

Peroxi-coagulation process: a comparison of the effect of oxygen level on color and TOC removals

Nurullah Yıldız^a, Ömür Gökkuş^{a,*}, Ali Savaş Koparal^b, Yalçın Şevki Yıldız^a

^aDepartment of Environmental Engineering, Faculty of Engineering, Erciyes University, TR-38039 Kayseri, Turkey, Tel. +903522076666, email: nurullahyildiz2012@gmail.com (N. Yıldız), Tel. +90 5054820842, email: omurgokkus@erciyes.edu.tr (Ö. Gökkuş), yyildiz@erciyes.edu.tr (Y.Ş. Yıldız) ^bFaculty of Engineering, Department of Environmental Engineering, Anadolu University, Eskişehir, Turkey, email: askopara@anadolu.edu.tr (A.S. Koparal)

Received 19 June 2018; Accepted 5 November 2018

ABSTRACT

The present study investigates the feasibility of using peroxi-coagulation (PC) process for the oxidative degradation of real textile wastewater and the Taguchi experimental method was adapted to the system variables to find optimum levels of the operational PC conditions. The PC experiments were carried out in an electrochemical cell using a carbon fiber cathode. Additionally, an iron wire electrode as source of Fe²⁺ (catalyst) was used in an undivided electrochemical cell. This investigation demonstrates the treatment performance in case of using metallic iron sources in electro-Fenton (EF) reactions. For this purpose, several experiments were carried out to investigate the effect of medium dissolved oxygen level applying air and N₂ gases in electrochemical cell. Experimental data showed that oxygen level in the solution medium had a positive effect on PC treatment performance. According to the results, PC process with iron anode and carbon fiber cathode pairs gave the best results as 69.8% TOC and 100% turbidity results in oxygenated medium. The removal rates were decreased to 66.8% and 62.4% for TOC and turbidity, respectively when the solution medium becomes oxygen-free.

Keywords: Carbon fiber cathode; Peroxi-coagulation; Textile; Color removal; TOC removal

1. Introduction

Access to clean water is one of the basic needs of human beings. Rapid population growth, urbanization and industrialization have increased water pollution worldwide. Among many industries, textile industries are one of the major water pollutants [1,2]. Textile effluents generally contain many textile dyes, suspended solids, mineral oils, electrolytes, etc. It is known that 280,000 ton of textile dyes are discharged in industrial effluents worldwide every year, with complex aromatic molecular structures. Most of aromatics are refractory to be removed by conventional treatment systems [3].

There are a lot of methods to treat colored wastewater, such as chemical oxidation, electrochemical oxidation, physical adsorption, chemical coagulation/precipitation, enhanced coagulation, and biological anaerobic/aerobic decomposition [4–6]. These methods are expensive and always lead to the another environmental pollution regardless of their convenient operation and excellent color removal efficiency [7].

In recent years, many researchers have focused on electrochemical advanced oxidation processes (EAOPs) in treatment of wastewater contaminated with non-biodegradable organics, because they produce strongly oxidizing radicals that can completely oxidize organic pollutants into CO_2 and H_2O [8]. Studies related to EF process to treat various organic contaminants are increasing and becoming popular day by day. The main mechanism for EF process is based on the in-situ production of H_2O_2 at a suitable cathode fed with O_2 or air, along with the addition of an iron catalyst to the polluted solution to produce oxidant (OH*) in the bulk

^{*}Corresponding author.

by Fenton's reaction. Moreover, in the EF process Fe^{2+} can be regenerated from the reduction of Fe^{3+} at the cathode [9]. Since Fe^{2+} ions is electro-regenerated according to Eq. (3) from ferric iron produced by Eq. (4) the process is electrocatalytic [10].

Anode:
$$Fe \rightarrow Fe^{2+} + 2e^{-}$$
 (1)

Cathode: $O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$ (2)

Cathode :
$$Fe^{3+} + e^- \rightarrow Fe^{2+}$$
 (3)

$$Overall: H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^* + OH^-$$
(4)

Alternatively, in the peroxi-coagulation (PC) process metallic iron can be used as anode which is electro dissolved supplying required amounts of Fe^{2+} to the effluent. Fe^{2+} reacts with electro generated H_2O_2 and the excess of Fe^{3+} formed precipitates as $Fe(OH)_3$. In PC process the main reactions can be summarized as follows:

Anode : The same as Eq. (1)

Cathode : The same as Eq. (2)

Contaminants are then expected to be removed by the combined action of their homogeneous degradation with OH* generated by Eq. (4) and their coagulation with the Fe(OH)₃ precipitate [11]. PC process does not require any external hazardous chemical when operated with an iron anode and carbon based cathode, thus, it is a better way to achieve complete mineralization of hazardous substances [12]. Additionally, less space for installation is needed in this process, no adjustment of the chemical properties of wastewater is required [13].

Using of different carbon-based cathodes, has high surface area, provide an acceleration of the abatement rate can be achieved in PC process [14]. According to the some researchers, the performance evaluation of a cathode material for EAOPs should account for two different abilities: the capability of reducing oxygen to electro-generate hydrogen peroxide and that of reducing ferric ions to restore ferrous ions thus, promoting the reaction leading to OH* production [15]. Therefore, the selection and performance evaluation of the cathode material is very important for PC reactions.

The aim of the study is to evaluate (1) H_2O_2 production potential of carbon fiber for PC reactions, (2) to investigate the utility of iron wire anode as a Fe²⁺ source (3) to determine optimum operational parameters for PC using Taguchi experimental design method.

2. Materials and methods

2.1. Effluent

The wastewater used in the experimental studies was obtained from a textile industry located in Kayseri, Turkey. The characterization of the raw textile wastewater is presented in Table 1. The wastewater sample was stored in a refrigerator before use to avoid any change.

As it **is** seen in Table 1, the values for COD_{total} and COD_{soluble} are almost the same. It means, only a small part of the wastewater has particular structure to be removed by physicochemical methods. This indicates that to achieve local wastewater discharge limits by using conventional methods such as chemical coagulation, biological treatment, adsorbtion etc. is not possible. These methods are less efficient because dyes are stable against biological degradation, which results in sludge formation, membrane fouling and incomplete mineralization [16]. For this reason, more effective treatment processes are required to treat textile wastewater.

2.2. Chemicals and electrodes

All the chemicals used in the study were analytical grade reagents. Solutions for the analyses were prepared with ultra-pure water obtained from an Elga Option Q7 system with a resistivity of 18.2 M Ω cm⁻¹. A sodium sulphate (Merck 99%) solution was used as the supporting electrolyte.

The carbon fiber with an area of 53.9 cm² was purchased from Spinteks Textile Co. (Denizli, Turkey). After each treatment period, the cathode was placed in a sulphuric acid solution for one night and then rinsed with distilled water and dried in air. The specific surface structure of carbon fiber was verified by using scanning electron microscope (SEM) images shown in Fig. 1.

Potassium titanium (IV) oxalate (Alfa Aesar) was used to determine the electro-generated H_2O_2 concentration. H_2O_2 (Merck, 35%) was used as a standard for hydrogen peroxide analysis. Potassium dichromate (Merck 99.5%),

Table 1

The main characteristics o	f the raw texti	le wastewater
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Parameter	Value	°Permissible Level
pН	13.31	6.5–10
Turbidity, NTU	34.80	_
Conductivity, ms/cm	11.96	_
Suspended solids (SS), mg/L	323	350
^a Soluble chemical oxygen demand (COD _{soluble}), mg/L	3398.6	_
Total chemical oxygen demand (COD_{total}), mg/L	3404.43	1000
TOC, mg/L	830.40	-
^b Color, abs	2.500	_

 $^{\rm a}{\rm COD}_{\rm soluble'}$ the samples are filtered through a 0.45 mm filter before COD analysis

^bColor measurement was performed at *λ*max = 670 nm ^cKayseri Water and Sewerage Administration (KASKİ) recommendations for effluent discharge in the sewer

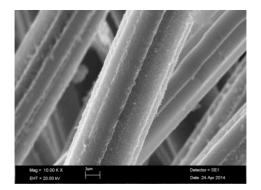


Fig. 1. SEM image of unused carbon fiber.

mercury chloride, and silver sulphate (Merck, 95–97%) were used as COD reagents. Potassium hydrogen phthalate (Carlo Erba, 99.5%) was used to prepare the standard calibration curves for COD and non-purgeable organic carbon (NPOC) analyses.

2.3. Electrolytic system

The PC experiments were carried out in an undivided cell (Plexiglas) and an open rectangular with a volume of 500 ml ($110 \times 50 \times 95$ mm), and the wastewater was continuously mixed with a magnetic stirrer (800 rpm) (Fig. 2). In addition, a measurement cell was used to monitor some parameters such as conductivity, pH, dissolved oxygen (DO), and temperature during the experiments. The measurement cell with a volume of 150 mL ($85 \times 50 \times 75$ mm), was connected to the main reactor to provide similar conditions with the main reactor. A peristaltic pump was used to water circulation between the main reactor and measurement cell while the experiments were carried out.

In the PC experiments, an iron wire (length = 100 mm) and carbon fiber electrodes were selected as anode and cathode, respectively. On the other hand, Pt wire anode was used in the H_2O_2 electro generation experiments instead of iron, the reason being to avoid its scavenging effect to OH* radicals [17]. To adjust the initial pH of the wastewater samples, 1 N H_2SO_4 and 1 N NaOH solutions were used. The

working electrode potential was monitored and adjusted by using a DC power supply (GWinstek SDP 3606, 30 V, 6 A). The reactor system had an air pump and a stone-diffuser to provide required oxygen levels which also enables to mix wastewater content. Then, the carbon fiber cathode was fed with variable air flow rates (Q_h) (0.1–0.5 L/min) to continuously generate H_2O_2 from the O_2 reduction. The inter-electrode gap was kept constant 4 cm during the experiment and the effect of the inter-electrode gap was not evaluated in the study.

Some preliminary tests were carried out before we specified the appropriate electrolyze time in order to reach steady-state conditions and set it as 400 min for each run. After the experiments, the samples were withdrawn from the reactor at 50-min time intervals, and aliquots of 2 mL were then withdrawn from the electrolyzed solutions and centrifuged at 4000 rpm before analysis. All of the experiments were carried out at room temperature.

2.4. Analytical procedures

The solution pH was monitored using a WTW inolab 7110 pH meter. Total carbon removal of textile wastewater was monitored from the TOC abatement and determined using a Shimadzu TOC-L analyzer. The color removal rate were measured by the absorbance at a maximum wavelength (λ_{m}) _w = 670 nm) using a spectrophotometer (Hach Lange DR 2500). The electro-generated hydrogen peroxide concentrations were measured by the absorbance measurement ($\lambda_{max} = 410 \text{ nm}$) of a colored complex formed by a reaction with potassium titanium oxalate [18-21]. The titanium (IV)-peroxide complex is yellow-orange in color and adsorbed a wavelength of 410 nm. DO, pH and conductivity were measured with a multi-parameter device (Hach Lange HQ40D). All of the experiments were repeated twice, and the averages were reported.

2.5. Experimental procedures

The experiments were carried out under constant current conditions using 500 ml of distilled water in a PC reactor system described in Section 2.3. In the H₂O₂ generation

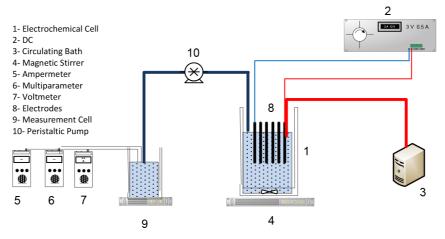


Fig. 2. Schematic diagram of the experimental setup.

experiments, a carbon fiber cathode was used to observe the production of H_2O_2 , and except where otherwise specified, 20 mM Na₂SO₄ was added as supporting electrolyte. The electrolytic system was fed with air through bubbling near the cathode to produce H_2O_2 by reduction of DO in acidic solutions containing a supporting electrolyte (Na₂SO₄). All of the H_2O_2 production trials were performed in the range of 60–100 mA current (*I*) at room temperature during 100 min of electrolysis. Before measurements, 2 mL samples were taken from the reactor at each 10 min to analyze the concentration of the H_2O_2 , and the cell potential values were recorded at every 10 min.

In the PC trials, electrolysis was performed with textile wastewater that was continuously saturated with oxygen by an air pumping system inside the reactor system at different flow rates of 0.1-0.5 L/min. In the range of 80-100 mA, a constant current was applied using a DC power supply during the PC reactions according to Taguchi experimental design. Unlike the H₂O₂ generation trials, an iron wire was used for the Fenton reactions as the sacrificial anode to provide the required iron catalyst, and any supporting electrolyte was added in the wastewater to provide high ionic strength. In these experiments, the electrolysis time was chosen as 400 min based on the preliminary tests.

All removal efficiencies were calculated according to Eq. (5);

$$\eta(\%) = \frac{A_o - A_f}{A_o} \times 100 \tag{5}$$

where A_o is the initial value before treatment and A_f is the final value after treatment for the wastewater.

At the deoxygenated PC trials, nitrogen gas (analytical grade) was bubbled into the solution during the 15 min before each electrolyzes, and a constant nitrogen flow was maintained over the solution during the experiment. At these deoxygenated experiments, there was no addition of external H_2O_2 to the solution, and similarly, the oxygenated reactions were conducted with the application of the current.

2.6. Taguchi's DOE method

Taguchi method applies fractional factorial designs, called OA, to reduce the number of experiments required to determine their influence over the process output [22], in this case the PC reactions after 400 min of operation. The effects of three factors, current, initial wastewater concentration and air flow rate on process performance were analyzed. The experimental design consisted of a set of nine trials corresponding to L_g orthogonal array under the specific conditions selected for this study: three factors and three levels, summarized in Table 2. At least two runs were performed for each trial to avoid nonlinearity effects.

3. Results and discussion

3.1. Investigation of H₂O₂ electro-generation

Since H_2O_2 production is essential for PC process, it is necessary to identify the H_2O_2 production capacity of carbon fiber cathode. Therefore, before determining of PC pro-

Table 2			
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Factors and levels in the experimenta	il design
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Levels	Factors							
	Current (C) (mA)	Initial wastewater concentration $(C_o) (C_o/$ dilution rate)	Air flow rate Q_h (L/min)					
1	80	C _o	0.1					
2	90	<i>C</i> _o /2	0.3					
3	100	$C_o/4$	0.5					

cess optimum conditions, potential of carbon fiber in terms of H_2O_2 production was tested. It is well known that pH 3 is the most appropriate value for EF reactions and it was confirmed by many works [23–25]. Fig. 3 presents the accumulation of H₂O₂ at different current values from 60 to 100 mA.

The results indicated the optimum current value for the H_2O_2 generation is 80 mA after the 100 min electrolysis, and the concentration of H_2O_2 reached 455.64 mg/L at this condition. On the other hand, the generation rate was decreased dramatically when current value increased more than 80 mA. This trend is in agreement with relevant literature and according to some researchers, at cell potentials higher than a certain value, the reduction in the amount of O_2 leads to the production of H_2O instead of H_2O_2 through Eq. (6) [26], which also results in a decrease in the H_2O_2 concentration when the current is above 80 mA.

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \tag{6}$$

According to these results, it can be concluded that carbon fiber is a favorable cathode material for the electro-generation of H_2O_2 . When the relevant literature is considered, Özcan et al. reached 273.7 and 91.8 mg/L at the end of the 180 min using carbon sponge and carbon felt cathode,

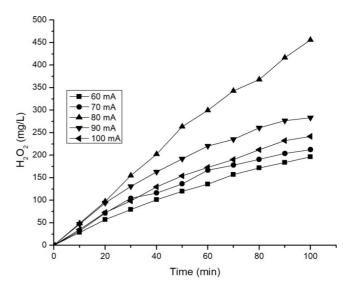


Fig. 3. Effect of applied current on H_2O_2 production [conditions: pHi 3, $Q_b = 0.3$ L/min, and 20 mM Na₂SO₄].

respectively [27]. On the other hand, Qiang et al. reported that especially H_2O_2 generation is favored at low temperatures and 80 mg/L H_2O_2 was reached by using graphite cathode material at the end of the 120 min [28].

3.2. Optimization of PC process

According to the previous studies, PC process is one of the most used treatment options for the treatment of textile waste waters [29–31]. To increase the performance of the process, it is necessary to analyze different factors that can influence the performance of the treatment. Therefore, Taguchi experimental design method was chosen optimizing the operational parameters for PC process. The experimental studies were carried out in different type of solution medium, which oxygenated and deoxygenated, to investigate of the effect of DO on PC reaction and all experimental trials were performed at an initial pH of 3. The obtained results of the experimental studies are presented for the comparison of both conditions.

In order to validate the used experimental design, a series of experiments were performed according to the L_g matrix using EF process in oxygenated and deoxygenated conditions. As seen in Table 3 and Table 4, the results of the

experimental runs for PC process are found to be very close to each other.

According to Tables 3 and 4, especially the removal percentages for color and TOC parameters in oxygenated conditions are higher than that of deoxygenated conditions. On the other hand, turbidity removals for deoxygenated conditions are higher than that of oxygenated conditions at some experimental conditions (Run 1). It can be explained by adsorption phenomena which takes place in EC mechanism due to lack of sufficient DO.

When the tables are considered, it can be seen that the parameter C_o is included in the design matrix. Because the wastewater characteristics change day after day, even hourly, the treatment performance of the treatment system depends strongly on the wastewater concentration. Accordingly, it was decided to include C_o in the orthogonal array as a design parameter for such real wastewater application.

To evaluate the influence of each factor on color, TOC, and turbidity removal, the signal to noise (S/N) ratios for each factor should be calculated. The mean S/N ratio for every factor was calculated and plotted in a graphical form. The peak points in these plots correspond to the optimum condition. Figs. 4a and b indicate the results of S/N ratios

Table 3

Experimental conditions,	measured turbidity	, color and TO	DC removals for	oxygenated	experiments

Exp.	С	C_{o}	Q_h	Turbidity removal (%)		Color ren	noval (%)	TOC rem	oval (%)
No				Run 1	Run 2	Run 1	Run 2	Run 1	Run 2
1	1	1	1	40.6	46.3	69.6	68.7	23.9	17.8
2	1	2	2	67.8	61.2	69.2	66.3	27.6	30.6
3	1	3	3	42.0	41.8	78.5	72.4	36.4	34.9
4	2	1	2	62.5	64.9	71.9	67.8	21.4	17.6
5	2	2	3	58.2	54.6	69.0	67.9	28.1	32.0
6	2	3	1	100	100	100	100	69.4	71.3
7	3	1	3	62.9	61.5	76.8	74.8	32.1	28.4
8	3	2	1	37.7	42.1	74.8	74.2	44.7	44.4
9	3	3	2	100	100	100	100	57.8	62.7

Table 4

Experimental conditions, measured turbidity, color and TOC removals for deoxygenated experiments

Exp.	С	C_{o}	Q_h	Turbidity	removal (%)	Color ren	noval (%)	TOC rem	oval (%)
No				Run 1	Run 2	Run 1	Run 2	Run 1	Run 2
1	1	1	1	53.0	52.4	45.0	46.7	20.9	25.9
2	1	2	2	17.1	15.5	44.6	44.4	22.7	17.2
3	1	3	3	17.1	19.0	97.2	98.3	61.0	56.6
4	2	1	2	30.2	31.7	50.1	47.6	13.4	11.3
5	2	2	3	13.8	17.7	86.6	84.8	22.9	26.7
6	2	3	1	8.2	9.2	98.1	97.5	46.8	49.2
7	3	1	3	51.3	51.4	73.9	74.4	34.1	30.6
8	3	2	1	37.1	35.3	85.4	84.3	51.7	55.4
9	3	3	2	25.1	27.5	100	100	65.0	68.6

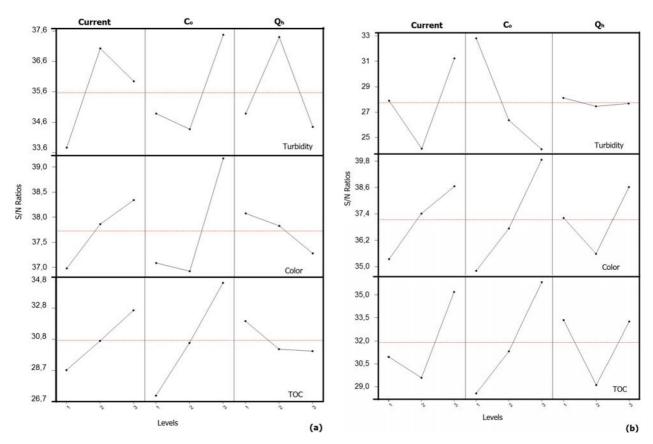


Fig. 4. S/N ratios for different factors (a) oxygenated medium, (b) deoxygenated medium.

for EF process with respect to C, C_o and Q_h at different parametric levels in oxygenated and deoxygenated medium.

It is known that the initial pollutant concentration in many process is one of the important factors [32]. It is seen from Fig. 4a and b that general tendencies of the C_o factor are same in all figures, and, removal efficiencies decrease with decreasing wastewater dilution rate, also, it is seen that the factor of C_o has the biggest variation around the mean S/N value, that is, it can be said that C_o is the system controlling factor for all removals in oxygenated and deoxygenated conditions. More hydroxyl radical is required to obtain the higher removal rate. However, applied current in the present conditions are not sufficient to produce enough *OH for higher concentrations of pollutant. Therefore, PC process performance decreases.

As expected, an increase in the applied current ranging from 80 to 100 mA leads to an increase in color and TOC removal rates for the both oxygenated and deoxygenated conditions. However, as seen from Fig. 1, the general tendency for applied current is not valid for turbidity removal (Figs. 1a and b). Also, Flores et al. reported that turbidity removal has affected by applied current, however, in their all trials, with more than 99% turbidity abatement at $j \ge 10$ mA cm⁻² was achieved by EC process [33]. Therefore, it can be said that the applied current is not the most important parameter in turbidity removal for EC like processes. It is widely known that the best way to remove turbidity is coagulation-flocculation method using Al and Fe metal hydroxides. In the present study, solution final pH values reached to 6–6.5 at the end of the electrolysis, and, these pH value were suitable for the iron species responsible for the agglomeration of pollutant particles (Fig. 5).

The flow rate had a great impact on not only the residence time of pollutants but also the accumulation of H_2O_2 in the E-Fenton process [34]. As it is seen from Fig. 4a, TOC and color removal rates decreased with increasing

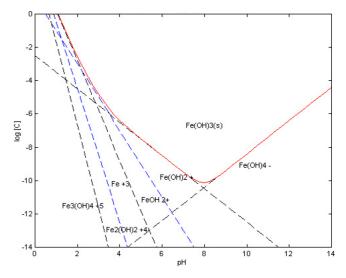


Fig. 5. Activity diagram of Fe(III).

amount of air flow rate. This behavior could be attributed to the scavenging effect of iron. It was reported that the excess H^+ ions would be resulted in the excess corrosion product (Fe²⁺) that also could act as hydroxyl radical scavenger [35]. The corresponding equations are given in Eqs. (7) and (8).

$$H^+ + OH^* + e^- \to H_2O \tag{7}$$

$$Fe^{2+} + OH^* \rightarrow OH^- + Fe^{3+}$$
(8)

The main mechanisms for removing TOC and color in EF process are mineralization and degradation by generated OH* radicals. However, in this study, excess iron particles that were electro-generated into the cell caused the surface of carbon fiber to be covered with iron particles towards the end of the reaction. Thus, required amount of H_2O_2 decreased and expected removal could not been achieved and the removal rate was decreased drastically. It can be seen from Figs. 6a and b.

As mentioned previously, the surface area of carbonaceous material is the most important point for H_2O_2 production. After the surface of the carbon fiber covered by iron, reduction of oxygen on the cathode surface has been prevented. This leads to a decrease in removal performance.

The best removal result for the turbidity was reached at the 2^{rd} level of air flow rate (0.3 L/h). The turbidity removal result can be attributed to the electrochemical coagulation

which occurs when iron dissolute with the effect of applied current. Thus, the applied air flow rate did not affect turbidity removal significantly. However, introduction of oxygen into the cell may cause a change in iron fraction from Fe²⁺ to Fe³⁺. In addition to this, the best turbidity removal should not be associated with the other parameters to be removed. According to some researchers, the best turbidity removal efficiency was closely related to reactor geometry [36].

On the other hand, when the deoxygenated conditions are compared each other with respect to turbidity, and color and TOC removal rates, the highest values are obtained at the 1st, 3rd and 1st, respectively.

3.3. Determination of contribution ratios

After all experiments were performed according to Taguchi OA matrix, the last step is to find optimum parametric conditions and calculate the contribution ratios in terms of their effect size on whole system performance. To this end, some confirmation tests were carried out and its results are given in Table 5.

As it is seen from Table 5, observed and predicted removal rates are close to each other, in other words, the Taguchi method can be used successfully with 5% error for the determination of optimum color, TOC, and turbidity removal by the PC process.

In Fig. 7, the contribution percentage of each factor on all system performance was given. According to Fig. 7, the

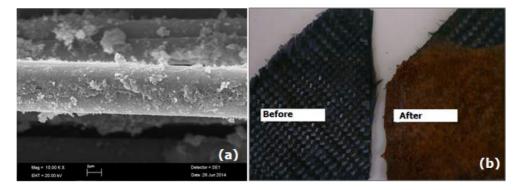


Fig. 6. (a) SEM images of carbon fiber covered with iron (b) photo of carbon fiber after and before PC.

Table 5
The optimum parametric conditions and their observed and predicted results

_	-					-			
Parameter	C (mA)		C_{o}		(Q_{02}/Q_{1})	_{N2}) (L/min)	Observed (%)	Predicted (%)	Confidence interval (%)
	Level	Value	Level	Value	Level	Value	-		
Oxygenated conditions									
Color	3	100	3	$C_o/4$	1	0.1	100	99.94	90.38-100
TOC	3	100	3	$C_o/4$	1	0.1	69.84	70.40	58.56-82.25
Turbidity	2	90	3	$C_o/4$	2	0.3	100	99.94	69.96–100
Deoxygenat	ted condit	ions							
Color	3	100	3	$C_o/4$	3	0.5	100	99.91	93.48-100
TOC	3	100	3	$C_o/4$	1	0.1	66.80	76.11	66.14-86.08
Turbidity	3	100	1	C	1	0.1	62.37	60.58	53.51-67.66

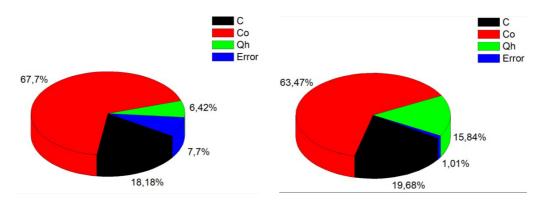


Fig. 7. Contribution ratios for each factor on PC process (a) oxygenated medium, (b) deoxygenated medium.

highest contribution rate belongs to C_o parameter, and C_o parameter almost manages to all system alone. On the other hand, current and Q_h have the smallest effect on PC process performance, and its effect on the whole system performance couldn't be understood clearly because of the C_o dominant parameter.

4. Conclusions

It has been proved that PC with iron wire anode and carbon fiber cathode is a very effective method for the treatment of textile wastewater. PC process efficiency depended on oxygen in the solution was evaluated using Taguchi orthogonal design matrix. In the study also, carbon fiber was investigated for the first time as cathode material in the electrochemical generation of H_2O_2 . According to the results, the removal efficiency of color and TOC parameters in oxygenated conditions are higher than those of deoxygenated conditions. The optimum conditions for PC process can be recommended as current of 100 mA, dilution rate of $C_{o}/4$, and oxygen flow rate of 0.1 L/min for oxygenated conditions. On the other hand, current of 100 mA, dilution rate of $C_{2}/4$, and nitrogen gas flow rate of 0.5 L/min for deoxygenated conditions provided the best results. At these conditions, almost complete color removal and >65% TOC removals were achieved for both medium. The study showed that this carbon fiber material was very promising in the field of electrochemical generation of H₂O₂ and PC degradation of real textile wastewater.

Acknowledgements

This work was supported by the TUBITAK-ÇAYDAG under Grant number 112Y160; the Research Fund of Erciyes University under Grant number FDA-2014-5597.

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