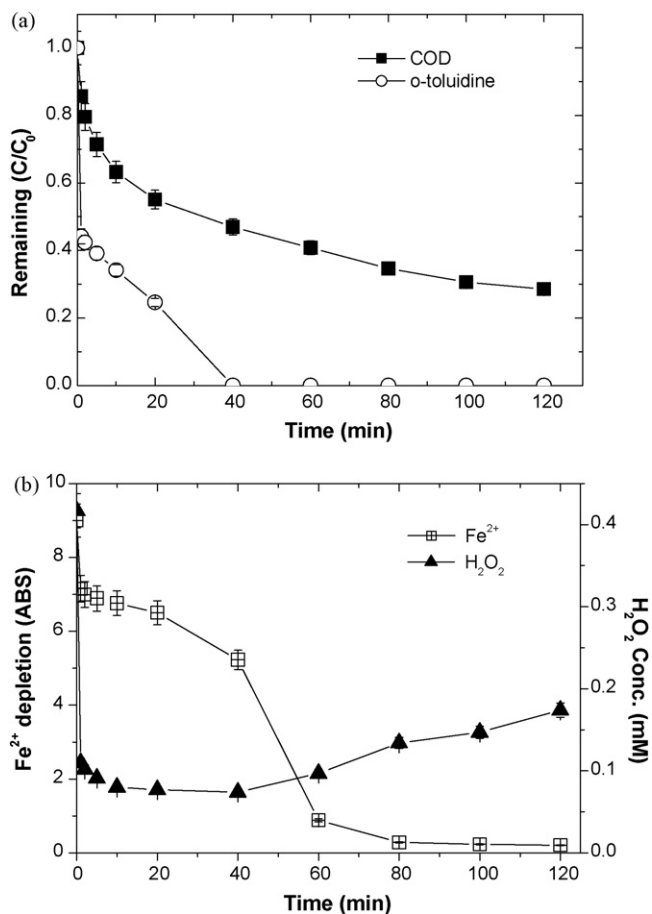


Fig. 3. The results from predicted optimum condition (a) *o*-toluidine and COD removal efficiency and (b) Fe²⁺ and H₂O₂ remaining. [OT] = 1 mM, [Fe²⁺] = 1.2 mM, [H₂O₂] = 8 mM, UVA = 85.7 wt/m³ at pH 3.

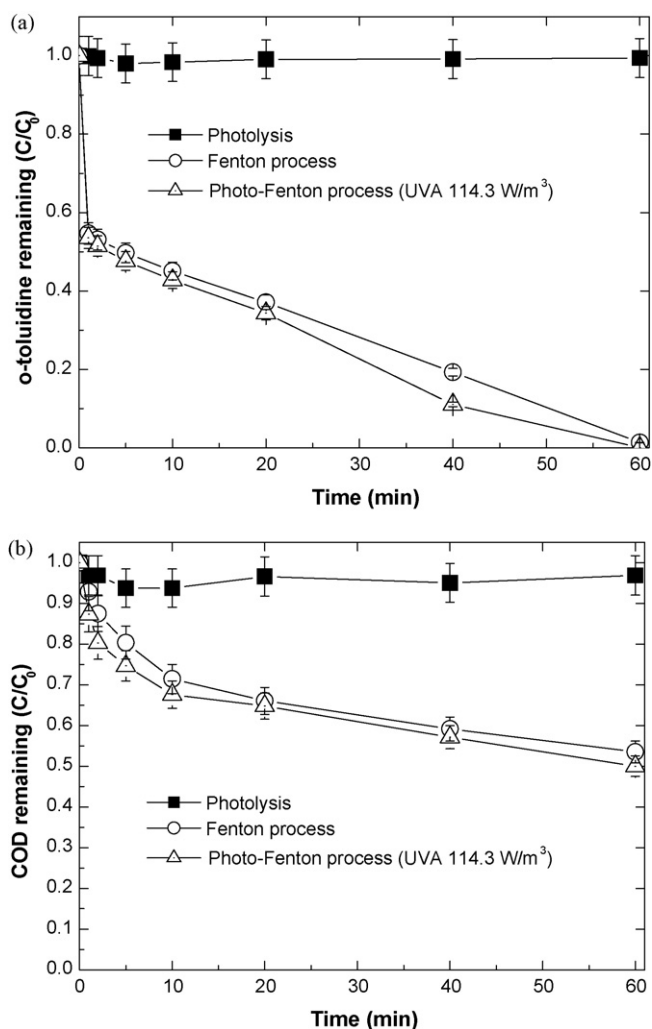


Fig. 4. Comparison between various processes on (a) OT removal and (b) COD removal efficiencies. [OT] = 1 mM, [Fe²⁺] = 1 mM, [H₂O₂] = 5 mM, pH = 3.

in range of 38.1–114.3 W/m³, ferrous ion concentration in range of 0.1–1.9 mM and hydrogen peroxide in range of 1–9 mM at pH 3 were applied.

Fig. 3 shows the results from the predicted optimum condition. The results show that *o*-toluidine was rapidly degraded in the first 5 min, after that the reaction rate was slower but it continued degrading to 100% of *o*-toluidine in 40 min. COD was also decreased with time, but at a lower rate, as shown in Fig. 3(a). For the Fenton's reagent, both ferrous ion and hydrogen peroxide decreased with time. However, for ferrous ion, the amount of ferrous ions increased after 40 min, due to the regeneration of ferrous ions from UVA irradiation, as shown in Eqs. (7) and (8). The hydrogen peroxide decreased with reaction time, and almost no hydrogen peroxide was found after 80 min (Fig. 3(b)).

3.4. Comparison between various processes

This part of the experiment aimed to show the effect of UVA irradiation, Fenton's reagent and photo-Fenton process on the *o*-toluidine degradation. The conditions used in this part were as follows: 1 mM of *o*-toluidine, 1 mM of Fe²⁺, 5 mM of H₂O₂ and pH 3. The results are shown in Fig. 4.

Fig. 4(a) shows that UVA irradiation alone can only slightly remove *o*-toluidine at about 1–2%. However, Fenton's reagent can remove 98% of *o*-toluidine with 1 mM of ferrous ion and 5 mM of

hydrogen peroxide. Moreover, 100% removal of *o*-toluidine can be achieved by applying photo-Fenton process (114.3 W/m³) for only 60 min. This means that UVA irradiation alone had no significant effect on *o*-toluidine removal. However, the removal of *o*-toluidine was due to the formation of the hydroxyl radicals produced from Fe²⁺ and H₂O₂ (Fenton's reagent) via Eq. (1). Moreover, with the assistance of UVA irradiation, the removal efficiency is higher than that without UVA irradiation as shown in Fig. 4(a). This is because ferrous ions in the solution were able to regenerate inside the reactor when UVA irradiation was applied, so more ferrous ions can react with hydrogen peroxide to produce hydroxyl radicals [14,15]. Thus applying UVA irradiation to the Fenton reaction can enhance the oxidation rate of organic compounds. This process utilizes the photoreduction of produced ferric ions (Fe³⁺) and ferric complexes. Ferrous ions will be continuously recycled by irradiation, and therefore they are not depleted during the course of the oxidation reaction, as shown in Eqs. (7) and (8).

The same result was found for COD removal efficiency, as shown in Fig. 4(b). UVA irradiation can remove almost no COD, but the Fenton process can remove 47% of COD. When UVA irradiation was combined with the Fenton process (photo-Fenton process), the COD removal efficiency was the highest (50%). The results indicate that the hydroxyl radicals from Fenton's reaction were responsible for the removal of *o*-toluidine and COD. Additionally, the removal efficiency of *o*-toluidine and COD can be improved by including UVA irradiation into the reactor.

4. Conclusion

The study uses the Box–Behnken statistical experiment design to show that *o*-toluidine can be completely degraded by the photo-Fenton process. The ferrous ion and hydrogen peroxide concentrations were found to be the most important factors in both *o*-toluidine and COD removal efficiency. UVA irradiation alone showed a slight improvement of *o*-toluidine and COD removal efficiency. Normally, the degradation efficiency increased with increasing ferrous ion and hydrogen peroxide concentrations. Furthermore, the COD removal also increased with increased concentration of ferrous ions and hydrogen peroxide. The optimum conditions for the maximum *o*-toluidine removal (100% according to both prediction and observation) and the maximum COD removal (73.8% from prediction and 71.4% from observation) were UVA 85.7 W/m³, 1.2 mM of Fe²⁺ and 8 mM of H₂O₂. Predictions for the *o*-toluidine and COD removal corresponded closely with the experimental results, indicating the reliability of the methodology used. The results showed that the hydroxyl radical from Fenton's reaction was responsible for removing of *o*-toluidine and COD. In addition, the removal efficiency of *o*-toluidine and COD can be improved by applying UVA irradiation.

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