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Effect of Fenton oxidation on the toxicity of carpet manufacturing effluents

A.S. Ciggin[a,*], O.O. Ozcan[a], H. Gökcekus[b], D. Orhon[b]

[a]*Environmental Engineering Department, Faculty of Engineering, Akdeniz University, 07058, Antalya, Turkey, emails: asliciggin@akdeniz.edu.tr (A.S. Ciggin), ozden.ozgur.ozcan@gmail.com (O.O. Ozcan)*

[b]*Environmental Engineering Department, Faculty of Civil and Environmental Engineering, Near East University, 99138 Nicosia, Mersin 10, Turkey, emails: huseyin.gokcekus@neu.edu.tr (H. Gökcekus), orhon@itu.edu.tr (D. Orhon)*

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ABSTRACT

Treatment of wastewater generated in carpet manufacturing is a problematic issue, mainly because of the toxic impact of chemicals used in different processes. Fenton oxidation may be a suitable approach for reducing toxicity but the cost of chemicals may be prohibitive to adopt this process as the main treatment phase. In this context, this study explored the feasibility of implementing either Fenton or Fenton-like oxidation process as a pretreatment stage before the biological treatment of carpet manufacturing effluents. It also included optimization of operation parameters using response surface methodology. Optimization was mainly focused on molar ratios of H_2O_2/COD and H_2O_2/Fe along with the reaction time for Fenton and Fenton-like advanced oxidation. For the Fenton process, the optimum H_2O_2/COD and H_2O_2/Fe^{2+} molar ratios were determined as 0.06 and 0.60 mol/mol, respectively. Different optimum values of 0.29 and 4 mol/mol, respectively, were applied to the same molar ratios for the Fenton-like oxidation. The Fenton process yielded 81% and 68% for COD removal and toxicity reduction, respectively. Similarly, removal yields of 62% for COD and 76% for toxicity were achieved by means of the Fenton-like oxidation. This process proved to be suitable as a pre-treatment step, where adequate toxicity reduction was achieved to allow effective COD removal in the following biological treatment phase.

Keywords: Advanced oxidation; Carpet manufacturing wastewaters; Fenton oxidation; Fenton-like oxidation; Toxicity

1. Introduction

The textile industry has a heterogeneous structure consisting of many sub-sectors such as synthetic fiber production, fiber preparation, yarn production, fabric weaving, knitting, non-woven fabric production and carpet manufacturing. Although numerous studies have been carried out to evaluate effective methods for the treatment of textile wastewaters, the carpet manufacturing effluents require particular evaluation due to the utilization of acid dyes for manufacturing carpets from synthetic fibers, which is different from most other textile products [1,2]. As Turkey is ranked second in the world in terms of the export of "carpets and other textile floor coverings" after China [3], the management of carpet manufacturing wastewaters is an important issue in Turkey.

The water consumption can reach up to 162.6 L/kg of carpet manufactured [4]. Although the water consumption is high similar to other textile industries, the color and turbidity are relatively low in the carpet manufacturing effluents due to the high stabilization rates of acid dyes on synthetic fibers [5]. However, auxiliary chemicals used during manufacturing process and aromatic amines formed from acid dyes are toxic and carcinogenic substances with high organic content [6]. Therefore, the removal of toxic substances and high chemical oxygen demand (COD) is more important than color removal during the treatment of carpet manufacturing effluents. Investigation of effective

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* Corresponding author.

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treatment methods is one of the most challenging issues in all sub-categories of the textile industry, as the majority of dyes and chemicals used in manufacturing contain organic substances with complex structures such as toxic substances, inhibitory compounds and resistant aromatic rings [7].

Many physicochemical and biological processes have been researched for the removal of organic matter and color from textile wastewaters. The main processes used in the treatment of textile wastewaters are adsorption, ion exchange, membrane processes, chemical oxidation, chemical precipitation and biological treatment methods. Although the efficiency of membrane processes in the treatment of carpet manufacturing effluents was established [5], biological methods are advantageous in terms of being economical and environmentally friendly compared with membrane processes. However, the toxic content of carpet manufacturing effluents limits the efficiency of biological processes. There are many parameters that affect the biological treatment efficiency of textile effluents negatively, such as heavy metals, sulfide, sulfur, salts and other components in addition to dyestuffs [8]. For example, the determination of low heterotrophic growth rate for wastewaters generated from the carpet finishing process was explained with the inhibitory effects of different chemicals in wastewaters [2].

High color removal efficiencies have been obtained in many studies by using advanced oxidation processes (AOPs) to treat organic synthetic dyes that are not biodegradable [9–11]. AOPs increase the biodegradability of textile wastewater and have the potential to decompose the materials contained in textile dyes that are resistant to breakdown. Among the AOPs, the Fenton process provides the desired water quality with high reaction efficiencies compared with traditional applications [12]. The Fenton process, which is applied by the use of ferrous ion (Fe^{2+}) as a catalyst to increase the conversion efficiency of hydrogen peroxide (H_2O_2) to hydroxyl radicals [13], is suggested as a suitable AOP for the oxidation of toxic matters such as hexavalent chromium from synthetic or real wastewaters [14,15]. In a study performed for the treatment of carpet manufacturing effluent, COD removal of 93% was achieved by Fenton oxidation [16]. However, the application of Fenton oxidation as the main treatment step is restricted due to the requirement of a high amount of chemical reagents in this process.

The combination of biological treatment with other technologies has been suggested as a good solution for the treatment of textile wastewaters [17,18]. The combined process consisting of biological and chemical stages can be a cost effective and sustainable solution for the treatment of textile wastewater. In the combined process, the efficiency depends on toxicity removal performance, whereas the cost of the process depends on the chemical consumption in the Fenton stage. It has been reported that chemical reagent was required five times less to achieve the same dye removal efficiency with the combined Fenton and biological process compared with the application of Fenton oxidation alone [19]. In the combined process, the removal efficiency largely depends on the operating conditions applied at the Fenton oxidation stage. The most important operating parameters for the Fenton process are determined as the H_2O_2/COD molar ratio, H_2O_2/Fe^{2+} molar ratio and pH [20].

In Fenton oxidation, the dominant removal mechanism may be oxidation or coagulation depending on the selected H_2O_2/Fe^{2+} molar ratios. Moreover, if the Fe^{2+} concentration is more than the H_2O_2 concentration, then the coagulation process may be the only process responsible for pollutant removal. Kang et al. [21] reported that COD removal was accomplished by coagulation reactions while color removal resulted from oxidation reactions. The application of the Fenton process leads to a high cost of reagent (hydrogen peroxide and iron) especially at high dye concentrations [22]. Although Fenton oxidation is theoretically initiated by Fe^{2+}, the utilization of ferric ion (Fe^{3+}) instead of Fe^{2+} has been suggested in order to decrease the cost of the iron source [23]. The oxidation process catalyzed by different iron sources instead of Fe^{2+} is considered as "Fenton-like oxidation", where other metal sources including Fe^{3+} and zero valent iron, replace Fe^{2+} [15]. Since Fe^{2+} and Fe^{3+} act as catalysts in Fenton reactions and these reactions occur as a cycle, the efficiency of these two processes is theoretically the same [24]. However, Fenton-like oxidation has been determined to be more efficient in the treatment of some industrial wastewaters [14,23,25].

The effect of the Fenton process on toxicity removal has been generally evaluated by acute toxicity tests using specific microorganisms such as *Daphnia magna, Vibrio fischeri* [26], *Pseudomonas* [27] and *Escherichia coli* [28]. Activated sludge respiratory inhibition tests are more direct methods to evaluate the activity of microorganisms that perform biological treatment compared with toxicity tests conducted with different microorganisms [29,30]. Different activated sludge respirometric techniques have been developed. The purpose of the activated sludge inhibition test proposed by the International Organization for Standardization (ISO) is to determine the concentrations that do not have an inhibitory effect that can be used in biological removal tests and to quickly identify substances that will adversely affect aerobic treatment [31]. In this method, the effect of different substances on the respiration rate of microorganisms is measured under certain conditions.

In this framework, the aim of this study is to optimize the operating parameters of Fenton and Fenton-like oxidation processes for decreasing the toxicity of carpet manufacturing effluents. In order to optimize the effect of H_2O_2/COD molar ratio, Fe concentration and reaction time on the treatment of carpet manufacturing effluents by Fenton and Fenton-like oxidations, the response surface methodology (RSM) based on central composite design (CCD) was used. In the last stage of the study, active sludge inhibition tests were carried out in order to evaluate the performance of the Fenton and Fenton-like oxidation processes in decreasing the toxic effects of carpet manufacturing effluents.

2. Materials and methods

2.1. Characterization of carpet manufacturing effluents

The carpet manufacturing effluents were obtained from a carpet manufacturing factory located in Gaziantep, Turkey. In the factory, all wastewaters were collected without separation of the dyeing effluents. The color from the dyes dilute with other wastewaters while the COD concentration is very high because of no differentiation in wastewater streams. As a result, the COD and color of the carpet manufacturing effluents were measured as 9,409.91 ± 17 mg COD/L and 7,879.60 ± 11 Pt-Co, respectively. Although the COD and color of the wastewater were very high, total suspended solids (TSS) and volatile suspended solids (VSS) concentrations were relatively low with 155 ± 5 mg TSS/L and 115 ± 15 mg VSS/L, respectively. After characterization, wastewaters were kept at +4°C until the experiments. COD concentrations were measured as described in the ISO6060 method [32]. The color, TSS and VSS concentrations were measured according to standard methods [33].

2.2. Design of experiments

The operating conditions for the treatment of carpet manufacturing effluents with Fenton and Fenton-like oxidation processes were optimized using RSM provided by Design-Expert software version 8.7.0.1 (Stat-Ease, USA). RSM is a widely accepted tool for investigating the effects of several independent variables on the process responses for the optimization of a process [34]. RSM enables a numerical relationship to be established between the operating parameters and the process response by the optimization model [35]. CCD is one of the design types used in evaluating the functions of RSM. CCD is designed to examine two factorial points, two level points and the central point. The level points consist of the highest and lowest levels of the process operating parameters (independent variables). The central point corresponds to the average level of all independent variables. Since CCD includes central points, it allows the estimation of second-order equations.

In this study, RSM was used for the optimization of the Fenton and Fenton-like oxidation processes with the experimental design created according to CCD. The H_2O_2/COD molar ratio, Fe concentration and reaction time were selected as independent variables. Because of the difficulty in applying two independent parameters depending of the same parameter (H_2O_2 concentration) for experimental design with CCD, the Fe concentration was selected as the independent variable instead of the H_2O_2/Fe molar ratio. The lowest and highest levels of the independent variables were determined by evaluating previous studies on the treatment of textile wastewater by Fenton oxidation. The lowest and highest levels of reaction time were selected as 30 and 90 min in optimization experiments for Fenton oxidation. As 30 min was determined as optimum in the first optimization experiments, the levels of reaction time were selected as 10 and 30 min in the Fenton-like oxidation process experiments. Thus, the levels of the independent process variables were determined as indicated in Table 1.

After determination of the levels of parameters, the lowest and highest levels of the independent variables (Table 1) were transferred to the trial version of the Design-Expert. According to these three variables, 16 experiments were proposed by CCD. All experiments were performed in triplicate. For optimization of the independent variables, COD concentration was considered as the process response. The regression models were established for process response with the analysis of the experimental data obtained from CCD by RSM. The adequacy of the models to express the relationship between the independent variables and process response was statistically determined by analysis of variance (ANOVA). ANOVA analysis includes testing of the variance coefficient and regression coefficients. The quality of the established regression models and independent variables was expressed by the regression coefficient (R^2) and adjusted regression coefficient (adj-R^2). The statistical significance of the models was checked by the Fisher F (Fisher variation ratio) test by the p (probability) > F value with 95% confidence levels [36]. This means that the values of $p > F$ less than 0.05 indicate that the model terms are significant.

2.3. Fenton and Fenton-like processes

After the design of the experiments, the Fenton and Fenton-like oxidation experiments were carried out with 100 mL of carpet manufacturing effluent. The beaker containing carpet manufacturing effluents was continuously stirred at 500 rpm by magnetic stirrer at the room temperature (around 25°C) throughout the oxidation experiments. During the experiments, after the addition of calculated amounts of H_2O_2 and Fe, the pH of the samples was adjusted to 3.5 ± 0.01 using 1 and 6 M sulfuric acid to initiate the oxidation reaction. The iron(II) sulfate heptahydrate ($FeSO_4·7H_2O$) and iron(III) chloride ($FeCl_3$) were used as Fe^{2+} and Fe^{3+} sources, respectively.

In the experiments where high concentrations of H_2O_2 and iron were applied, pH adjustment was not necessary since the pH was between 3.41 and 3.5. At the end of the experiments, the pH of the samples was immediately adjusted to pH > 12 using 1 M and 6 M sodium hydroxide to stop the oxidation reaction. Samples were taken to measure the remaining H_2O_2 concentration in order to determine the necessity of COD correction in order to avoid errors during COD measurement [37]. Then, the samples were allowed to settle down for 1 h. Subsequently, the samples were

Table 1
Levels of independent process variables used in the RSM

Variable no	Independent variable	Fenton process		Fenton-like process	
		Lowest level (–1)	Highest level (+1)	Lowest level (–1)	Highest level (+1)
A	H_2O_2/COD ratio (mol/mol)	0.06	0.3	0.15	0.45
B	Fe concentration (mmol)	0.69	3.44	1.15	3.44
C	Reaction time (min)	30	90	10	30

centrifuged at 4,500 rpm for 15 min and the supernatants were filtered through a 0.45 μm diameter membrane filter. The samples were then stored in a refrigerator at +4°C until the COD analyses. COD concentrations were measured as described in the ISO6060 method [32]. The residual hydrogen peroxide concentrations were determined by spectrophotometer at 410 nm according to the titanium sulfate method [38].

2.4. Activated sludge inhibition tests

After the determination of the optimum operating conditions for COD removal in each Fenton oxidation process, activated sludge inhibition tests were performed according to ISO 8192 [31] in order to determine the effect of the Fenton oxidation processes on decreasing the toxic effects of carpet manufacturing effluents. In this method, the effect of different wastewaters on the respiration rate of microorganisms was measured under certain conditions. The toxicity of carpet manufacturing effluents was determined by measuring the respiration rates of microorganisms when treating raw or pretreated carpet manufacturing wastewaters under certain conditions at different incubation times ranging between 30 and 180 min. The oxygen consumption rate of aerobic microorganisms is usually expressed in mgO_2 (mgO_2/L h) per hour in milligrams of sludge.

The same concentration of microorganisms was exposed to synthetic wastewater (control) and carpet manufacturing wastewater in all inhibition tests. For calculation of percentage inhibition, the decrease in dissolved oxygen concentrations was measured at different times in each sample. Oxygen consumption rates were calculated from the linear part of the dissolved oxygen consumption graphs using Eq. (1):

$$R = \frac{\left(\mathrm{DO}_1 - \mathrm{DO}_2\right)}{\Delta t} \tag{1}$$

The oxygen consumption rate expressed by Eq. (1) represents oxygen consumption rate (R) as mgO_2/L h, the dissolved oxygen concentration at the start of the selected linear phase (DO_1) as mgO_2/L, at the end of the selected linear phase (DO_2) as mgO_2/L and time interval between measurements of DO_1 and DO_2 (Δt) as a second.

After the calculation of oxygen consumption rates of aerobic microorganisms, the inhibition percentages for raw and pretreated carpet manufacturing effluents were calculated by comparing with the respiration rate measured in control sample using Eq. (2):

$$I = \frac{\left(R_0 - R_W\right)}{R_0} \times 100 \tag{2}$$

The percentage inhibition (I) expressed by Eq. (2) represents the oxygen consumption rate calculated for the control sample (R_0) and the oxygen consumption rate calculated for the raw and pretreated carpet manufacturing wastewaters (R_W).

3. Results and discussion

3.1. Treatment of carpet manufacturing effluents by Fenton oxidation

The COD removal efficiencies obtained with the implementation of Fenton oxidation on carpet manufacturing effluents are illustrated in Fig. 1. As seen in the figure, a COD removal efficiency of close to zero was obtained at the lowest Fe^{2+} concentration with Fenton oxidation independently from H_2O_2/COD molar ratio and reaction time. The COD removal efficiency increased as the Fe^{2+} concentration increased. Interestingly, the highest COD removal efficiency was obtained at the lowest H_2O_2/COD molar ratio. The optimum operating conditions for the Fenton oxidation were determined as 0.06 mol H_2O_2/mol COD, 3.44 mmol Fe^{2+} and a reaction time of 30 min.

A CCD model was generated for COD removal by Fenton oxidation in order to evaluate the effect of each independent process parameter and its interactions. The compatibility of the process response (COD removal efficiency) with linear, two-factor interaction (2FI), quadratic and cubic

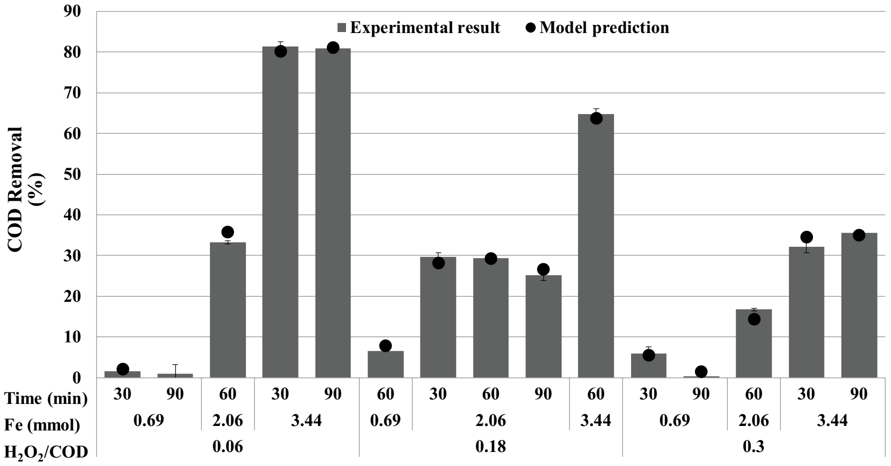


Fig. 1. COD removal efficiencies obtained with Fenton oxidation of carpet manufacturing effluents.

polynomial models was evaluated using Design-Expert software. The quadratic (second order) model was determined as the most appropriate model as it had the highest regression coefficient (R^2: 0.9967) and adjusted R^2 (adj-R^2: 0.9917). The adequately close model predictions with actual experimental results revealed that the model has reliability in terms of prediction accuracy (Fig. 1). The quadratic model equation in terms of actual factors was obtained as shown in Eq. (3):

$$\text{COD removal}(\%) = -21.27285 + (170.79619 \times A) + (17.73379 \times B) + (0.15674 \times C) - (74.39130 \times A \times B) - (0.032230 \times A \times C) + (0.027448 \times B \times C) - (290.72516 \times A^2) + (3.46105 \times B^2) - (1.94551 \times 10^{-3} \times C^2) \quad (3)$$

The model expressed by Eq. (3) represents COD removal efficiency as a function of H_2O_2/COD ratio (mol/mol) (A), Fe^{2+} concentration (mmol) (B) and reaction time (min) (C). The statistical significance of the model and effects of the independent variables on the process response were determined by ANOVA (Table 2). The small p-values ($p < 0.05$) showed the significance of the model and independent variables.

As shown in Table 2, the H_2O_2/COD molar ratio and Fe^{2+} concentration had high significant effects on the COD removal efficiency, while the reaction time had no significant effect. The interaction effect between the H_2O_2/COD molar ratio and Fe^{2+} concentration (AB) had a statistically significant effect on the COD removal efficiency. The quadratic terms belonging to H_2O_2/COD molar ratio (A^2) and Fe^{2+} concentration (B^2) had also determined as significant terms for COD removal efficiency with Fenton oxidation.

In numerical process optimization, it is possible to define the values of the independent process parameters as none, maximum, minimum, target and within range in Design-Expert software. The optimum combination of independent variables to obtain the highest possible COD removal efficiency was determined by defining the H_2O_2/COD molar ratio and Fe^{2+} concentration within range. As the reaction time is determined as an insignificant term for COD removal efficiency, it was set at 30 min for standardization purposes.

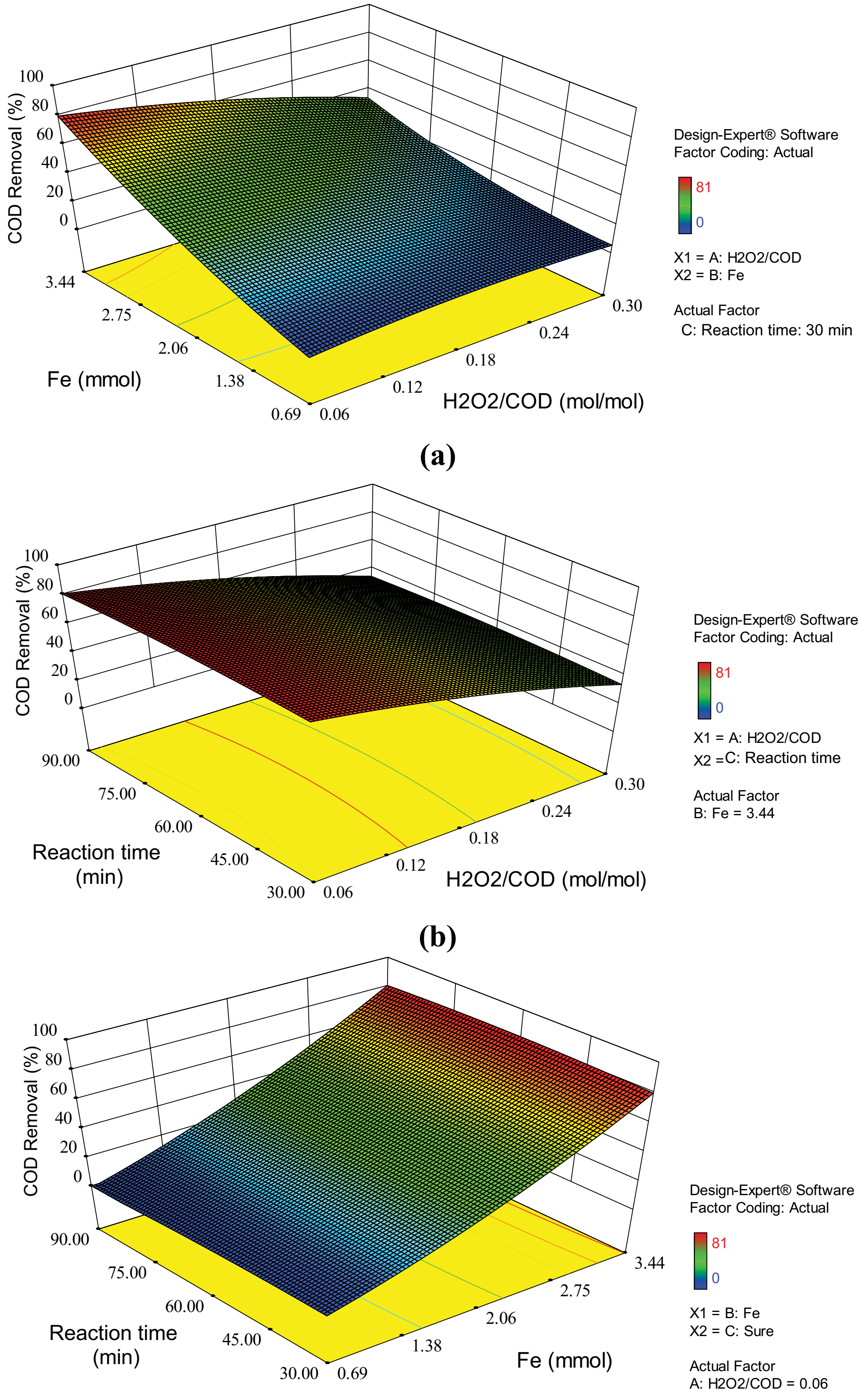
The optimum COD removal efficiency was predicted as 80.17% at the lowest level of H_2O_2/COD molar ratio (0.06 mol/mol) and highest level of Fe^{2+} concentration (3.44 mmol), similar to be determined by the experimental results. The determined optimum Fe^{2+} concentration corresponds to a H_2O_2/Fe^{2+} molar ratio of 0.6 mol/mol. In the only study on the treatment of carpet manufacturing effluents by Fenton oxidation, the optimum H_2O_2/COD molar ratio was determined to be approximately 5 mol/mol and H_2O_2/Fe^{2+} molar ratio of 12.32 mol/mol to achieve a COD removal efficiency of 93% [16].

The optimum H_2O_2/COD molar ratio determined in this study is comparatively lower than the ratio determined in the mentioned study. At the optimum conditions, the relationship between the COD removal efficiency and independent variables was visualized by 3D response surface plots, as shown in Fig. 2. While the effects of two independent variables on the COD removal efficiency were illustrated in a response surface plot, the third independent variable was kept constant at the determined optimum value.

According to the response surface plot shown in Fig. 2a, the increase in the H_2O_2/COD molar ratio was ineffective on the COD removal efficiency at low Fe^{2+} concentrations. However, the COD removal efficiency decreased with an increase in the H_2O_2/COD molar ratio at Fe^{2+} concentrations higher than 2.06 mmol. The decrease in the COD removal efficiency after an optimum H_2O_2/COD molar ratio was also observed in the treatment of carpet dyeing wastewater [16]. This may have been caused by the inhibition of oxidation because of the reaction of excess H_2O_2 with hydroxyl radicals [39]. The Fe^{2+} concentration played a more important role in the COD removal efficiency at lower H_2O_2/COD molar ratios compared with higher H_2O_2/COD molar ratios. The effects of the H_2O_2/COD molar ratio and reaction time on COD removal are presented in Fig. 2b. With an increase in H_2O_2/COD molar ratio, the COD removal efficiency decreased linearly, while no changes were observed in the COD removal efficiency according to changes in the reaction time. Similarly, the COD removal efficiency was not affected by changes in the reaction time at different Fe^{2+} concentrations, as shown

Table 2
ANOVA results for Fenton oxidation of carpet manufacturing effluents

Source	Sum of squares	Mean square	F-value	p-value
Model	10,279.58	1,142.18	199.00	<0.0001
A-H_2O_2/KOİ	1,151.33	1,151.33	200.59	<0.0001
B-Fe^{2+}	7,779.10	7,779.10	1,355.31	<0.0001
C-Time	6.01	6.01	1.05	0.3456
AB	1,205.32	1,205.32	210.00	<0.0001
AC	0.11	0.11	0.019	0.8955
BC	10.26	10.26	1.79	0.2298
A^2	46.21	46.21	8.05	0.0297
B^2	112.88	112.88	19.67	0.0044
C^2	8.08	8.08	1.41	0.2802
Lack of fit	34.40	6.88	188.05	0.0553



(a)

(b)

(c)

Fig. 2. Impacts of independent variables on COD removal efficiency in Fenton oxidation (a) H_2O_2/COD molar ratio and Fe^{2+} concentration, (b) H_2O_2/COD molar ratio and reaction time, and (c) Fe^{2+} concentration and time.

in Fig. 2c. At the constant mol/mol H_2O_2/COD molar ratio of 0.06, the COD removal efficiency reached a plateau with the increase in the Fe^{2+} concentration. This suggests that the application of higher iron concentrations will not increase the COD removal efficiency much more.

3.2. Treatment of carpet manufacturing effluents by Fenton-like oxidation

The optimization experiments were repeated with Fe^{3+} instead of Fe^{2+} as catalyst in Fenton-like oxidation process. When carpet manufacturing effluents was treated by Fenton-like oxidation, considerable differences were observed in the effects of the process parameters on the COD removal efficiencies compared with Fenton oxidation. The obtained COD removal efficiencies are illustrated in Fig. 3. The COD removal efficiency increased linearly in line with increases in the independent process parameters. The optimum operating conditions for the Fenton-like oxidation were determined as 0.45 mol H_2O_2/mol COD, 3.44 mmol Fe^{3+} and a reaction time of 30 min. The COD removal efficiency obtained under these conditions was 53.08%.

Based on the CCD experimental design of Fenton-like oxidation, the relationship between the independent variables (H_2O_2/COD ratio, Fe^{3+} concentration and reaction time) and process response (COD removal efficiency) was defined using a quadratic model with the R^2 of 0.9520 and adj-R^2 of 0.9040. The quadratic model equation in terms of actual factors was obtained as shown in Eq. (4):

$$\text{COD removal}(\%) = +5.35896 + (199.44221 \times A) - (23.80130 \times B) - (0.12559 \times C) + (17.15319 \times A \times B) + (0.12166 \times A \times C) + (0.28417 \times B \times C) - (372.90974 \times A^2) + (4.98338 \times B^2) \tag{4}$$

The model expressed by Eq. (4) represents the COD removal efficiency as a function of H_2O_2/COD ratio (mol/mol) (A), Fe^{3+} concentration (mmol) (B) and reaction time (min) (C). The ANOVA results for the COD removal model are presented in Table 3.

According to the ANOVA analysis, while the Fe^{3+} concentration and reaction time had high significant effects on COD removal efficiency, the H_2O_2/COD molar ratio had a statistically less significant effect on COD removal efficiency. Among the interaction effects, the interaction between Fe^{3+}

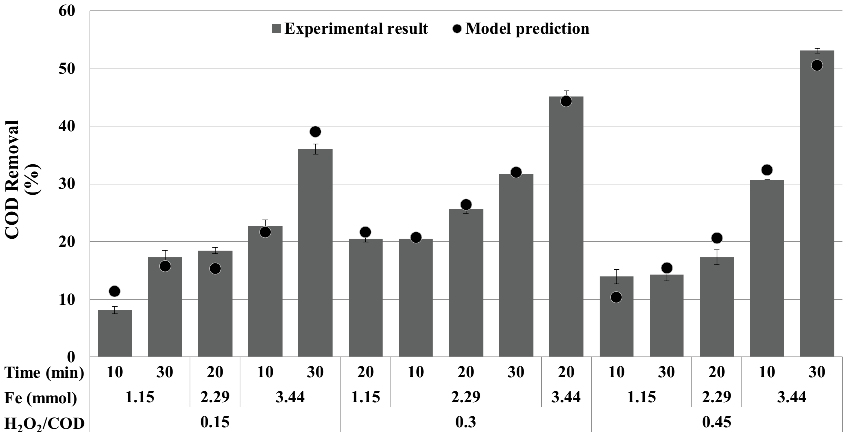


Fig. 3. COD removal efficiencies obtained with Fenton-like oxidation of carpet manufacturing effluents.

Table 3
ANOVA results for Fenton-like oxidation of carpet manufacturing effluents

Source	Sum of squares	Mean square	F-value	p-value
Model	2,490.22	311.28	19.82	0.0002
A-H_2O_2/KOİ	70.10	70.10	4.46	0.0676
B-Fe^{3+}	1,369.20	1,369.20	87.20	<0.0001
C-Time	337.10	337.10	21.47	0.0017
AB	71.73	71.73	4.57	0.0650
AC	0.27	0.27	0.017	0.8982
BC	92.19	92.19	5.87	0.0416
A^2	215.29	215.29	13.71	0.0060
B^2	133.29	133.29	8.49	0.0195
Lack of fit	119.87	17.12	2.98	0.4194

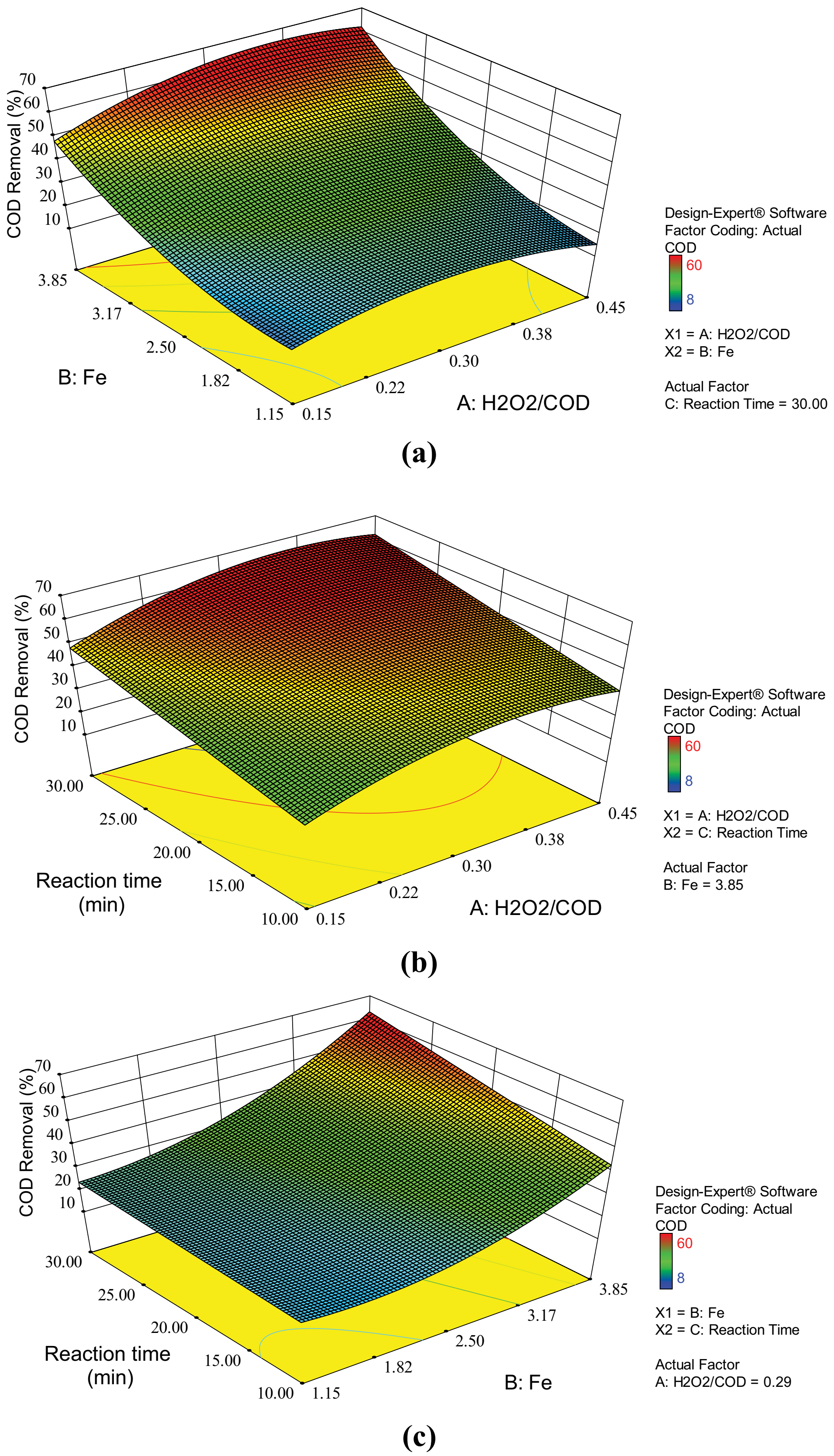


Fig. 4. Impacts of independent variables on COD removal efficiency in Fenton-like oxidation (a) H_2O_2/COD molar ratio and Fe^{3+} concentration, (b) H_2O_2/COD molar ratio and reaction time, and (c) Fe^{3+} concentration and time.

concentration and reaction time (*BC*) had the most significant effect, while the interaction between H_2O_2/COD molar ratio and Fe^{3+} concentration (*AB*) had a less significant effect on COD removal. The interaction between H_2O_2/COD molar ratio and reaction time (*AC*) had no significant effect on COD removal. The quadratic terms for H_2O_2/COD molar ratio (A^2) and Fe^{3+} concentration (B^2) were also determined as significant terms for COD removal efficiency.

For optimization of the treatment of carpet manufacturing effluents by Fenton-like oxidation, the reaction time of 30 min was set as constant, while the H_2O_2/COD molar ratio and Fe^{3+} concentration were set as within range. Differently from the optimization of Fenton oxidation, the maximum level of Fe^{3+} concentration was set as 4 mmol in order to evaluate the effect of higher Fe^{3+} concentrations on COD removal. As a result of numerical optimization, the optimum COD removal efficiency was predicted as 63.33% at a H_2O_2/COD molar ratio of 0.29 mol/mol and Fe^{3+} concentration of 3.85 mmol. The COD removal efficiency of 62.28% obtained with the validation experiments confirmed the satisfactoriness of the model and optimum process conditions. The determined optimum Fe^{3+} concentration corresponds to a H_2O_2/Fe^{3+} molar ratio of 4.0 mol/mol.

At the optimum conditions, the relationship between the independent variables for COD removal was visualized by 3D response surface plots, as shown in Fig. 4. At a reaction time of 30 min, the COD removal efficiency increased linearly with the increase in Fe^{3+} concentration (Fig. 4a). When the H_2O_2/COD molar ratio increased from 0.15 to 0.30 the COD removal efficiency increased, whereas increasing H_2O_2/COD molar ratio from 0.30 to 0.45 resulted in a decrease in COD removal efficiency. The effect of the H_2O_2/COD ratio was not as high as the effect of Fe^{3+} concentration. According to Fig. 4b, the H_2O_2/COD molar ratio and the reaction time had minimal effects on the COD removal efficiency at a Fe^{3+} concentration of 3.85 mmol. While the COD removal efficiency was not affected by the reaction time until the Fe^{3+} concentration was raised to nearly 2.5 mmol, the reaction time significantly affected the COD removal efficiency at high Fe^{3+} concentrations, as shown in Fig. 4c.

3.3. Effect of Fenton and Fenton-like oxidation processes on the toxicity of carpet manufacturing effluents

For evaluating the effect of Fenton and Fenton-like oxidation processes on the toxicity of carpet manufacturing effluents, activated sludge inhibition tests were performed with raw and pretreated carpet manufacturing effluents. The obtained oxygen uptake rates (OURs) in the inhibition tests are illustrated in Fig. 5a along with the OURs obtained in the control experiment (without OMW). The percentage inhibitions calculated from the OURs are illustrated in Fig. 5b.

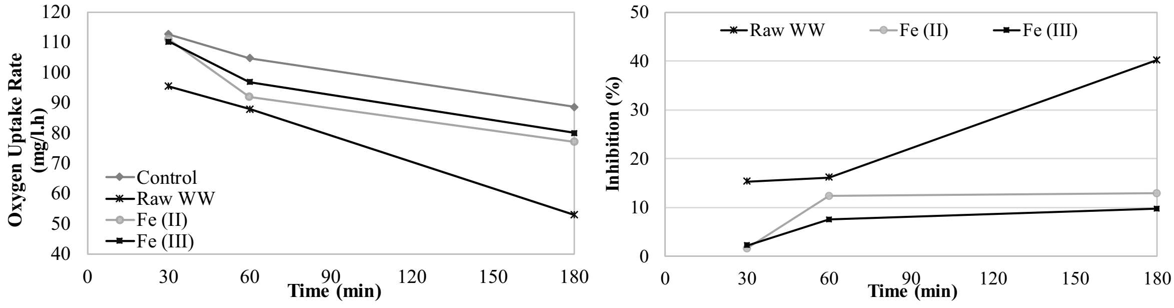
The addition of raw carpet manufacturing effluents to activated sludge resulted in an inhibition of 16% at the 60th min while the inhibition reached 40% at the 180th min. While there was little increase in the inhibition between the 30th min and 60th min of the test, the inhibition nearly tripled between the 60th and 180th min. The huge increase in the inhibition may have originated from the slow degradation of the soluble slowly biodegradable COD fraction in carpet manufacturing effluents as suggested by Yildiz et al. [40].

When Fenton oxidation was applied to carpet manufacturing effluents, inhibition of 13% was observed at the 180th min. The implementation of Fenton-like oxidation on carpet manufacturing effluent resulted in a decrease of inhibition to 10% at the end of the 180th min. As a result, the treatment of carpet manufacturing effluents with Fenton and Fenton-like oxidation processes resulted in 67.9% and 75.8% decreases in inhibition, respectively. The high toxicity removal efficiency may be attributed to the precipitation of heavy metals with Fe^{3+} [41].

4. Conclusion

This study addressed a major dilemma in wastewater management: Assessing the optimal treatment scheme that would achieve the maximum possible level of removal. A complex wastewater generated in carpet manufacturing process was selected for this evaluation. This issue is still a significant problem for a single parameter, COD, representing an intricate mixture of different organics. The problem tackled in the study involved two parameters, namely toxicity and COD with antagonistic nature with respect to treatment.

The Fenton oxidation was determined as more effective process for COD removal under optimum conditions (H_2O_2/COD: 0.06 mol/mol, H_2O_2/Fe^{2+}: 0.60 mol/mol) with approximately 80% of COD removal. On the other hand, the Fenton-like oxidation was determined as more efficient for toxicity removal at optimum conditions (H_2O_2/COD: 0.29 mol/mol,



(a) (b)

Fig. 5. Result of activated sludge inhibition tests (a) oxygen uptake rates and (b) % inhibition.

H_2O_2/Fe^{2+}: 4 mol/mol). At these optimum conditions, inhibitory character of the raw carpet manufacturing effluent was decreased by 67.8% and 75.8% by Fenton and Fenton-like processes, respectively. Pilot and real-scale experiments were required for the verification of these results.

The experimental results reflecting meaningful combinations of major operating conditions, such as molar ratios of H_2O_2/COD, H_2O_2/Fe and reaction time, indicated that the Fenton-like reaction catalyzed by Fe^{3+} was the optimal pre-treatment, achieving the maximum toxicity removal and ensuring safe operation for the following biological treatment that would complete COD removal. The study also showed that the response surface methodology based on CCD proved to be a reliable modeling tool to identify optimum values for the operating parameters in the treatment scheme.

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