



Application of Iron Electrode in Textile Industry Wastewater Treatment Using Electro-fenton Technique: Experimental and Statistical Study

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ABSTRACT

The application of synthetic colors in textile industries and their entry into the water and groundwater is an environmental problem because of being very toxic material. The synthetic colors which are used in textile dyeing (polyacrylic and polyester) are usually dispersing colorants. They derive the azo and anthraquinone chemicals. Electro-Fenton process is an efficient technique which can degrade the recalcitrant wastewaters. The main goal of the present study was to examine the effect of iron electrodes (as a cheap and available material) on industrial textile wastewater treatment by electro-Fenton technique. The experiments were conducted to evaluate the effects of reaction time, current density, pH, H_2O_2/Fe^{2+} molar ratio and volume ratio of H_2O_2 to textile wastewater (TW) (ml/l) on the process. Response surface methodology (RSM) was used to consider the effects of five independent variables on the COD and color removal from the wastewater and optimize the operating conditions. The optimum conditions were obtained at reaction time of 71.74 min, current density of 40.11 mA/cm², pH 2.84, H_2O_2/TW of 2.03 (ml/l), H_2O_2/Fe^{2+} molar ratio of 3.89 for COD removal of 76.33%. Furthermore, optimum conditions were found at reaction time of 75.97 min, current density of 67.04 mA/cm², pH 2.98, H_2O_2/TW of 1.69 (ml/l), H_2O_2/Fe^{2+} molar ratio of 2.98 for color removal of 79.33%.

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1. INTRODUCTION

A great amount of wastewater in the textile industry is generated from dyeing operations [1]. Various methods have been used for textile industry wastewater treatment such as adsorption [2], coagulation [3], electro-coagulation [4] and sonication [5]. A combination of Fenton and electrochemical processes which is called electro-Fenton (EF) process can improve the oxidation efficiency [1]. The traditional Fenton process is widely used as a suitable treatment method for highly concentrated wastewater due to producing hydroxyl radicals [6, 7].

Applicability of the traditional Fenton process is limited by the acidic pH, the formation of iron sludge and high cost of hydrogen peroxide [6, 8]. Electro-chemical advanced oxidation processes (EAOPs) based on

Fenton's reaction chemistry are eco-friendly methods that have recently received much attention for wastewater remediation (such as photo-Fenton, Fenton-like and electro-Fenton processes) [8]. The most popular EAOP is the electro-Fenton process which can proceed by a chain reaction [9-11]. The hydroxyl radicals obtained from the initial reaction are generated at the surface of a high-oxygen over voltage anode.

The anode has a good resistance against the redox reactions and limits the corrosion. Furthermore, the electrode resists against hydrogen peroxide decomposition [12]. The amount of hydroxyl radicals produced by the electro-Fenton process is more than that of the Fenton method. Therefore, H_2O_2 consumption decreases. The produced ferric ions (from the initial reaction) can be converted into the ferrous ions by the electro chemical regeneration of Fe^{2+} on the cathode surface.

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TABLE 1. Characteristics of the used wastewater

Parameter	Unit	Value
Chemical oxygen demand (COD)	mg/l	540
Biochemical oxygen demand (BOD ₅)	mg/l	135
Color	Color unit	100
BOD ₅ /COD	-	0.25
pH	-	8.1
Temperature	°C	27
Appearance	-	Brown

The dyeing sewage contains the toxic and resistant molecules. According to the literature, some methods such as coagulation and flocculation cannot remove these molecules. The other techniques such as activated carbon only substitute a contaminant with another molecule. Therefore, a supplementary treatment is requested. The electro-Fenton process completely decomposes the organic contaminants and converts them into CO₂, H₂O and non-toxic materials [13]. The electrode material is an effective parameter in the electro-Fenton process. The reaction rate on electrode surface has a direct relation with anode material. The most applied electrode (as an anode) in electro-Fenton process is platinum. Since it is an expensive material, a cheaper one is encouraged [6, 14, 15]. The efficiency of electro-Fenton process highly depends on the cathode material because the regeneration of hydrogen peroxide and Fe²⁺ ions in cathode surface are accelerated. Iron as cathode can also be used as a proper material for the electro-Fenton process. It increases Fe²⁺ ions regeneration and reduces the iron salts [9, 11, 14]. Cruz-Gonzalez optimized the operating conditions for the acid yellow 36 decolorization by electro-Fenton process to remove 98% of color [16]. The color removal from textile wastewater by electro-Fenton process using a three-dimensional graphite cathode was carried out by Chih-Tawang. 70.6% of removal was investigated in this research [17]. According to another research, COD was reduced from industrial textile wastewater by electro-Fenton process using an activated carbon fiber cathode. The maximum efficiency was reported around 75.2% [18].

In this research, the effects of various parameters such as reaction time, pH, current density, H₂O₂/Fe²⁺ molar ratio and H₂O₂/TW (ml/l) on the COD and color removal from industrial textile wastewater were carefully considered during treating by the electro-Fenton process. Furthermore, the iron electrodes (as a cheap source of Fe²⁺ ions) were used. The response surface methodology (RSM) was used to minimize the number of experiments and optimize the operating conditions [9, 19-22].

2. EXPERIMENT

2. 1. Materials and Methods

2. 1. 1. Wastewater Sampling and Characterization The study was conducted on industrial wastewater samples obtained from Khomein Textile Company (Khomein, Iran). The main contaminant agents of water in the textile industry are the synthetic fibers like polyacrylic and polyester. The wastewater sample was taken from the industrial sewage basin. The industrial sewage basin is a product of the function of dyeing system and is an output of this system. The sewage basin is a large tank in which the wastewater is treated by several processes. There are various sewage basins such as stabilization, aeration and sedimentation basin. The sewage enters into a close tank for stabilization purpose for 12 h. The oxidation process occurs in the presence of 1 g/l calcium hypochlorite at 10 min. The oxidized sewage is then pumped to the aeration basin. The surplus COD which was not treated by chemical method is treated by microorganisms (activated sludge). According to the factory report, the efficiency of this process is around 57% for COD removal and around 65% for color removal. According to the literature, electro-Fenton as an efficient, rapid and compressed technique can treat the toxic wastewater. Furthermore, the colloids and suspended particles are removed from the reaction environment during the electro-Fenton process. Therefore, this is ecologically more acceptable [6, 23].

The wastewater sample used in this research was taken from the stabilization basin before any treatment. 40 liter of sample from the industrial sewage basin was taken and saved in a plastic container. It was immediately transported to Arak University (Chemical Engineering Research Lab). All experiments were done during few days and all samples were kept inside a refrigerator (at a temperature of 4 °C). COD and color of processed samples were tested by an online UV visible. COD and color were evaluated by the standard method [24]. COD was determined by acidic digestion (open reflux) method at 150 °C for 2h, using potassium dichromate as oxidant, followed by titration with iron (II) sulfate and ammonia. In this measurement, pH was adjusted to 4. The initial color was evaluated and reported by the company. The characteristics of this wastewater are presented in Table 1.

2. 1. 2. Electro-fenton Process The electro-Fenton experiments were conducted at room temperature (25±2 °C) and atmospheric pressure. Since the reaction rate normally decreases at low temperatures and hydrogen peroxide decomposes at high temperatures, a mild temperature (25°C) was considered in this research [14]. pH was initially adjusted using sulfuric acid (Merck, Germany) and sodium hydroxide (Merck, Germany)

and measured by a pH meter (model: METTLE-TOLEDO 320, UK). In each run, 250 cm³ of the sample was placed in an electrolytic cell and pH was adjusted. The cell was a beaker with 400 cm³ capacity, which functioned as a reactor at laboratory scale. The chemicals [H₂O₂ 30%, FeSO₄·7H₂O, sulfuric acid and sodium hydroxide (Merck grades, Germany)] were added into the wastewater and electro-Fenton reactions were started with switching on the power supply. Hydrogen peroxide easily releases an active oxygen atom. Therefore, H₂O₂ concentration is normally expressed by the active oxygen. The cell was placed on the magnetic stirrer (Labinco, Netherland) and iron sulfate was entirely dissolved. A pair of electrodes (anode and cathode) made of iron was placed in the cell and solution was mixed at 400 rpm. Stirrer should integrate the mixture without vortex creation because it will change the current density [9, 25]. The effective area of the electrodes in the solution was 1 cm² with dimensions of 1 cm × 1 cm and the spacing between the electrodes was 2.5 cm. The distance between electrodes and their areas have direct influence on the current density although it does not affect the process in the distance range of 1.5-2.5 cm [6]. After placing the electrodes in the solution a direct current (DC) power supply [Kala Gostaran-e-Farda, Iran (30V & 3A)] was used to provide the desired current. The electro-Fenton apparatus used in this research is shown in Figure 1.

At the end of each run, samples were filtered through the filter paper [Whatman, England (S&S 5891)] and the filtrate was then analyzed in terms of COD and color. COD and color were respectively measured at wavelenths of 438 and 647 nm using a UV-Vis spectrophotometer (HACH, US) calibrated by the supplier. The filtered samples were put in the spectrophotometer while the blank was water. The absorption amount for each sample was found at 438 and 647 nm for COD and color, respectively.

According to the chromate test as explained above and the reported wavelength validation, the initial sample was diluted in five different volumes (50, 100, 200, 500 and 1000 cm³) and absorption amounts were obtained for these five samples at 438 nm (calibration curve for COD). Similar procedure was carried out for color (at 647 nm), as well. Finally, the COD and color removal can be calculated by Equation (1):

$$\text{Removal (\%)} = \frac{C_i - C_0}{C_i} \times 100 \quad (1)$$

where, C_i and C₀ are initial and final sample concentrations, respectively.

2. 1. 3. Experimental Design and Statistical Analysis

In this research, the amounts of consumed salt and H₂O₂ were exactly determined by two ratios. In fact, 250 cm³ of textile wastewater was utilized and H₂O₂ mole was obtained from H₂O₂/TW (ml/l). Then, the salt mole was found from H₂O₂/Fe²⁺ molar ratio. However there are several researches on these ranges selection [9, 11, 25, 26] but, some experiments were done to confirm or modify them for this case-study. The applied ranges for various parameters are shown in Table 2.

The design expert software (Stat-Ease, US, 7.0.0 open source) was used for the experimental design, data analysis, suitable model correlation and graph plotting. The independent variables were reaction time (X₁), current density (X₂), pH (X₃), H₂O₂/TW (ml/l) (X₄) and H₂O₂/Fe²⁺ molar ratio (X₅). COD and color removal (Y₁ and Y₂, respectively) were considered as the dependent variables. The performance of this process was evaluated by COD and color removal.

Furthermore, the experimental design and optimization were conducted using the Central Composite Design (CCD). Each variable was coded with low, medium and high level (-1, 0, 1) in the CCD as shown in Table 3. As shown in Table 4 (matrix design obtained from the design expert software) 46 experiments with their conditions were designed.

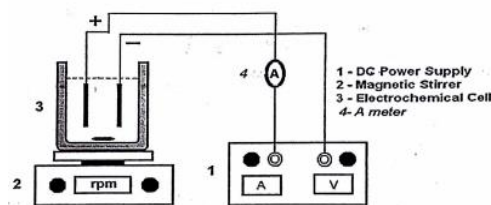


Figure 1. Electro-Fenton process apparatus

TABLE 2. The used ranges for various parameters in electro-Fenton process

3	Range	Reference
Reaction time	10-80 (min)	[9, 11, 25, 26]
Current density	10-80 (mA/cm ²)	[9, 11, 25]
pH	2-5	[9, 11, 25]
H ₂ O ₂ /TW	0.25-2.3 (ml/l)	[11]
H ₂ O ₂ /Fe ²⁺	0.5-5 (mole/mole)	[9, 11, 25]

TABLE 3. Independent variables and their levels obtained from the statistical software

Symbol	Factor	Coded levels of variables					
		-1	0	+1	-alpha	alpha	+alpha
x ₁	Reaction time	10	45	80	-38.24	45	128.24
x ₂	Current density	10	45	80	-38.24	45	128.24
x ₃	pH	2	3.5	5	-0.06	3.5	7.06
x ₄	H ₂ O ₂ /TW	0.25	1.27	2.3	-1.16	1.27	3.71
x ₅	H ₂ O ₂ /Fe ²⁺	0.5	2.75	5	-2.60	2.75	8.10

TABLE 4. Experimental matrix design for overall optimization

Run	Block	Reaction time	Current density	pH	H ₂ O ₂ /TW	H ₂ O ₂ /Fe ²⁺
1	block 1	10	45	2	1.275	2.75
2	block 1	45	10	2	1.275	2.75
3	block 1	10	45	3.5	2.3	2.75
4	block 1	45	80	3.5	1.275	0.5
5	block 1	45	80	2	1.275	2.75
6	block 1	45	45	5	2.3	2.75
7	block 1	10	45	3.5	0.25	2.75
8	block 1	45	45	3.5	1.275	2.75
9	block 1	80	80	3.5	1.275	2.75
10	block 1	45	45	3.5	1.275	2.75
11	block 1	45	45	3.5	1.275	2.75
12	block 1	80	45	3.5	0.25	2.75
13	block 1	80	45	2	1.275	2.75
14	block 1	80	10	3.5	1.275	2.75
15	block 1	45	45	3.5	2.3	0.5
16	block 1	45	10	3.5	0.25	2.75
17	block 1	45	45	3.5	1.275	2.75
18	block 1	45	10	3.5	1.275	0.5
19	block 1	45	45	3.5	2.3	5
20	block 1	45	45	2	0.25	2.75
21	block 1	45	45	2	1.275	0.5
22	block 1	10	45	3.5	1.275	0.5
23	block 1	45	10	5	1.275	2.75
24	block 1	45	80	5	1.275	2.75
25	block 1	45	45	5	0.25	2.75
26	block 1	45	45	5	1.275	0.5
27	block 1	45	10	3.5	2.3	2.75
28	block 1	45	45	2	1.275	5
29	block 1	45	45	5	1.275	5
30	block 1	80	45	5	1.275	2.75
31	block 1	45	45	2	2.3	2.75
32	block 1	45	80	3.5	2.3	2.75
33	block 1	45	80	3.5	0.25	2.75
34	block 1	80	45	3.5	1.275	0.5
35	block 1	45	10	3.5	1.275	5
36	block 1	10	10	3.5	1.275	2.75
37	block 1	80	45	3.5	2.3	2.75
38	block 1	45	45	3.5	1.275	2.75
39	block 1	10	80	3.5	1.275	2.75
40	block 1	45	80	3.5	1.275	5
41	block 1	80	45	3.5	1.275	5
42	block 1	45	45	3.5	0.25	0.5
43	block 1	10	45	3.5	1.275	5
44	block 1	45	45	3.5	0.25	5
45	block 1	45	45	3.5	1.275	2.75
46	block 1	10	45	5	1.275	2.75

3. RESULTS AND DISCUSSION

3. 1. Regression Models and Statistical Analysis

For the purpose of data analysis, analysis of variance (ANOVA) was continuously controlled. The regression model in the software was chosen. The combined effect of parameters on removal was checked by R^2 . Some small coefficients were ignored. The final correlations for COD [Equation (2)] and color removal [Equation (3)] prediction were investigated as:

$$\begin{aligned} \text{COD removal (\%)} = & 73.95 + 7.33 A + 4.43 B - 3.64 \\ & C + 5.08D + 2.95 E + 1.19AB - AC + 2.32 AD + \\ & 3.65 AE - 1.5 BC + 1.13 BE - 0.87 CD - 1.14 CE - \\ & 0.052 DE - 4.04 A^2 - 9.28 B^2 - 7.06 C^2 - 7.67D^2 - 8E^2 \end{aligned} \quad (2)$$

$$\begin{aligned} \text{Color removal (\%)} = & 74.12 + 7.86 A + 3.54B - 2.81 \\ & C + 4.78 D + 3.2 E + 1.49 AB - 1.25 AC + 1.75 AD \\ & + 2.94 AE - 1.53 BC - 1.22 BD + 2.06 BE - 0.77 \\ & CD + 0.68 CE + 1.51 DE - 2.45 A^2 - 9.69B^2 - \\ & 6.92C^2 - 9.22D^2 - 7.75 E^2 \end{aligned} \quad (3)$$

where, A, B, C, D and E are reaction time, current density, pH, H_2O_2/TW (ml/l) and H_2O_2/Fe^{2+} molar ratio, respectively. The experimental data (observed) and predicted ones (based on the above equations) for COD and color removal are shown in Table 5.

Tables 6 and 7 show the ANOVA for quadratic equation terms of COD and color removal, respectively. Analysis of variance which contains fitness test was conducted for evaluation of meaningful effects of process variables on each response. The meaningfulness of fitness test for a model means that the model is so well superposed on the points that it can be used for value prediction. The high amounts of F-value show that major differences in responses can be explained by regression model and the models are meaningful for COD and color removal. The $\text{prob} > F$ -value shows that the correlation terms statistically are significant (for less than 0.05) or insignificant (for more than 0.05) [11, 14].

The statistical results for quadratic equation for COD and color removal are represented in Table 8. High amounts of R^2 (0.9181 and 0.9758 for COD and color removal, respectively) show that quadratic equation is consistent with experimental data [11, 14, 27]. The closeness of R^2 , R^2 adjusted, R^2 predicted to one indicate that regression model is in good agreement with the experimental data. The coefficient of variance (CV) as the ratio of the standard error of estimate for the mean value of the observed response shows reproducibility of the model [14, 28]. The adequate precision (AP) measures the signal to noise ratio. AP is compared to the range of the predicted values at the design points to the average prediction error [11, 14]. The AP value greater than four is favorable and shows a proper signal. It means that the predicted models can direct the defined space by CCD.

TABLE 5. Observed and predicted data for COD and color removal

Run	COD removal		Color removal	
	Observed	Predicted	Observed	Predicted
1	58.1	58.15	58.82	58.44
2	55.69	55.31	56.13	55.25
3	59.49	57.66	60.12	57.61
4	59.22	57.02	57.26	54.97
5	65.39	67.17	66.19	65.39
6	59.75	59.78	58.42	59.17
7	52.37	52.14	53.32	51.56
8	73.28	73.94	73.18	74.12
9	73.08	73.58	73.2	74.87
10	73.28	73.94	73.18	74.12
11	73.28	73.94	73.18	74.12
12	61.93	62.17	65.56	63.78
13	74.3	74.82	77.31	76.67
14	62.87	62.34	63.82	64.83
15	60.12	60.46	59.05	57.23
16	47.64	47.48	48.17	45.68
17	73.28	73.94	73.18	74.12
18	50.28	50.42	52.25	52.00
19	66.34	66.25	67.33	66.63
20	55.57	56.9	50.29	55.23
21	60.95	58.44	60.82	59.74
22	51.46	55.28	50.31	55.79
23	52.11	51.04	50.84	52.7
24	55.81	56.89	54.77	56.71
25	51.23	51.36	50.28	51.16
26	54.37	53.44	53.97	52.76
27	56.4	57.64	57.33	57.67
28	68.63	66.61	70.75	64.76
29	57.5	57.06	66.63	60.51
30	64.72	65.54	67.75	68.56
31	67.57	68.80	61.52	66.33
32	66.1	66.50	60.68	62.32
33	57.34	56.34	56.38	55.18
34	61.36	62.65	64.63	65.65
35	51.2	54.06	50.15	54.28
36	52.18	50.06	55.81	52.07
37	78.33	76.97	79.38	76.85
38	77.28	73.94	78.83	74.12
39	57.62	56.53	59.24	56.17
40	64.66	65.17	63.38	65.47
41	77.34	75.84	77.49	77.91
42	50.15	50.19	50.54	50.67
43	52.84	53.87	51.43	56.31
44	56.58	56.2	52.8	54.06
45	73.28	73.94	73.18	74.12
46	52.52	52.87	54.25	55.32

TABLE 6. Analysis of variance for response surface quadratic model terms for COD removal

Source	Sum of squares	DF	Mean square	F-value	Prob> F	Remark
Model	3312.20	20	165.61	50.39	< 0.0001	Significant
A	860.69	1	860.69	261.87	< 0.0001	Significant
B	313.73	1	313.73	95.45	< 0.0001	Significant
C	211.63	1	211.63	64.39	< 0.0001	Significant
D	413.00	1	413.00	125.66	< 0.0001	Significant
E	139.12	1	139.12	42.33	< 0.0001	Significant
AB	5.69	1	5.69	1.73	0.2003	Significant
AC	4.00	1	4.00	1.22	0.2805	Significant
AD	21.53	1	21.53	6.55	0.0169	Significant
AE	53.29	1	53.29	16.21	0.0005	Significant
BC	9.00	1	9.00	2.74	0.1105	Significant
BD	0.000	1	0.000	0.000	1.0000	Significant
BE	5.11	1	5.11	1.55	0.2241	Significant
CD	3.03	1	3.03	0.92	0.3464	Significant
CE	5.18	1	5.18	1.57	0.2211	Significant
DE	0.011	1	0.011	3.354E-003	0.9543	Significant
A ²	142.25	1	142.25	43.28	< 0.0001	Significant
B ²	751.68	1	751.68	228.70	< 0.0001	Significant
C ²	435.28	1	435.28	132.43	< 0.0001	Significant
D ²	513.50	1	513.50	156.23	< 0.0001	Significant
E ²	558.05	1	558.05	169.79	< 0.0001	Significant
Residual	82.17	25	3.29			
Lack of fit	68.84	20	3.44	1.29	0.4208	Not significant
Pure error	13.33	5	2.67			
Cor. total	3394.37	45				

TABLE 7. Analysis of variance for response surface quadratic model terms for color removal

Source	Sum of squares	DF	Mean square	F-value	Prob> F	Remark
Model	3434.86	20	171.74	14.02	<0.0001	Significant
A	989.73	1	989.73	80.77	<0.0001	Significant
B	200.22	1	200.22	16.34	0.0004	Significant
C	126.11	1	126.11	10.29	0.0036	Significant
D	365.67	1	365.67	29.84	<0.0001	Significant
E	163.39	1	163.39	13.33	0.0012	Significant
AB	8.85	1	8.85	0.72	0.4035	Significant
AC	6.23	1	6.23	0.51	0.4826	Significant
AD	12.32	1	12.32	1.01	0.3256	Significant
AE	34.46	1	34.46	2.81	0.1060	Significant
BC	9.39	1	9.39	0.77	0.3896	Significant
BD	5.9	1	5.9	0.48	0.4940	Significant
BE	16.89	1	16.89	1.38	0.2514	Significant
CD	2.39	1	2.39	0.19	0.6627	Significant
CE	1.86	1	1.86	0.15	0.6999	Significant
DE	9.06	1	9.06	0.74	0.3980	Significant
A ²	52.32	1	52.32	4.27	0.0493	Significant
B ²	818.65	1	818.65	66.81	<0.0001	Significant
C ²	418.35	1	418.35	34.14	<0.0001	Significant
D ²	742.06	1	742.06	60.56	<0.0001	Significant
E ²	524.55	1	524.55	42.81	<0.0001	Significant
Residual	306.34	25	12.25			
Lack of fit	279.74	20	13.99	2.63	0.1438	Not significant
Pure error	26.60	5	5.32			
Cor. total	3741.20	45				

TABLE 8. Quadratic model ANOVA results for COD and color removal

Variable	COD removal	Color removal
Standard deviation	1.81	3.50
Mean	61.41	61.59
R ²	0.9758	0.9181
R ² adjusted	0.9564	0.8526
R ² predicted	0.9132	0.6907
Coefficient of variance	2.95	5.68
Press	294.54	1157.26
Adequate precision	24.072	13.629

3. 2. Process Optimization and Validation The optimum operating conditions for COD and color removal were obtained using the software. In this software, numerical optimization was used to achieve the maximum amounts of COD and color removal. In fact, all variables were targeted to be in a range and COD and color removal were goaled to be maximized. In order to confirm the reliability of the obtained optimum conditions, the theoretical and experimental data were compared. Both data are illustrated in Table 9. There is a very good agreement between the experimental data (observed) and theoretical ones (predicted).

Furthermore, Figure 2 compares the predicted data with the experimental ones. Both data properly cover each other when line R² comes close to 1.

As found in this research, the optimum removal data were around 76.33% and 79.33% for COD and color removal, respectively. Moreover, the wastewater was analyzed in terms of BOD₅ at the optimum condition. Therefore, BOD₅/COD ratio was at 0.36.

In order to compare the electro-Fenton with Fenton process, an experiment was done at the optimum conditions without power supply. According to the recent experiment, the COD and color removals were around 66.59% and 67.47%, respectively (while they were 76.33% and 79.33% in the electro-Fenton process).

According to the literature, Torrades and García-Montaño reported 62.9% and 76.3% for COD removal by Fenton and photo-Fenton process from two effluents obtained from polyamide and polyester dyeing processes, respectively [29]. Duarte et al. obtained 66.3% COD removal by heterogeneous Fenton process in a continuous packed-bed reactor using Fe/activated carbon as catalyst [24]. Manenti et al. reduced the COD of wastewater from 1.2 g/l to 139 mg/l (around 88%) using a three-step process (electrocoagulation, photo-Fenton and biological oxidation) [30].

3. 3. Three-dimensional Plots of the Regression

Using design expert software, the 3D plots for COD and color removal were drawn as shown in Figures 3 and 4 which show the effect of various operating parameters on COD and color removal, respectively. All variables have important roles in creating the optimum state and reaching the maximum amount of responses. The reaction time has a positive effect on COD and color removal. As shown in Figures 3 (a,b,c,d) and 4 (a,b,c,d), the removal increases with reaction time while the removal rate decreases. This is due to the reactants reduction and undesirable side reactions possibility in the cell [15]. The current density plays an important role in the electro-Fenton process because it controls the formation of the hydroxyl radical and the concentration of ferrous ions in the solution [6, 9, 11].

As shown in Figure 3 (e,f,g), COD removal increases when the current density increases from 10 to 40.11 mA/cm². As shown in Figure 4 (e,f,g), color removal increases when the current density increases from 10 to 67 mA/cm². This trend can be attributed to greater production of OH[•] at the surface of the anode and also higher electro-regeneration of ferrous ions from ferric ions at high current density, which increased the efficiency of Fenton chain reactions. The continuous conversion of Fe³⁺ into Fe²⁺ is a great advantage compared to chemical Fenton system [9, 25]. Hydrogen peroxide decomposes on the anode when the current density increases (more than the optimum value). In fact, OH[•] and hydrogen peroxide on the cathode generate water and the removal consequently decreases [14, 31].

Moreover, the value of pH solution is an important factor in the electro-Fenton process. Most of the studies show that the optimal value of pH is 2-5 [6-9, 11]. The pH enhancement (for pH>5) decreases the E-Fenton efficiency, rapidly. This is due to the H₂O₂ instability in the basic solution (H₂O₂ rapidly decomposes to water). Furthermore, H₂O₂ exchanges to H₃O₂⁺ (H₂O₂ cannot be changed to OH[•] by Fe²⁺) when pH decreases (for pH<2) [6, 7, 11].

As shown in Figure 3 (h,i), COD removal decreases when pH increases from 2.84 to 5. Moreover, color removal decreases with pH increasing from 2.98 to 5 as illustrated in Figure 4 (h,i). In fact, pH has an optimum level in the electro-Fenton process. Iron ions (in special Fe³⁺) settle when pH increases (more than the optimum value). Therefore, the Fenton reaction and removal decrease. More OH⁻ and iron hydroxide [Fe(OH)₂] are also produced at optimum pH. Therefore, it (with coagulant factors) causes more aggregation of suspended materials. The electro-Fenton efficiency will finally be improved [6, 23].

H₂O₂/TW (ml/l) and H₂O₂/Fe²⁺ molar ratio have a considerable effect on the COD and color removal.

TABLE 9. Optimum conditions found by software (predicted) and experimental verification (observed) for COD and color removal

Response	Reaction time (min)	Current density (mA/cm ²)	pH	H ₂ O ₂		Removal (%)		Error%
				TW (ml/l)	Fe ²⁺ (mole/mole)	Observed	Predicted	
COD removal	71.74	40.11	2.84	2.03	3.89	76.33	78.93	3.4
Color removal	75.97	67.04	2.98	1.69	3.09	79.33	81.04	2.2

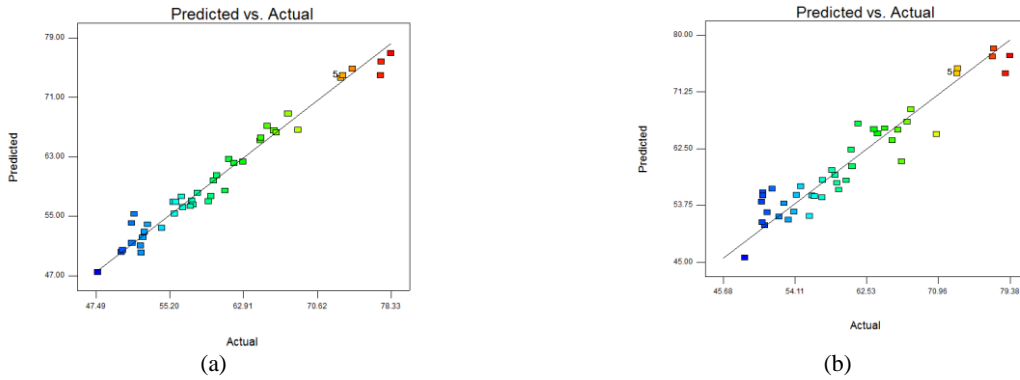


Figure 2. Predicted vs. actual values for (a) COD removal and (b) color removal

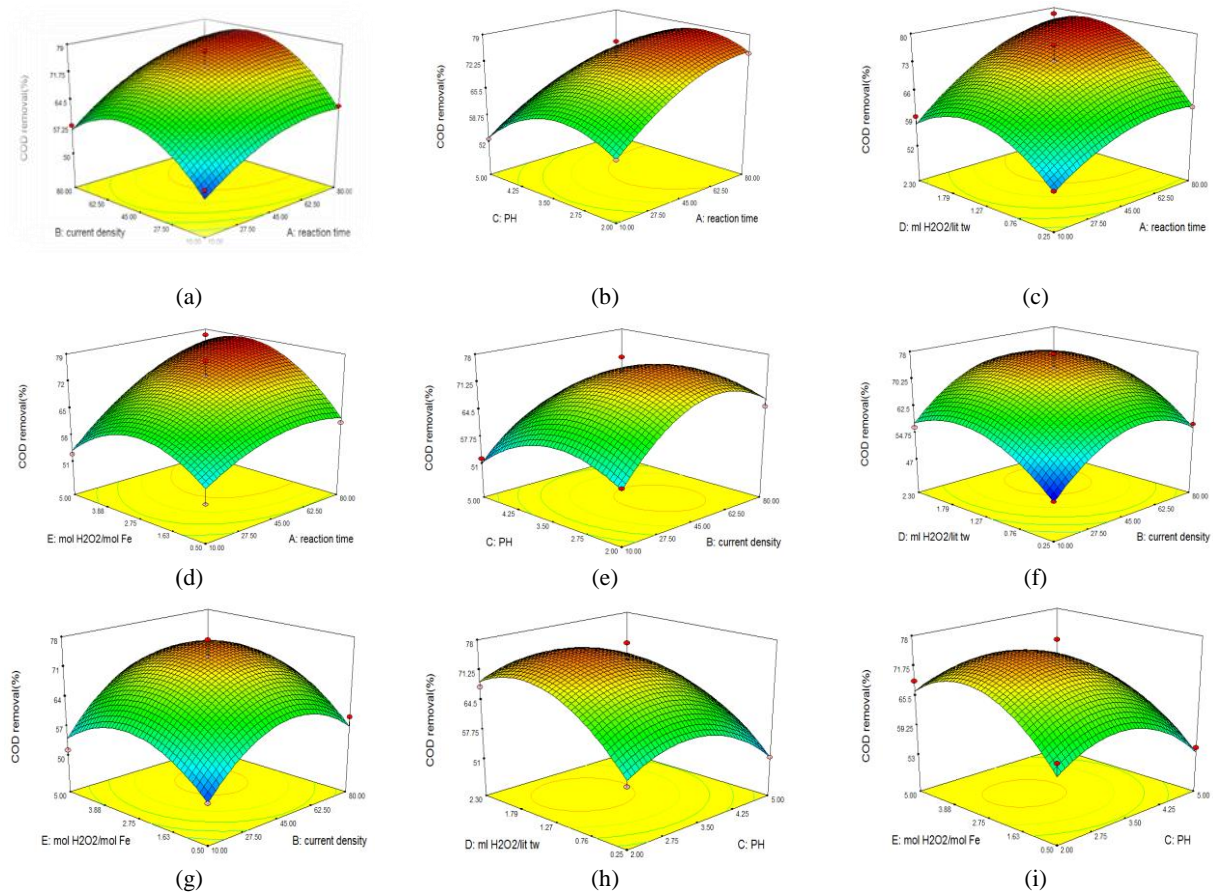


Figure 3. Three-dimensional diagram of COD removal as a function of: (a) reaction time and current density, (b) reaction time and pH, (c) reaction time and H₂O₂/TW (ml/l), (d) reaction time and H₂O₂/Fe²⁺ molar ratio, (e) current density and pH, (f) current density and H₂O₂/TW (ml/l), (g) current density and H₂O₂/Fe²⁺ molar ratio, (h) pH and H₂O₂/TW (ml/l) and (i) pH and H₂O₂/Fe²⁺ molar ratio.

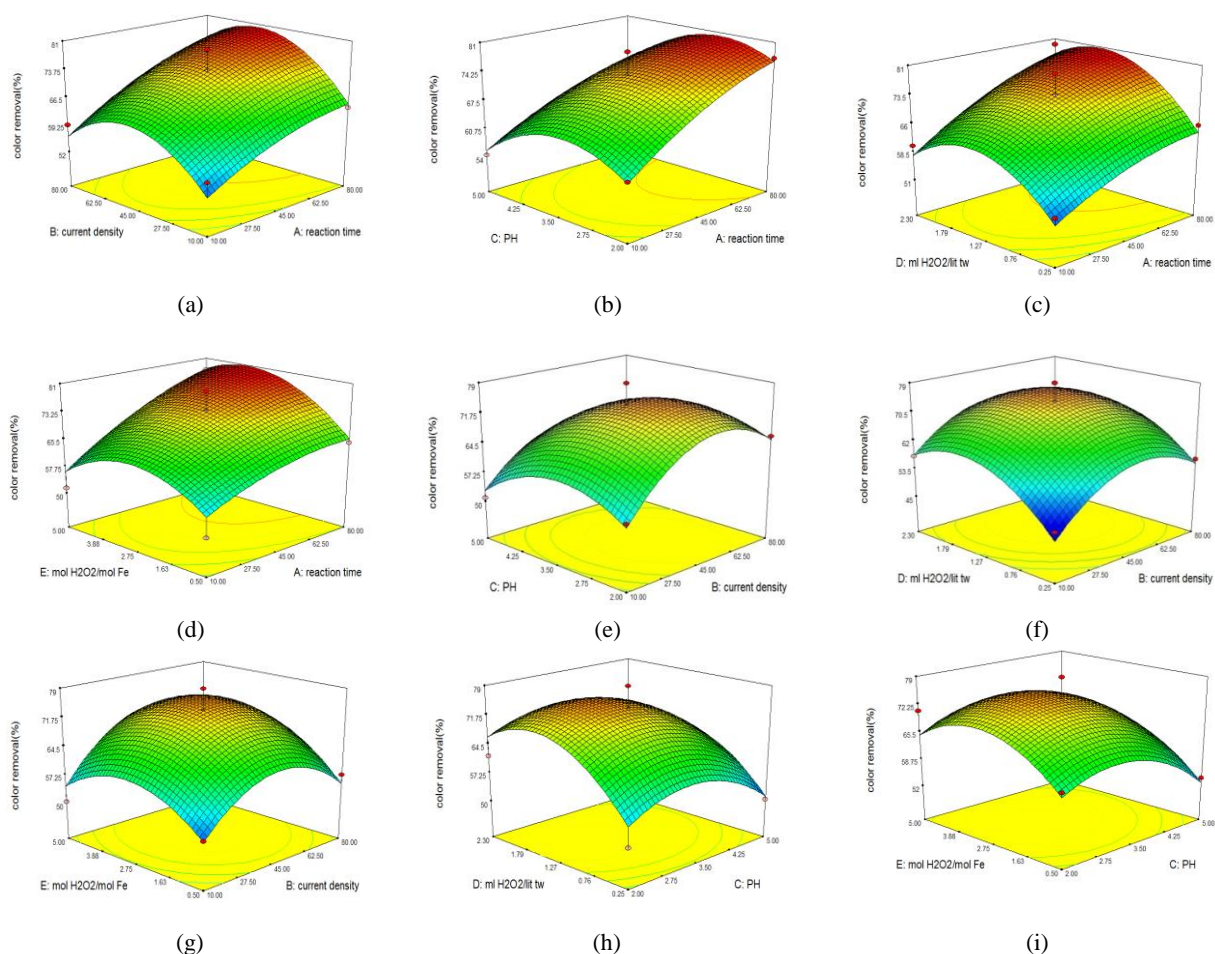


Figure 4. Three-dimensional diagram of color removal as a function of: (a) reaction time and current density, (b) reaction time and pH, (c) reaction time and $\text{H}_2\text{O}_2/\text{TW}$ (ml/l), (d) reaction time and $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratio, (e) current density and pH, (f) current density and $\text{H}_2\text{O}_2/\text{TW}$ (ml/l), (g) current density and $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratio, (h) pH and $\text{H}_2\text{O}_2/\text{TW}$ (ml/l) and (i) pH and $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratio.

An increase in H_2O_2 amount (an increase in a reactant) leads to COD and color removal. COD and color removal decrease when H_2O_2 increases (more than the optimal amount). This is due to hydroxyl radicals absorption [8, 9] and their conversion into hydroperoxyl radicals which have weaker oxidation power [9, 32].

The efficiency decreases when Fe^{2+} increases (more than the optimum value). This is due to the hydroxyl radicals consumption. Moreover, the generated ferric ions (Fe^{3+}) decompose hydrogen peroxide in the cell. This has an undesired effect on the electro-Fenton process due to the OOH^\ominus generation [15, 32].

As shown in Figure 3 (j), COD removal decreases when $\text{H}_2\text{O}_2/\text{TW}$ (ml/l) increases from 2.03 to 2.3. Furthermore, color removal decreases when $\text{H}_2\text{O}_2/\text{TW}$ (ml/l) increases from 1.69 to 2.3 as shown in Figure 4 (j).

Moreover, there is an optimum level for $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratio as shown in Figures 3 (j) and 4 (j).

4. CONCLUSION

In this research, the effect of various operating parameters such as reaction time, current density, pH, $\text{H}_2\text{O}_2/\text{TW}$ (ml/l) and $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratio on COD and color removal from textile industry wastewater by electro-Fenton process was carefully investigated. RSM as a statistical technique was used to determine the optimum operating conditions. The proposed quadratic model by software was properly matched with experimental data ($R^2 > 0.91$). The optimum data for COD removal were found to be 76.33 (experimentally) and 78.93% (theoretically) which were obtained at reaction time of 71.74 min, current density of 40.11 mA/cm^2 , pH 2.84, $\text{H}_2\text{O}_2/\text{TW}$ of 2.03 ml/l and $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratio of 3.89 while they were 75.97 min, 67.04 mA/cm^2 , 2.98, 1.69 ml/l and 3.09 molar ratio for the optimum removal of color (experimentally at 79.33% and theoretically at 81.04%).

It is also concluded that iron electrode (as a cheap and available material) can properly treat an industrial textile wastewater by electro-Fenton process in terms of COD and color.

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Application of Iron Electrode in Textile Industry Wastewater Treatment Using Electro-fenton Technique: Experimental and Statistical Study

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استفاده از رنگ های مصنوعی در صنایع نساجی و ورود آن ها به آب و سیستم های آبی یک مشکل زیست محیطی است زیرا شامل مواد بسیار سمی هستند. رنگ های مصنوعی استفاده شده در صنعت نساجی (پلی اکریلیک و پلی استر) معمولا مواد رنگ زای دیسپرس هستند. آنها از مشتقات آزو و آنتراکینون می باشند. فرایند الکترو-فنتون یک تکنیک کارآمد است که میتواند سختی فاضلابها را کاهش دهد. در این مطالعه هدف اصلی آن است که کارایی الکترو-فنتون (به عنوان یک ماده ی ارزان و قابل دسترس) را در تصفیه ی پساب نساجی به روش الکترو-فنتون بررسی کنیم. آزمایشات به گونه ای هدایت شدند تا تاثیر زمان واکنش، چگالی جریان، درجه ی اسیدی و بازی، نسبت مولی پراکسید هیدروژن به یون آهن و نسبت حجمی پراکسید هیدروژن به پساب نساجی را روی عملکرد فرآیند ارزیابی کنند. روش رویه ی پاسخ استفاده شد تا تاثیر پنج متغیر مستقل را روی حذف دو پارامتر اکسیژن شیمیایی مورد نیاز و رنگ در پساب ارزیابی کند و شرایط عملیاتی را بهینه کند. شرایط بهینه در زمان ۷۱/۷۴ دقیقه، چگالی جریان ۴۰/۱۱ میلی آمپر بر سانتی متر مربع، درجه ی اسیدی برابر ۲/۸۴، نسبت حجمی پراکسید هیدروژن به پساب برابر ۲/۰۳ میلی لیتر بر لیتر و نسبت مولی پراکسید هیدروژن به یون آهن برابر ۳/۸۹ برای حذف اکسیژن شیمیایی مورد نیاز به مقدار ۷۶/۳۳٪، به دست آمد. به علاوه شرایط بهینه در زمان ۷۵/۹۷ دقیقه، چگالی جریان ۶۷/۰۴ میلی آمپر بر سانتی متر مربع، درجه ی اسیدی برابر ۲/۹۸، نسبت حجمی پراکسید هیدروژن به پساب برابر ۱/۶۹ میلی لیتر بر لیتر و نسبت مولی پراکسید هیدروژن به یون آهن برابر ۲/۹۸ برای حذف رنگ به مقدار ۷۹/۳۳٪، به دست آمد.

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