Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2022.28821

272 (2022) 266–276
October

Removal of reactive blue 171 dye from aqueous solution and textile industrial wastewater using peroxi-electrocoagulation process by iron electrode: application of response surface methodology

Azam Mahroudi[a], Majid Aghasi[b,*], Maryam Dolatabadi[c], Saeid Ahmadzadeh[d,e,*]

[a]*Student Research Committee, Kerman University of Medical Sciences, Kerman, Iran, email: Azammahrodi@yahoo.com*
[b]*Department of Environmental Health, School of Public Health, Kerman University of Medical Sciences, Kerman, Iran, email: Aghasi.Majid@yahoo.com*
[c]*Environmental Science and Technology Research Center, Department of Environmental Health Engineering, School of Public Health, Shahid Sadoughi University of Medical Sciences, Yazd, Iran, email: Health.dolatabadi@gmail.com*
[d]*Neuroscience Research Center, Institute of Neuropharmacology, Kerman University of Medical Sciences, Kerman, Iran, email: Chem_Ahmadzadeh@yahoo.com*
[e]*Pharmaceutics Research Center, Institute of Neuropharmacology, Kerman University of Medical Sciences, Kerman, Iran*

Received 18 March 2020; Accepted 11 August 2022

ABSTRACT

Dyes are organic compounds with very complex structures that are used in various industries. The remaining dyes have a significant environmental impact on the environment and can change the physical and chemical properties of the aquatic solution. Therefore, removing them from the environment is essential. In this study, the removal of reactive blue 171 dye from aqueous solution and textile industrial wastewater using peroxi-electrocoagulation process by response surface methodology. According to the results, 99.4% of reactive blue 171 dye under optimal conditions in the peroxi-electrocoagulation (PEC) process, including the concentration of 43.1 mg·L^{-1}, pH with 3, 9.2 mA·cm^{-2} current density, 2.5 cm distance between the electrodes, 4 mM H_2O_2, and 7.7 min the reaction time. Under these conditions, energy consumption was equivalent to 0.275 kWh·m^{-3}. The removal process follows from the first-order kinetics with R^2 = 0.9771. This study showed that the PEC process can remove high levels of dye with the least amount of energy consumed from aqueous solutions and it can be used as an economical process.

Keywords: Removal; Reactive blue 171; Textile industrial; Peroxi-electrocoagulation process; Response surface methodology

1. Introduction

Industrial wastewater is one of the most potent sources of contamination of the environment. The pollutants in industrial effluents depend on the production line and can produce different types of contaminants. These compounds consist mainly of chemical and toxic substances that are created by human activities related to the processing and production of raw materials, washing, cooling, heating, extraction, reaction products, separation, and etc. The textile industry is one of the most-used industries in the world, and there are a lot of dyes and other pollutants in the effluent of this industry. A large number of textile industries have not estimated the discharge wastewater standard according to environmental laws, and this mentioned issue and non-compliance laws have created serious and acute consequences on the water ecological system. In general, the textile industry has more stringent limits

* Corresponding authors.

on wastewater disposal [1,2]. One of the most important contaminants in the textile industry is dyes. Dyes are aromatic organic compounds that absorb light in the visible light region (wavelength 700–350 nm). Based on the chemical structure or chromophore, the dyes are divided into 30–20 groups [3,4]. Today more than 10,000 types of synthetic dyes are commercially used in various industries such as textiles, food, paper, plastics, cosmetics, etc. In the textile industry, about 1,000 types of different dyes and pigments are used in the textile industry [5]. That more than 50% of them have a double bond N=N and contain 1–4 azo groups. About 20%–30% of dyestuff dyes are reactive dyes and most reactive dyes (about 80%) are azo dyes. The reactive dyes are used to dye cellulose fibers like flax and it includes more than half of the used fiber throughout the world [6,7].

The presence of these dyes in water resources causes major problems, such as dermatitis, carcinogenesis, mutagenesis, and ecosystem disruption [8,9]. Therefore, it is necessary to remove dyes from water environments to reduce the problems caused by their presence in the aqueous media. So far, various techniques have been used for the treatment of dye wastewater that can refer to different process, including adsorption with various adsorbents such as activated carbon, chitosan, nanoparticles, etc. [10,11], coagulation and flocculation processes [12,13], use of membrane processes, biological processes [14,15], and advanced oxidation process [16–18].

The peroxi-electrocoagulation (PEC) process is one of the most popular electrochemical oxidation processes that have recently attracted attention researchers. The Fenton process is a processing in which bivalent iron ion and H_2O_2 are used simultaneously to oxidize contaminants using insitu generation of hydroxyl radical ($^{\bullet}OH$) (Reaction 1).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH \tag{1}$$

This process is called PEC if in the Fenton process, instead of Fe ion, the electric current and iron electrodes are used to produce bivalent iron ion. The $^{\bullet}OH$ is ability to react rapidly with organic compounds and by hydroxylation or hydrogenation of these compounds through a radical mechanism to complete the mineralization of these compounds [19–21]. The Fenton process is a powerful technique that can oxidize decomposition-resistant pollutants in a short time. However, the Fenton process has main disadvantages, including the creation of an acidic solution for the reaction and neutralization of treated wastewater, as well as the need for more iron ions during the Fenton process than PEC process, so in the Fenton process, management requires the sludge produced during the process [22]. Nevertheless, in the PEC process, the Fe^{3+} produced in the Fenton reaction is regenerated in the cathode electrode and produces Fe^{2+}, and again it may react with H_2O_2 to produce it, and therefore the production of sludge is less than in the PEC process [23,24]. The reactive blue 171 (RB 171) dye has been widely used in the textile industry due to its high solubility, brightness, ease of use, optimum durability during washing and low energy consumption. Reactive blue 171 (RB 171) dye is considered as azo and reactive dye. It causes a lot of danger if it reaches the water resources. Therefore, in this study, it has been investigated the usage of the PEC process to purify and remove RB 171 dye from water sources.

2. Material and methods

2.1. Materials

The RB 171 dye ($C_{40}H_{23}O_{19}$ $N_9Na_6S_6C_{12}$) was purchased and used from the Shadilon Dye Factory of Mashhad with a purity ≥ 99.0%. hydrogen peroxide (H_2O_2, grade: 30%), sodium chloride (NaCl, purity: ≥99.9%), sodium sulfate (Na_2SO_4, purity: ≥99.0%), sodium hydroxide (NaOH, purity: ≥98.0%), hydrochloric acid fuming (HCl, purity: 37%), sulfuric acid (H_2SO_4, purity: 95%–97%), and tert-butanol ($C_4H_{10}O$, purity: ≥99.5%), potassium chloride (KCl, purity: ≥99.0%), and potassium nitrate (KNO_3, purity: ≥99.0%) were purchased from the Merck Co.

2.2. Reactor set up

The PEC reactor, to perform the PEC process on a laboratory scale, was designed to be batch and was made of cylindrical Plexiglas with 300 mL. To set up the PEC reactor, 250 mL wastewater synthetic was made at each stage with pre-set RB 171 dye concentrations and distilled water.

The pH of the samples was adjusted using H_2SO_4 and NaOH using a pH meter (Metrohm 827 pH lab). The reactor was placed on a magnetic stirrer at 100 rpm (rotation per minute) rotational speed. The electrodes were used with 5.0 cm length, 1.5 cm wide, 0.1 cm thick, and the electrode immersion dimensions with 3.0 cm length, 1.5 cm width, and 0.1 cm thickness were used for wastewater treatment.

The electrode contacting area with wastewater, ignored of the electrode thickness, was 9 cm^2. The distance between the electrodes in this reactor was made up of two plastic holders which did not create any limitation in the electrodes' surfaces contacting with the wastewater refining. The iron electrodes were rinsed with HCl and polished their surfaces with sandpaper at the desired intervals inside the reactor and they have been connected to the Megatek power supply. Simultaneously by adding the H_2O_2 predetermined quantities in the reactor, the Megatek power supply was switched on and the desired current was adjusted. After the reaction time, the reactor contents transferred to the test tube. In order to eliminate the residual H_2O_2 and stop the Fenton reaction, for each mole of primary H_2O_2, 1 mL sodium thiosulfate 5 mM (manually) was added to the samples. Then the samples were centrifuged at 1,000 rpm (rotation per minute) for 5 min and they measured with the UV/Vis spectrophotometer Optizen 3220 at 610 nm wavelengths. The PEC process efficiency in the RB 171 dye removing was calculated from Eq. (2) and the energy amount was consumed using Eq. (3) [25].

$$\text{Removal}\left(\%\right) = \frac{\left(C_0 - C_t\right)}{C_0} \times 100 \tag{2}$$

where C_0 is the concentration of RB 171dye in mg·L^{-1}, C_t is the concentration of RB 171 dye at time t (after the PEC process) in mg·L^{-1}.

$$\text{EEC} = \left(\frac{\text{UIt}}{V}\right) \tag{3}$$

where EEC is the electrical energy consumed amount (kWh·m^{-3}), I is the applied current intensity (A), t is the electrolysis time (h), U is the applied voltage (V), V is the volume of solution (L) [26].

2.3. Analytical procedure

Designing the study using the Design–Expert software was performed by the response surface methodology (RSM) method to determine the main factors and the interaction between them and the quadratic effects, with the aim of minimizing the number of experiments, and saving time and cost. The five independent variable's effects on the dye removal efficiency were investigated by the PEC process. The variables included RB 171 concentration, current density, H_2O_2 concentration, the distance between electrodes, and reaction time. Experiments were designed and implemented in five levels ($-\alpha$, –1, 0, +1, $+\alpha$) according to Table 1 and based on the RSM method. The PEC process efficiency was considered as a dependent variable (as the response) in the RB 171 dye removal.

Variance analysis (ANOVA) was used to analyze the data. The response variable in the form of a polynomial regression model presented in Eq. (4) is presented as a function of independent variables [27,28].

$$Y = b_0 + \sum_{i=1}^{n} b_i x_i + \sum_{i=1}^{n}\sum_{j=1}^{n} b_{ij} x_i x_j + \sum_{i=1}^{n} b_{ii} x_i^2 \tag{4}$$

where Y is the response (removal efficiency), b_0 is the intercept, and b_i is the calculated regression coefficient which is obtained from Y and X_i values in the independent variables encoded levels.

The X_iX_j and x_i^2 parameters include interaction and quadratic effects, respectively.

The equation fitting quality was balanced using regression coefficients (R^2), adjusted R^2 (Adj. R^2) and predicted R^2 (Pred. R^2) it was evaluated. P-value < 0.05 was considered as statistically significant. The contribution effect of the investigated variables on the removal RB 171 dye was determined by Pareto analysis according to Eq. (5) [29].

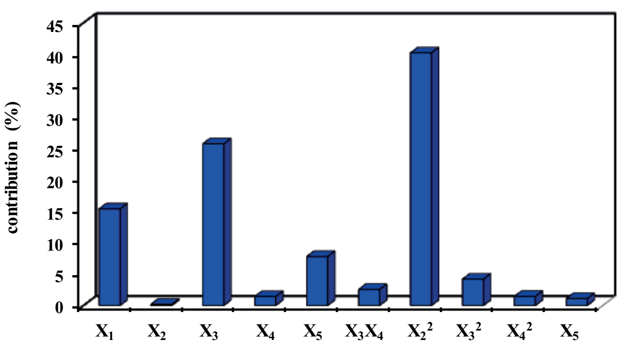

Fig. 1. Pareto analysis for removal RB 171 dye using PEC process.

$$P_i = \frac{b_i^2}{\sum b_i^2} \times 100 \left(i \neq 0\right) \tag{5}$$

where P_i is the percentage of each effect contribution and b_i is each effect influence coefficient.

2.4. Characterizes of the real textile industrial wastewater

The real wastewater was supplied from the output of the unit of wastewater treatment plant's balancing unit. The physical and chemical characteristics of the real samples of the factory wastewater are given in Table 2.

2.5. Plant wastewater treatment system and sampling

Dropper and balancing (to adjust the temperature and pH, also for mixing), the importance of temperature modification is the ratio of photoconductivity in the chemical treatment of wastewater with coagulation and flocculation. However, in the biological treatment section, anaerobic treatment was first treated as an anaerobic lagoon, a relaxing pond, a discontinuous reactor with the upstream flow, and a sedimentation reservoir. Then the waste was introduced into the aerobic system. There were two activated sludge pots with continuous aeration. Thereafter, an aerobic settling pond was located. The blast furnace returns the sludge to the aerobic system, and then the wastewater from the rotary bridge was introduced into the sand filter by pumping and eventually fired from the outlet. The sampling was done at the end of the equilibrium match. The maximum wavelength after centrifugation was determined using a spectrophotometer, which obtained 580 nm.

3. Results and discussion

In order to evaluate the RB 171 dye removal efficiency by the PEC process, central composite design (CCD), which is one of the RSM, was used. The dye concentration effects, current density, H_2O_2 concentration, the distance between electrodes and reaction time were investigated. The design matrix with the experimental and predicted results are presented in Table 3. The results of the EF process efficiency in the RB 171 dye removal from synthetic wastewater were analyzed by the experimental design software to develop the best model that can describe the observed response.

The analyses were selected polynomial type and quadratic models. The validity of the proposed model was assessed by analysis of variance (ANOVA). In addition, it can be determined the statistical significance of the main effect, interaction, and quadratic effect. The ANOVA test results are presented in Table 4.

In Table 4, X_1, X_2, X_3, X_4, and X_5 represent the independent variable main effects which are including the RB 171 dye concentration, current density, H_2O_2 concentration, electrodes distance, and reaction time. The variable X_3X_4 represents the effect of H_2O_2 concentration (X_3) and the distance between the electrodes (X_4). The variable X_2^2 represents the square effect of factor X_2 (current density) on the desired response. P-value was determined less than 0.05 (P-value > 0.00001) for the PEC process efficiency

Table 1
Actual and coded values of independent variables in the PEC process

Variable	Unit	Coded value	Actual value	Levels				
				$-\alpha$	–1	0	+1	$+\alpha$
RB 171 concentration	mg·L^{-1}	X_1	A	20.0	43.2	60.0	76.8	100.0
Current density	mA·cm^{-2}	X_2	B	3.0	6.5	9.0	11.5	15.0
H_2O_2 concentration	mM	X_3	C	1.0	2.2	3.0	4.0	5.0
Distance between electrodes	cm	X_4	D	1.0	1.9	2.5	3.1	4.0
Reaction time	min	X_5	E	2.0	4.3	6.0	7.7	10.0

Table 2
Physical and chemical characteristics of the real samples of the factory wastewater

Parameters	Units	Value
Temperature	°C	22.2 ± 1.8
pH	–	4.8 ± 0.26
TDS	mg·L^{-1}	1,060 ± 56
TSS	mg·L^{-1}	105 ± 12
BOD	mg·L^{-1}	763 ± 25
COD	mg·L^{-1}	1,963 ± 44
Color	mg·L^{-1}	56.2 ± 8.5

proposed model in the removal of RB 171 dye using PEC process. *P*-value was less than 0.3713 for the main effects of X_1, X_2, X_3, X_4, X_5, and intervention X_3X_4, square effects, X_2^2, X_3^2, X_4^2, and X_5^2. Also, it was calculated 0.0579 to the lack of fit statistic. The regression analysis is a test that was used to validate the model. The regression analysis showed good fit of the experimental data to the second-order polynomial model with coefficient of determination (R^2) value of 0.9219, adjust correlation coefficient (Adj. R^2) value of 0.9019 and predicted correlation coefficient (Pred. R^2) value of 0.8166. The R^2 indicates the model predicted values fitting against the actual values which are obtained from the experimental tests and the predicted determination coefficient indicate the model adequacy.

The model final equation for the PEC process efficiency in the dye removing (Y) based on the coded factors is as follows.

$$Y(\%) = 88.91 - 4.79X_1 + 0.53X_2 + 6.20X_3 + 1.46X_4 + 3.41X_5 - 1.95X_3X_4 - 7.75X_2^2 - 2.50X_3^2 - 1.47X_4^2 - 1.28X_5^2 \quad (6)$$

The PEC process efficiency model in the RB 171 dye removal is also shown in Eq. 6. Y is the PEC process efficiency for the removal RB 171 dye. In this equation, X_1, X_2, X_3, X_4, and X_5 are the coded values of the RB 171 dye concentration, the current density, the H_2O_2 concentration, the distance between the electrode, and the reaction time.

This model consists of a fixed number and a variable section. The fixed section shows the fixed efficiency 88.91% to the dye removal. The model variable section states the dye removal efficiency that among the main effects, the factor X_3 and X_2 have the highest and the least effect on the PEC process efficiency in dye removal, with coefficients +6.2 and +0.53, respectively. The H_2O_2 concentration and the distance between electrodes (X_3X_4) intervention effect was the only effective interventional effect. While among the factors square effects the X_2^2 and X_5^2 equal to –7.75 and –1.28, that had the most and the least effect on the dye removal efficiency by the PEC process. According to Pareto analysis (Fig. 1), That among the main effects, factors X_3 (H_2O_2 concentration) and X_1 (RB 171 dye concentration) had the highest contribution to the dye removal that their share in PEC efficiency was 25.7% and 13.6%, respectively, while other factors such as X_2, X_4, and X_5 have been effective in dye removal with 0.19%, 1.4%, and 7.8% contribution share, respectively. X_3 and X_4 interventional effect with 2.5% effective factor were known as the only effective interventional factor. From the five independent variables, the H_2O_2 concentration factors (X_3) and the distance between the electrodes (X_5) have the highest and lowest effect on the dye removal efficiency, respectively. Among the efficiency square effects on the PEC process in dye removal, the factors X_2, X_3, X_4, and X_5 have a contribution share 40.2%, 4.2%, 1.4%, and 1.1%, respectively. Among them, X_2 (current density) was most effective, and X_5 (reaction time) had the least effect on the dye removal.

3.1. Effect of operating parameter for removal RB 171 dye sing PEC process

pH is one of the most important affecting parameters on the chemical processes. In order to determine the effect of pH on the PEC process efficacy in the dye removal pH ranging from 2–12 was investigated. At this stage, the other studied parameters including the dye concentration of 50 mg·L^{-1}, the current density of 7.5 mA·cm^{-2}, the H_2O_2 concentration of 2.5 mM, the distance between the electrodes of 2.0 cm have remained fixing, and time removal efficiency rate in 10.0 min was investigated. According to the results (Fig. 2), the RB 171 dye removal efficacy in 10 min after the PEC process at pH of 2.0, 3.0, 5.0, 7.0, 10.0 and 12.0 was 81.5%, 87.2%, 52.7%, 25.4%, 10.9% and 1.6%, respectively.

The results show that the maximum removal efficiency took place at pH 3. The general trend of removal efficiency of RB 171 dye was decreasing by increasing pH. In very acidic pH (pH ≤ 3), the removal efficiency decreases. The reason for this is that H_2O_2 at pH which is less than 3.0 it transforms to the oxonium ion ($H_3O_2^+$) (Reaction 7), and its reactivity by a Fe^{2+} ion is very slight. As a result, the

Table 3
Experimental condition and values obtained responses through the CCD

STD	RB 171 concentration (mg·L^{-1})	Current density (mA·cm^{-2})	H_2O_2 concentration (mM)	Distance between electrodes (cm)	Reaction time (min)	Experimental removal efficiency (%)	Predicted removal efficiency (%)
1	43.2	6.5	2.2	1.9	4.3	69.5	67.1
2	76.8	6.5	2.2	1.9	4.3	58.6	57.6
3	43.2	11.5	2.2	1.9	4.3	73.6	68.2
4	76.8	11.5	2.2	1.9	4.3	57.3	58.6
5	43.2	6.5	4.0	1.9	4.3	82.7	83.5
6	76.8	6.5	4.0	1.9	4.3	76.5	73.9
7	43.2	11.5	4.0	1.9	4.3	85.6	84.5
8	76.8	11.5	4.0	1.9	4.3	79.9	74.9
9	43.2	6.5	2.2	3.0	4.3	79.4	74.0
10	76.8	6.5	2.2	3.0	4.3	65.4	64.4
11	43.2	11.5	2.2	3.0	4.3	78.2	75.1
12	76.8	11.5	2.2	3.0	4.3	63.5	65.5
13	43.2	6.5	4.0	3.0	4.3	80.8	82.5
14	76.8	6.5	4.0	3.0	4.3	78.3	72.9
15	43.2	11.5	4.0	3.0	4.3	89.5	83.5
16	76.8	11.5	4.0	3.0	4.3	73.4	73.9
17	43.2	6.5	2.2	1.9	7.7	78.5	73.9
18	76.8	6.5	2.2	1.9	7.7	67.5	64.4
19	43.2	11.5	2.2	1.9	7.7	72.4	75.1
20	76.8	11.5	2.2	1.9	7.7	61.3	65.5
21	43.2	6.5	4.0	1.9	7.7	86.1	90.3
22	76.8	6.5	4.0	1.9	7.7	79.6	80.7
23	43.2	11.5	4.0	1.9	7.7	93.6	91.3
24	76.8	11.5	4.0	1.9	7.7	85.8	81.8
25	43.2	6.5	2.2	3.0	7.7	83	80.8
26	76.8	6.5	2.2	3.0	7.7	70.2	71.2
27	43.2	11.5	2.2	3.0	7.7	79.6	81.8
28	76.8	11.5	2.2	3.0	7.7	74.8	72.3
29	43.2	6.5	4.0	3.0	7.7	85.4	89.3
30	76.8	6.5	4.0	3.0	7.7	83.4	79.7
31	43.2	11.5	4.0	3.0	7.7	95.4	90.3
32	76.8	11.5	4.0	3.0	7.7	76.5	80.8
33	20.0	9.0	3.0	2.5	6.0	100	100.0
34	100.0	9.0	3.0	2.5	6.0	80.6	77.5
35	60.0	3.0	3.0	2.5	6.0	40.3	43.8
36	60.0	15.0	3.0	2.5	6.0	43.5	46.3
37	60.0	9.0	1.0	2.5	6.0	57.1	60.1
38	60.0	9.0	5.0	2.5	6.0	86.1	89.5
39	60.0	9.0	3.0	1.0	6.0	74.3	77.1
40	60.0	9.0	3.0	4.0	6.0	80.5	84.0
41	60.0	9.0	3.0	2.5	2.0	64.5	73.6
42	60.0	9.0	3.0	2.5	10.0	92.5	89.8
43	60.0	9.0	3.0	2.5	6.0	84.5	88.9
44	60.0	9.0	3.0	2.5	6.0	85.4	88.9
45	60.0	9.0	3.0	2.5	6.0	88.7	88.9
46	60.0	9.0	3.0	2.5	6.0	87.8	88.9
47	60.0	9.0	3.0	2.5	6.0	86.5	88.9
48	60.0	9.0	3.0	2.5	6.0	86.5	88.9
49	60.0	9.0	3.0	2.5	6.0	92.01	88.9
50	60.0	9.0	3.0	2.5	6.0	86.5	88.9

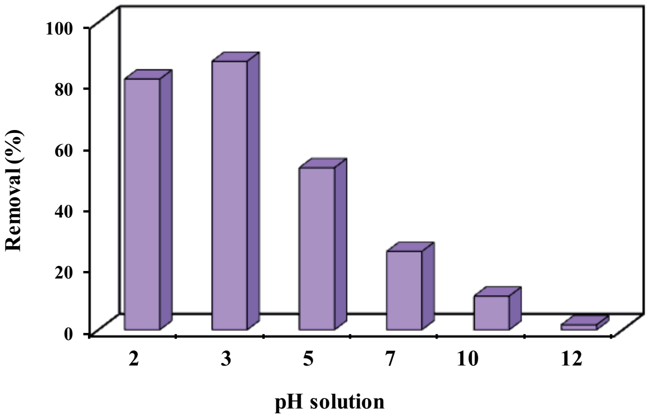

Fig. 2. Effect of pH on the removal efficiency RB 171 dye.

$^{\bullet}OH$ generation decreases and subsequently removal efficiency of RB 171 was decreased. Furthermore, at the pH ≤ 3, in addition to decreasing Fe^{2+} ions concentration, the H^+ ion concentration is increased, which is itself one of the radical scavengers, and decreased the removal efficiency.

$$H_2O_2 + H^+ \rightarrow H_3O_2^+ \quad (7)$$

According to the obtained results, by increasing the pH from 3.0 to 12.0, the removal efficiency decreased. At pH about 2.0 to 3.0, the Fe^{2+} ions available to the reactor is maximum and through the reaction with H_2O_2 in the PEC reactor, the production of the $^{\bullet}OH$ is maximized, thus it is increasing the Fenton reaction rate. On the other words, in acidic pHs especially in the pH between 2.0 and 3.0 Fe ions is soluble form in the reactor (Fe^{2+} species), and resulted in the Fe^{2+} ions reacts with H_2O_2 and it generation of $^{\bullet}OH$ which is having high oxidizing properties ($E°$ = 2.8 eV). Therefore, the $^{\bullet}OH$ generation in a sufficiently amounts at pH 3 and it improves the dye removal efficiency by the PEC process. The reason for reducing the removal efficiency by increasing the pH from 3.0 to 12.0 is that by increasing the pH the oxidizing potential of the $^{\bullet}OH$ decreases.

Moreover, at the pH values more than 5.0, due to the Fe^{2+} ions (as catalyst) deactivation and insoluble complexes formation, the resituated H_2O_2 accordance with reactions (8) and (9) electrochemically in the cathode is turned into water and oxygen and they release into the environment.

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \quad (8)$$

$$2H_2O_2 \rightarrow O_2 + 2H_2O \quad (9)$$

According to the results of this study, the conversion of H_2O_2 rate to $^{\bullet}OH$ depends on pH and it increases under acidic conditions [30,31]. Moreover, pH increase causes the Fe^{3+} ions instability and it leads to an increase in the hydroxide iron formation. At alkaline pH, iron species is converting to hydroxide compounds such as $[Fe(OH)^{4+}$, $[Fe(OH)_2]^+$, $[Fe(OH)]^{2+}$ and hydroxy compounds such as $[Fe(OH_2)_2]^+$ and $[Fe(OH)(OH_2)]^+$ are removed from the reaction medium [31,32]. The removal mechanism for removal of RB 171 dye in acid pH, especially below 4, has been the Fenton reaction pathway.

One of the most important affecting parameters in the treatment process is the initial concentration of contaminants. In this study, the dye concentration was studied in the range of 20–100 mg·L^{-1}. Fig. 3 shows the simultaneous effect of two variables which are the RB 171 dye concentration and the current density on the PEC process for removal efficiency of RB 171 dye. Fig. 3 shows the dye removal efficiency under conditions that H_2O_2 concentration is equal to 60 µL·L^{-1}, the distance between the electrodes is 2.5 cm and the reaction time is equal to 6 min.

Table 4
ANOVA for removal of RB 171 dye using PEC process

Factor	Sum of squares	df	Mean squares	*F*-value	*P*-value
Model	6,939.1	10	693.9	46.0	<0.0001
X_1	993.4	1	993.4	65.9	<0.0001
X_2	12.33	1	12.33	0.81	0.3713
X_3	1,666.5	1	1,666.5	110.5	<0.0001
X_4	91.7	1	91.7	6.1	0.0181
X_5	502.6	1	502.6	33.3	<0.0001
X_3X_4	122.0	1	122.0	8.1	0.0070
X_2^2	3,393.7	1	3,393.7	225.1	<0.0001
X_3^2	352.4	1	352.4	23.3	<0.0001
X_4^2	122.4	1	122.4	8.1	0.0070
X_5^2	92.1	1	92.1	6.1	0.0179
Residual	587.7	39	15.1	–	–
Lack of fit	550.0	32	17.2	3.1	0.0579
Pure error	37.7	7	5.4	–	–
Cor. total	7,526.9	49	–	–	–

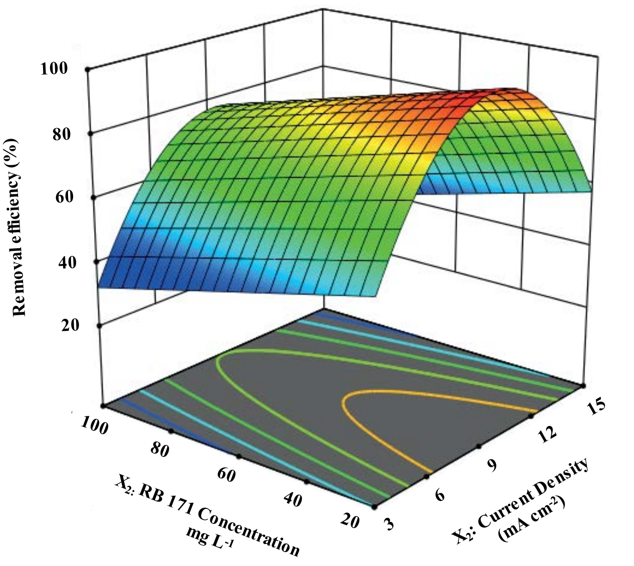

Fig. 3. Effect of RB 171 dye concentration and current density on the dye removal efficiency.

Fig. 3 shows that when the RB 171 dye concentration of 43.0 mg·L^{-1} and the current density equivalent to 0.6 0 mA·cm^{-2}, then the dye removal efficiency is 85.7%. At the same level of current density, when the dye concentration reaches 77.0 mg·L^{-1}, the removal efficiency of RB 171 dye is 76.3%. Also, according to Fig. 3, when the dye concentration is 43.0 mg·L^{-1} and the current density is 12.0 mA·cm^{-2}, the removal efficiency reaches 86.7%. As can be seen, if the dye concentration and current density are at its high level (dye concentration 77.0 mg·L^{-1} and current density 12.0 mA·cm^{-2}), the dye removal efficiency reaches 77.5%.

The results showed that increases in the dye concentration have a negative effect on the PEC process efficiency. The cause of reduced efficiency by increasing the concentration of the contaminant in the PEC process may be due to the fact that at the higher concentrations, the competitive consumption of $^{\bullet}$OH by middle-produced products is increased and resulting in the lower amounts of $^{\bullet}$OH can react with contaminating molecules. On the other hand, increasing in contaminants concentrations leads to an increase in the collisions number between molecules contaminants, resulting in a reduction in the collisions number with $^{\bullet}$OH, and the removal efficiency decreases with increasing dye concentration. It should be noted that by increasing the concentration of the contaminant, the required time increases to remove a certain contaminant percentage.

The current density effect on the dye removal efficiency using the PEC process is shown in Fig. 3 as a curve. According to Fig. 3, in the mid-range between –1 and +1, the removal efficiency was greater than in the $-\alpha$ and $+\alpha$ levels. According to Eq. (6), the current density quadratic effect (X_2^2) with –7.75 coefficient was higher than the current density main effect X_2 with 0.53 coefficient value. Also, current density was known as the most effective factor in the process. Current density is one of the most important factors in the chemical process. Based on the results obtained in the PEC process, the current density has a direct effect on the RB 171 dye removal efficiency. By increasing the current density to the optimum 9.2 mA·cm^{-2}, the removal efficiency increases, based on Pareto analysis, the current density square effect with high participation share (15.3%) was the most important affecting factor the removal efficiency.

The current density controls the Fe ions amount which is released from the anode electrode. Finally, the $^{\bullet}$OH concentration is controlled by current density. In the absence of Fe^{2+}, H_2O_2 by itself cannot degrade and decompose the dye molecule and on the other hand, the side and intervention reactions increase with increasing current density. These reactions will reduce the PEC process efficiency in dye removal. Also, H_2O_2 decomposes at high current density and reduces the process efficiency as excessive current density increases, the ion in the anode solution is oxidized to the ferric ion. Increasing the current density up to 6.0 mA·cm^{-2} will increase the RB dye removal efficiency using the PEC process.

Fig. 4 shows the simultaneous effect of two variable dye concentrations and H_2O_2 concentrations on the removal efficiency.

Fig. 4 shows that when the RB 171dye concentration is 43.17 mg·L^{-1} and the H_2O_2 concentration is 2.2 mM, the removal dye efficiency reaches of 85.1%. At the same level of dye concentration, when the H_2O_2 reaches 4.0 mM, the removal dye efficiency is 97.3%.

Fig. 4 also shows that if wastewater containing 77.0 mg·L^{-1} for 6.0 min is entered into the PEC treatment reactor which is containing 2.2 mM, removal efficiency of dye will be equal to 77.7% and if the H_2O_2 concentration increases to 4.0 mM, the removal efficiency reaches 87.9%. Considering that the presence of H_2O_2 on the one hand due to $^{\bullet}$OH production is necessary for the Fenton reaction, on the other hand, its excess values can act as radicals and reduce the PEC process efficiency, therefore, one of the most important factors that have an effect on the PEC process. In this study, in order to determine the effect of the H_2O_2 concentration, the concentrations of 1.0–5.0 mM were investigated. According to the results, the H_2O_2 concentration changing process on the PEC process efficiency in the removal efficiency of RB 171 dye is initially increasing and then decreasing. Based on Pareto analysis and Eq. 6, H_2O_2 concentration is the second most effective factor in the RB 171 dye removal efficiency. Increasing the removal efficiency due to the fact that according to Eq. 1, H_2O_2 is one of the Fenton main reactants, and in suitable concentration, it can produce sufficiently $^{\bullet}$OH in the presence of ferrous ion. Further, increasing in H_2O_2 leads to radical hydroxylation radical parasitic reactions and causes the use of this radical.

As a result, the dye removal efficiency decreases. In fact, the excessive increase in the H_2O_2 concentration due to the $^{\bullet}$OH reaction with H_2O_2 or the two $^{\bullet}$OH combinations with each other and the oxygenated water production leads to the $^{\bullet}$OH production (Eq. 10). This has the inhibitory effect on $^{\bullet}$OH production and reduces the PEC removal efficiency [32,33].

$$OH^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O \quad (10)$$

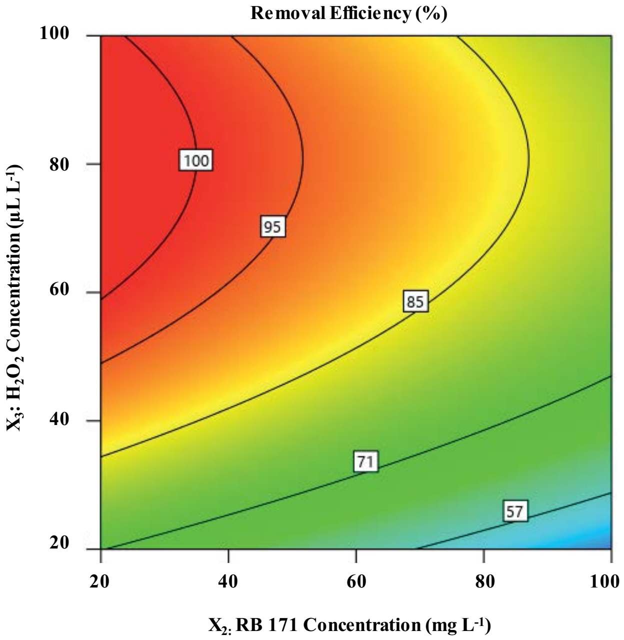

Fig. 4. Effect of RB 171 dye concentrations and H_2O_2 concentrations on the dye removal efficiency.

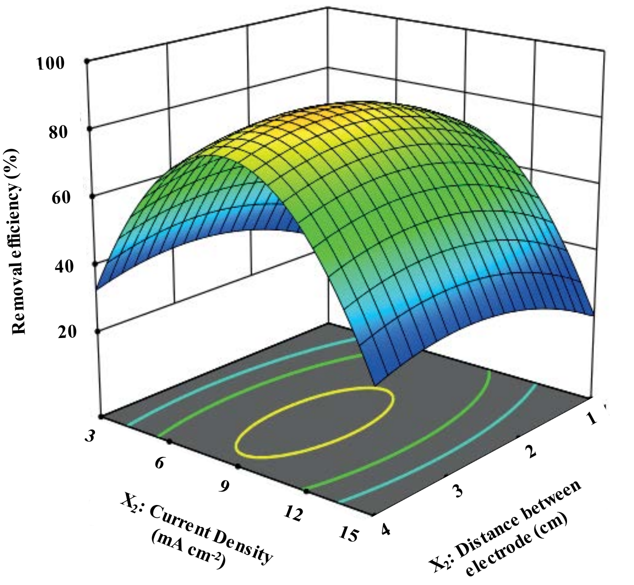

Fig. 5. Effect of current density and distance between electrodes on the removal dye efficiency.

Fig. 5 shows the simultaneous effect of two variables of current density and distance between electrodes on the PEC process efficiency in the dye removal efficiency.

The distance between electrodes is one of the factors that affect chemical processes. In this study, the distance between electrodes in the range of 1–4 cm was investigated. Based on Pareto's analysis, the distance between electrodes contributes in the PEC process with 1.43% and their share is 1.4% in the dye removal efficiency. Fig. 5 shows that when the current density is equivalent to 6.0 mA·cm^{-2} and the distance between the electrodes is 1.8 cm, the PEC efficiency in the dye removal is 78.1%. At the same current density level, when the distance between the electrodes is 3.1 cm, the dye removal efficiency reaches 80.9%. Furthermore, according to the diagram, when the current density is 12.0 mA·cm^{-2} and the distance between the electrodes is 1.8 cm, the dye removal efficiency is 79.1%. It can be seen that if the current density and the distance between the electrodes are at their upper level (the current density is equivalent to 12.0 mA·cm^{-2} and the distance between the electrodes is equivalent to 3.1 cm), the dye removal efficiency is 81.9%. When the distance between the two electrodes is very short, the generated ions are oxidized to the ferric ions easily in the anode and are removed from the reaction of the Fenton. By increasing the distance between the two electrodes to the optimal value, the system's resistance is increased and, due to the constant current rate, the power of the system is also increased according to reaction 11. As a result, more quantities of bivalent iron are produced and participate in the Fenton reaction, and consequently the system efficiency increases. In contrast, with a further increase in the distance between the electrodes (more than the optimal value), the produced ions' motion is slower and the collision possibility with H_2O_2 is reduced. As a result, the system efficiency is reduced to produce $^{\bullet}$OH.

$$P = \mathrm{RI}^2 \tag{11}$$

In the PEC process to determine the reaction time effect on the dye removal the times with duration 2–10 min were investigated. According to the corresponding diagrams, the dye removal efficiency increases by spending time, and the maximum removal efficiency was 7.7 min. When the H_2O_2 is 2.2 mM and the reaction time is equivalent to 4.3 min the dye removal efficiency is 75.8%. At the same level of hydrogen peroxide, when the reaction time reaches 7.7 min, the dye removal efficiency is 82.5%. Also, according to the diagram, when the H_2O_2 is 4.0 mM and the reaction time is 4.3 min, the dye removal efficiency is 88.0%. As seen, if H_2O_2 and reaction time are at their highest level (H_2O_2 of 4.0 mM, and reaction time of 7.7 min), the dye removal efficiency is 94.7%.

After this time, the removal efficiency graph ramp is almost constant so that the graph ramp afterward 7 min reaches less than 2%. This could be due to the injected H_2O_2 depletion into the reactor. Also, increasing time leads to the amount of the intermediate product from the H_2O_2 decomposition being increased, on the other hand, by mixing in the reactor environment the ion contact chance with the intermediate products, which are resulting from the H_2O_2 decomposition, increased, and against it, the $^{\bullet}$OH are produced less. In the early electrolysis stages, the ferroelectric ion concentration in the solution is low, and almost all of produced ferroelectric ion by the H_2O_2 in the reactor reacts and it the produces $^{\bullet}$OH. But by increasing reaction time, the ferrite ion in the reactor is converted to iron hydroxides and insoluble iron compounds such as $[Fe(H_2O)_8(OH)_2]^{+4}$, $[Fe_2(H_2O)_7(OH)_3]^{+3}$, $[Fe_2(H_2O)_7(OH)_4]^{+5}$ that in contact with H_2O_2 non-radicals they produce $^{\bullet}$OH with lower oxidation potentials [34,35]. As a result, in PEC processes, after the optimum time, the organic compounds oxidation process will have a slower ramp. This slowdown speed in increasing efficiency is also justified by the collision theory. Because the lifespan of •OH is very short (in a few nanoseconds), they react with organic molecules that are present in their formation. Over time, the residual dye concentration decreased as a result of the collisions number between the dye molecules and •OH (increasing the by-products) and it leads to reduce the dye removal efficiency ramp during PEC removal process.

3.2. EF optimization and Validation studies in the RB 171 dye removal

The developed model in Eq. 6 was used to determine PEC process efficiency optimal conditions in dye removal from synthetic wastewater. In order to optimize, we must select the desired inputs with expected outputs based on an arbitrary approach. In this study, the approach to achieve the PEC process efficacy was performed to remove the dye values which its value was more than 90%. Based on these conditions, the software lists various solutions to satisfy this proposed approach and according to desirability. In Table 5, the proposed first solution for the PEC process is presented.

As shown in Table 5, among the proposed solutions in the variables range, based on the desirability factor and the removal efficiency, the first solution is chosen as optimal conditions. Based on the results, if the wastewater with a dye concentration of 43.2 mg·L^{-1} is introduced into the EF reactor, at current densities 9.2 mA·cm^{-2}, and the distance between electrodes of 2.5 cm at time 7.6 min, 99.4% of the wastewater dye is removed. To ensure the proper function of the developed model for the RB 171 dye removal by the PEC process, 5 experiments were tested experimentally and separately. The results of this test with the 95% confidence coefficient were determined by the software that is presented in Table 6. According to Table 6, the experimental values and predictive values are within the range which is predicted by the software and it confirms the performed tests validity.

3.3. Kinetic study

To study the RB 171 dye kinetic study in the PEC process in the optimal condition including pH of 3.0, RB 171 dye concentration of 44.0 mg·L^{-1}, current density of 9.2 mA·cm^{-2}, H_2O_2 concentration of 0.77 μL·L^{-1}, the distance between electrodes of 2.5 cm, in time duration of 0 to 15 min was investigated. The kinetic coefficients are including the reaction rate constant (k) and the determination coefficient (R^2) were calculated. The RB 171 dye decomposition using the PEC process with the first-order kinetic had the highest R^2 of 0.9771.

3.4. Investigation the molar ratio of H_2O_2/Fe^{2+} in EF process

The H_2O_2/Fe^{2+} molar ratio is one of the affected parameters to the PEC process efficiency. Therefore, in this study the optimal H_2O_2/Fe^{2+} molar ratio at the same experiments, that is, pH of 3.0, dye concentration of 44 mg·L^{-1}, current density of 9.2 mA·cm^{-2}, H_2O_2 concentration of 0.77 μL·L^{-1}, the distance between electrode of 2.5 cm. The optimal H_2O_2/Fe^{2+} molar ratio for the high efficiency is equivalent to 2.1, which is in the range 2–3.5.

3.5. Investigation of the removal mechanism using radical scavenger

In order to ensure •OH production, the PEC process was investigated using 50 mM radical scavenger concentration, KCl, NaCl, Na_2SO_4, $NaHCO_3$, ethanol (C_2H_6O), and TB under the EF optimal conditions (pH = 3.0, dye concentration 44 mg·L^{-1}, current density 9.2 mA·cm^{-2}, H_2O_2 concentration 0.77 μL·L^{-1}, the distance between the electrodes 2.5 cm). Each experiment was repeated 3 times. The PEC process efficiency in optimal conditions as well as the PEC process in the radical scavengers presence KCl, NaCl, Na_2SO_4, $NaHCO_3$, ethanol, and TB were 81.6%, 79.4%, 86.4%, 66.3%, 47.5% and 40.6%, respectively (Fig. 6). The results show that the EF efficiency decreases in the core radicals' presence. This decrease in the EF process performance at presence different radical compounds is likely to indicate that the PEC process through the •OH production leads to the dye removal.

The steady state reaction rate of TB with •OH is very high. For this reason, this compound is widely used in advanced oxidation processes as radicals to determine the •OH roles. TB is usually preferred to free •OH that relative to surface radicals. While chloride, sulfate and carbonate anions disable active sites on the catalyst surface and thus prevent the surface radicals' formation. In this study, TB radicals had the highest reduction in the efficacy of dye removal compared to other cores radical. Therefore, free •OH are likely to have a greater effect on the PEC process

Table 5
Proposed solutions in the dye removal PEC process optimal condition

No	Concentration (mg·L^{-1})	Current density (mA·cm^{-2})	H_2O_2 concentration (mM)	Reaction time (min)	Distance between electrode (cm)	Removal efficiency (%)	Desirability
1	43.2	9.2	4.0	7.7	2.5	99.4	0.996
2	43.2	9.1	4.0	7.7	2.4	99.5	0.993
3	50.0	9.0	4.0	7.7	2.3	97.6	0.960
4	43.2	11.5	4.0	7.7	2.1	92.3	0.935
5	76.8	9.0	4.0	7.7	2.4	90.0	0.912

Table 6
Validation test of the dye removal using PEC process

Dye concentration	Current density (mA·cm^{-2})	H_2O_2 dosage (Mm)	Distance electrodes (cm)	Reaction time (min)	95% PI low	95% PI High	Predicted values	Experimental values
43.0	9.0	4.0	2.3	7.6	85.3	100.0	99.58	99.3
76.8	6.5	4.0	2.3	7.7	72.4	87.5	91.7	82.8
76.0	9.0	4.0	2.3	7.7	80.2	95.4	89.9	86.6
60.0	11.2	3.0	2.7	10.0	74.2	89.8	82.5	83.8
80.0	9.1	5.0	2.2	10.0	81.8	96.5	87.7	85.3

than surface type. The authors suggested that carbonate, by reacting with Fe^{3+} ion, removes this catalyst from the reaction medium, thereby reducing the •OH production.

In order to determine the electrocoagulation process contribution in the dye removal by PEC process under optimal conditions that is including pH of 3.0, the dye concentration of 43.2 mg·L^{-1}, the distance between electrode of 2.5 cm, the current density of 9.2 mA·cm^{-2}, and the time of 7.7 min the PEC process was done without H_2O_2 injection, and it was found that in the H_2O_2 absence, the dye removal rate by electrocoagulation is 1.5%. In order to determine the dye removal ratio by the Fenton-like process, the PEC process without applying the current density in optimal conditions. Accordingly, the Fenton-like process share in the dye removal is 2.3%. The results of the study showed that the dye removal efficiency by electrocoagulation was only 1.5%, while in the presence of H_2O_2 the PEC process efficiency was 99.4%, which indicates that the main mechanism of the dye removal was chemical oxidation and only 1.5% has been removed due to the coagulation mechanism. It was found that Fenton's reaction was mainly through the PEC process. The cause of the Fenton-like low efficiency process was the pH of the reaction medium, which is made it difficult to release the Fe^{3+} ion. According to Faraday's law, in a process of PEC by establishing current a certain amount of Fe^{2+} compounds is released from the electrode and reacted in the reaction intermediate, and after reacting with the H_2O_2 present in the •OH production medium.

3.6. The energy consumption amount in the PEC process

In order to determine the consumed energy amount in optimal conditions based on the treated wastewater volume was calculated from Eq. (3). Regarding the determined optimal conditions in the PEC process which is including pH of 3.0, dye concentration 43.2 mg·L^{-1}, the current density 9.2 mA·cm^{-2}, the distance between the electrodes 2.5 cm, the H_2O_2 concentration equivalent to 4.0 mM, and time 7.7 min, the consumed energy amount is 0.275 kWh·m^{-3}.

3.7. Real sample textile wastewater

The real sample of the factory wastewater was refined according to the optimum conditions obtained from the PEC process. (All experiments were performed three times). The results showed that the efficiency of removing dye in optimal conditions using PEC process on the real textile waste dye was 73.3%, and compared to the synthetic sample with 98.4% efficiency, it was 25.1% decreased. Also, in addition, the amount of energy consumed in the treatment of real samples compared to the synthetic samples in the PEC process was 0.546 and 0.275 kWh·m^{-3}.

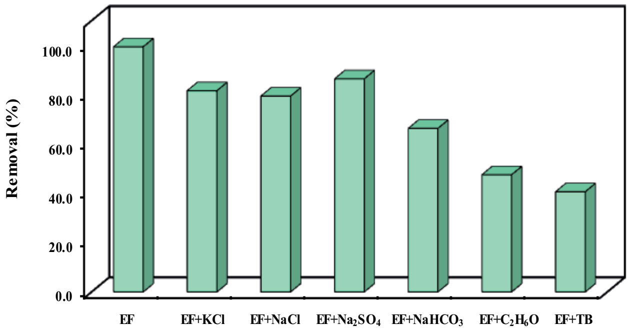

Fig. 6. Effect of radical scavenger on the removal efficiency of RB 171 dye.

4. Conclusion

The PEC process under the optimum conditions including dye concentration 43.2 mg·L^{-1}, the current density of 9.2 mA·cm^{-2}, pH of 3.0, H_2O_2 concentration of 4.0 mM, the distance between the electrode of 2.5 cm and the reaction time of 7.7 min, 98.4% can be treated by the RB 171 dye. In this condition, the energy consumption is 0.275 kWh·m^{-3}. Therefore, it can be concluded that the PEC process can be used as an effective, fast and high efficiency method for the treatment of textile wastewater. The reason for the reduction of efficiency in actual samples can be attributed to the presence of other complex organic substances, including the compounds of other colors, solvents and heavy metals, and salts used in the process of production of yarn and fabric, which reduces the efficiency of the PEC process in the real treatment samples.

Acknowledgements

The authors express their appreciation to Department of Environmental Health, School of Public Health, Kerman University of Medical Sciences, Kerman, Iran for supporting the current work.

References

[1] L. Bulgariu, L.B. Escudero, O.S. Bello, M. Iqbal, J. Nisar, K.A. Adegoke, F. Alakhras, M. Kornaros, I. Anastopoulos, The utilization of leaf-based adsorbents for dyes removal: a review, J. Mol. Liq., 276 (2019) 728–747.

[2] S. Thakur, M.S. Chauhan, Treatment of Dye Wastewater From Textile Industry by Electrocoagulation and Fenton Oxidation: A Review, V. Singh, S. Yadav, R. Yadava, Eds., Water Quality Management. Water Science and Technology Library, Vol. 79, Springer, Singapore, 2018, pp. 117–129.

[3] F. Ghanbari, M. Moradi, Electrooxidation Processes for Dye Degradation and Colored Wastewater Treatment, CRC Press LLC, London, 2016.

[4] A.G. Gutierrez-Mata, S. Velazquez-Martínez, A. Álvarez-Gallegos, M. Ahmadi, J.A. Hernández-Pérez, F. Ghanbari, S. Silva-Martínez, Recent overview of solar photocatalysis and solar photo-Fenton processes for wastewater treatment, Int. J. Photoenergy, 2017 (2017) 8528063, doi: 10.1155/2017/8528063.

[5] A. Najafpoor, H. Alidadi, H. Esmaeili, T. Hadilou, M. Dolatabadi, A. Hosseinzadeh, M. Davoudi, Optimization of anionic dye adsorption onto *Melia azedarach* sawdust in aqueous solutions: effect of calcium cations, Asia-Pac. J. Chem. Eng., 11 (2016) 258–270.

[6] T.W. Seow, C.K. Lim, Removal of dye by adsorption: a review, Int. J. Appl. Eng. Res., 11 (2016) 2675–2679.

[7] M.T. Yagub, T.K. Sen, S. Afroze, H.M. Ang, Dye and its removal from aqueous solution by adsorption: a review, Adv. Colloid Interface Sci., 209 (2014) 172–184.

[8] G. Crini, Non-conventional low-cost adsorbents for dye removal: a review, Bioresour. Technol., 97 (2006) 1061–1085.

[9] M. Davoudi, H. Alidadi, M. Mehrabpour, M. Dolatabadi, Competitive removal of cationic dye (BR 46) and heavy metal (copper II) from synthetic textile effluent using adsorbent of *Melia azedarach* sawdust, Desal. Water Treat., 118 (2018) 326–335.

[10] A.M. Herrera-González, M. Caldera-Villalobos, A.-A. Peláez-Cid, Adsorption of textile dyes using an activated carbon and crosslinked polyvinyl phosphonic acid composite, J. Environ. Manage., 234 (2019) 237–244.

[11] H. Ma, A. Kong, Y. Ji, B. He, Y. Song, J. Li, Ultrahigh adsorption capacities for anionic and cationic dyes from wastewater using only chitosan, J. Cleaner Prod., 214 (2019) 89–94.

[12] N. de Camargo Lima Beluci, G.A.P. Mateus, C.S. Miyashiro, N.C. Homem, R.G. Gomes, M.R. Fagundes-Klen, R. Bergamasco, A.M.S. Vieira, Hybrid treatment of coagulation/flocculation process followed by ultrafiltration in TIO_2-modified membranes to improve the removal of reactive black 5 dye, Sci. Total Environ., 664 (2019) 222–229.

[13] M. Hasanzadeh, A. Simchi, H.S. Far, Nanoporous composites of activated carbon-metal organic frameworks for organic dye adsorption: synthesis, adsorption mechanism and kinetics studies, J. Ind. Eng. Chem., 81 (2020) 405–414.

[14] N.C. Cinperi, E. Ozturk, N.O. Yigit, M. Kitis, Treatment of woolen textile wastewater using membrane bioreactor, nanofiltration and reverse osmosis for reuse in production processes, J. Cleaner Prod., 223 (2019) 837–848.

[15] D. Lv, R. Wang, G. Tang, Z. Mou, J. Lei, J. Han, S. De Smedt, R. Xiong, C. Huang, Ecofriendly electrospun membranes loaded with visible-light-responding nanoparticles for multifunctional usages: highly efficient air filtration, dye scavenging, and bactericidal activity, ACS Appl. Mater. Interfaces, 11 (2019) 12880–12889.

[16] S.H.S. Chan, T. Yeong Wu, J.C. Juan, C.Y. Teh, Recent developments of metal oxide semiconductors as photocatalysts in advanced oxidation processes (AOPs) for treatment of dye waste-water, J. Chem. Technol. Biotechnol., 86 (2011) 1130–1158.

[17] C. Martínez-Sánchez, I. Robles, L.A. Godínez, Review of recent developments in electrochemical advanced oxidation processes: application to remove dyes, pharmaceuticals, and pesticides, Int. J. Environ. Sci. Technol., (2022) 1–68, doi: 10.1007/s13762-021-03762-9.

[18] L.B. Bezerra, T.D. Carlos, A.P.N. das Neves, W.A. Durães, R. de Almeida Sarmento, D.H. Pereira, G.S. Cavallini, Theoretical-experimental study of the advanced oxidative process using peracetic acid and solar radiation: removal efficiency and thermodynamic elucidation of radical formation processes, J. Photochem. Photobiol., A, 423 (2022) 113615, doi: 10.1016/j.jphotochem.2021.113615.

[19] A.K. Abdessalem, N. Bellakhal, N. Oturan, M. Dachraoui, M.A. Oturan, Treatment of a mixture of three pesticides by photo-and electro-Fenton processes, Desalination, 250 (2010) 450–455.

[20] S. Lanzalaco, I. Sirés, M.A. Sabatino, C. Dispenza, O. Scialdone, A. Galia, Synthesis of polymer nanogels by electro-Fenton process: investigation of the effect of main operation parameters, Electrochim. Acta, 246 (2017) 812–822.

[21] X. Liu, D. Yang, Y. Zhou, J. Zhang, L. Luo, S. Meng, S. Chen, M. Tan, Z. Li, L. Tang, Electrocatalytic properties of N-doped graphite felt in electro-Fenton process and degradation mechanism of levofloxacin, Chemosphere, 182 (2017) 306–315.

[22] L. Xu, J. Wang, A heterogeneous Fenton-like system with nanoparticulate zero-valent iron for removal of 4-chloro-3-methyl phenol, J. Hazard. Mater., 186 (2011) 256–264.

[23] M. Dolatabadi, H. Naidu, S. Ahmadzadeh, A green approach to remove acetamiprid insecticide using pistachio shell-based modified activated carbon; economical groundwater treatment, J. Cleaner Prod., 316 (2021) 128226, doi: 10.1016/j.jclepro.2021.128226.

[24] T. Yao, W. Jia, Y. Feng, J. Zhang, Y. Lian, J. Wu, X. Zhang, Preparation of reduced graphene oxide nanosheet/FexOy/nitrogen-doped carbon layer aerogel as photo-Fenton catalyst with enhanced degradation activity and reusability, J. Hazard. Mater., 362 (2019) 62–71.

[25] A. Mohseni-Bandpei, S.M. Ghasemi, A. Eslami, M. Rafiee, M. Sadani, F. Ghanbari, Degradation of atenolol by $CuFe_2O_4$/visible light/oxidant: effects of electron acceptors, synergistic effects, degradation pathways, and mechanism, J. Photochem. Photobiol., A, 418 (2021) 113425, doi: 10.1016/j.jphotochem.2021.113425.

[26] L. Labiadh, M.A. Oturan, M. Panizza, N.B. Hamadi, S. Ammar, Complete removal of AHPS synthetic dye from water using new electro-Fenton oxidation catalyzed by natural pyrite as heterogeneous catalyst, J. Hazard. Mater., 297 (2015) 34–41.

[27] B. Bazaria, P. Kumar, Optimization of spray drying parameters for beetroot juice powder using response surface methodology (RSM), J. Saudi Soc. Agric. Sci., 17 (2018) 408–415.

[28] H. Harfouchi, D. Hank, A. Hellal, Response surface methodology for the elimination of humic substances from water by coagulation using powdered Saddled sea bream scale as coagulant-aid, Process Saf. Environ. Prot., 99 (2016) 216–226.

[29] F. Jamali-Behnam, A.A. Najafpoor, M. Davoudi, T. Rohani-Bastami, H. Alidadi, H. Esmaily, M. Dolatabadi, Adsorptive removal of arsenic from aqueous solutions using magnetite nanoparticles and silica-coated magnetite nanoparticles, Environ. Prog. Sustainable Energy, 37 (2018) 951–960.

[30] P. Nidheesh, R. Gandhimathi, Trends in electro-Fenton process for water and wastewater treatment: an overview, Desalination, 299 (2012) 1–15.

[31] V. Poza-Nogueiras, E. Rosales, M. Pazos, M.Á. Sanromán, Current advances and trends in electro-Fenton process using heterogeneous catalysts–a review, Chemosphere, 201 (2018) 399–416.

[32] Ö. Gökkuş, N. Yıldız, A. Koparal, Y. Yıldız, Evaluation of the effect of oxygen on electro-Fenton treatment performance for real textile wastewater using the Taguchi approach, Int. J. Environ. Sci. Technol., 15 (2018) 449–460.

[33] N. Oturan, C.T. Aravindakumar, H. Olvera-Vargas, M.M.S. Paul, M.A. Oturan, Electro-Fenton oxidation of para-aminosalicylic acid: degradation kinetics and mineralization pathway using Pt/carbon-felt and BDD/carbon-felt cells, Environ. Sci. Pollut. Res., 25 (2018) 20363–20373.

[34] A. Chmayssem, S. Taha, D. Hauchard, Scaled-up electrochemical reactor with a fixed bed three-dimensional cathode for electro-Fenton process: application to the treatment of bisphenol A, Electrochim. Acta, 225 (2017) 435–442.

[35] N. Wang, T. Zheng, G. Zhang, P. Wang, A review on Fenton-like processes for organic wastewater treatment, J. Environ. Chem. Eng., 4 (2016) 762–787.