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Carbofuran, one of the most toxic and biorefractory carbamate compounds, is widely used in insecticides in Taiwan (9–18% of total insecticides production per year). In the present study, a central composite design experiment was used to study the effect of photo-Fenton treatment on carbofuran solution and to optimize the process variables such as carbofuran concentration (1–100 mg L^{-1}), H_2O_2 dosage rate (0.25–6 mg L^{-1} min^{-1}) and Fe^{3+} dosage (1–50 mg L^{-1}), which influenced the efficiency of carbofuran degradation and mineralization. The results indicated that all the variables investigated in this study had significant roles in the degradation and mineralization of carbofuran in solution. The carbofuran degradation and mineralization efficiencies were increased with increase in H_2O_2 dosage rate and Fe^{3+} dosage, and with decrease in carbofuran concentration. Furthermore, optimum values of both H_2O_2 dosage rate and Fe^{3+} dosage were found to shift to higher values as carbofuran concentration increased. Based on the model obtained in this study, optimum H_2O_2 dosage rate and Fe^{3+} dosage were found to be 4 mg L^{-1} min^{-1} and 20 mg L^{-1}, respectively, for 51 mg L^{-1} of carbofuran concentration. Under these conditions, carbofuran was completely removed within 30 min and coupled with 78% mineralization at the end of experiment.

Keywords: Carbofuran, central composite design, mineralization, photo-Fenton treatment.

Introduction

Carbofuran is widely used in agriculture in many countries. In the past, carbofuran annual usages in the United States and Italy were more than 2,200 tons and 1,200 tons, respectively.[1] In Taiwan, carbofuran accounts for about 9–18% of total insecticide production per year.[2] Normally, carbofuran is moderately persistent in water due to its chemical stability and has been frequently detected in the surface and groundwaters of seven states in the United States[1,3] as well as in Europe and Asia over the last two decades. Since the carbofuran exhibits a special biorefractory character due to its toxicity and requires longer biodegradation time and specific microorganisms, its complete degradation in a shorter time could only be achieved by using advanced oxidation processes (AOPs).[4,5] In the past, photo-Fenton treatment which is a combination of H_2O_2 and UV irradiation less than 400 nm with Fe^{3+} or Fe^{2+} has shown very high efficiency in the mineralization of biorefractory pesticides and other organic pollutants.[6–11]

However, high electrical energy demand and chemical reagents consumption are major drawbacks of the photo-Fenton process.[12] In order to reduce the operational cost along with high degradation performance of the target compound degradation, the experimental conditions or process parameters must be optimized. In earlier studies, the effect of each variable (process parameter) on the response was studied based on a step-by-step procedure, that is, varying one factor at a time while keeping the other variables at constant level. This approach is time-consuming and also does not consider the cross effects between variables on the overall reaction.[13,14] Hence, statistically based designs of experiments (DOE) are used to identify or screen out the important variables that have significant effects on response and to develop statistically empirical models; in fact, with a minimum number of experiments. Also, the importance of each variable along with their interaction effect can be observed by DOE. Among the DOE, central composite design (CCD) has been widely used for optimizing process variables in various scientific areas owing to its simple procedure and its advantage in the full evaluation on interactions between variables.[7,12,15–18] Effects of pH, pollutant concentration, temperature, UV intensity, reaction time and Fenton reagent concentrations on the oxidation performance by AOPs have been investigated by CCD in earlier studies.[7,19,20] For effective application

of AOPs in the wastewater treatment, the optimization of operational parameters plays an important role in target compounds degradation. For such a goal, CCD along with RSM has been used extensively in several wastewater treatments including photocatalytic oxidation,[21–23] Fenton,[24–26] Fenton-like reaction[14,20] and photo-Fenton reaction[7,27] to generate a quadratic model and to yield the most desirable response that considers the synergistic and antagonist effects between the variables.[7,12, 19] Besides, the three-dimensional response surface plots can be constructed to determine the optimal conditions that produce a maximum or minimum value of response.[16]

Therefore, the objective of the present study was to investigate the degradation and mineralization of carbofuran by photo-Fenton reaction. Also, a three-factors CCD followed by RSM was used to study the effect of carbofuran concentration, H_2O_2 dosage rate and Fe^{3+} dosage on carbofuran degradation for optimizing the conditions of photo-Fenton reaction.

Materials and methods

Chemical reagents

Carbofuran was obtained from the 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). Ferric iron (Fe^{3+}) stock solution was prepared by dissolving ferric sulfate powders ($Fe_2(SO_4)_3$, Yakuri Pure Chemicals, Japan) in distilled and deionized water and stored in the dark. All other chemicals used in the study were of reagent grade and all the solutions were prepared using distilled and deionized water.

Experimental apparatus

A 1.6 L double-walled reactor equipped with two 8-W monochromatic UV lamps of 312 nm (UV intensity of 60 μW cm^{-2}), pH probe, thermal probe, mixer, temperature controller and syringe pump was used to carry out the degradation experiments. In the photo-Fenton experiment, H_2O_2 was added continuously into the reactor by a syringe pump. The reaction temperature was maintained at 25 $\pm$ 1°C.

Photo-Fenton procedures

Diluted carbofuran solution (1 L), corresponding to an initial concentration of 1–100 mg L^{-1} (as per the statistical design shown in Table 1) was added into the reactor. The initial pH was adjusted to 3.0 using 0.1 N H_2SO_4. The UV lamps were turned on for 30 min before experiment then mark the starting point of the experiment. A designed

Table 1. Experimental arrangement of a three factor CCD for photo-Fenton degradation of carbofuran.

Experimental runs	Natural value (Coded value)		
	Carbofuran concentration (mg L^{-1}, X_1)	H_2O_2 dosage rate (mg L^{-1} min^{-1}, X_2)	Fe^{3+} concentration (mg L^{-1}, X_2)
1	51 (0)	0.25 (-1.68)	25 (0)
2	21 (-1)	1.3 (-1)	10 (-1)
3	100 (α^*)	3 (0)	25 (0)
4	51 (0)	3 (0)	50 (1.68)
5	21 (-1)	1.3 (-1)	40 (1)
6	51 (0)	3 (0)	25 (0)
7	51 (0)	6 (1.68)	25 (0)
8	51 (0)	3 (0)	25 (0)
9	80 (1)	1.3 (-1)	10 (-1)
10	21 (-1)	4.8 (1)	10 (-1)
11	21 (-1)	4.8 (1)	40 (1)
12	80 (1)	1.3 (-1)	40 (1)
13	51 (0)	3 (0)	25 (0)
14	1 ($-\alpha^*$)	3 (0)	25 (0)
15	51 (0)	3 (0)	1 (-1.68)
16	80 (1)	4.8 (1)	40 (1)
17	80 (1)	4.8 (1)	10 (-1)

*α is equal to 1.68.

quantity of Fe^{3+} was added into the reactor and the contents were mixed thoroughly and the H_2O_2 was introduced into the reactor simultaneously at a constant flow rate. At regular intervals, samples were withdrawn from the reactor, quenched with sodium hydrogen sulphite to avoid further reaction and filtered through a 0.45 μm membrane filter paper before taking measurements.

Experimental design and data analysis

The CCD has been applied to optimize the levels of the selected variables viz. carbofuran concentration (X_1), H_2O_2 dosage rate (X_2) and Fe^{3+} dosage (X_3) and to study their effects on carbofuran degradation and mineralization. Each variable was assessed at 5 different levels coded as $-\alpha$, -1, 0, +1, +α and total 17 experiments were performed with 3 central point replicates. The full experimental design along with the coded and uncoded (natural) values of all variables is shown in Table 1. The three significant independent variables X_1, X_2 and X_3 and, their mathematical relationship with response Y can be approximated by the quadratic (second-degree) polynomial equation as shown in Equation 1:

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 \quad (1)$$

where, Y represents predicted response; the set of regression coefficients consist the intercept (β_0), linear ($\beta_1, \beta_2, \beta_3$), interaction ($\beta_{12}, \beta_{13}, \beta_{23}$) and quadratic coefficients

$(\beta_{11,}\beta_{22,}\beta_{33})$.[15] The statistical software MINITAB® 14, USA was used to design the experiments, to analyze the experimental data and to plot the response surface and contour plots.

Analytical methods

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). An amount measuring 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. Carbofuran mineralization was estimated in terms of dissolved organic carbon (DOC) concentrations. A TOC analyzer (O.I. Analytical Model 1030) was used 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 thermo meter (Suntex TS-2, Taiwan), respectively.

Results and discussion

It is understood that pH, dosages of H_2O_2 and Fe^{3+} and carbofuran concentration affect the degradation and mineralization efficiency of carbofuran in the photo-Fenton system. The optimum pH value varies with different target compounds treated by photo-Fenton reaction. However, degradation of pollutants by the Fenton or photo-Fenton reaction is most effective in acidic solution (pH~3) which keeps Fe^{3+} species soluble. In our earlier study, we investigated the effect of pH (2.0 to 4.0) on the degradation of carbofuran and pH 3.0 was found best for complete carbofuran degradation within 30 min reaction.[28] Therefore, in this study, the initial pH level was fixed at 3.0 in all the experiments. Throughout the experiments, the solution pH remains relatively unchanged (2.8–3.4). The levels of other variables (carbofuran concentration, H_2O_2 dosage rate and Fe^{3+} dosage) were optimized in this study.

Comparison of carbofuran and DOC removals with UV/H₂O₂, UV/Fe³⁺ and photo-Fenton method

As an example, run 4, 8 and 13 from Table 1 were compared with UV with H_2O_2 (3 mg L^{-1} min^{-1}) and UV with Fe^{3+} (25 mg L^{-1}). The initial carbofuran concentration in all these experiments was 51 mg L^{-1}. Figures 1a and 1b show the evolution of the carbofuran and DOC removal percentage by UV/H₂O₂, UV/Fe³⁺ and photo-Fenton methods (run

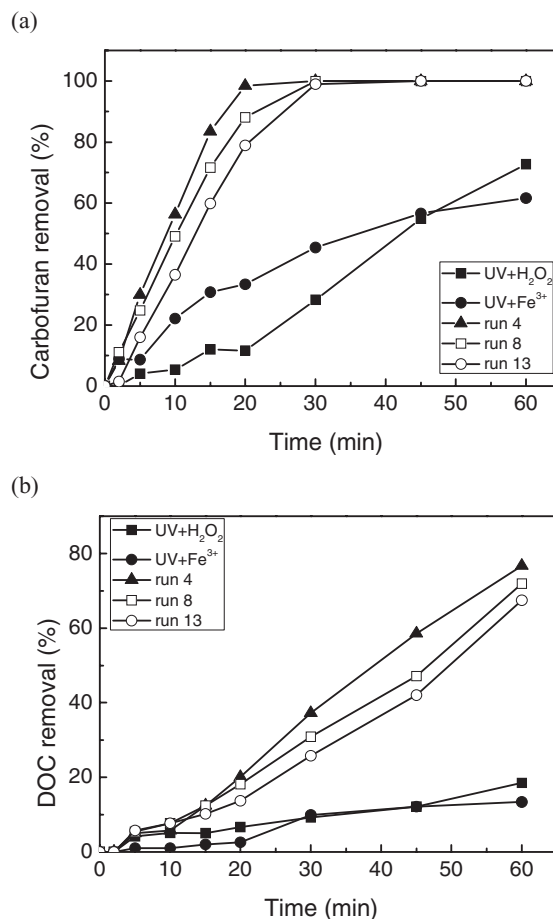**Fig. 1.** Variations of (a) carbofuran and (b) DOC removals with reaction time. UV+H₂O₂ with H_2O_2 dosage rate at 3 mg L^{-1} min^{-1} and UV+Fe³⁺ with Fe^{3+} dosage at 25 mg L^{-1}.

4, 8 and 13). In these figures, the carbofuran was initiated at 51 mg L^{-1}; H_2O_2 dosage rate and Fe^{3+} dosage were designed at 3 mg L^{-1} min^{-1} and 25 and 50 mg L^{-1}, respectively. Degradation of carbofuran was found to be linearly dependent on reaction time in UV/H₂O₂ and UV/Fe³⁺ experiments, where the carbofuran removals were 70% and 60%, and DOC removals were 17% and 11%, respectively, after 60 min reaction (Fig. 1a and 1b). Lu et al.[29] proposed that only 7% of carbofuran could be degraded during 120 min reaction in sole UV system. Therefore, the presence of Fe^{3+} or H_2O_2 would be advantageous for improving the carbofuran degradation and mineralization. Further, the results of Figures 1a and 1b confirmed that the carbofuran and DOC removals increased dramatically with the presence of both H_2O_2 and Fe^{3+} in the reaction (run 4, 8 and 13). It can be noticed that only 20 min is needed for a complete carbofuran removal (run 4) and up to 77% of DOC removed after 60 min of reaction, which can be identified as a synthetic fact in photo-Fenton system.

Table 2. Experimental results of carbofuran and DOC removals by photo-Fenton method.

Experimental runs	Carbofuran degradation (%) 30 min	DOC removal (%) 60 min	DOC removal/ carbofuran degradation 30 min	DOC removal/ carbofuran degradation 60 min
1	72	34	0.19	0.43
2	100	77	0.33	0.77
3	68	39	0.28	0.40
4	100	77	0.37	0.77
5	100	77	0.47	0.77
6	100	69	0.22	0.69
7	100	78	0.41	0.78
8	99	68	0.26	0.68
9	53	18	0.13	0.22
10	100	76	0.50	0.76
11	100	87	0.70	0.87
12	74	35	0.20	0.36
13	100	72	0.31	0.72
14	100	75	0.20	0.75
15	54	37	0.37	0.44
16	97	74	0.30	0.74
17	68	34	0.17	0.34

Optimization of variables for maximum carbofuran and DOC removal

Table 2 shows the result of carbofuran removal (30 min), DOC removal (60 min), ratio of DOC removal to carbofuran removal (30 and 60 min) for 17 experimental runs. It can be seen from Table 2 that the removals of carbofuran were reached 100% in nine runs, where the carbofuran concentration, H_2O_2 dosage rate and Fe^{3+} dosage were in a range of 1 to 51 mg L^{-1}, 1.3 to 6 mg L^{-1} min^{-1} and 10 to 40 mg L^{-1}, respectively. It was also found in Runs 5 and 11 that the H_2O_2 dosage rate of 1.3 and 4.8 mg L^{-1} min^{-1} both showed the satisfactory carbofuran degradation efficiency where the initial carbofuran and Fe^{2+} concentrations were

in same range. In addition, Run 2 showed comparable result of carbofuran degradation with lower Fe^{3+} dosage than Run 5, where the initial carbofuran and H_2O_2 dosage rate were the same. These results indicate that finding the suitable dosages of oxidants in reaction is necessary to reduce the formation of ferric iron sludge and save the operational cost. In the experimental run, where the carbofuran concentration was greater than 80 mg L^{-1}, removal of carbofuran was in a range of 53 to 97%. Therefore, it is estimated that increase of Fenton's reagent is necessary to enhance the degradation of carbofuran. To effectively estimate the better carbofuran degradation results at different reaction conditions, this study used the second-order polynomial equations to obtain the simulation equations for determining the optimal experimental parameters. Three parameters viz. initial carbofuran concentration, H_2O_2 dosage rate and Fe^{3+} dosage were defined as X_1, X_2, and X_3, respectively, and Y_1, Y_2, Y_3 and Y_4 were defined as carbofuran removal at 30 min, DOC removal at 60 min and ratio of DOC removal to carbofuran degradation at 30 and 60 min, respectively. The estimated regression coefficient and corresponding P-value for these responses were shown in Table 3 and the full equations were shown as Equations 2–5. The responses (Y_1 to Y_4) can be estimated from these empirical equations; moreover, the surface and contour plot constructed based on these equations can be used to find out the optimal reaction condition.

$$Y_1 = 99.33 - 11.85X_1 + 6.23X_2 + 9.33X_3 - 4.38X_1^2 - 3.67X_2^2 - 6.86X_3^2 + 4.75X_1X_2 + 6.25X_1X_3 + 1.00X_2X_3 \qquad (2)$$

$$Y_2 = 69.42 - 15.86X_1 + 10.11X_2 + 9.90X_3 - 3.62X_1^2 - 3.97X_2^2 - 3.62X_3^2 + 5.75X_1X_2 + 5.75X_1X_3 + 4.25X_2X_3 \qquad (3)$$

$$Y_3 = 0.260 - 0.078X_1 + 0.067X_2 + 0.040X_3 + 0.001X_1^2 + 0.022X_2^2 + 0.048X_3^2 - 0.033X_1X_2 - -0.018X_1X_3 + 0.015X_2X_3 \qquad (4)$$

Table 3. Estimated regression coefficient and corresponding P-value for response.

Component	Y_1 Coefficient	Y_1 P	Y_2 Coefficient	Y_2 P	Y_3 Coefficient	Y_3 P	Y_4 Coefficient	Y_4 P
Constant	99.33	0.000	69.42	0.000	0.260	0.012	0.696	0.000
X_1	−11.85	0.001	−15.86	0.000	−0.078	0.068	−0.154	0.000
X_2	6.23	0.016	10.11	0.002	0.067	0.108	0.086	0.002
X_3	9.33	0.002	9.91	0.003	0.040	0.311	0.088	0.002
X_1^2	−4.38	0.084	−3.62	0.175	0.002	0.970	−0.040	0.090
X_2^2	−3.67	0.135	−3.97	0.142	0.023	0.586	−0.029	0.193
X_3^2	−6.86	0.016	−3.62	0.175	0.048	0.272	−0.029	0.193
X_1X_2	4.75	0.108	5.75	0.083	−0.033	0.514	0.051	0.070
X_2X_3	6.25	0.051	5.75	0.083	−0.018	0.723	0.054	0.060
X_1X_3	1.00	0.710	4.25	0.179	0.015	0.761	0.046	0.095

$$Y_4 = 0.696 - 0.154X_1 + 0.086X_2 + 0.088X_3 - 0.040X_1^2$$
$$- 0.029X_2^2 - 0.029X_3^2 + 0.051X_1X_2 + 0.054X_1X_3$$
$$+ 0.046X_2X_3 \qquad (5)$$

In Table 3, these coefficients represent the contribution of each variable to individual response (Y_1 to Y_4), i.e. the contribution of first-order, quadratic and cross effects, the trend of response and interaction among variables. A positive sign for the coefficients of H_2O_2 dosage rate and Fe^{3+} dosage in the fitted model for Y_1 to Y_4 indicates that the responses increased with an increase level of reagent dosage. On the other hand, the negative coefficient of carbofuran concentration indicates that the response decreased with an increase in carbofuran concentration. The P-value is used to estimate the statistical significance and its value less than 0.05 in ANOVA indicates that the component is considered as statistically significant.[30] The results showed that the P-values for all variables (X_1 to X_3) were smaller than 0.05, indicating these three variables affected the responses (Y_1, Y_2 and Y_4) significantly. In addition, carbofuran concentration had greater impact on the responses than the H_2O_2 dosage rate and Fe^{3+} dosage. The quadratic and cross effects were negligible except the quadratic effect of Fe^{3+} dosage (X_3^2) for carbofuran removal at 30 min.

Since the coefficients (R^2) always increases with increasing regressor variables in a regression model. Therefore, the adjusted R^2 considering the number of regressor variables is usually selected in statistical modeling.[15] The adjusted R^2 coefficients determined for all responses in this study were ranged from 0.63 to 0.89, which indicate that at least 63–89% of quadratic model was in a good agreement with experimental data. As can be seen in Figure 2, the values calculated by second-order polynomial equations show satisfactory agreement with experimental data. In Figure 2a, the graph of carbofuran removal reveals that there were some problems with fitting the second-order polynomial equation in wide range, therefore several calculated values were above 100%. This observation is in good agreement with the results reported by other researchers where they point out that the failure of this approach is often obtained due to the complexity of the system while the model covers with wide range of results.[14,31]

To understand the effect of reaction variables on the degradation of carbofuran and to find out the optimal conditions for carbofuran degradation by a photo-Fenton method, the results of seventeen runs shown in Table 2 were collected to draft the response surface and contour plots by RSM and shown in Figures 3 to 5. It can be noticed from Figures 3a and 3b that carbofuran concentration has a great negative effect on carbofuran degradation, regardless of the amount of H_2O_2 dosage rate and Fe^{3+} dosage employed. Also, carbofuran removal increased with increase in H_2O_2 dosage rate and Fe^{3+} dosage at a high carbofuran concentration. The low requirements of H_2O_2 and Fe^{3+} were found for low carbofuran concentration, where the
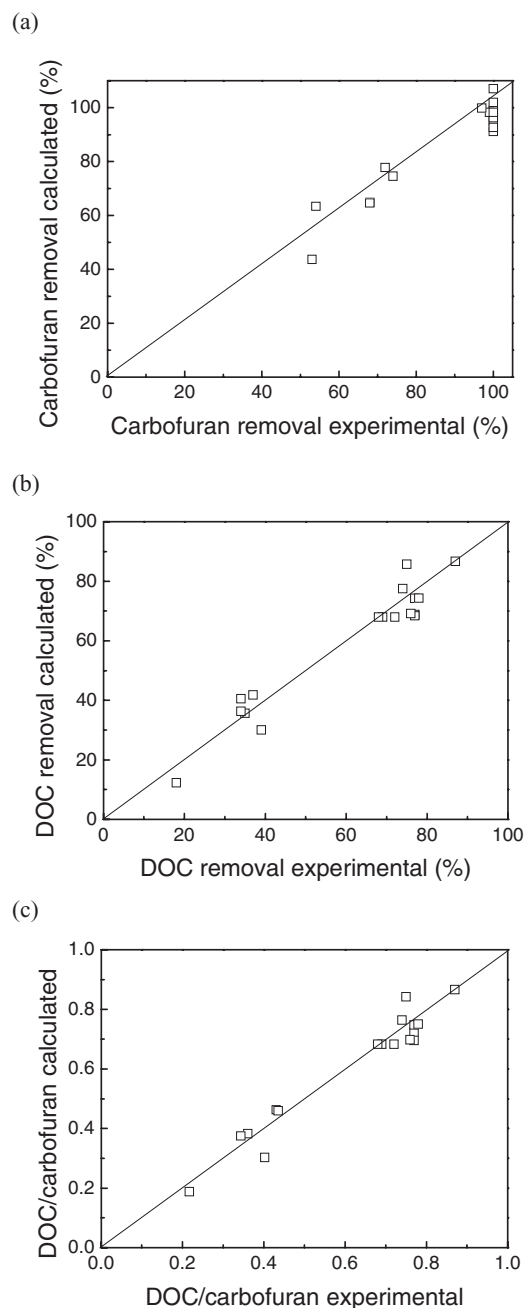
Fig. 2. Experimental and calculated values for (a) carbofuran removal at 30 min (b) DOC removal at 60 min (c) DOC removal/carbofuran degradation at 60 min in the photo-Fenton degradation of carbofuran.

detrimental effect on carbofuran removal caused by an excessive H_2O_2 dosage rate and Fe^{3+} dosage were observed. Comparable profiles were also found in DOC removal and ratio of DOC removal to carbofuran degradation. Figure 3c shows an obvious curvature in three-dimensional surface plot while the carbofuran concentration was fixed at 51 mg L^{-1}. From the bending extent of curvature, it was also observed that carbofuran reduction was more
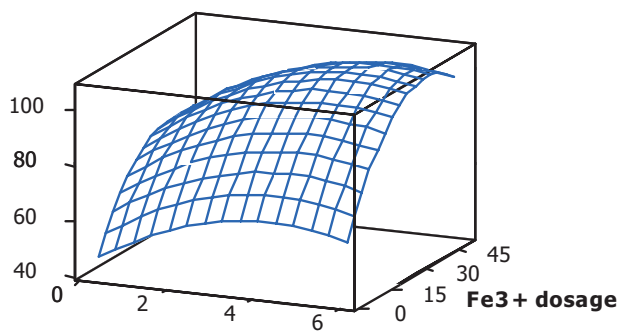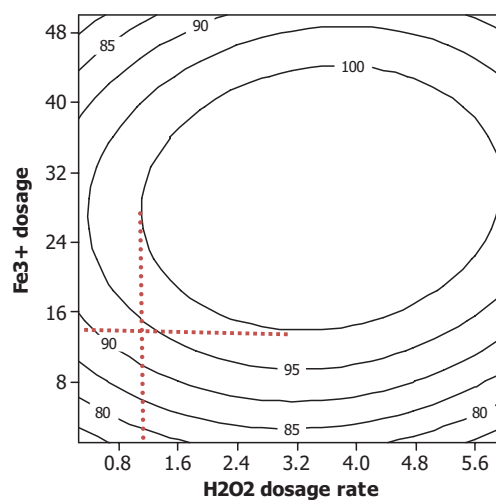
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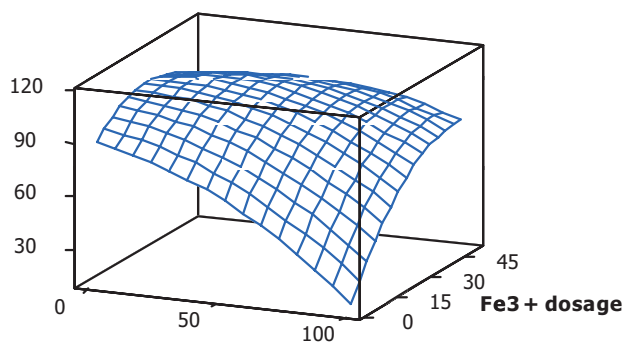
(b)

(c)
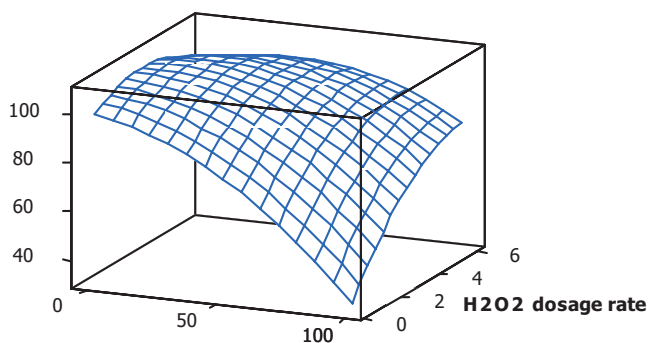
Fig. 3. The response surface plots as a function of carbofuran concentration, H_2O_2 dosage rate and Fe^{3+} dosage of carbofuran removal at 30 min (a) H_2O_2 dosage rate at 3 mg L^{-1} min^{-1} (b) Fe^{3+} dosage at 25 mg L^{-1} (c) carbofuran concentration at 51 mg L^{-1} (color figure available online).

(a)

(b)
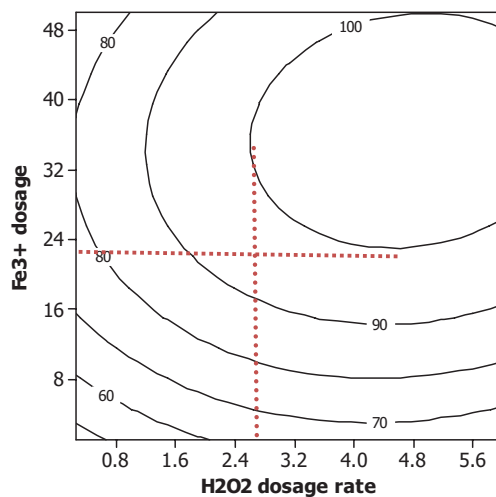
(c)

Fig. 4. The contour plots as a function of H_2O_2 dosage rate and Fe^{3+} dosage of carbofuran removal at 30 min with different carbofuran concentrations (a) 21 mg L^{-1} (b) 51 mg L^{-1} (c) 80 mg L^{-1} (color figure available online).

(a)

(b)

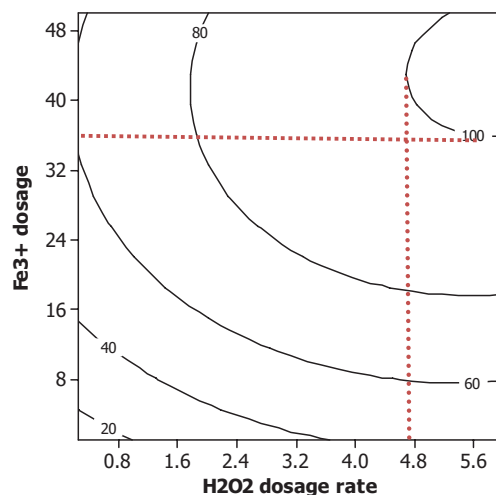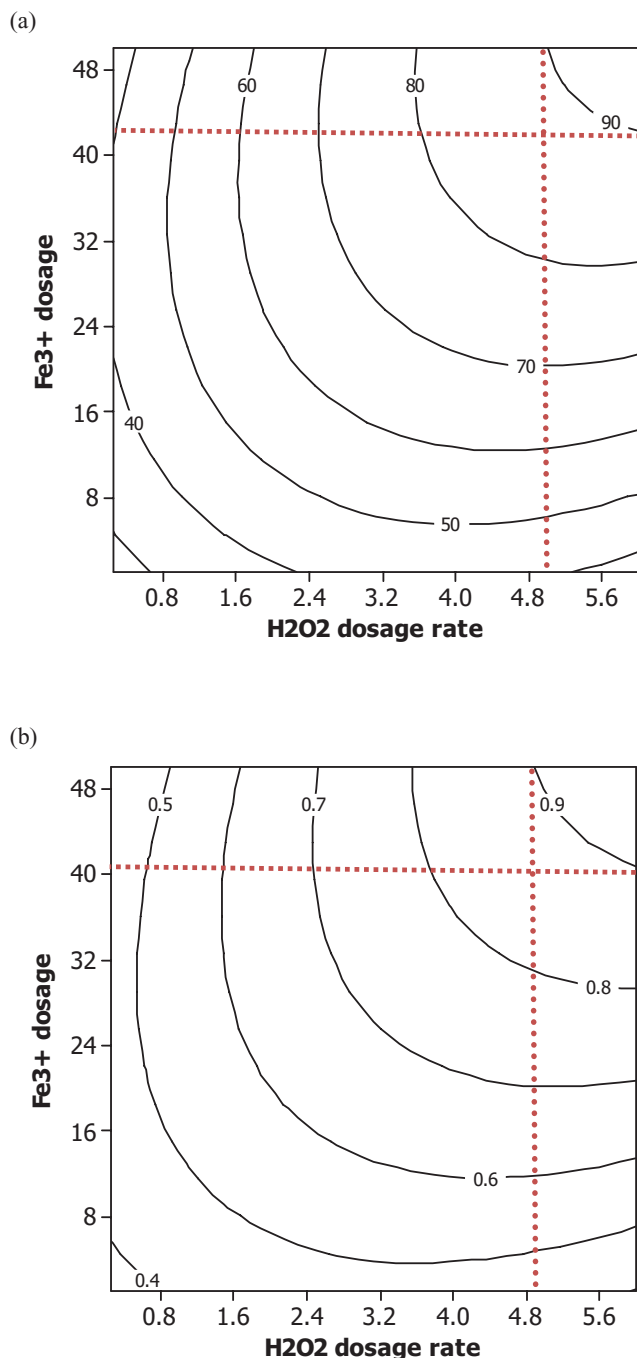**Fig. 5.** The contour plots as a function of H_2O_2 dosage rate and Fe^{3+} dosage of (a) DOC removal at 60 min (b) DOC removal/carbofuran degradation at 60 min at carbofuran concentration of 51 mg L^{-1} (color figure available online).

influenced by Fe^{3+} dosage than the H_2O_2 dosage rate. Also, carbofuran removal decreases at higher levels of H_2O_2 dosage rate and Fe^{3+} dosage. Many researchers also reported the negative effect of H_2O_2 and Fe^{3+} dosages under overdosed system for the degradation of various target compounds.[12,32,33]

Figure 4 shows three contour plots for carbofuran removal at carbofuran concentration of 21, 51 and 80 mg L^{-1} (Fig. 4a to 4c) and different H_2O_2 dosage rate and Fe^{3+} dosage. These contour plots are useful to point out the minimal requirement of oxidants for complete degradation of carbofuran. For 21 mg L^{-1} carbofuran concentration, only 1.1 mg L^{-1} min^{-1} of H_2O_2 and 28 mg L^{-1} of Fe^{3+} or 3.0 mg L^{-1} min^{-1} of H_2O_2 and 15 mg L^{-1} of Fe^{3+} were necessary for maximum carbofuran removal within 30 min (Fig. 4a). This observation provides the information about what amounts of Fenton's reagent are required in advance and the minimal or optimal dosages of oxidants, based on economic considerations. In Figure 4b where the carbofuran concentration was 51 mg L^{-1}, minimal requirements of H_2O_2 dosage rate and Fe^{3+} dosage were found to be 3 mg L^{-1} min^{-1} and 35 mg L^{-1} or 4 mg L^{-1} min^{-1} and 20 mg L^{-1}, respectively. If the carbofuran concentration increased to 81 mg L^{-1}, optimum H_2O_2 dosage rate and Fe^{3+} dosage should be increased to 4.8 mg L^{-1} min^{-1} and 45 mg L^{-1} or 5.6 mg L^{-1} min^{-1} and 36 mg L^{-1}, respectively, for 100% carbofuran removal. Based on the above observation, lower Fe^{3+} dosages should be considered as the optimal condition due to the lower iron sludge produced in the treatments. In addition, according to the shape of these contour plots (elliptical, circular or saddle point) we can know that if there is any interaction effect between the variables[34]. Figure 4 shows that there was no significant interaction between H_2O_2 dosage rate and Fe^{3+} dosage. This result is in good agreement with results mentioned in Table 3.

The optimum conditions of variables for maximum DOC removal and ratio of DOC removal to carbofuran degradation were also investigated. In Table 2, the maximum 87% of DOC removal efficiency was observed in run 11 in which the initial carbofuran concentration was 21 mg L^{-1} with H_2O_2 dosage rate of 4.8 mg L^{-1} min^{-1} and Fe^{3+} dosage of 40 mg L^{-1}. It could be seen from the table that the DOC removal efficiency increased with increase in H_2O_2 dosage rate and Fe^{3+} concentration and with decrease in carbofuran concentration. However, this table can only provide the results of carbofuran and DOC removals at certain experimental conditions. It is interesting to estimate the maximum DOC removal at different carbofuran concentrations.

The contour plot (Fig. 5a) indicated that for 51 mg L^{-1} carbofuran concentration, 90% of DOC could be removed at H_2O_2 dosage rate and Fe^{3+} dosage of more than 5.8 mg L^{-1} min^{-1} and 42 mg L^{-1} or 5.0 mg L^{-1} min^{-1} and 50 mg L^{-1}, respectively. In Runs 1, 4, 6, 7, 8, 13 and 15, the maximum DOC removal was 78% (Run 7, Table 2). Therefore, comparing the results shown in Table 2, it is understood that CCD coupled with contour plot can help the researchers to find out the optimal reaction condition. As for the ratio of DOC removal to carbofuran degradation, conclusions are similar to those described for DOC removal. Higher values of H_2O_2 dosage rate and Fe^{3+} dosage are required to achieve greater ratio of DOC removal to carbofuran degradation (Fig. 5b). The increase in ratio of DOC removal to

Table 4. Comparison of the simulated data of carbofuran degradation and DOC removal with experimental data.

| Item | Carbofuran degradation at 30 min (%) | | | DOC removal at 60 min (%) | | |
	Experimental	Simulated	Differences (%)	Experimental	Simulated	Differences (%)
Set 1[a]	100	100	0	66	73	−10.6
Set 2[b]	100	97	3	78	70	10.3

[a]Experimental result obtained at initial carbofuran concentration, H_2O_2 dosage rate and Fe^{3+} concentration were at 51 mg L^{-1}, 3 mg L^{-1} min^{-1} and 35 mg L^{-1}.
[b]Experimental result obtained at initial carbofuran concentration, H_2O_2 dosage rate and Fe^{3+} concentration were at 51 mg L^{-1}, 4 mg L^{-1} min^{-1} and 20 mg L^{-1}.

carbofuran degradation demonstrates that the addition of H_2O_2 and Fe^{3+} are useful for enhancing the mineralization of carbofuran in the photo-Fenton process. The differences between the results of 30 and 60 min are evidence to prove that carbofuran was strongly mineralized and several intermediates were formed.

The experimental results indicated that the presence of high loading reagent dosages was required to achieve a good mineralization degree within a short reaction period. However, many researchers proposed that it was dispensable to introduce large amount of oxidants to achieve a very high level of DOC removal, based on the high production of iron sludge and cost of chemicals. Since the results revealed that the optimal reagent dosages varied with carbofuran concentration, the model optimized values of H_2O_2 dosage rate and Fe^{3+} dosage were found to be 4 mg L^{-1} min^{-1} and of 20 mg L^{-1} for 51 mg L^{-1} carbofuran and 5.6 mg L^{-1} min^{-1} and 36 mg L^{-1} for 81 mg L^{-1} carbofuran, respectively, for 100% carbofuran removal within 30 min. Ma et al. reported that the 57% carbofuran was removed using Fenton reaction with carbofuran concentration of 50 mg L^{-1}, H_2O_2 dosage of 200 mg L^{-1} and Fe^{2+} dosage of 5 mg L^{-1} in 30 min reaction.[35] Under the optimized reagent dosage in this study, carbofuran (51 mg L^{-1}) can be completely removed within 30 min reaction.

To confirm the applicability of the second-order quadratic model, two optimized experiments with designed H_2O_2 dosage rate (3 and 4 mg L^{-1} min^{-1}) and Fe^{3+} concentration (35 and 20 mg L^{-1}) were conducted at carbofuran concentration of 51 mg L^{-1}. Table 4 shows the comparison of simulated data of carbofuran degradation and DOC removal with real experimental results. It was found that the simulated and experimental data are comparable with only 0–10.6% differences.

Conclusion

This study demonstrates that coupling the CCD and RSM can provide statistically reliable results to design the optimum values of process variables for maximum carbofuran degradation and mineralization by a photo-Fenton method. The developed second-order polynomial equations, which can be used to estimate the treatment efficien-

cies, were reasonably agreed with the experimental data in certain conditions. The response surface and contour plots obviously proposed the effect of carbofuran concentration, H_2O_2 dosage rate and Fe^{3+} concentration on the degradation and mineralization of carbofuran. Optimum values of both H_2O_2 dosage rate and Fe^{3+} dosage were found to shift to higher values as carbofuran concentration increased.

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