Photo-Fenton pretreatment of carbofuran – Analyses via experimental design, detoxification and biodegradability enhancement

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ABSTRACT

The central composite design (CCD) and response surface methodology (RSM) were employed to evaluate the effect of H_2O_2 dosage rate (1–10 mg L^{-1} min^{-1}) and Fe^{3+} dosage (1–100 mg L^{-1}) in the photo-Fenton treatment of carbofuran and to develop the second-order polynomial equations in terms of carbofuran and dissolved organic carbon (DOC) removals and BOD_5/DOC ratio with different reaction times. Both H_2O_2 dosage rate and Fe^{3+} dosage have significant effects on the dependable variables. Based on the results of carbofuran removal and BOD_5/DOC ratio, H_2O_2 dosage rate of 5.4 mg L^{-1} min^{-1} and Fe^{3+} dosage of 59 mg L^{-1} were found to be the favorable reagent dosages for carbofuran degradation. Under these conditions, the toxicity unit measured by Microtox® test with 5 min exposure was decreased from 47 to 6 and the biodegradability evaluated by BOD_5/COD ratio was increased from 0 to 0.76 after 60 min reaction. The results obtained in this study demonstrate that the photo-Fenton process is a promising pretreatment before the application of biological treatment for carbofuran removal from contaminated water/wastewater.

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1. Introduction

Carbofuran (2,3-dihydro-2,2-dimethylbenzofuran-7-yl methylcarbamate) is a broad spectrum carbamate pesticide and nematicide, which has been used against various foliar pests observed in fruit, vegetable and forest crops. This carbamate pesticide is highly soluble in fresh water (700 mg L^{-1}) [1]. Recent findings reporting the presence of carbofuran in surface water and groundwater illustrate the fact that carbofuran can enter ground water through leaching and surface water through runoff from applied fields [2–5]. Carbofuran usage has received intensive concern not only due to its high solubility but also due to its high oral toxicity. The LD_{50} for carbofuran is 5–13 mg kg^{-1} body weight in rats whereas the LD_{50} for atrazine (a triazine herbicide of low to moderate toxicity) is 1300 mg/kg [4,6,7].

As carbofuran exhibits a special biorefractory characteristic and requires longer biodegradation time, its complete degradation in a shorter time could only be achieved by advanced oxidation processes (AOPs). Moreover, AOPs can be an attractive alternative for the treatment of biorecalcitrant wastewater. AOPs are characterized by the generation of hydroxyl radical (·OH) with an E^0 of

2.8 V/SHE, which is capable to oxidize and mineralize organic pollutants [8,9]. A variety of effective treatment techniques such as ultrasonication, direct photolysis, ultra-violet (UV) irradiation in the presence of ozone or Fenton reagent, electro-Fenton, anodic Fenton treatment (AFT) and TiO_2 as a photocatalyst have been successfully applied for carbofuran removal from contaminated water [2,4,10–15]. Among these processes, the photo-Fenton treatment has revealed very high efficiency in the mineralization of biorefractory pesticides and other organic pollutants [16–21]. The photo-Fenton reaction, a combination of H_2O_2 and UV irradiation less than 400 nm with Fe^{3+} or Fe^{2+}, is a promising treatment, which can produce relatively more ·OH compared to the Fenton treatment [22].

Comparing with biological treatment, the major limitation of AOPs is their relatively high operational costs for complete oxidation of organic compounds [23,24]. In order to reduce the operational cost and achieve high performance of AOPs, the experimental conditions, i.e. pH, temperature and dosages of reactants, must be optimized. For such a goal, the statistical based optimization methodology such as the CCD is appropriate to be applied in a multifactor system with minimum number of well-chosen experiments [8,25]. The CCD is a modern experimental design approach, which has been widely used in several applications [16,26–28] to fit the experimental data and develop a statistically significant second-order polynomial equation. Along with RSM, it is possible to assess the conditions that could yield the most desirable response.

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Besides, the response surface plots can be constructed to locate the optimum points of the multifactor system [29].

A step forward in the cost reduction of pesticide bearing wastewater treatment could be achieved by combining the AOPs with a conventional biological treatment [30–35]. The combination of the photo-Fenton process (as a pretreatment) followed by biological treatment has great potential for enhancing the biodegradability of pesticide contaminated wastewater [23,35–37]. Nevertheless, incomplete oxidation may result the formation of more toxic intermediates than the parents, which can decrease the biodegradability [24,37]. Therefore, the biodegradability and toxicity assessment of degradation intermediates are essential for evaluating the success of the photo-Fenton process as a pretreatment for pesticide bearing wastewater treatment.

In the present study, the CCD and RSM were chosen to evaluate the effects of H_2O_2 dosage rate and Fe^{3+} dosage in the photo-Fenton pretreatment of carbofuran and to develop the second-order equations in terms of carbofuran and DOC removals and BOD_5/DOC ratio with different reaction times. Moreover, the objective of this study was extended to explore the favorable Fentron reagent dosages using the experimental design, and to investigate the detoxification and biodegradability enhancement at different stages of the photo-Fenton reaction.

2. Materials and methods

2.1. Chemical reagents

Carbofuran was obtained from Shida Chemical Industries (Taoyuan, Taiwan) and was used as received (HPLC grade >98% purity). Hydrogen peroxide (H_2O_2, 33%, w/w) was supplied by Panreac Chemicals (Spain). Exactly 1000 mg L^{-1} Fe^{3+} stock solution was prepared by dissolving ferric sulfate ($Fe_2(SO_4)_3$), Yakuri Pure Chemicals, Japan and used for the experiments. The HPLC grade methanol was used in carbofuran analysis. All other chemicals were of reagent grade and the solutions were prepared using double distilled water.

2.2. Experimental apparatus

A 1.6 L double-walled reactor as shown and described in our previous study was used in all the experiments [38]. Several ports were provided in the reactor for feeding the reactants and sampling the solution. Moreover, pH and temperature probes were permanently fixed in the reactor. A Teflon-coated stirrer was installed in the reactor to mix the solution at 175 rpm. During the experiment, H_2O_2 was added continuously into the reactor at a flow rate of 1 mL min^{-1} with a syringe pump. Two 8-W monochromatic UV lamps of 312 nm (with emission range between 280 and 360 nm) were placed axially in the reactor and kept in place with a quartz sleeve; the UV intensity of one 8-W UV lamp is 60 μW cm^{-2}. The reaction temperature was maintained at 25 ± 1 °C using a water bath.

2.3. Photo-Fenton procedures

Exactly 1 L of diluted carbofuran solution corresponding to an initial concentration of 100 mg L^{-1} was added into the reactor. The initial pH was adjusted to 3 using 0.1 N H_2SO_4 based on the literature and our previous findings [20,39–41]. Subsequently, a designed quantity of Fe^{3+} was added into the reactor and the contents were mixed thoroughly. The UV lamp was then turned on to mark the start point of the experiment and continued with the simultaneous addition of H_2O_2 at a constant flow rate. At regular intervals, samples were withdrawn from the reactor,

quenched with sodium hydrogen sulfite to avoid further reaction and filtered through a 0.45 μm membrane filter paper. Finally, the samples were analyzed for residual carbofuran, H_2O_2, DOC, BOD_5, COD and Microtox® test.

2.4. Analytical measurements

Carbofuran concentration in the samples was analyzed by the high performance liquid chromatography (HPLC) (Hitachi Co., Japan) equipped with a Hitachi L-2420 UV detector and a RP-18 GP 250 separation column (250 mm × 4.6 mm i.d., Kanto Chemicals, Japan). Exactly 20 μL of the sample was injected manually and analyzed at 280 nm. The mobile phase composed of methanol and water (50:50, v/v), and was pumped at a flow rate of 1 mL min^{-1}. Under these separation conditions, the retention time of carbofuran was observed around 12 min. For determining the residual H_2O_2 concentration, the samples were mixed with 5% titanium sulfate solution (the volume ratio of H_2O_2 sample to titanium sulfate solution is 10:1 v/v) and analyzed in a spectrophotometer (Hitachi U-3010, Japan) at 412 nm. Carbofuran mineralization was estimated from DOC concentrations. A TOC analyzer (O.I. Analytical Model 1030) was adopted for measuring the DOC of the samples using sodium persulphate and phosphoric acid as oxidizing and acid reagents, respectively. Throughout the study, the reaction pH and temperature were continuously monitored by a pH probe and thermometer (Suntex TS-2, Taiwan), respectively. Variation in BOD_5 and COD at different stages of the photo-Fenton treatment were measured as per the Standard Methods [42].

2.5. Microtox® test

Acute toxicity of initial carbofuran solution and the samples collected at different time periods of the photo-Fenton treatment were measured by the Microtox® test using *Vibrio fischeri* strains. Microtox® test was performed using a model M500 analyzer and standard procedures recommended by the Microbics Corporation, USA. Toxicity is expressed as EC_{50} value, i.e. the concentration of sample that causes a 50% reduction of the bioluminescence (*V. fischeri*). In this paper, toxicity was evaluated at 5 and 15 min from the time of mixing at various dilutions with the *V. fischeri*. Before conducting the Microtox® test, the pH value of the samples was adjusted to 7. Moreover, the EC_{50} value used in this study was converted to toxicity unit (TU) using Eq. (1). Thus, TU is inversely proportional to EC_{50} value, lower EC_{50} value relates to a higher TU.

$$TU = \frac{100}{EC_{50}} \qquad (1)$$

2.6. Experimental design and data analysis

In order to correlate the independent variables, i.e. H_2O_2 dosage rate and Fe^{3+} dosage, and dependent variables, i.e. carbofuran and DOC removals and BOD_5/DOC ratio, a two factors CCD was used in this study. The total number of experiments (N) required for two independent variables was determined as per the Eq. (2) [28,43,44].

$$N = 2^K + 2K + n_c \qquad (2)$$

Where K represents the number of independent variables and n_c is the center point. Predetermined ranges of independent variables, i.e. H_2O_2 dosage rate (1, 2.3, 5.5, 8.7 and 10 mg L^{-1} min^{-1}) and Fe^{3+} dosage (1, 15, 51, 86 and 100 mg L^{-1}), were selected for CCD. Three replications of center point were selected for CCD and 11 photo-Fenton experiments were arranged by the software. Due to

Table 1
Experimental results of CCD for the photo-Fenton degradation of carbofuran.

Experimental runs	Actual value (coded value)		Carbofuran removal (%)		DOC removal (%)		BOD$_5$/DOC ratio (mg-O$_2$ mg-C^{-1})
	H$_2$O$_2$ dosage rate (mg L^{-1} min^{-1})	Fe^{3+} dosage (mg L^{-1})	45 min	60 min	45 min	60 min	60 min
1	2.3 (−1)	15 (−1)	68	81	17	26	0.37
2	2.3 (−1)	86 (1)	72	86	15	25	0.41
3	5.5 (0)	100 (1.414)	90	100	24	30	0.82
4	5.5 (0)	51 (0)	97	100	30	42	0.93
5	5.5 (0)	51 (0)	93	100	29	39	0.81
6	5.5 (0)	51 (0)	95	100	27	41	0.86
7	5.5 (0)	1 (−1.414)	55	67	7	15	0.36
8	8.7 (1)	86 (1)	92	100	24	43	0.53
9	10.0 (1.414)	51 (0)	100	100	42	70	0.38
10	1.0 (−1.414)	51 (0)	68	81	17	27	0.33
11	8.7 (1)	15 (−1)	80	95	17	25	0.24

the varying units of the different factors (actual values), H$_2$O$_2$ dosage rate and Fe^{3+} dosage were normalized in the form of dimensionless coded values from −1.414 to 1.414, which is also useful to obtain more accurate estimate of the regression coefficient and reduce the interrelationship between linear and quadratic terms [45]. A second-order polynomial equation and its corresponding regression coefficients were obtained from the experimental data using the MINITAB® 14 statistical software.

3. Results and discussion

3.1. CCD of experiments for the photo-Fenton process

A two factors CCD was carried out using H$_2$O$_2$ dosage rate ranging from 1 to 10 mg L^{-1} min^{-1} and Fe^{3+} dosage from 1 to 100 mg L^{-1} to investigate their influence on carbofuran degradation under the photo-Fenton process. The ranges considered for these two independent variables were chosen according to our preliminary study [46]. The dependent variables of photo-Fenton process including carbofuran and DOC removals and BOD$_5$/DOC ratio with different reaction times are shown in Table 1. The influences of H$_2$O$_2$ dosage rate and Fe^{3+} dosage were determined by carbofuran and DOC removals at 45 and 60 min, and BOD$_5$/DOC ratio at 60 min. The center point was repeated three times (Runs 4, 5 and 6) in Table 1 to check the reproducibility and experimental error in the CCD results. The remained H$_2$O$_2$ concentrations of eleven runs after 60 min reaction were around 16–72%.

The coefficients of the second-order polynomial equation corresponding to each dependent variable were developed by multiple regression analysis using the MINITAB® 14 statistical software. Carbofuran removals ($Y_{1, 45 min}$, $Y_{2, 60 min}$), DOC removals ($Y_{3, 45 min}$, $Y_{4, 60 min}$) and BOD$_5$/DOC ratio ($Y_{5, 60 min}$) were expressed as a function of H$_2$O$_2$ dosage rate (X_1) and Fe^{3+} dosage (X_2) as per Eqs. (3)–(7). As can be seen in the Fig. 1, the experimental results are in good agreement with the values calculated by the second-order polynomial equations. The coefficient of variable in the equation represents the weight of itself to each dependent variable. Based on Eqs. (3) and (5)–(6) all the dependent variables are more influenced by H$_2$O$_2$ dosage rate than Fe^{3+} dosage due to the greater regression coefficients of X_1 than X_2. In addition, both H$_2$O$_2$ dosage rate and Fe^{3+} dosage have positive effect on all the dependent variables.

$$Y_{1,45min} = 95.0 + 9.7X_1 + 8.2X_2 - 5.6X_1^2 - 11.3X_2^2 + 2.0X_1X_2 \quad (3)$$

$$Y_{2,60min} = 100.0 + 6.9X_1 + 7.1X_2 - 3.9X_1^2 - 7.4X_2^2 \quad (4)$$

$$Y_{3,45min} = 28.7 + 5.5X_1 + 3.6X_2 - 0.6X_1^2 - 7.6X_2^2 + 2.3X_1X_2 \quad (5)$$

$$Y_{4,60min} = 40.7 + 9.7X_1 + 4.8X_2 + 2.5X_1^2 - 10.5X_2^2 + 4.8X_1X_2 \quad (6)$$

$$Y_{5,60min} = 0.867 + 0.008X_1 + 0.123X_2 - 0.277X_1^2 - 0.160X_2^2 + 0.063X_1X_2 \quad (7)$$

3.2. Influence of H$_2$O$_2$ dosage rate and Fe^{3+} dosage on the performance of photo-Fenton process

In order to better understand the influence of independent variables, the 3-D response surface plot and contour plot were constructed according to the second-order polynomial equations as
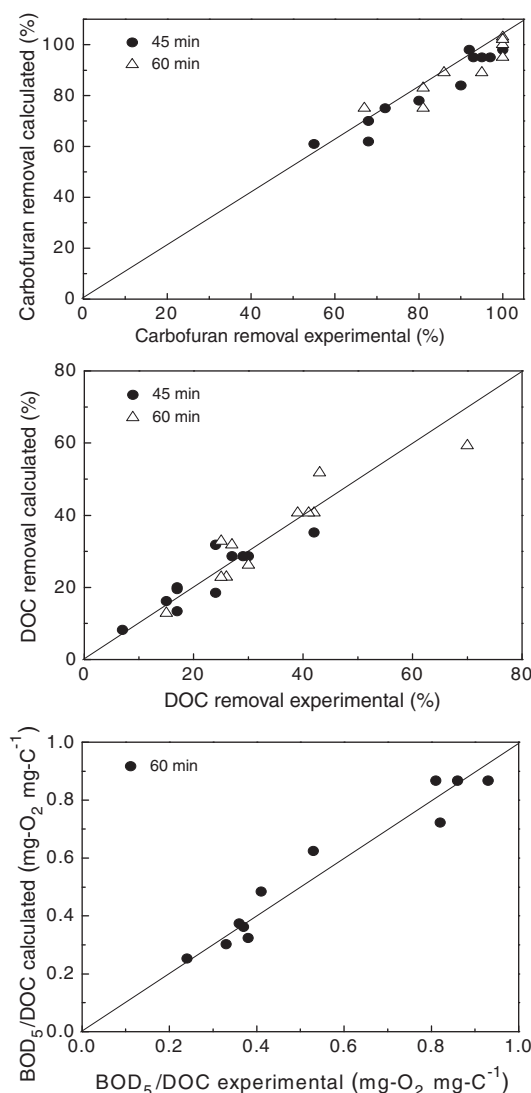

Fig. 1. Experimental and calculated values for carbofuran and DOC removals and BOD$_5$/DOC ratio in the photo-Fenton degradation of carbofuran.
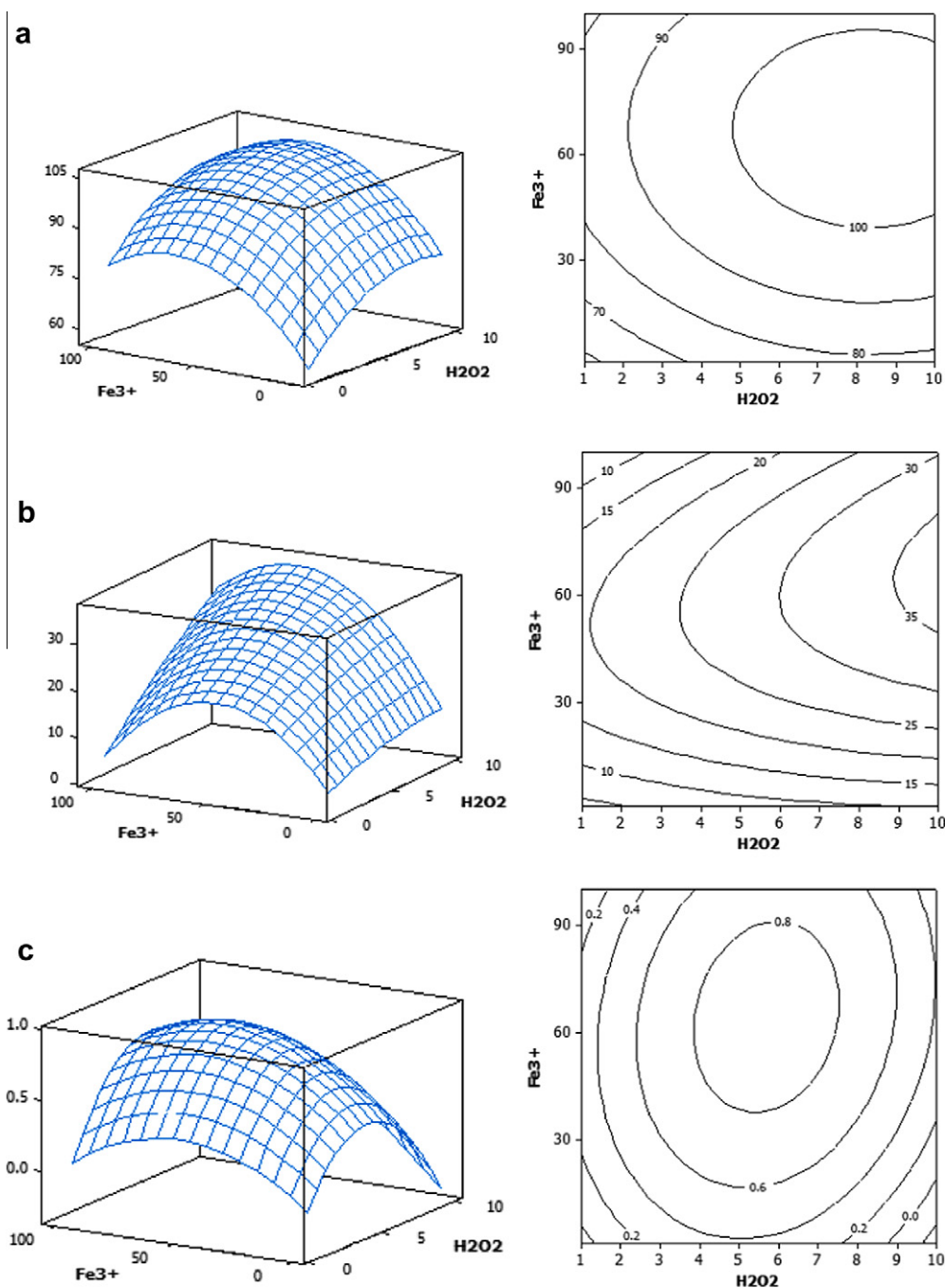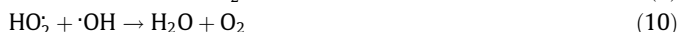
Fig. 2. The response surface and contour plot as a function of H_2O_2 dosage rate and Fe^{3+} dosage of (a) carbofuran removal at 60 min; (b) DOC removal at 45 min (c) BOD_5/DOC ratio at 60 min.

shown in Fig. 2. It can be noticed in Fig. 2(a) that H_2O_2 dosage rate has little effect on carbofuran removal at low Fe^{3+} dosage. This may be caused by low Fe^{3+} dosage restricting the generation of $\cdot$OH. The carbofuran degradation increases with the increasing H_2O_2 dosage rate under higher Fe^{3+} dosage, which is mainly due to the generation of $\cdot$OH with extra H_2O_2 addition. However, there is no furthur improvement in the carbofuran removal while the H_2O_2 dosage rate beyond 5 mg L^{-1} min^{-1}. This is in good agreement with the results obtained in previous studies [47,48]. Under this overdosed rate, H_2O_2 could react with $\cdot$OH or $\cdot$H; thus, a less powerful $HO_2^{\cdot}$ is formed as shown in Eqs. (8) and (9). Moreover, $HO_2^{\cdot}$ could further react with $\cdot$OH and form water and oxygen as per Eq. (10)

[20,29,33]. Therefore, the scavenging effect can reduce the oxidative capacity of the photo-Fenton reaction by decreasing the amount of $\cdot$OH and oxidant in the system [39].

$$H_2O_2 + \cdot OH \rightarrow H_2O + HO_2^{\cdot} \tag{8}$$

$$H^{\cdot} + H_2O_2 \rightarrow H_2 + HO_2^{\cdot} \tag{9}$$

$$HO_2^{\cdot} + \cdot OH \rightarrow H_2O + O_2 \tag{10}$$

A similar behavior was observed in the effect of Fe^{3+} dosage on carbofuran removal. The increase in Fe^{3+} dosage enhances the production of more $\cdot$OH through the Fenton reaction and primary reaction of photoreduction of ferric species and facilitates the higher

carbofuran removal efficiencies. Moreover, no significant improvement in carbofuran removal is observed when the Fe^{3+} dosage is increased beyond 60 mg L^{-1}.

Fig. 2(b) shows that the carbofuran mineralization is significantly influenced by H_2O_2 dosage rate. DOC removal reflects the extent of mineralization of target compound and highly depends on the amount of H_2O_2 dosage rate. The increase in H_2O_2 dosage rate enhances the mineralization of carbofuran. However, H_2O_2 dosage rate reveals little effect on DOC removal with Fe^{3+} dosage below 30 mg L^{-1} due to the limitation of ·OH production. Moreover, the DOC removal is maximized at Fe^{3+} dosage range of 55–65 mg L^{-1} while H_2O_2 dosage rate controlled at 10 mg L^{-1} min^{-1}.

It can be seen in Fig. 2(c) that both H_2O_2 dosage rate and Fe^{3+} dosage have positive effect on BOD_5/DOC ratio to a certain dosage level and then negative effect on BOD_5/DOC ratio is observed. A maximum BOD_5/DOC ratio (>0.8 mg-O_2 mg-C^{-1}) was observed when the H_2O_2 dosage rate and Fe^{3+} dosage were controlled at the range of 5–6 mg L^{-1} min^{-1} and 55–65 mg L^{-1}, respectively.

3.3. Favorable reagent dosages for carbofuran degradation under the photo-Fenton as a pretreatment process

Table 2 shows the optimum levels of H_2O_2 dosage rate and Fe^{3+} dosage for maximizing carbofuran removal, DOC removal and BOD_5/DOC ratio with different reaction times. For carbofuran removal, it is observed that as the reaction time increases, the optimum H_2O_2 dosage rate shifts toward low level of dosage rate. For example, an initial carbofuran concentration of 100 mg L^{-1} was completely degraded while H_2O_2 dosage rate and Fe^{3+} dosage controlled at 6.9 mg L^{-1} min^{-1} and 62 mg L^{-1}, respectively, at 45 min reaction time. As the reaction time extend to 60 min, optimum Fe^{3+} dosage is 61 mg L^{-1} and optimum H_2O_2 dosage rate is reduced to 4.9 mg L^{-1} min^{-1} for 100% carbofuran removal.

In addition, a maximum DOC removal of 61% is achieved after 60 min reaction at H_2O_2 dosage rate of 10 mg L^{-1} min^{-1} and Fe^{3+} dosage of 61 mg L^{-1}. Several researchers reported that DOC removal is highly related with H_2O_2 concentration in the system [22,48,49]. Therefore, high loading of H_2O_2 dosage rate must be employed to achieve high carbofuran mineralization within a short reaction time. Residual DOC after the photo-Fenton reaction indicates that the carbofuran intermediates generated in the treatment are not completely degraded. In the aspect of BOD_5/DOC ratio, a maximum BOD_5/DOC ratio of around 0.89 mg-O_2 mg-C^{-1} is obtained at H_2O_2 dosage rate of 5.4 mg L^{-1} min^{-1} and Fe^{3+} dosage of 59 mg L^{-1}. Higher BOD_5/DOC ratio represents that more organic carbon compounds are oxidized to easily biodegradable intermediates. In this study, the photo-Fenton reaction is selected as a pretreatment for carbofuran degradation; thus, mineralization efficiency is not a concerning parameter. Based on the results of carbofuran removal and BOD_5/DOC ratio, H_2O_2 dosage rate of 5.4 mg L^{-1} min^{-1} and Fe^{3+} dosage of 59 mg L^{-1} are found to be the favorable reagent dosages for pretreating carbofuran in the photo-Fenton process.

Table 2
Optimum levels of H_2O_2 dosage rate and Fe^{3+} dosage for obtaining maximum carbofuran removal, DOC removal and BOD_5/DOC ratio.

Dependent variable	Reaction time (min)	H_2O_2 (mg L^{-1} min^{-1})	Fe^{3+} (mg L^{-1})	Calculated value
Carbofuran removal (%)	45	6.5	62	100
	60	4.9	61	100
DOC removal (%)	45	10	61	37
	60	10	61	61
BOD_5/DOC (mg-O_2 mg-C^{-1})	60	5.4	59	0.89

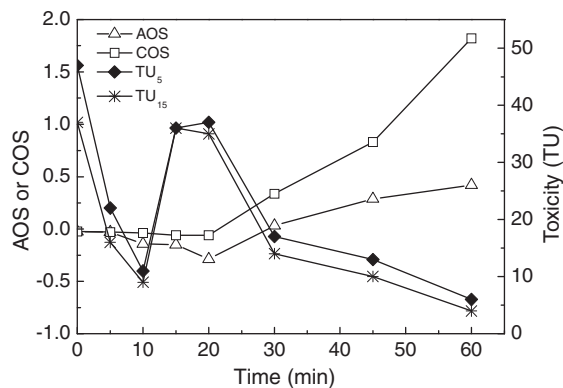**Fig. 3.** Variations in the Microtox® test, AOS and COS as a function of reaction time (H_2O_2 dosage rate at 5.4 mg L^{-1} min^{-1} and Fe^{3+} dosage at 59 mg L^{-1}).

3.4. Toxicity and oxidation state assessment

Microtox® test has been proved to be a suitable global indicator to evaluate the biodegradability of effluent pretreated by phototreament process [24]. Therefore, acute toxicity of the photo-Fenton effluent was evaluated by Microtox® test to find out the extent of carbofuran detoxification in the photo-Fenton process under the predetermined H_2O_2 dosage rate of 5.4 mg L^{-1} min^{-1} and Fe^{3+} dosage of 59 mg L^{-1}. TU_5 and TU_{15} profiles of the photo-Fenton effluent at different reaction times are shown in Fig. 3. Both the profiles have shown similar trends throughout the treatment process. A sharp decrease in toxicity was observed in the first 10 min of the photo-Fenton reaction. Subsequently, a sudden increase in TU_5 as well as TU_{15} profiles were observed between 10 and 20 min, which demonstrate that the intermediates produced during the photo-Fenton degradation of carbofuran are toxic than the parent compound. However, the toxicity decreased gradually after 20 min reaction time and reached a lowest TU value of 4 at the end of reaction. This behavior agrees with the toxicity results of single pesticide solutions obtained in previous studies [24,36,37].

On the other hand, average oxidation state (AOS) and carbon oxidation state (COS) are the useful parameters that can be employed for evaluating the extent of carbofuran oxidation and also the oxidation of intermediates. AOS and COS were calculated according to Eqs. (11) and (12) [32,34], respectively, where DOC_0 represents the initial DOC of carbofuran.

$$AOS = 4 - 1.5 \frac{COD}{DOC} \qquad (11)$$

$$COS = 4 - 1.5 \frac{COD}{DOC_0} \qquad (12)$$

As shown in Fig. 3, the initial AOS and COS of 100 mg L^{-1} carbofuran were −0.03, indicating the presence of rather reduced organic matter. After 60 min of reaction, AOS and COS values increased from −0.03 to 0.42 and 1.82, respectively. These results clearly evidence the strong mineralization and generation of oxidized organic intermediates during the photo-Fenton treatment of carbofuran. Moreover, this proves the improvement of carbofuran biodegradability. The AOS and COS values at the end of experiment may be characteristic of well oxidized compounds such as carbamic acid resulting in the reduction of pH value from 3 to 2.89 (data not show).

3.5. Biodegradability assessment

The BOD_5/COD ratio has been reported as an important indicator for biodegradability [32]. Results of BOD_5 and BOD_5/COD ratio
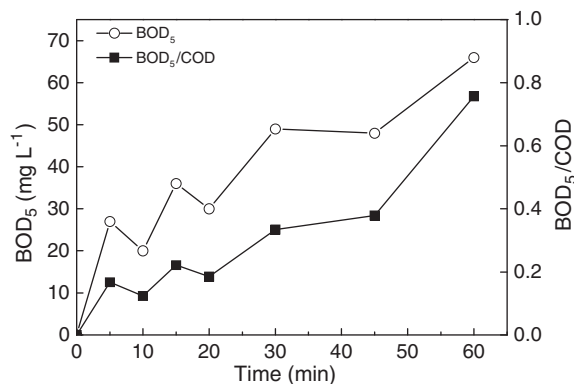
Fig. 4. Variations in the BOD_5 and BOD_5/COD ratio as a function of reaction time (H_2O_2 dosage rate at 5.4 mg L^{-1} min^{-1} and Fe^{3+} dosage at 59 mg L^{-1}).

at different treatment times under predetermined H_2O_2 dosage rate of 5.4 mg L^{-1} min^{-1} and Fe^{3+} dosage of 59 mg L^{-1} are shown in Fig. 4. The BOD_5 of initial 100 mg L^{-1} carbofuran solution was around zero, confirming the biorefractory characteristic of carbofuran. The BOD_5 of the photo-Fenton effluent increases gradually with the treatment time indicating the improvement of biodegradability due to the generation of biodegradable intermediates under the photo-Fenton reaction. At initial stage of photo-Fenton process, the biodegradable intermediates may also present in the system, but the activity of microorganism is inhibited by carbofuran. Throughout the study, the profile of BOD_5/COD ratio followed similar trend as BOD_5 profile. After 30 min reaction time, BOD_5/COD ratio was increased greater than 0.3 due to the enhancement in BOD_5 together with the reduction in COD, representing an easily biodegradable effluent. The highest BOD_5/COD ratio of 0.76 was achieved at the end of experiment. It has been widely reported in the literature that BOD_5/COD ratio greater than 0.5 is an indication of readily biodegradable effluent [31,34]. Based on effective adaptation, microorganism would be profitable to degrade the biorefractory pollutant. However, the photo-Fenton process can be used as the pretreatment to convert the bio-refractory pollutant into biodegradable ones after degradation. Subsequently, the effluent could be treated in a biological treatment unit that will shorten the adaptation period. The result of high BOD_5/COD ratio is in good agreement with the results of AOS and COS. Besides, the results of BOD_5/COD ratio are in good correlation with the COS values, which can be noticed in Fig. 5. This implies that the enhancement of BOD_5/COD ratio may be contributed by the oxidation degree of organic carbon during the photo-Fenton degradation of carbofuran. Based on the results of Microtox® test and BOD_5/COD ratio, a
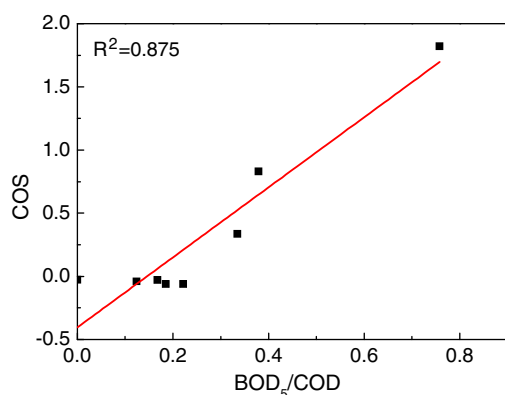
reaction time of 45 min is chosen as the appropriate time for coupling the photo-Fenton process with biological treatment. Under this circumstance, around 96% carbofuran removal can be achieved, the toxicity unit can be reduced to 10 and the BOD_5/COD ratio can be increased to 0.38.

4. Conclusions

This study has demonstrated that CCD and RSM can provide statistically reliable results in the photo-Fenton degradation of carbofuran. The second-order polynomial equations for carbofuran with DOC removals and BOD_5/DOC ratio at different reaction times have been successfully developed. Both H_2O_2 dosage rate and Fe^{3+} dosage have significant and positive effects on dependent variables. According to the results of carbofuran removal and BOD_5/DOC ratio, H_2O_2 dosage rate of 5.4 mg L^{-1} min^{-1} and Fe^{3+} dosage of 59 mg L^{-1} are the favorable reagent dosages for degradation of carbofuran. Based on the results of Microtox® test and BOD_5/COD ratio, a reaction time of 45 min is chosen as the appropriate time for coupling the photo-Fenton process with biological treatment. Under this circumstance, around 96% carbofuran removal was achieved, the toxicity unit was reduced to 10 and the BOD_5/COD ratio increased to 0.38. The significant reduction of toxicity and increase of biodegradability confirm that the photo-Fenton process is a promising pretreatment to deal with carbofuran comtainated water.

Acknowledgements

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