



Advanced oxidation and mineralization of simazine using Fenton's reagent

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ABSTRACT

Removal of simazine from aqueous solution by Fenton's reagent oxidation was investigated. Box–Behnken statistical experiment design and the response surface methods were used to investigate the effects of simazine, H_2O_2 and Fe (II) concentrations on simazine degradation and mineralization. Total organic carbon (TOC) and simazine removals were investigated at different reagent doses to determine the experimental conditions yielding the highest removal of simazine and TOC. Fe (II) concentration had more profound effect than H_2O_2 for simazine removal while all parameters affected mineralization (TOC removal). Complete disappearance of simazine was achieved within 6 min reaction period. However, only 32% of simazine was mineralized after 15 min indicating formation of some intermediate products. The optimal H_2O_2 /Fe (II)/simazine ratio resulting in the maximum pesticide (100%) and TOC removal (32%) was found to be 55/15/3 ($mg L^{-1}$). The initial rate of simazine degradation was found to be first-order with respect to the initial simazine concentration.

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1. Introduction

Pollution of soil and aquatic environment by chemicals used in agriculture is one of the major environmental problems. Simazine (6-chloro-*N,N'*-diethyl-1,3,5-triazine-2,4-diamine), one of the most commonly used pesticides, belongs to the triazine family of chemical compounds (six-member ring containing three carbon and nitrogen atoms). In addition to the aromatic carbon/nitrogen ring, simazine contains one chlorine and two ethylamine groups attached to the ring. Important physico-chemical characteristics of simazine are presented in Table 1. Other members of the triazine family include prometryn and atrazine [1]. Simazine is used to control broad-leaf weeds and annual grasses in crop fields such as fruit orchards. Fish farm ponds, aquariums, and cooling towers were some of the water systems where simazine was used to control algae prior to 1992 [2].

Due to bio-recalcitrant and toxic characteristics, pesticides cannot be removed by the conventional wastewater treatment plants utilizing activated sludge bacteria. New technologies need to be developed for effective treatment of pesticide containing wastewaters. In recent years, advanced oxidation processes (AOPs) were given special attention for removal of toxic compounds from wastewater. AOPs are capable of transforming the pollutants into harmless substances [3] and almost all rely on the generation of reactive hydroxyl radicals (OH^*) with a redox potential of 2.8 V [4]. Hydroxyl radicals react rapidly and indiscriminately with most of the organic compounds, either by addition to a double bond or by

abstraction of a hydrogen atom from an aliphatic organic molecule [5]. The resulting organic radicals then react with oxygen to initiate a series of oxidation reactions ultimately leading to mineralization products of CO_2 and H_2O [6].

Therefore, advanced oxidation is a promising alternative for removal and mineralization of pesticides from water samples. Simazine is a highly toxic pesticide present in surface and ground water sources in concentrations of 0.5–2 $\mu g L^{-1}$. However, in some agricultural areas before dilution by the surface water sources, simazine may be as high as 2–5 $mg L^{-1}$. For this reason, simazine is listed as the priority substances by the EU (Decision No. 2455/2001/EC of the European Parliament and of the Council of 20 November 2001). Limited number of studies was reported in literature on photolysis [7], photo-catalytic degradation [8] and oxidation of simazine [9]. However, the reported studies were mainly focused on the analysis and identification of the main products with proposals for the reaction mechanisms.

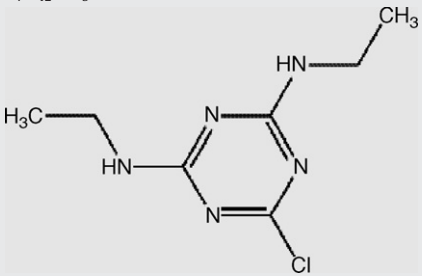
In the light of the literature studies, simazine oxidation and mineralization (TOC removal) by the Fenton's reagent was investigated in this study. The major objective was to determine the effects of the reagent doses (initial pesticide, H_2O_2 and Fe (II) doses) on percent simazine and TOC removals by using a Box–Behnken statistical experiment design approach. Reagent doses maximizing the simazine and TOC removals were determined. Kinetics of simazine degradation was investigated and the kinetic constants were determined using the experimental data.

2. Design of experiments

The classical approach of changing one variable at a time to study the effect of variables on the objective function is a time consuming

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Table 1
Some physico-chemical characteristics of simazine.

Molecular name	6-Chloro-N2,N4-diethyl-1,3,5-triazine-2,4-diamine (simazine)
CAS number	[122-34-9]
Water solubility (mg/L) at 20 °C	5
Water solubility (mg/L) at 85 °C	84
Melting point (°C)	225–227 °C
Molecular formula	C ₇ H ₁₂ ClN ₅
	
Molecular weight (g/mol)	201.657
Vapor pressure (mm Hg) at 20 °C	6.1×10^{-9}
Density at 20 °C (g/mL)	0.436
Henry's law constant (atm m ³ /mol)	9.48×10^{-10}

method particularly for multivariable systems. Design of experiments by using statistical methods can be used for optimization of the process variables in multivariable systems. Response surface methodology (RSM) can be used when only several significant factors are involved in optimization. Pesticide removal from aqueous medium can be studied with a minimum number of experiments by using statistical experiment design and the RSM. The RSM and statistical experiment design comprises a group of statistical techniques for model building and model exploitation [10,11].

Different types of RSM designs include 3-level factorial design, central composite design (CCD) [12,13], Box–Behnken design [14], and D-optimal design [15]. A modified central composite experimental design known as the Box–Behnken design is an independent, rotatable quadratic design containing no embedded factorial or fractional factorial design [13,14]. Among all the statistical experiment design methods, Box–Behnken design requires fewer runs than the other design methods, such as 15 runs for a 3-factor experiment design. Moreover, the method allows calculation of the response function at intermediate levels which is not experimentally studied [10,11].

The Box–Behnken statistical experiment design was reported to be useful in optimization of the response of a three variable response function [16–20]. The optimization process involves evaluating the response of the statistically designed combinations, estimating the coefficients by fitting the experimental data to the response function, predicting the response of the fitted model and checking the adequacy of the model. Therefore, the Box–Behnken statistical experiment design was used in this study to optimize and evaluate the effects of reagent concentrations (H₂O₂, Fe (II) and pesticide dose) on simazine and TOC removals by the Fenton's reagent treatment.

3. Materials and methods

3.1. Chemicals

Simazine of high purity (99.4%) grade was purchased from Riedel-de-Haen (Germany). Chromatographic grade acetonitrile and analytical grade ferrous sulfate (FeSO₄·7H₂O), hydrogen peroxide solution (30% (w/w)), H₂SO₄ (98–99%) and NaOH were all purchased from Merck (Germany). Concentrated stock solution of Fe (II) (3000 mg L⁻¹) was prepared for further dilution to obtain solutions of desired concentrations and was stored at dark. pH adjustments were done by using either sodium hydroxide or sulfuric acid solutions. All other chemicals were of analytical grade

and used without any further purification. Water used for chemical solutions was purified using a Mili-Q system (milipore filtration).

3.2. Analytical methods

Fenton's reagent experiments were carried out at room temperature (23 ± 2 °C) using different H₂O₂ and Fe (II) doses at pH 3.5 which was reported to be the most suitable pH for Fenton treatment [21]. Since the pH of the surface and ground waters are usually around pH 6–7, pH adjustment to 3.5 is required before treatment. Fe (II) was mixed well with wastewater before the addition of hydrogen peroxide solution in batch experiments. The experiments were started by addition of the H₂O₂ as the oxidant. Samples withdrawn from the reactor at certain time intervals were analyzed immediately to avoid further reaction. Samples (20 mL) of raw and treated pesticide solutions were analyzed for pesticide and TOC concentrations. pH levels were also determined for every sample.

Simazine was analyzed using an HPLC (Agilent 1100 model), equipped with a UV-detector and a C18 column. The mobile phase composition was H₂O/acetonitrile with a ratio of 40/60. The UV-detection was operated at 214 nm. The flow rate was 1 mL min⁻¹ and the injection volume was 20 μL. Under these conditions, the retention time for simazine was 4 min. Calibration curve for simazine was constructed using the peak areas of the standard samples under the same conditions as that of the experimental samples. Stock solution of simazine was prepared every other day by dissolving the proper amount of the herbicide in 1 L water and was stored in dark to protect from the light for a day or two. Simazine calibration curve was prepared for concentrations between 0.0015 and 5 mg L⁻¹ with a correlation coefficient of $R^2 = 0.9997$. Higher concentrations of simazine could not be prepared due to low solubility (5 mg L⁻¹ at 20 °C) of simazine.

A Shimadzu TOC Analyzer was used to determine the total organic carbon (TOC) content of the samples. For the TOC measurements, potassium phthalate solution was used as calibration standards with the concentrations between 0 and 5 mg L⁻¹. Samples were analyzed in triplicates and the standard deviations were less than 3% of the average. A pH meter (WTW, Germany) was used to monitor pH.

4. Results and discussion

Box–Behnken statistical experiment design and the response surface methodology [20] was used to investigate the effects of

Table 2
Results of the Box–Behnken experiments at the pre-determined experimental points.

Run no.	Actual and coded levels of variables			Experimental percent removals	
	X ₁ (simazine) (mg L ⁻¹)	X ₂ (H ₂ O ₂) (mg L ⁻¹)	X ₃ (Fe (II)) (mg L ⁻¹)	Y ₁ (pesticide)	Y ₂ (TOC)
1	0.5 (-1)	10 (-1)	15 (0)	100	11.93
2	5 (+1)	10 (-1)	15 (0)	99.79	15.93
3	0.5 (-1)	100 (+1)	15 (0)	98.50	11.74
4	5 (+1)	100 (+1)	15 (0)	97.16	14.69
5	0.5 (-1)	55 (0)	0 (-1)	5.62	8.72
6	5 (+1)	55 (0)	0 (-1)	4.17	8.15
7	0.5 (-1)	55 (0)	30 (+1)	100.	5.95
8	5 (+1)	55 (0)	30 (+1)	100.	14.00
9	2.75 (0)	10 (-1)	0 (-1)	2.60	3.19
10	2.75 (0)	100 (+1)	0 (-1)	3.49	4.20
11	2.75 (0)	10 (-1)	30 (+1)	100.00	9.10
12	2.75 (0)	100 (+1)	30 (+1)	100.00	5.19
13	2.75 (0)	55 (0)	15 (0)	99.05	31.97
14	2.75 (0)	55 (0)	15 (0)	99.68	31.80
15	2.75 (0)	55 (0)	15 (0)	100.	31.64

three independent variables on percent simazine and TOC removals and also to determine the optimal conditions maximizing the removals. The independent variables were the initial dose of pesticide (X₁), hydrogen peroxide (X₂), and ferrous ion (X₃). The response functions were the percent pesticide (Y₁) and TOC (Y₂) removals. The experimental points and the observed results are presented in Table 2 for every experimental point. The center point (0,0,0) was repeated three times and nearly the same results were obtained indicating the reproducibility of the data. The observed and predicted percent removals for simazine, and TOC are compared in Table 3.

4.1. The regression model

The application of RSM offers an empirical relationship between the response function (Y) and independent variables (X) which can be approximated by a quadratic polynomial equation as follows:

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 \quad (1)$$

This model contains one block (b₀), three linear (X_i), three quadratic (X_i²), and three interaction (X_iX_j) 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. Response functions with determined coefficients are presented in Eqs. (2)–(4). The goodness of the fit was tested by using the ANOVA (analysis of variance) test for every response function. The ANOVA test for

Table 3
Comparison of the observed and predicted percent simazine and TOC removals.

Run no	Predicted percent removals		Observed percent removals	
	Y ₁ (pesticide)	Y ₂ (TOC)	Y ₁ (pesticide)	Y ₂ (TOC)
1	100	11.93	99.36	12.05
2	99.79	15.93	99.17	16.18
3	98.50	11.74	99.11	11.49
4	97.16	14.69	97.80	14.57
5	5.62	8.72	5.17	8.31
6	4.17	8.15	3.70	7.61
7	100	5.95	100	6.49
8	100	14.00	100	14.41
9	2.60	3.19	3.69	3.48
10	3.49	4.20	3.32	4.86
11	100	9.10	100.17	8.44
12	100	5.19	98.91	4.90
13	99.05	31.97	99.58	31.80
14	99.68	31.80	99.58	31.80
15	100	31.64	99.58	31.80

percent simazine removal is presented in Table 4 which is used 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 2789.45 implies that the model is significant. The P value of <0.05 for any factor in the ANOVA test indicates a significant effect of the corresponding variable on the response. In this case, X₃ (Fe) and X₃² were significant terms affecting percent pesticide removal.

The response function for percent pesticide removal (Y₁) at the end of 6 min has the following form:

$$Y_1 = 3.96 - 0.289X_1 + 4.81 \times 10^{-2}X_2 + 9.487X_3 - 2.790 \times 10^{-3}X_1X_2 + 1.074 \times 10^{-2}X_1X_3 - 3.296 \times 10^{-4}X_2X_3 + 2.082 \times 10^{-2}X_1^2 - 4.047 \times 10^{-4}X_2^2 - 0.210X_3^2 \quad (R^2 = 0.999) \quad (2)$$

The response function coefficients indicate that the pesticide dose has a negative, but H₂O₂ and Fe (II) doses have positive effects on percent pesticide removal. In other words, percent simazine removal decreases with increasing simazine dose, but increases with increasing peroxide and Fe (II) doses. Fe (II) dose has the most profound effect on pesticide removal with the largest coefficient.

The response function for percent TOC removal (Y₂) at the end of 15 min has the following form:

$$Y_2 = -12.858 + 7.833X_1 + 0.620X_2 + 2.058X_3 - 2.592 \times 10^{-3}X_1X_2 + 6.385 \times 10^{-2}X_1X_3 - 1.822 \times 10^{-3}X_2X_3 - 1.426X_1^2 - 5.436 \times 10^{-3}X_2^2 - 6.833 \times 10^{-2}X_3^2 \quad (R^2 = 0.998) \quad (3)$$

Table 4
ANOVA test for the response function Y₁ (% pesticide removal).

Source	Sum of squares	d.f.	Mean square	F ratio	P value
Model	26,761.07	9	2973.45	2789.45	<0.0001
X ₁ (pesticide)	1.13	1	1.13	1.06	0.3514
X ₂ (H ₂ O ₂)	1.31	1	1.31	1.23	0.3177
X ₃ ((Fe (II)))	18,443.52	1	18,443.52	17,302.21	<0.0001
X ₁ X ₂	0.32	1	0.32	0.30	0.6077
X ₁ X ₃	0.53	1	0.53	0.49	0.5139
X ₂ X ₃	0.20	1	0.20	0.19	0.6844
X ₁ ²	0.041	1	0.041	0.038	0.8522
X ₂ ²	2.48	1	2.48	2.33	0.1877
X ₃ ²	8237.93	1	8237.93	7728.15	<0.0001
Residual	5.33	5	1.07		
Lack of fit	4.86	3	1.62	6.94	0.1286
Pure error	0.47	2	0.23		
Total (corr)	26,766.40	14			

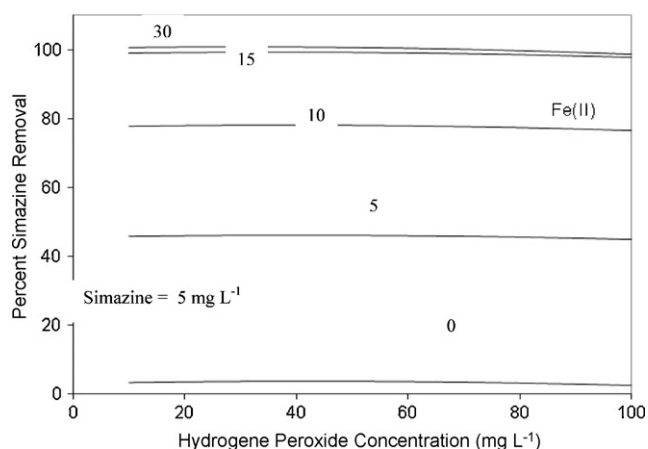


Fig. 1. Variation of percent simazine removal with H₂O₂ concentration at different Fe (II) doses at the end of 6 min reaction time. Simazine = 5 mg L⁻¹. Numbers on the curves represent Fe (II) doses in mg L⁻¹.

The coefficients indicated that pesticide, H₂O₂ and especially Fe (II) doses have positive effects on percent TOC removal. That is, percent mineralization (TOC removal) increases with the peroxide and Fe (II) doses. Simazine dose has the most significant effect on TOC removal due to the largest coefficient. High correlation coefficients for both Y₁ and Y₂ indicated the good fit between the experimental data and the model predictions.

Simazine concentration was varied between 0.5 and 5 mg L⁻¹ which was lower than simazine concentrations in surface and ground waters (0.1–2 μg L⁻¹) although simazine concentrations as high as 5 mg L⁻¹ are encountered in some agricultural areas. Simazine removal performance of the Fenton treatment should be valid for lower concentrations to cover surface and ground water treatments.

4.2. Disappearance of simazine

Response functions with determined coefficients were used to estimate variations of percent simazine and TOC removals as function of the reagent concentrations. Fig. 1 depicts the effect of initial H₂O₂ concentration on percent simazine removal at different Fe (II) concentrations after 6 min of reaction time when the initial simazine dose was 5 mg L⁻¹. Simazine removal was not affected from hydrogen peroxide doses above 10 mg L⁻¹ since simazine dose was low (5 mg L⁻¹) and peroxide doses were relatively high. However, Fe (II) dose significantly affected percent simazine removal which increased with increasing Fe (II) dose up to Fe (II) = 15 mg L⁻¹. Further increases in Fe (II) doses did not yield higher simazine removals. The minimum Fe (II) concentration for complete removal of simazine was 15 mg L⁻¹. Percent pesticide removals were 3.5, 99.4 and 100% for an initial pesticide dose of 5 mg L⁻¹ and Fe (II) doses of 0, 15 and 30 mg L⁻¹, respectively when H₂O₂ dose was 20 mg L⁻¹. High Fe (II) doses above 30 mg L⁻¹ had adverse effects on pesticide removal due to hydroxyl ion scavenging effect of Fe (II). The results are in agreement with the literature reports, where a beneficial effect of increasing Fe (II) was observed in photo-degradation of pesticides [22,23]. Complete degradation of simazine (5 mg L⁻¹) was accomplished at a hydrogen peroxide and Fe (II) doses of 20 and 15 mg L⁻¹, respectively after 6 min reaction time. Lower concentrations of Fe (II) did not result in complete simazine removal.

Effects of simazine and H₂O₂ concentrations on percent simazine oxidation by the Fenton treatment are depicted in Fig. 2 at a Fe (II) dose of 15 mg L⁻¹. Percent simazine removal increased with decreasing initial simazine concentrations for all perox-

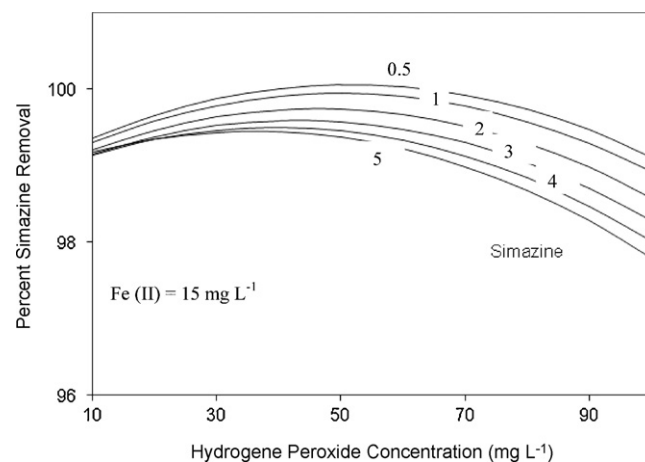


Fig. 2. Variation of percent simazine removal with H₂O₂ concentration at different simazine doses at the end of 6 min reaction time. Fe (II) = 15 mg L⁻¹. Numbers on the curves represent simazine doses in mg L⁻¹.

ide doses. However, simazine removals were between 98 and 100% indicating rather slight changes in percent removals with simazine concentration since the initial simazine doses were low (0.5–5 mg L⁻¹). Simazine removals increased with H₂O₂ concentration up to 50 mg L⁻¹ due to H₂O₂ limitations at low peroxide doses. Further increases in peroxide dose resulted in decreases in percent simazine removals probably due to hydroxyl radical scavenging effects of high peroxide doses. At constant simazine and Fe (II) doses of 5 and 15 mg L⁻¹ and variable H₂O₂ doses of 10, 50 and 100 mg L⁻¹ percent pesticide removals were calculated from the response function as 99.0, 99.5 and 98.2%, respectively. Therefore, peroxide dose of 50 mg L⁻¹ was optimal maximizing the pesticide removal.

Rivas et al. [9] investigated the effects of pH, temperature and Fe (II) concentration on simazine removal at a constant peroxide dose. Unlike the Rivas study, peroxide dose was considered as a variable in our study and the effects of peroxide on both simazine and TOC removals were investigated. Fe (II) dose was found to have more profound effect on simazine removal as compared to peroxide dose. Furthermore, both Fe (II) and peroxide doses had adverse effects on simazine removal above certain concentrations due to hydroxyl ion scavenging effects of those reagents. The ANOVA analysis indicated that Fe (II) dose (X₃, X₃²) played an important role in simazine oxidation by the Fenton' reagent treatment (*p*-value < 10⁻⁴). Due to low solubility of simazine in water, simazine doses were less than 5 mg L⁻¹ and peroxide doses were in excess and therefore, not much affecting the simazine removal. Fe (II) doses up to 15 mg L⁻¹ were needed for effective simazine removal.

4.3. TOC removal: mineralization of simazine

Overall mineralization of simazine using oxygen as oxidizing agent can be written as follows:



Complete mineralization of simazine was not achieved within 60 min of oxidation although simazine disappeared within 6 min. This difference indicated formation of intermediate products during the oxidation reaction which were not completely degraded to CO₂ and H₂O.

2-hydroxy-4,6-bis(ethylamino)-s-triazine, 2-chloro-4-amino-6-ethylamino)-s-triazine (deisopropylatrazine), and 2-chloro-4,6-diamino-s-triazine (diamino chlorotriazine) were reported to be the main photochemical degradation intermediates [24,25].

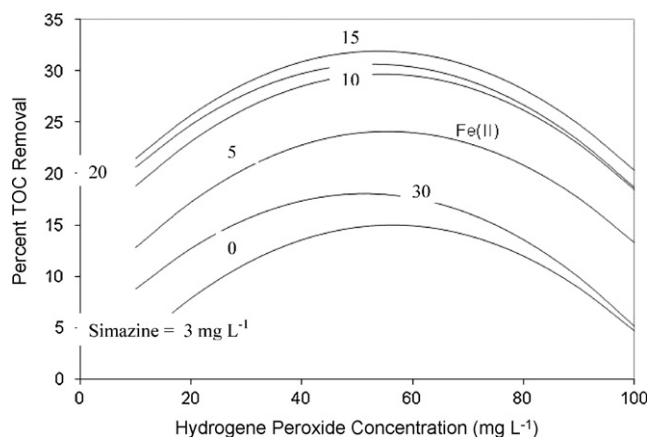


Fig. 3. Variation of percent TOC removals with H₂O₂ concentration at different Fe(II) doses at the end of 15 min reaction time. Simazine = 3 mg L⁻¹. Numbers on the curves represent Fe(II) doses in mg L⁻¹.

As depicted in Fig. 3, percent mineralization or TOC removal increased with peroxide dose up to 50 mg L⁻¹ for all Fe(II) doses between 0 and 30 mg L⁻¹ indicating peroxide limitations at low peroxide concentrations. Peroxide concentrations above 50 mg L⁻¹ resulted in decreases in percent TOC removal indicating adverse effects of high H₂O₂ concentrations. Therefore, the optimum peroxide dose was 50 mg L⁻¹ under the experimental conditions used. In agreement with Glaze et al. [26] and Beltran et al. [27], a reduction in TOC removal was observed at high peroxide concentrations indicating the adverse effects of excess peroxide doses. This is due to hydroxyl ion (HO[•]) scavenging by excess H₂O₂ and consequent formation of the less reactive radical HO₂[•] as presented by the following reactions:



At constant simazine and Fe(II) doses of 3 and 15 mg L⁻¹ and variable H₂O₂ doses of 10, 50 and 100 mg L⁻¹ percent TOC removals can be calculated using the response function as 21.5, 31.8 and 20.4%, respectively indicating the optimum peroxide dose of 50 mg L⁻¹. Percent TOC removals were much lower than simazine removals indicating incomplete degradation of simazine and formation of some intermediate products.

Percent TOC removals also increased with Fe(II) doses up to 15 mg L⁻¹ due to Fe(II) limitations at low Fe doses (Fig. 3). Further increases in Fe(II) dose above 15 mg L⁻¹ resulted in decreases in simazine removal probably due to hydroxyl ion scavenging effects of high Fe(II) doses. Therefore, the optimum Fe(II) dose was 15 mg L⁻¹. The highest TOC removal was 32.5% obtained at peroxide and Fe(II) doses of 50 and 15 mg L⁻¹ when simazine was 3 mg L⁻¹. At a simazine concentration of 5 mg L⁻¹ (not shown in Fig. 4), percent TOC removals were calculated from the response function as 7.4, 26.4 and 14.5%, respectively, at Fe(II) doses of 0, 15 and 30 mg L⁻¹ and peroxide dose of 50 mg L⁻¹ indicating the same optimum doses of peroxide (50 mg L⁻¹) and Fe (15 mg L⁻¹).

Variation of percent TOC removal (mineralization) with the peroxide dose at different simazine concentrations is depicted in Fig. 4 at a constant Fe(II) dose of 15 mg L⁻¹. Percent TOC removal steadily increased when simazine dose was increased from 0.5 to 3 mg L⁻¹ due to limitations by low simazine doses while peroxide and Fe(II) were in excess. Further increases in simazine dose above 3 mg L⁻¹ resulted in decreases in TOC removal due to limitations by the peroxide and Fe(II) at high simazine doses. The optimum simazine dose was 3 mg L⁻¹ under the specified experimental conditions. Similarly, percent TOC removal increased with increasing peroxide

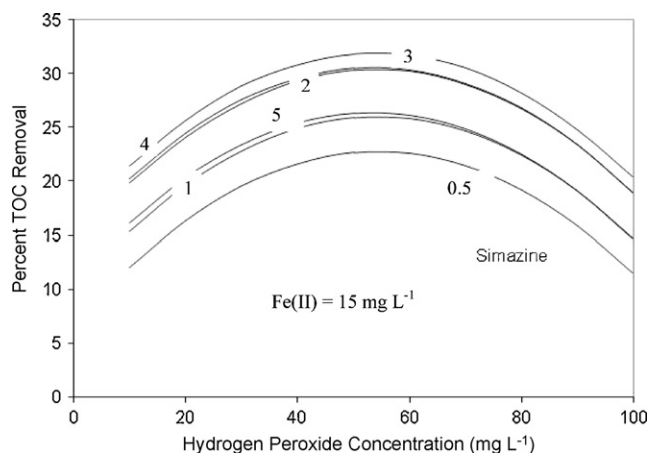


Fig. 4. Variation of percent TOC removal with H₂O₂ concentration at different initial simazine doses at the end of 15 min reaction time. Fe(II) = 15 mg L⁻¹. Numbers on the curves represent simazine concentrations in mg L⁻¹.

dose up to 50 mg L⁻¹ due to peroxide limitations at low concentrations. TOC removals decreased when peroxide dose increased above 50 mg L⁻¹ due to adverse effects of high peroxide concentrations by scavenging hydroxyl ions. Therefore, the optimum doses of peroxide (oxidant) and Fe (catalyst) was found to be 50 and 15 mg L⁻¹, respectively.

Initial simazine concentration was the most important parameter affecting the efficiency of simazine removal by the Fenton oxidation. At low simazine dose of 0.5 mg L⁻¹, the optimal H₂O₂/Fe(II)/simazine dose yielding the highest TOC removal (22.1%) was 45/13/0.5 mg L⁻¹, while at a simazine concentration of 3 mg L⁻¹ this ratio was 55/15/3 mg L⁻¹ yielding 31.9% TOC removal.

4.4. Kinetics of simazine degradation

Time course of variations of simazine concentrations for different experiments of the Box–Behnken design are depicted in Fig. 5. Simazine concentration decreased steadily with time and the reaction was almost completed within 6–12 min in most cases. Simazine oxidation by the Fenton reagent can be described by the following reaction:

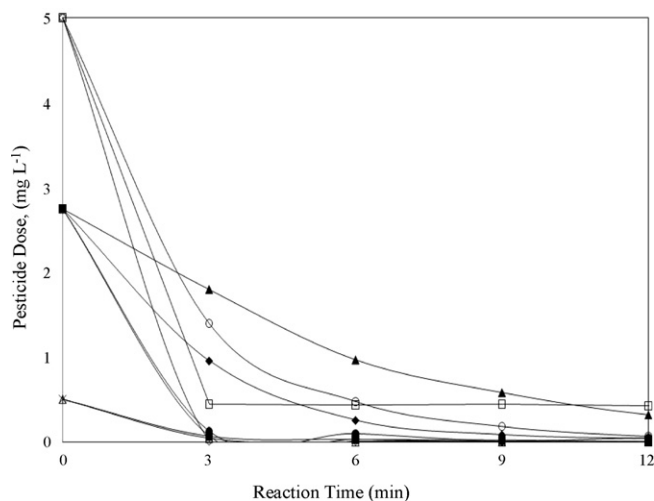
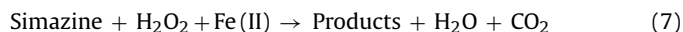


Fig. 5. Time course of variations of simazine concentration for different experiments: (□) A₂, (Δ) A₃, (◆) A₄, (●) A₆, (■) A₇, (▲) A₉, (×) A₁₂, and (○) A₁₃.

Table 5
Initial rates of simazine degradation at different experimental conditions of the Box–Behnken design.

Run no.	A ₁	A ₂	A ₃	A ₄	A ₅	A ₆	A ₇	A ₈	A ₉	A ₁₀	A ₁₁	A ₁₂	A ₁₃
R ₀ (mg L ⁻¹ min ⁻¹)	0.32	1.66	0.31	1.48	0.00	0.07	0.32	1.68	0.02	0.03	0.96	0.96	0.95
Simazine ₀ (mg L ⁻¹)	0.5	5	0.5	5	0.5	5	0.5	5	2.75	2.75	2.75	2.75	2.75
(H ₂ O ₂) ₀ (mg L ⁻¹)	10	10	100	100	55	55	55	55	10	100	10	100	55
Fe (II) ₀ (mg L ⁻¹)	15	15	15	15	0	0	30	30	0	0	30	30	15

The initial reaction rates of simazine degradation can be expressed in terms of initial simazine, H₂O₂ and Fe (II) concentrations as follows:

$$R_0 = \left(\frac{-dS}{dt} \right)_0 = kS_0^\alpha HP_0^\beta Fe_0^\gamma \quad (8)$$

where R_0 is the initial rate of simazine degradation (mg S L⁻¹ min⁻¹); k is the rate constant; S_0 , HP_0 and Fe_0 are the initial simazine, peroxide and Fe (II) concentrations, respectively (mg L⁻¹).

In linearized form the rate equation can be written as

$$\ln R_0 = \ln k + \alpha \ln S_0 + \beta \ln HP_0 + \gamma \ln Fe_0 \quad (9)$$

The initial rates obtained within the first 3 min are presented in Table 5 for every experiment of the Box–Behnken design. The experimental data were used for calculation of the initial rates for every experiment by using the equation $R_0 = -\Delta S/\Delta t$ where $\Delta t = 3$ min. The initial rates were correlated with the initial simazine, peroxide and Fe (II) concentrations by using the STATISTICA 5.0 computer program to determine the exponents and the coefficient of the rate expression. The following constants were determined from the regression analysis:

$$k = 0.009, \quad \alpha = 0.957, \quad \beta = -0.03, \quad \gamma = 1.297 \quad (R^2 = 0.96)$$

Therefore, the rate equation takes the following form,

$$R_0 = \left(\frac{-dS}{dt} \right)_0 = 0.09S_0^{0.957} HP_0^{-0.03} Fe_0^{1.297} \quad (10)$$

The rate of simazine degradation is almost first-order (0.957) with respect to simazine concentration; almost zeroth-order with respect to peroxide and 1.3rd-order with respect to Fe (II) concentration. Peroxide concentrations were in excess due to low simazine concentrations yielding almost zero-order kinetics with respect to peroxide concentration. In agreement with our previous findings, the rate of simazine degradation is more profoundly affected from the Fe (II) dose as compared to the simazine and peroxide doses.

5. Conclusions

The response surface methodology and the Box–Behnken statistical experiment design were used to generate statistically reliable results for oxidation of simazine by Fenton's reagent and also for determination of optimum conditions maximizing the simazine and TOC removals. Predictions obtained from the response functions were in good agreement with the experimental results indicating the reliability of the method used. The response surface methodology also provided better understanding of the roles of Fe (II) and H₂O₂ doses on degradation of simazine for a large range of concentrations. Independent variables and their interactions were found to be effective in pesticide and TOC removals by the Fenton's reagent.

High simazine removals indicated effective breakdown of simazine. However, low TOC removals (low mineralization) indicated incomplete simazine degradation and formation of intermediary products. Fe (II) dose was found to affect simazine degradation more profoundly than the peroxide dose. Percent

simazine removal decreased with increasing initial simazine concentration. At a constant simazine concentration, percent TOC removal increased with increasing H₂O₂ and Fe (II) concentrations up to 15 mg L⁻¹ Fe (II) and 50 mg L⁻¹ peroxide above which mineralization decreased due to scavenging effects of H₂O₂ on hydroxyl radicals. Maximum pesticide (100%) and TOC removals (32%) were obtained with a H₂O₂/Fe (II)/simazine ratio of 55/15/3 (mg L⁻¹). Simazine degradation was incomplete yielding formation of intermediates which were not completely mineralized to CO₂ and H₂O.

The initial rate of simazine degradation was found to be first-order with the initial simazine concentration, almost zeroth-order with respect to peroxide and nearly 1.3rd-order with the Fe (II) concentration.

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