Optimized Removal of Sodium Dodecylbenzenesulfonate by Fenton-Like Oxidation Using Response Surface Methodology

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ABSTRACT: *This study investigates the degradation of sodium dodecylbenzenesulfonate (SDBS) in aqueous solution by Fenton-like oxidation process. The effects of different parameters such as concentrations of ferric chloride and hydrogen peroxide, pH and reaction time on the SDBS removal and Chemical Oxygen Demand (COD) reduction were evaluated. Response Surface Methodology (RSM) with Central Composite Design (CCD) was used to study and optimize the oxidation process. A quadratic polynomial equation could accurately model the SDBS removal with an R^2 of 0.98. The results showed that pH and time were the most significant parameters affecting SDBS removal and COD reduction, respectively. A high SDBS (90.5%) and COD (70.7%) reduction efficiency was obtained at the optimal conditions of 60 min, pH 4 and 8.82 mM of H_2O_2 and 3.67mM of Fe^{+3}. In this work, the effects of some organic compounds on the degradation of SDBS by Fenton-like process were examined. The results showed that 50 $mgL^{-1}$of oxalic acid slightly enhanced the SDBS degradation efficiency while acetic acid and Ethylenediaminetetraacetic acid (EDTA) reduced it.*

KEYWORDS: *Degradation; Fenton-like process; Response surface methodology; Sodium dodecylbenzenesulfonate.*

INTRODUCTION

Surfactants are surface-active chemicals used in high volumes in the formulation of detergents, household cleaning and personal care products [1]. They are also widely used in the oil, textile, food, pharmaceuticals, paints, polymers, pulp and paper, fibbers, electroplating and mining industries [2]. Based on their ionic nature, surfactants are divided into four categories namely, anionic, cationic, nonionic and amphoteric [1,3]. Anionic surfactants are the major class used in detergent formulations, and hence the most frequently detected

113

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Iran. J. Chem. Chem. Eng.   *Taghavi K. et. al.*   *Vol. 35, No. 4, 2016*

surfactants in urban wastewaters [1]. The presence of surfactants in the aquatic environments could seriously affect the ecosystem [4]. The toxicity of surfactants to various organisms such as algae, invertebrate and fish is well documented [4]. Surfactants are also responsible for causing foams and reducing the quality of water. These foams are possible habitat for disinfectant-resistant bacteria and therefore affect the human health when arrive into drinking water [5]. In addition, the use of water polluted by surfactants as the source of irrigation leads to groundwater contamination, generates soil depletion, and adversely affects plant growth [5]. Biological treatment, either aerobic or anaerobic, is the dominant conventional treatment process for surfactants discharged into water bodies. However, at high surfactant concentrations, >50 mg/L, biodegradation may be restricted and even inhibited [6]. Therefore, exploring the potential of alternative advanced treatment techniques would be of great interest.

Fenton oxidation is a proven and effective technology for degradation of a large number of hazardous organic pollutants [7].The mixture of ferrous iron and hydrogen peroxide (Fenton's reagent) at low enough pH, results in the formation of a strong oxidizing agent (hydroxyl radicals) that destructs organic compounds in a short time[8,9].

Besides Fenton process, Fenton-like reactions in which ferric ions or other transition metal ions are utilized have been effective at organic components degradation in wastewater [10,11]. *Jiang et al.* [12] studied the effect of various parameters such as H_2O_2 concentration, iron dosage and pH on the phenol degradation in Fenton and Fenton-like reactions. The results of their study demonstrated that although the reaction mechanisms and effects of parameters were different, the overall degree of phenol degradation at the optimal conditions was equivalent for the two reactions.

Fenton degradation of anionic surfactant linear alkylbenzenesulphonates (LAS) and optimization of the operating parameters have been reported previously [13]. The results showed that the degradation capacity of the Fenton's reagent was highly dependent on the concentration of H_2O_2 and Fe^{+2}. The optimum $FeSO_4/H_2O_2$ ratio obtained was higher than 1 and the optimum pH was around 3. Under the optimum conditions, the LAS surfactant removal was over 95%.
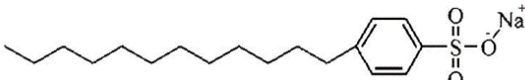
Fenton-like agent, $Fe(0)/H_2O_2$, has been used to degrade the anionic surfactant, sodium dodecylbenzenesulphonate (SDBS). Approximately, 90% of SDBS degradation efficiency was accomplished at a pH range from 3.0 to 6.5 [14]. Fenton oxidation of SDBS by ferrous sulfate and hydrogen peroxide was also studied by Ahmadi and Gorgani [15]. Initial concentration of hydrogen peroxide was found to be the most important parameter for Chemical Oxygen Demand (COD) reduction. Optimum condition for maximum COD reduction (38.5%) was obtained at pH=3.7 where the initial SDBS concentration was 1.68 mM and the H_2O_2 concentration was 2.27 mM.

Since that Fenton and Fenton-like reactions are affected by several parameters such as iron and hydrogen peroxide concentrations, in addition to the pH of the reaction medium, the treatment conditions are specific to each case and therefore have to be carefully optimized [16]. Response Surface Methodology (RSM) is a set of mathematical and statistical techniques useful for analyzing the effects of several independent variables on the response [17]. RSM has been successfully applied for optimization and modeling of Fenton oxidation of various types of wastewater [18].

In the present study, the anionic surfactant SDBS was chosen as the model compound due to its widespread use in detergents and cleaning products. The potential of Fenton-like $FeCl_3/H_2O_2$ system for mineralization of SDBS was evaluated. Although, Fenton-like Fe^0/H_2O_2 system have been used previously for degradation of SDBS [14], however, so far, there is no report on the application of $FeCl_3/H_2O_2$ system for the treatment of wastewater containing SDBS. Furthermore, a detailed study aiming to evaluate the operating parameters involved in the Fenton-like oxidation of SDBS using mathematical models was not presented before. On the other hand, the effect of some organic compounds such as oxalic acid, acetic acid and Ethylenediaminetetraacetic acid (EDTA) on the SDBS removal efficiency of the Fenton-like system was studied for the first time.

The aim of the present work was to investigate the possibility of degradation of SDBS surfactant by Fenton-like $FeCl_3/H_2O_2$ system. RSM was used to analyze the effect of operational parameters including pH, oxidation time, H_2O_2 and $FeCl_3$ concentrations on the SDBS degradation efficiency. In this study, COD reduction

Table 1: Chemical properties of sodium dodecylbenzene sulfonate (SDBS) [19].

Formula and structure	MW (g mol^{-1})	Color	Melting point	Solubility in water (g/100ml, 25°C)	Octanol/water partition coefficient
$CH_3(CH_2)_{11}C_6H_4SO_3Na$	348.48	Light yellow	>300°C	20	0.45

was also determined in order to explain the degradation of SDBS in the Fenton-like process.

EXPERIMENTAL SECTION
Materials

All reagents used in this work were of analytical grade. Sodium dodecylbenzenesulfonate (SDBS) was purchased from Sigma-Aldrich and used as received without further purification to prepare simulated wastewater. The chemical structure and properties of SDBS is presented in Table 1. Hydrogen peroxide (H_2O_2, 30% w/w) and acetic acid were purchased from Merck. Ferric chloride ($FeCl_3.6H_2O$), oxalic acid, ethylenediaminetetraacetic acid disodium salt and calcium hydroxide were obtained from Sigma-Aldrich.

Analytical methods

The pH was measured by using a pH meter (Aqualytic AL15, Germany). The amount of anionic surfactant in each sample was determined by a UV–Vis spectrophotometer (Jenway 7315, UK) as the Methylene Blue Active Substances (MBAS) in 652 nm. The MBAS method is a standard method for determination of anionic surfactants. This method is based on the emergence of ionic pairs, including anionic surfactant and the cationic dye (methylene blue), and their transport from water phase to organic phase (chloroform). The analytical procedure is carried out with a triple extraction of the ionic pairs from 100 mL of a previously alkalized sample and measuring the absorbance of the extract [20]. The SDBS removal percentage was calculated using the following equation:

$$SDBS\ removal\,(\%) = \frac{c_i - c_f}{c_i} \times 100 \qquad (1)$$

where C_i is the initial SDBS concentration (mg SDBS/L) and C_f is the final concentration (mg SDBS/L).

Potassium dichromate analysis was utilized for measuring COD according to the standard methods for the examination of water and wastewater [21]. COD reduction percentage was determined by the following equation:

$$COD\ reduction\,(\%) = \frac{COD_i - COD_f}{COD_i} \times 100 \qquad (2)$$

where COD_i and COD_f are the measured COD values before and after the Fenton-like process, respectively.

Fenton-like oxidation of SDBS solution with a concentration of 150 mg/L and COD of 456 mg/L was carried out in batch mode using a 500 mL jar. The reaction temperature was 25 ±1 °C for all experiments. After pH adjustment, ferric chloride and hydrogen peroxide were added to the reactor. During the oxidation process, a large amount of small flocs in the solution was observed. The flocs were not easy to settle out because of their small sizes. To rapidly remove the flocs, chemical coagulation is highly effective. In addition, coagulation can also remove dissolved iron concentration from the wastewater after the oxidation process. After completion of Fenton-like reaction, calcium hydroxide, $Ca(OH)_2$, was added and the solution was stirred rapidly for 1 min. Then, 5 M NaOH solution was added to adjust the pH to 7-8, and a small amount of acrylamide-based anionic polyelectrolyte solution was added for flocculation. After that, the solution was kept undisturbed for 1 hour for settling of the flocs. The supernatant was analyzed for COD and SDBS.

Design of experiments, statistical analysis and optimization

To reduce the number of experiments and to optimize the treatment conditions, a Central Composite Design (CCD), with seven replicates at the center point was employed with 31 experiments. All experiments were performed in triplicate. The variables selected for the Fenton-like oxidation of SDBS were pH, H_2O_2 and Fe^{3+}

115

Table 2: Range of variables for the central composite design.

Variable		Levels	
	-1	0	1
pH, A	3	4	5
H_2O_2 (mM), B	2.95	8.82	14.70
Fe^{3+} (mM), C	1.85	3.78	5.50
Time (min), D	20	60	100

concentrations and time. The range of variables and their levels is shown in Table 2. SDBS removal and COD reduction were analyzed as the responses. The employed design of experiments is presented in Table 3.

For statistical calculations, the variables X_i were coded as χ_i according to the following equation:

$$\chi_i = \frac{X_i - X_0}{\partial X} \tag{3}$$

The response could be simply related to the independent variables by the following quadratic equation:

$$Y = \beta_0 + \sum_{i=1}^{K} \beta_i X_i^2 + \sum_{i=1}^{K} \beta_{ii} X_i^2 + \sum_{i=1}^{k-1} \times \sum_{j=2}^{k} \beta_{ij} X_i X_j \tag{4}$$

where Y is the response; X_i and X_j are the independent variables; β_0 is the constant coefficient; and β_i, β_{ii}, and β_{ij} are the interaction coefficients of linear, quadratic, and second-order terms, respectively.

The results of the experimental design were analyzed and interpreted by Design Expert Version 6.0.6 (Stat-Ease, Statistics Made Easy, Minneapolis, MN, USA) statistical software. An analysis of variance (ANOVA) was performed to examine whether the developed models were adequate to describe the observed data.

RESULTS AND DISCUSSION

Model fitting and ANOVA

Design matrix of the variables along with obtained SDBS removal percentage is given in Table 3. Fitting of the data to the full quadratic multiple regression model and the subsequent ANOVA showed that the SDBS removal by Fenton-like oxidation could suitably described by the following equation:

$$\text{SDBS removal}(\%) = 88.09 - 10.19A + 0.65B + \tag{5}$$

$$1.78C + 9.31D - 15.97A^2 - 7.25D^2 + 3.71AB - 1.73AC + 3.39AD + 2.89BD$$

Where A is pH, B hydrogen peroxide concentration (mM), C Fe^{3+} concentration (mM), and D the time.

The ANOVA for the model is shown in Table 4. The insignificant terms were removed from the model. The F value of the model (103.14) with a P value less than 0.0001 implies that the model is significant at the 95% confidence level. The model showed no lack of fit at the 95% level of significance. The small P value and a very high coefficient of determination (R^2=0.9810) also indicate the adequacy of the model for representing the real relationship among the parameters [22]. The predicted R^2 of 0.9447 is in reasonable agreement with the adjusted R^2 of 0.9715 and thus implies that the model can be used to navigate the design space.

Table 3 also presents the COD reduction percentage for each experiment. According to ANOVA, a quadratic polynomial model was statistically significant to represent the actual relationship between the response (COD reduction) and the variables, with a very small P value (<0.0001) and a high coefficient of determination (R^2= 0.9744). The model also showed no lack of fit at 95% level of significance. The equation of the model (based on the coded values) is as follows:

$$\text{COD reduction}(\%) = 68.16 - 0.91A + 1.42B + \tag{6}$$

$$3.32C + 8.08D - 6.04A^2 - 12.14B^2 - 7.50C^2 - 6.56D^2 - 1.84AC - 4.07AD + 6.61BC$$

Where A is pH, B hydrogen peroxide concentration (mM), C Fe^{3+} concentration (mM), and D the time.

Effect of parameters

The significance of each parameter in the model was evaluated by testing the null hypothesis. If the P value

116

*Table 3: Composition of various experiments of t0he CCD, and SDBS and COD reduction responses
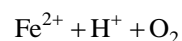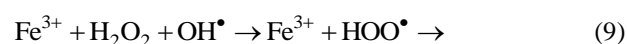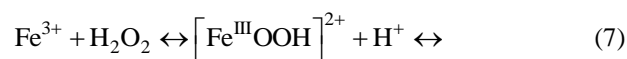for the Fenton-like oxidation process.*

Exp. no.	Variable				SDBS Removal (%)	COD Reduction (%)
	pH	H_2O_2 (mM)	Fe^{3+} (mM)	time (min)		
1	0	0	0	0	90.46	70.66
2	1	-1	-1	-1	40.37	35.26
3	1	1	1	1	75.14	45.41
4	0	0	0	0	89.59	73.48
5	0	0	0	0	87.29	74.22
6	-1	1	1	-1	65.18	40.15
7	-1	-1	-1	-1	71.85	25.39
8	0	0	0	0	88.17	70.06
9	-1	1	-1	-1	60.35	16.54
10	1	1	-1	-1	45.12	25.25
11	0	0	1	0	90.20	65.63
12	-1	-1	1	-1	79.19	20.37
13	-1	1	-1	1	73.15	40.43
14	1	1	-1	1	73.25	30.58
15	1	1	1	-1	43.28	40.35
16	0	1	0	0	84.17	55.30
17	-1	-1	-1	1	80.41	48.49
18	1	0	0	0	60.78	60.23
19	1	-1	1	1	60.71	33.30
20	0	0	0	0	92.64	68.32
21	0	0	0	0	89.81	68.13
22	-1	0	0	0	83.40	58.91
23	0	0	0	1	91.25	70.51
24	0	-1	0	0	83.24	51.64
25	0	0	0	-1	70.38	47.60
26	1	-1	-1	1	60.44	45.60
27	0	0	0	0	87.29	67.55
28	-1	-1	1	1	80.38	45.25
29	0	0	-1	0	86.20	50.60
30	1	-1	1	-1	40.23	25.26
31	-1	1	1	1	88.87	62.12

Table 4: ANOVA for the quadratic models used for the Fenton-like oxidation process.

Source	Sum of squares	Degree of freedom	Mean square	F value	P value
SDBS removal (%)					
Model	7689.63	10	768.96	103.14	< 0.0001
A, pH	1869.87	1	1869.87	250.80	< 0.0001
B, H_2O_2 concentration	7.59	1	7.59	1.02	0.3250
C, Fe^{3+} concentration	57.03	1	57.03	7.65	0.0119
D, time	1561.47	1	1561.47	209.43	< 0.0001
A^2	885.56	1	885.56	118.78	< 0.0001
D^2	182.39	1	182.39	24.46	< 0.0001
AB	219.93	1	219.93	29.50	< 0.0001
AC	47.89	1	47.89	6.42	0.0197
AD	184.28	1	184.28	24.72	< 0.0001
BD	133.29	1	133.29	17.88	0.0004
Residual	149.11	20	7.46		
Lack of fit	126.91	14	9.07	2.45	0.1385
Pure error	22.20	6	3.70		
Corrected total	7838.74	30			
COD reduction (%)					
Model	8779.64	11	798.15	65.67	< 0.0001
A, pH	14.96	1	14.96	1.23	0.2811
B, H_2O_2 concentration	36.32	1	36.32	2.99	0.1001
C, Fe^{3+} concentration	198.00	1	198.00	16.29	0.0007
D, time	1176.45	1	1176.45	96.79	< 0.0001
A^2	94.80	1	94.80	7.80	0.0116
B^2	382.72	1	382.72	31.49	< 0.0001
C^2	145.94	1	145.94	12.01	0.0026
D^2	111.64	1	111.64	9.19	0.0069
AC	54.06	1	54.06	4.45	0.0484
AD	264.63	1	264.63	21.77	0.0002
BC	699.47	1	699.47	57.55	< 0.0001
Residual	230.94	19	12.15		
Lack of fit	189.10	13	14.55	2.09	0.1879
Pure error	41.84	6	6.97		
Corrected total	9010.58	30			

is less than 0.05 (at 95% level of significance), the null hypothesis is rejected, which means that the parameter is significant [22]. According to ANOVA (Table 4), pH, time and Fe^{3+} concentration are the significant parameters in the Fenton-like oxidation and removal of SDBS, whereas time and Fe^{3+} concentration are the most significant parameters that affect the COD reduction.

According to Ahmadi and Gorgani [15], H_2O_2 concentration was the most significant parameter in Fenton oxidation of SDBS using ferrous sulfate and hydrogen peroxide. However, Fenton-like reactions are highly sensitive to pH and more dependent on iron dosage because of the demand of the conversion of Fe(III) to Fe(II) [12].The corresponding mechanism of Fenton-like oxidation is as follows:

$$Fe^{3+} + H_2O_2 \leftrightarrow \left[Fe^{III}OOH\right]^{2+} + H^+ \leftrightarrow \qquad (7)$$
$$Fe^{2+} + HOO^\bullet + H^+$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + 2OH^\bullet \qquad (8)$$

$$Fe^{3+} + H_2O_2 + OH^\bullet \rightarrow Fe^{3+} + HOO^\bullet \rightarrow \qquad (9)$$
$$Fe^{2+} + H^+ + O_2$$

According to ANOVA (Table 4), the interaction terms AB, AC, AD and BD are significant in the Fenton-like oxidation and removal of SDBS. Fig. 1a presents the response surface plot in a three dimensional (3D) representation reflecting the effects of pH and H_2O_2 concentration on the removal of SDBS. As can be seen in Table 4, pH is the most significant parameter (F value = 250.8) that affects the Fenton-like reaction. Maximum SDBS removal was obtained at pH = 3.6 and 8.1 mM H_2O_2. Increasing the concentration of H_2O_2 from 2.95 to 14.7 did not have a significant effect on the SDBS removal. At the optimum pH, by increasing H_2O_2 concentration from 2.95 to 8.12 mM, SDBS removal increased slightly from 86.7 to 90.0%, and then a decrease in the removal efficiency was observed by increasing H_2O_2 concentration to 14.7 mM. As it was mentioned previously, Fenton-like oxidation is highly pH-dependent. The pH-dependent nature of the Fenton-like reactions might be caused by the inhibition of the Fe(III)-H_2O_2 complex formation at extremely low pH according to reaction 1. In addition, Fe(III) can precipitate as ferric hydroxideat higher pH levels. Therefore, an optimum amount of pH would be favorable for

the reaction. The results were in agreement with the previous studies on the Fenton-like oxidation of various organic compounds [23].

Fig. 1b depicts the 3D response surface plot regarding the effect of Fe^{3+} concentration, pH, and their interactions on the SDBS removal at H_2O_2 concentration of 8.82 mM and 60 min (center point of the experimental design). Maximum SDBS removal (93.5%) was obtained at pH=3.6 and 5.5 mM of Fe^{3+}. At the optimum pH (3.6), SDBS removal increased as the dose of Fe(III) increased. According to reaction 1, a low Fe(III) dose would lead to a low concentration of $[Fe^{III}OOH]^{2+}$ complex. As the Fe(III) dose increased, the formation of the complex enhanced and consequently accelerated the formation of Fe(II) and $OH^\bullet$ [11]. In addition, higher concentrations of Fe(III) ions might have been advantageous in terms of SDBS removal due to the post coagulation process. Fig. 1c shows the effect of varying pH and reaction time on the removal of SDBS using 3.67 mM Fe^{3+} and 8.82 mM H_2O_2. Finding the optimum reaction time is important in Fenton and Fenton-like processes. If the reaction time exceeds the equilibrium, the process will be no longer economical. The result showed that by prolonging the reaction time, the SDBS removal increased. At the optimum pH, the equilibrium time was obtained at 60 min. The SDBS removal percentage increased from 75.7 to 90.0% by increasing the time from 20 to 60 min. After the equilibrium time, the SDBS removal did not change significantly. The equilibrium time is probably attributed to the recalcitrant nature of the oxidation by-products, which cannot undergo further degradation by hydroxyl radicals.

The effect of varying time and H_2O_2 concentration is shown in Fig. 1d. The main chemical cost of Fenton/Fenton like reagent is the cost of H_2O_2. Therefore, it is important to optimize the amount of H_2O_2 in the process. At pH=4 (center point of the design), 90% SDBS removal was obtained at 69 min and H_2O_2 concentration of 11.6 mM. A slight decrease was observed by increasing the H_2O_2 concentration from 11.6 to 14.7 mM. By increasing the H_2O_2 concentration, the H_2O_2 decomposition increases until an optimal H_2O_2 concentration is achieved. When the H_2O_2 concentration exceeds the optimal concentration, the decomposition of H_2O_2 decreases as a result of the scavenging effect and regeneration of H_2O_2 according to the following reactions [12]:
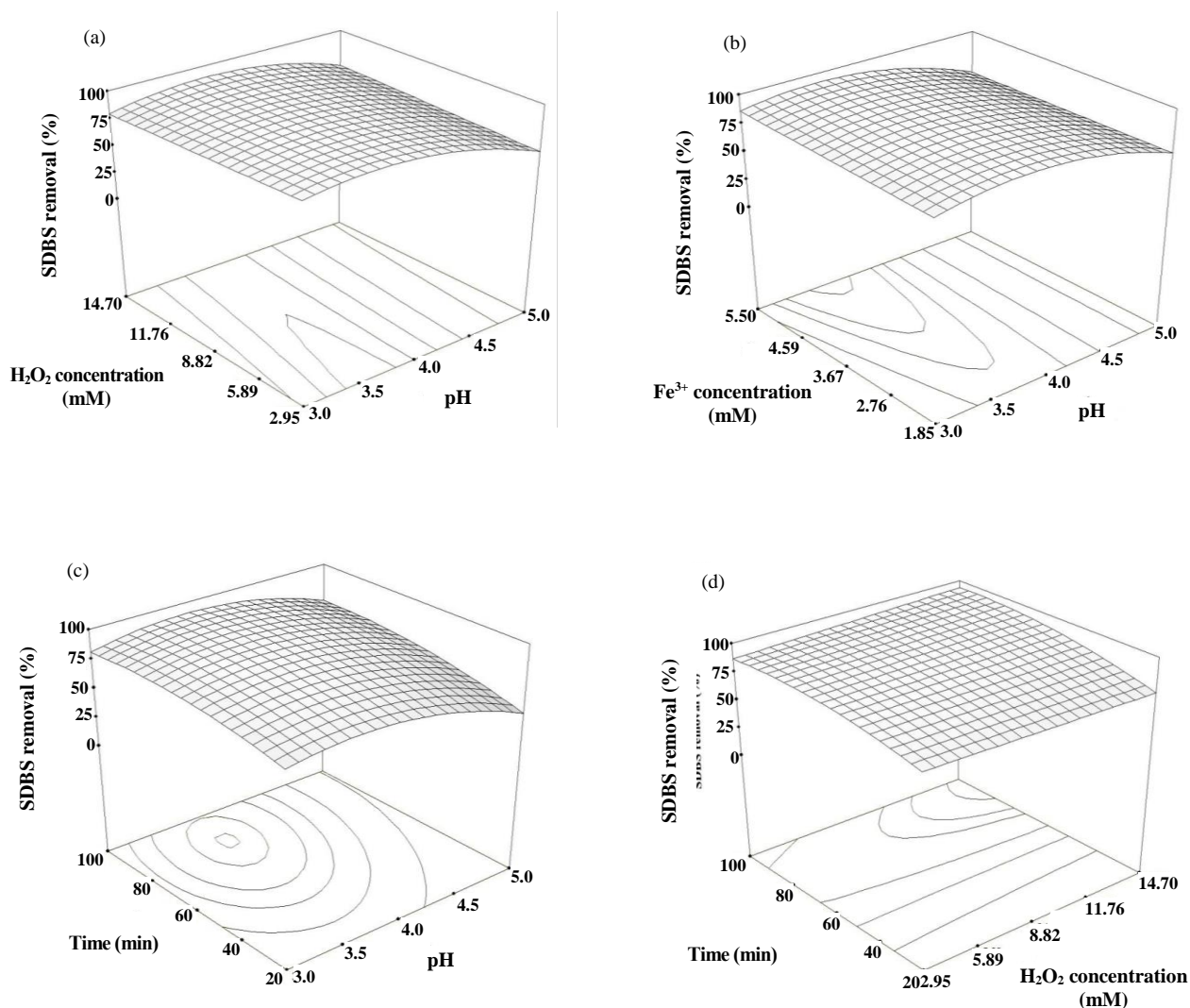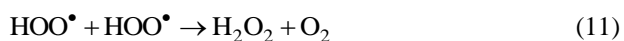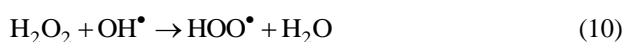
119

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Iran. J. Chem. Chem. Eng.   *Taghavi K. et. al.*   *Vol. 35, No. 4, 2016*

Fig. 1: Response surface plots showing the interaction between two parameters, pH and H₂O₂ concentration (a), pH and Fe³⁺ concentration (b), pH and time (c) and time and H₂O₂ concentration (d) on the SDBS removal percentage. Other variables are constant at their center points.

$$H_2O_2 + OH^\bullet \rightarrow HOO^\bullet + H_2O \tag{10}$$

$$HOO^\bullet + HOO^\bullet \rightarrow H_2O_2 + O_2 \tag{11}$$

$$OH^\bullet + OH^\bullet \rightarrow H_2O_2 \tag{12}$$

In addition, due to decomposition of H_2O_2 and generation of hydrogen gas, application of H_2O_2 more than the optimal value can cause flotation of generated iron sludge [24].

According to ANOVA, the interaction terms AC, AD and BC are significant in the reduction of COD. Fig. 2a presents the effects of pH and Fe^{3+} concentration on the

COD reduction. Maximum COD reduction was achieved at the pH range of 3.6-4.1 and Fe^{3+} concentration of 4.07 mM. According to the results, an optimum amount of Fe^{3+} was required for the efficient reduction of COD, However, the SDBS removal percentage was increased by increasing the concentration of Fe^{3+} at the optimum pH. By increasing the amount of Fe^{3+} ions, decomposition of the anionic surfactant molecules will be enhanced. However, a high dosage of iron ions can scavenge the hydroxyl/hydroperoxyl radicals according to Reaction 3, which decreases the complete mineralization of the surfactant molecules and reduction of COD [17].
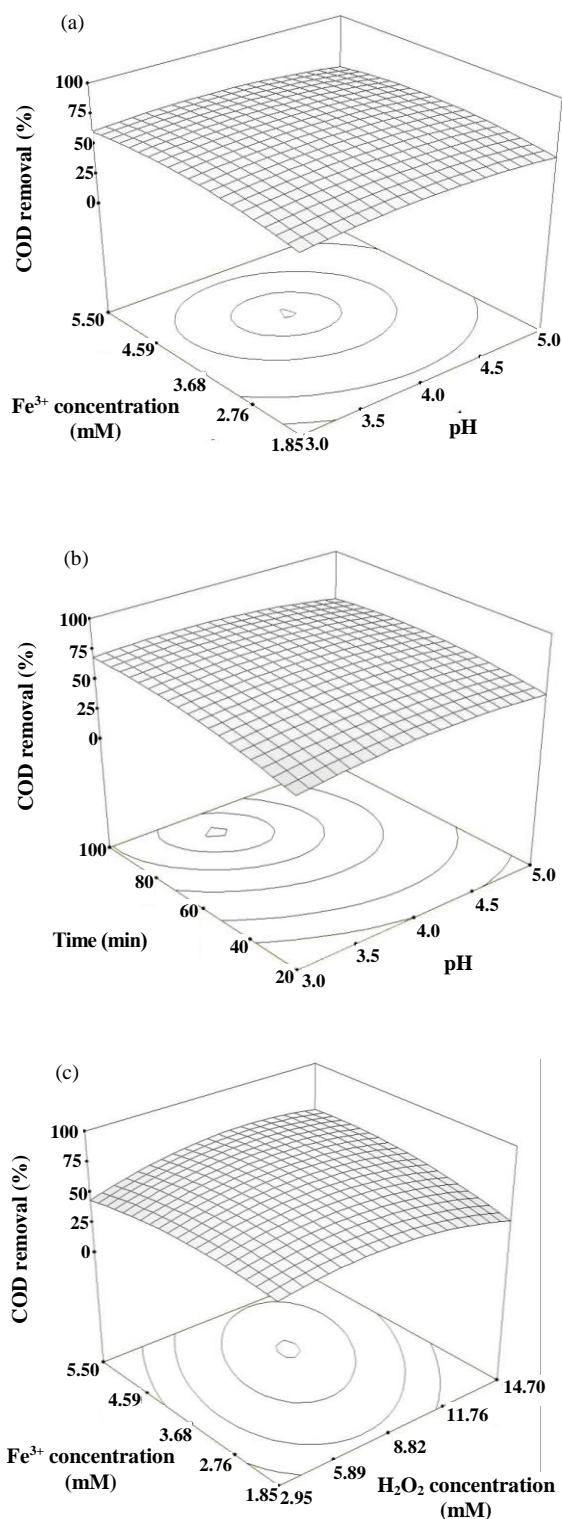
120

(a)

(b)

(c)

Fig. 2: Response surface plots showing the interaction between two parameters, pH and Fe³⁺ concentration (a), pH and time (b) and Fe³⁺ and H₂O₂ concentrations (d) on the COD reduction percentage. Other variables are constant at their center points.

Fig. 2b represents the effect of varying pH and reaction time on the COD reduction. The effects of pH and reaction time were similar to those obtained for SDBS removal. Maximum COD reduction was observed at pH=3.6. The predominant soluble ferric iron species in the pH range of 3-4 is hydrated ferric iron complex ($[Fe(OH)(H_2O)_5]^{2+}$). At pH<3, the efficiency of the process would be low due to the formation of $[Fe(III)(H_2O)_6]^{3+}$ complex, which reacts more slowly with H_2O_2 than $[Fe(OH)(H_2O)_5]^{2+}$ and therefore produces lower hydroxyl radicals. In addition, at pH<3, OH radicals can be consumed by the scavenging effects of H^+ according to the following equation [25]:

$$OH^\bullet + H^+ + e^- \rightarrow H_2O \tag{13}$$

On the other hand, if the solution pH is too high, the iron precipitates in the form of $Fe(OH)_3$ which catalytically decomposes the H_2O_2 into molecular oxygen, without forming hydroxyl radicals.

The effect of Fe^{3+} and H_2O_2 concentrations on the COD reduction is presented in Fig. 2c. The interaction of Fe^{3+} and H_2O_2 concentrations was highly significant. Maximum COD reduction (68.7%) was obtained at H_2O_2 concentration of 9.55 mM and Fe^{3+} concentration of 4.21 mM when pH and time were set at their center points. Determination of the optimum amount of iron and hydrogen peroxide is highly important in Fenton/Fenton-like processes since these reagents affect the operation cost as well as efficiency. Increasing the H_2O_2 concentration leads to increase in the concentration of hydroxyl radicals and hence increase in the COD reduction. However, excessive amount of H_2O_2 has adverse effects on the removal efficiency due to the hydroxyl radical scavenging effect and the recombination of hydroxyl radicals according to Equations 10-12. A high dosage of Fe^{3+} more than an optimum value can scavenge the hydroxyl/hydroperoxyl radicals according to Reaction 3.

The optimal conditions were determined using the ridge maximum analysis and the canonical analysis. The maximum SDBS and COD reduction (93.3 and 70.6%, respectively) was predicted under treatment conditions of pH 3.7, H_2O_2 9.16 mM, Fe^{3+} 4.77 mM and 78 min. The actual experimental values obtained were 92.5% with 0.8% deviation for SDBS removal and 71.1% with 0.5% deviation for COD reduction. According to the
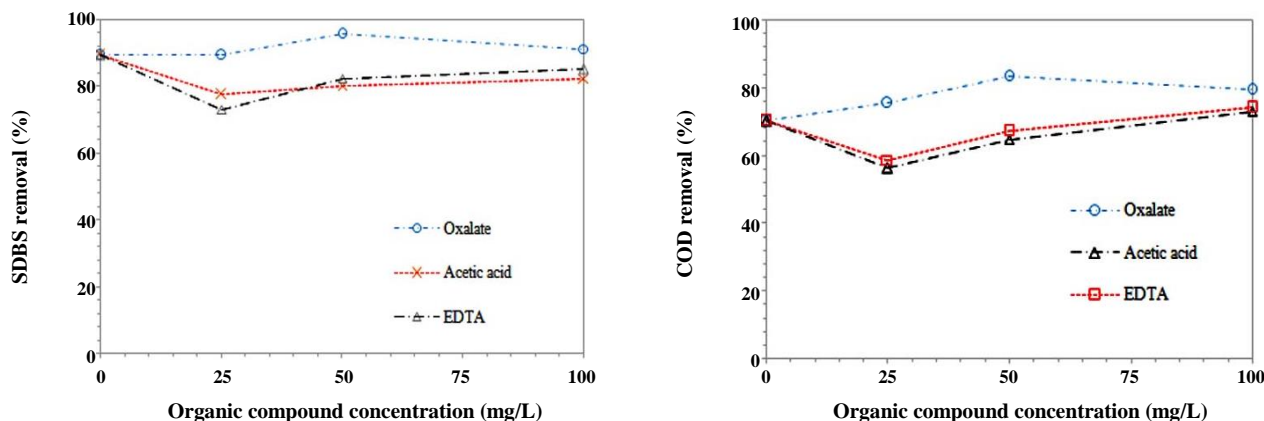
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Iran. J. Chem. Chem. Eng.   *Taghavi K. et. al.*   *Vol. 35, No. 4, 2016*

Fig. 3: Effect of different organic compounds on the removal of SDBS (a) and COD (b) (pH= 4, Fe³⁺ = 3.78 mM, H₂O₂ = 8.82 mM, time = 60 min).

experiments conducted, experiment no.1 with treatment conditions of pH 4, H_2O_2 8.82 mM, Fe^{3+} 3.67 mM and 60 min seems to be a better optimum condition with a shorter reaction time and minimum amount of H_2O_2 and Fe^{3+}. At this condition, SDBS and COD reduction were 90.5 and 70.7%, respectively.

Effect of organic compounds on the removal efficiency

One of the major concerns of the application of Fenton/Fenton-like processes is the interference of chemical species available in the wastewater or formed as intermediates during degradation of organic pollutants. Interference of inorganic ions on phenol degradation by Fenton reaction has been studied by *Friedrich et al.* [26]. *deLuna et al.* [27] studied the effect of organic acids on the degradation of acetaminophen molecules in the Fenton process. Iron solubility, redox potentials and concentration of Fe^{2+} and Fe^{3+} are dependent on the ligands that coordinate iron. Strong iron chelators can inhibit the formation of hydroxyl radicals due to the absence of accessible coordination sites for H_2O_2 to bind to [26].

In this study, the effects of three organic compounds including oxalic acid (dicarboxylic acid), acetic acid (simplest carboxylic acid) and EDTA on the SDBS and COD reduction efficiency of Fenton-like oxidation process have been investigated. The experiments were performed at the conditions that maximum reduction of SDBS and COD were obtained (i.e., 92.6 and 74.2%, respectively). The results are presented in Figs. 3a and b.

The removal efficiency of Fenton-like oxidation in the presence of oxalate is greater than the other two organic compounds. By addition of 50 mg/L oxalate, the SDBS removal efficiency increased from 92.6 to 95.7% and COD reduction increased from 74.2 to 83.5%. In Fenton-like reactions the effects of carboxylic acids on the generation of hydroxyl radicals correspond to the changes in Fe^{2+} concentration. According to *Baba et al.* [28], addition of oxalic acid accelerates the rate of iron redox cycle. The formation of Fe (II)-oxalic acid complex leads to the enhancement of the OH radical generation in the Fenton reaction. In the present study, further increase in oxalate concentration (>50 mgL⁻¹) lead to decrease in the removal efficiency. This can be attributed to the radical scavenging effect of oxalate at higher concentrations.

Addition of 25 mg/L EDTA and acetic acid leads to a decrease in the removal efficiency. By increasing the EDTA and acetic acid concentration up to 100 mg/L, the removal efficiency increased gradually. However, maximum SDBS removal and COD reduction was observed in the absence of EDTA and acetic acid. Low-molecular organic acids such as acetic acid can affect the mechanism and efficiency of the Fenton process [29]. The results showed that acetic acid acted as a hydroxyl radical scavenger and inhibited the complete mineralization of organic pollutants. The removal efficiency depends on the concentration of the acid and the initial composition of the wastewater. *Whebi et al.* [30] reported that degradation of methyl red dye by Fenton's reagent decreased with increase in EDTA concentration. Fe(II) and Fe(III) forms very stable complexes with EDTA which inhibits the formation of hydroxyl radicals.

CONCLUSIONS

Mineralization of sodium dodecylbenzenesulfonate (SDBS) was successfully performed by Fenton-like process using $FeCl_3/H_2O_2$ system. Response surface methodology and central composite design were effectively applied to the modeling and optimization of the four main reaction parameters. The result of ANOVA showed that the developed model was highly significant and could be used to predict the SDBS removal from the initial experimental conditions. Over 90% of SDBS was removed within 60 min at pH 4.0, and H_2O_2/Fe^{3+} molar ratio of 2.4. The results showed that the reaction was highly sensitive to pH, in terms of SDBS removal, and dependent on Fe^{3+} dosage and oxidation time. Investigating the effect of some organic compounds on the degradation of SDBS showed that an optimal value of oxalic acid (50 mg/L) could increase the removal up to 95.7%.Optimization of the Fenton-like process makes this technology a cost-effective and suitable option in treating surfactant-contaminated wastewaters.

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