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Treatment of raw tannery wastewater by electrocoagulation technique: optimization of effective parameters using Taguchi method

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ABSTRACT

In this study, the electrocoagulation (EC) technique for tannery wastewater treatment was examined using iron and aluminum electrodes. The effects of operating parameters that include current density, initial pH, and electrolysis time on EC performance were accomplished. In addition, Taguchi method was carried out in order to design the experiments and to optimize the experimental results. L_{25} orthogonal array (OA, three factors in five levels), signal-to-noise (S/N) ratio (the larger-the-better), and analysis of variance were applied to find the optimum levels and relative magnitude of the effects of parameters. The removal efficiency of chemical oxygen demand (COD), total chrome, and color are considered as the response parameters. In the case of iron electrodes, the optimum conditions of COD were found to be at the fifth level of current density (50 mA/cm^2), the fourth level of initial pH (7), and fifth level of electrolysis time (25 min). According to total chrome, they were found at the third level of current density (30 mA/cm^2), the fifth level of initial pH (8), and the fifth level of electrolysis time (25 min). In addition, with regard to color removal efficiency, they were determined to be at the fifth level of current density (50 mA/cm^2), the fourth level of initial pH (7), and the fifth level of electrolysis time (25 min). At the optimum conditions of COD, total chrome and color removal efficiencies were achieved as 63.3, 99.7, and 82%, respectively. Also, operating costs for both COD and color removals were evaluated as 0.88 \$/m^3; but for chrome removal, they were 0.70 \$/m^3. In the case of aluminum electrode, the optimum conditions of COD, total chrome, and color removal were found to be at the fifth level for each operating parameter corresponding to current density (50 mA/cm^2), initial pH (7), and electrolysis time (25 min). As a result, the observed removal efficiencies of COD, total chrome, and color under these optimum conditions were 64.4, 99, and 88%, respectively. In addition, operating costs for COD, chrome, and color removals were 0.94 \$/m^3.

Keywords: Taguchi method; Electrocoagulation; Aluminum electrodes; Iron electrodes; Total chrome; Tannery wastewater

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1. Introduction

A few decades ago, water and energy sources were classified as the top two challenges for the twenty-first century [1]. Wastewater treatment has been considered as an efficient tool for managing water and energy sources. Until relatively recently, little has been done of effective technique "zero effluent" to conserve them.

Leather and environment can be described as two sides of the same coin due to the fact that potential wastes from meat industry (i.e. skins and/or hides) are used in the leather industry via tanning process [2]. Tannery industry is known widely as one of the highest consumers of water as well as playing a key role in the economic sector of many countries. The global leather industry produces about 18 billion square feet of leather yearly with an estimated value of about $40 billion [3]. Tanneries, ultimately, generate wastewater in the range of 30–35 L/kg skin/hides processed with high concentrations of organic and inorganic pollutants. On the other hand, tannery is characterized as an influential pollutant that can cause severe environmental problems due to its high chemical oxygen demand (COD), biochemical oxygen demand (BOD), total suspended solids (TSS), total Kjeldahl nitrogen (TKN), sulfides, chromium, deep color content together with variable pH, and low biodegradability [4–6]. Therefore, it is extremely vital to search for cleaner, cost effective as well as environment-friendly sustainable techniques for tannery wastewater treatment [7].

There are many options that are utilized for the treatment of tannery wastewater, such as biological process [4,8,9] and physical–chemical process [10–12]. In this context, the conventional biological treatment does not always achieve satisfactory performance due to the toxicity of the tannery wastewater that affects the development of the bacteria. In addition, traditional physical–chemical processes are comparatively expensive, and may lead to secondary pollution. This is because it needs additional chemicals [13]. The drawbacks mentioned above have forced various industries to seek for effective alternative treatment technologies for pollutants removal, ideally by electrochemical methods.

Nowadays, electrochemical treatment methods have reached such a state that they are not only comparable with other technologies in terms of cost, but they are also more efficient and more effective [14]. Ultimately, it is a great attention to use these methods in treatment of water/wastewater owing to its attractive advantages such as environmental compatibility, versatility, energy efficiency, safety, selectivity, amenability to automation, and cost effectiveness [15].

Recently, electrochemical technologies have been investigated in environmental applications, especially for treating water/wastewater. One of these processes is electrocoagulation (EC) which has achieved much attention due to its attractive advantages as: simple, reliable, and cost-effective operation for the treatment of wastewater. In fact, it involves dissolution of metal from the anode with simultaneous formation of hydroxyl ions, and generation of hydrogen gas at the cathode which can be recovered for use as energy source or a reactant for other industrial applications [16]. There are vital advantages of EC as a low sludge production technology; secondly, the EC flocs are relatively large, contain less bound water, more stable, and amenable to filtration [17]. The fitting choice of EC materials is very essential electrode materials, generally, are aluminum and iron. They are cheap, readily available, and have been proven effective [18].

However, the chemistry of aqueous medium, especially its conductivity, is playing a vital role for EC mechanism. The driving force of EC is a direct current source between metal electrodes engrossed in wastewater. In EC process, the coagulating ions are produced "*in situ*" and it involves six main processes: (i) electrophoresis and aggregation due to charge neutralization; (ii) precipitation due to collective cation or hydroxyl ion with pollutant; (iii) bridge coagulation resulting by interaction between metallic cation with OH^- to form a hydroxide, which has high adsorption properties, therefore bonding to the pollutant; (iv) sweep coagulation when the hydroxides form larger lattice-like structures and sweep through the water; (v) oxidation of pollutants to less toxic species; (vi) electroflotation or sedimentation and adhesion to bubbles lead to remove the pollutants [14,17]. In general, there are two metals that utilized in EC process as electrodes, aluminum, and iron. An electrical current is passed through a metal electrode; the anode material undergoes oxidation, while the cathode will be subjected to reduction or reductive deposition of elemental metals [19]. In the case of aluminum, main reactions can be given as [20]:

$$\text{Anode} \quad Al_{(s)} \rightarrow Al^{3+} + 3e^- \tag{1}$$

$$\text{Cathode} \quad 3H_2O + 3e^- \rightarrow \frac{3}{2}H_{2(g)} + 3OH^- \tag{2}$$

Al^{3+} and OH^- react with each other to form $Al(OH)_{3(s)}$ according to complex precipitation kinetics.

$$Al^{3+} + 3H_2O \rightarrow Al(OH)_3 + 3H^+ \quad (3)$$

In the case of iron, two mechanisms for the reduction of metal hydroxide have been proposed:

Mechanism I

$$\text{Anode} \quad 4Fe_{(s)} \rightarrow 4Fe^{2+}_{(aq)} + 8e^- \quad (4)$$

$$4Fe^{2+}_{(aq)} + 10H_2O_{(l)} + O_{2(g)} \rightarrow 4Fe(OH)_{3(s)} + 8H^+_{(aq)} \quad (5)$$

$$\text{Cathode} \quad 8H^+_{(aq)} + 8e^- \rightarrow 4H_{2(g)} \quad (6)$$

$$\text{Overall} \quad 4Fe_{(s)} + 10H_2O_{(l)} + O_{2(g)} \rightarrow 4Fe(OH)_{3(S)} + 4H_{2(g)} \quad (7)$$

Mechanism II

$$\text{Anode} \quad Fe_{(s)} \rightarrow Fe^{2+}_{(aq)} + 2e^- \quad (8)$$

$$Fe^{2+}_{(aq)} + 2OH^-_{(aq)} \rightarrow Fe(OH)_{2(s)} \quad (9)$$

$$\text{Cathode} \quad 2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aq)} \quad (10)$$

$$\text{Overall} \quad Fe_{(s)} + 2H_2O_{(l)} \rightarrow Fe(OH)_{2(s)} + H_{2(g)} \quad (11)$$

Yet, EC has satisfactory been utilized for decades to treat wastewater of olive mills [21,22], metal plating [23], domestic [24], tannery [25–28], rose processing [29], chromium removal (VI) [30], textile industry [31], etc.

Taguchi's orthogonal array (OA) analysis is applied to achieve the best parameters for the optimum process design with the least number of experiments. Recently, the Taguchi method has been utilized to establish optimum parameters due to having vital advantages over the other statistical experiment design methods. It can investigate the effects of parameters as controlling or none controlling and also, it can be utilized to an experimental design involving large number of design factors [32,33]. Thus, the Taguchi method has been proven as an effective tool in terms of quality and costs.

Based on literature reviews, so far no other studies have taken into account the effective factors on EC treatment of tannery wastewater using the Taguchi method. This paper was carried out to determine the optimum operating conditions of tannery wastewater treatment by EC process with iron and aluminum electrodes. In addition, it was investigated the influence of the variables such as current density, initial pH, and electrolysis time on treatment efficiency. The experiments were implemented in Taguchi OA experimental design (larger is better) with five levels and three factors.

2. Materials and methods

2.1. Experimental setup and procedure

A schematic diagram of the experimental setup is shown in Fig. 1. Hence, the experimental setup of the electrochemical reactor operated in a lab-scale batch mode of operation. It consists of a Plexiglas reactor with volume work 0.6 L, a pair of electrodes (Al or Fe), and DC regulated power supply. The anode and cathode, that have the dimensions of 9.0–5.0 cm, are placed vertically and parallel to each other with an inter-electrode distance of 5 cm. The available effective electrode area is 37 cm^2 for anodic reactions. The electrode plates are cleaned manually by washing them in distilled water prior to every run. The volume of effluent taken is 250 ml in the electrochemical reactor and the electrodes are connected to DC power supply (GPS-3030DD, 0–30.0 V, and 0.0–3.0 A). Thus, at the beginning of the experiment, the EC cell is thoroughly washed and rinsed with deionized water followed by rinsing with the sample solution. The cell voltage is periodically noted. The samples are taken at regular interval of time from the reactor and filtered using Whatman 42 filter paper.

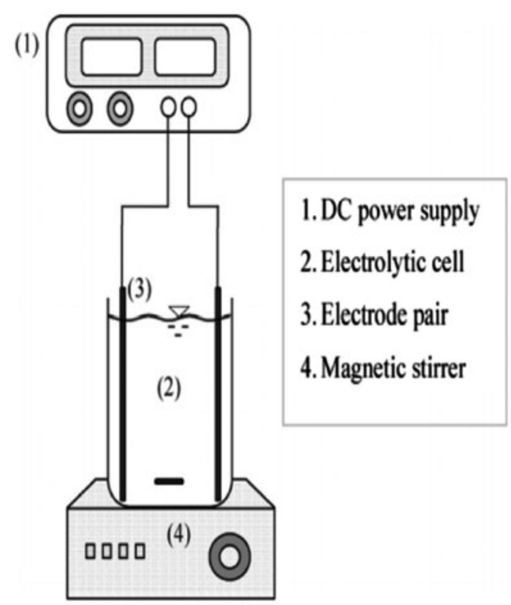

Fig. 1. Schematic diagram of the experimental setup.

2.2. Analytical procedure

The wastewater analyses were carried out in accordance with the Standard Methods for Examination of Water and Wastewater [34]. "pH, conductivity, COD, total chrome, and color were determined with (A Jenway 3040 brand, HACH HQ40d, closed reflux titrimetric method 5220C, A-Analyst 400, atomic absorption spectrometer, and HACH LANGE GmbH DR 5000 (spectrophotometer), respectively)". Merck analytical quality chemicals were used in the preparation of reagents.

2.3. Experimental design based on Taguchi method

Taguchi method was used to create a set of designed experiments by MINITAB software (version 16). The Taguchi method applies OA to reduce the number of experiments. OA refers to experimental matrix designed by L_i, where i is the number of trials of experimental matrix or total degree of freedom and includes a set of experiments where the settings of process parameters are changed. OA allows evaluating the effects of several process parameters to be determined efficiently. The selection of a suitable OA depends on the number of control factors and their levels [35]. In this study, Taguchi method was applied to determine the optimum condition of EC process. Similarly, the current density, initial pH, and electrolysis time were selected as control factors (parameters) during Taguchi orthogonal arrays experimental design. Each factor, that consisted of five levels and L_{25} orthogonal array, was taken to establish the optimal conditions for iron and aluminum electrodes with minimum number of experiments. The factors and their levels are presented in Table 1.

However, the following steps should be determined to optimize performance characteristics that can be given as:

(1) Recognition of the recital characteristics and choosing the process parameters to be assessed.
(2) Determination of the number of parameter levels.
(3) Selection of the suitable orthogonal array.
(4) Conduction of the experiments depends on the arrangement of the orthogonal array.
(5) Calculation of the performance characteristics.
(6) Analysis of the experimental results using the performance characteristics and ANOVA.
(7) Selection of the optimal levels of process parameters.
(8) Validation of the optimal process parameters through the confirmation experiment [36].

In order to optimize the COD, total chrome, and color removal efficiencies process, experimental variables, their levels, and results were investigated as illustrated in Table 2.

Taguchi method suggests the use of signal-to-noise (S/N) ratio to measure the quality characteristic deviating from the desired value. The optimum conditions should be determined using the S/N ratio of the results achieved from experiments designed by OA technique. There are three cases of S/N ratios: the larger-the-better, the smaller-the-better, and the nominal-the-better. In this study, the higher removal efficiency of pollutants is required for optimization EC process. Thus, the larger-the-better was selected based on COD, total chrome, and color removal efficiencies in two cases (iron and aluminum electrodes). The performance characteristics were evaluated using the following equation (Eq. (12)) [37]:

$$\mathrm{SNL} = -10\log\left(\frac{1}{n}\sum_{i=1}^{n}\frac{1}{y^2}\right) \tag{12}$$

where SNL is the S/N ratio or the performance characteristics as "the larger-the-better", y_i is the comparison variable in experiment i for a certain combination of control factor levels, and n is the number of experiments performed for that combination.

In such cases, optimum operation conditions may have not been attained during the entire experimental section. So, an additive model may be needed in order to predict the performance value corresponding to the optimum operation conditions, where the following additive model may be applied, as (Eq. (13)):

$$y_i = \mu + X_i + e_i \tag{13}$$

where μ is the overall mean of the performance value, X_i is the fixed effect of the quantity level combination used in i_{th} experiment, and e_i is the random error in the i_{th} experiment.

Since Eq. (13) is a point estimation, which is calculated using experimental data in order to determine whether results of the confirmation experiments are sufficient or not, the confidence interval must be evaluated. At the selected error level, the confidence interval is calculated using the following equation (Eq. (14)) [38]:

$$Y_i \pm \mathrm{CI}\left(\mathrm{CI} = \sqrt{F_\alpha(1, f_\mathrm{e}) \times v_\mathrm{e} \times \left[\frac{1}{n_{\mathrm{eff}}} + \frac{1}{S}\right]}\right) \tag{14}$$

Table 1
Factors and their values corresponding to their levels to be studied in EC experiments (aluminum and iron electrodes)

	Levels									
	1		2		3		4		5	
Factors	I	II	I	II	I	II	I	II	I	II
A: Current density (mA/cm^2)	10	10	20	20	30	30	40	40	50	50
B: pH	4	3	5	4	6	5	7	6	8	7
C: Time (minute)	5	5	10	10	15	15	20	20	25	25

Notes: I: iron electrode; II: aluminum electrode.

Table 2
Experimental variables, their levels, and results of conducted experiments corresponding to L_{25} experimental plan

	Variables and their levels			COD_{Re}		Cr_{Re}		$Color_{Re}$	
Trail no.	A	B	C	I	II	I	II	I	II
1	1	1	1	21.0	17.0	47.9	20.0	5	10
2	1	2	2	29.0	32.3	63.2	30.0	25	30
3	1	3	3	33.9	38.0	80.0	60.0	53	39
4	1	4	4	38.5	40.7	94.0	78.0	77	60
5	1	5	5	40.5	47.5	96.7	88.0	85	70
6	2	1	2	36.0	30.1	83.6	33.0	35	33
7	2	2	3	40.0	41.6	95.2	55.0	77	43
8	2	3	4	44.6	45.8	99.5	88.0	85	72
9	2	4	5	48.6	49.8	100	94.1	82	71
10	2	5	1	36.0	36.0	93.8	64.0	64	45
11	3	1	3	45.9	33.6	95.6	50.0	90	53
12	3	2	4	48.0	50.0	97.8	92.5	83	75
13	3	3	5	50.2	54.9	98.7	100	79	79
14	3	4	1	40.6	38.2	95.0	72.0	80	57
15	3	5	2	43.0	55.0	100	94.6	77	76
16	4	1	4	49.7	40.7	98.7	77.0	87	70
17	4	2	5	55.0	54.9	100	100	86	80
18	4	3	1	40.0	37.8	89.5	64.0	67	50
19	4	4	2	47.5	55.8	96.3	96.9	85	73
20	4	5	3	48.5	57.4	99.1	100	76	78
21	5	1	5	55.3	46.5	98.2	98.9	89	84s
22	5	2	1	42.6	43.0	90.0	60.0	70	50
23	5	3	2	55.7	50.9	97.7	98.2	89	78
24	5	4	3	60.7	62.0	100	100	86	84
25	5	5	4	59.6	64.1	100	100	84	88

where F_α (1, f_e) is the F-ratio at a confidence level of (1 − α) against DOF 1, f_e is the error degree of freedom (DOF), n_{eff} is (N/(1 + (total DOF associated in the estimate of mean))), N is the total number of results, S is the sample size for confirmation test, v_e is the error variance, and CI is the confidence interval.

When the experimental results are presented in percentages (%) "As in our work" before estimating Eqs. (13) and (14), Ω transformation for percentage values should be applied first using the following equation (Eq. (15)) [37]. The values of interest are then determined later by carrying out reverse transformation using the same equation.

$$\Omega\,(\mathrm{db}) = -10\log\left(\frac{1}{P} - 1\right) \tag{15}$$

where Ω (db) is the decibel value of the percentage value subjected to omega transformation and P is the percentage of the product obtained experimentally.

3. Results and discussion

3.1. Wastewater sources and characteristics

The samples analyzed in this work were collected from different outflow wastewaters of the Organized Tannery Industrial Region (OTIR) which is located in the Tuzla quarter of Istanbul, Turkey. With regard to OTIR, the treatment plant receives wastewater from 100 small tannery plants based on chrome and vegetables tanning. Generally, it has four treatment steps that can be given as: equalization, settling, aerobic activated sludge, and physiochemical treatment by chemical coagulation. The samples were put into PE containers, transported to laboratory in one hour, mixed very well, and conserved at 4˚C during the experiments. The composition of the wastewater sample is presented in Table 3. The sample was collected in December 2014.

3.2. Determination of optimum parametric levels

The collected data were analyzed using Minitab ˝16 version" statistical software for the estimation of the effect of each parameter on the optimization criteria. Experimental results, with regard to the model, were liberated from Taguchi method and

Table 3
Characteristics of raw tannery wastewater used in this study

Parameter	Value
pH	4.10 at 6.5°C
Conductivity (mS cm^{-1})	11.71
COD	2,200–3,000
Soluble COD	1,436–1959
Suspended solids	912
Chloride	1,691
Total chromium	570
Color	824

Note: Color ADMI (10) Pt–Co, all other parameters as mg/L.

demonstrated in Table 2. On the other hand, all levels of variables are situated in Table 1. During this work, COD, total chrome, and color results are expressed as percentage of removal (%) through the following equation (Eq. (16)):

$$\%\ \text{removal} = \left[\frac{(C_i - C_f)}{C_i}\right] \times 100 \quad (16)$$

where C_i is the initial concentration and $C_f$is the final concentration of the pollutant (mg/L and ptc).

The obtained results are shown in Figs. 2a, 2b, 2c, and 3a, 3b, 3c for iron and aluminum electrodes, respectively. The numerical value of the maximum point in each graph clarifies the best value of that particular parameter, situated in Table 2 for each parameter, and indicates the optimum conditions within the range of experimental conditions.

3.3. Effect of current density on EC process

Current density is considered as a vital parameter for pollutants removal efficiency in EC process due to its power. Current density is in charge of the metal hydroxide concentrations, reaction rate of the process, coagulant dosage, bubble production, moreover, the effects on growth of flocs. During this work, current density was examined at the range of 10–50 mA/cm^2 in order to assess effects on tannery wastewater treatment efficiency of EC process. Either iron or aluminum electrode can be noticed from Figs. 2a and 3a that when current density increased, the COD removal efficiency was increased but not as likely, and also, the removal efficiency of total chrome and color was increased, so the best level for total chrome and color removal efficiency was obtained at the fifth level (50 mA/cm^2) for aluminum electrode as shown in Figs. 3b and 3c, and for color removal efficiency in the case of iron electrode as demonstrated in Fig. 2c. It can be pointed out that the optimum removal efficiency of total chrome in iron electrode was attained at the third level (30 mA/cm^2) as shown in Fig. 2b.

3.4. Effect of initial pH on EC process

It was reported in prior studies that pH is a central factor that affects the performance of EC process [18]. In the case of iron electrode, Figs. 2a, 2b, and 2c illustrates the effects of all performance criteria on COD, total chrome, and color removal efficiencies. As it can be seen in Table 1, original pH value of the wastewater is 4.1. The pH experiments were performed within the examined range demonstrated that optimal pH value was 7 (fourth level) for the best COD removal efficiency as founded in Fig. 2a. It can be noticed from Fig. 2c, COD removal is similar to the best color removal at pH 7 (fourth parametric level). Whereas the best removal efficiency of total chrome is pH 8 (fifth level) as shown in Fig. 2b. And also, Figs. 3a, 3b, and 3c explains the optimum pH values for COD, total chrome, and color removal efficiencies for the

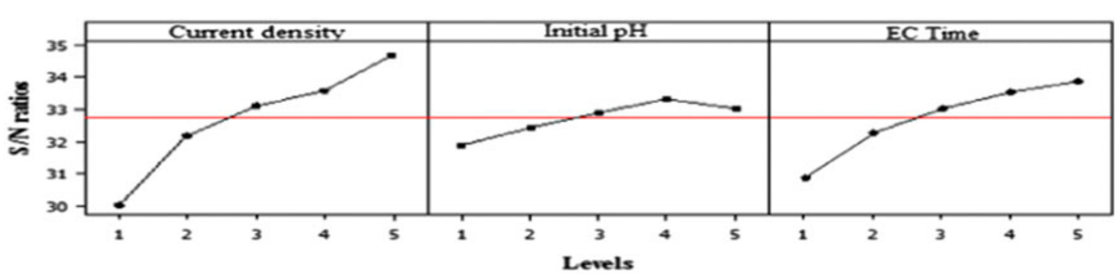

Fig. 2a. The effect of each parameter on COD removal efficiency for iron electrode. On the left side, it shows the current density with different currents (10–50 mA/cm^2). In the middle, it presents different initial pH values from 4 to 8. On the right side, it explains EC time with different intervals from 5 to 25 min.

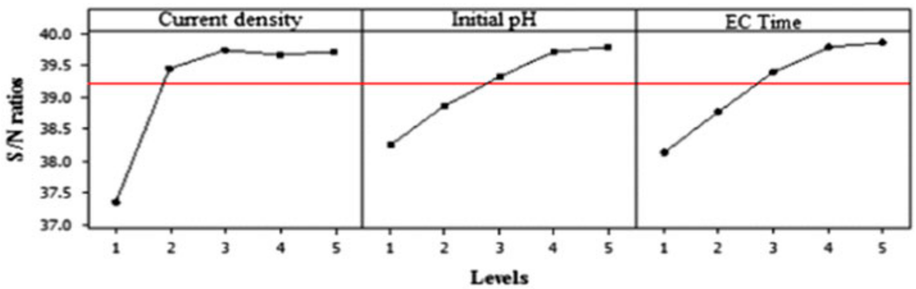

Fig. 2b. The effect of each parameter on Cr removal efficiency for iron electrode. On the left side, it shows the current density with different currents (10–50 mA/cm^2). In the middle, it presents different initial pH values from 4 to 8. On the right side, it explains EC time with different intervals from 5 to 25 min.

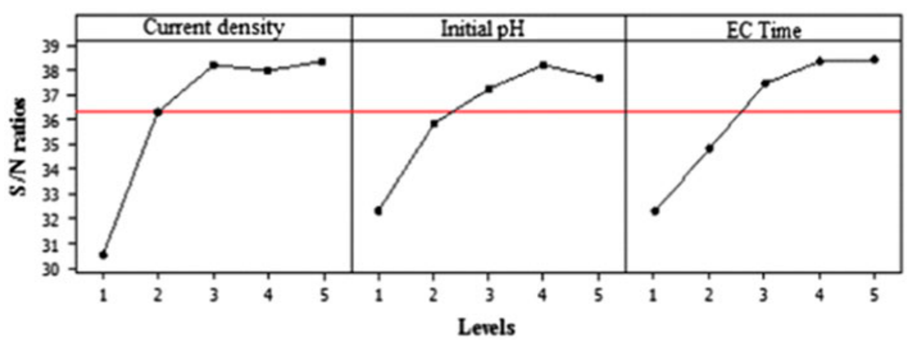

Fig. 2c. The effect of each parameter on color removal efficiency for iron electrode. On the left side, it shows the current density with different currents (10–50 mA/cm^2). In the middle, it presents different initial pH values from 4 to 8. On the right side, it explains EC time with different intervals from 5 to 25 min.

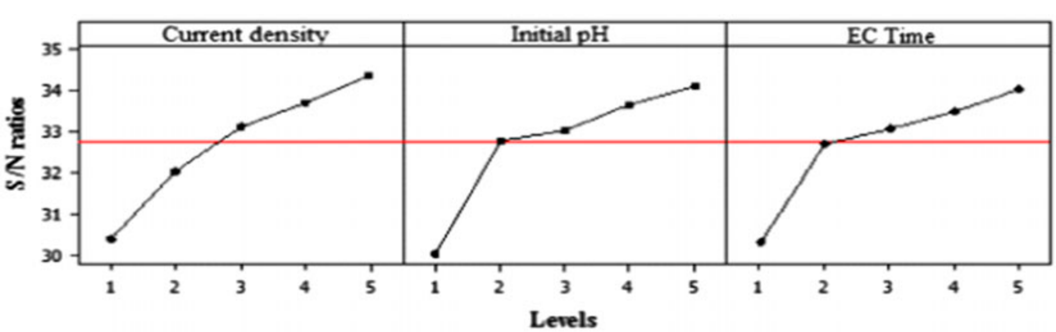

Fig. 3a. The effect of each parameter on COD removal efficiency for aluminum electrode. On the left side, it shows the current density with different currents (10–50 mA/cm^2). In the middle, it presents different initial pH values from 3 to 7. On the right side, it explains EC time with different intervals from 5 to 25 min.

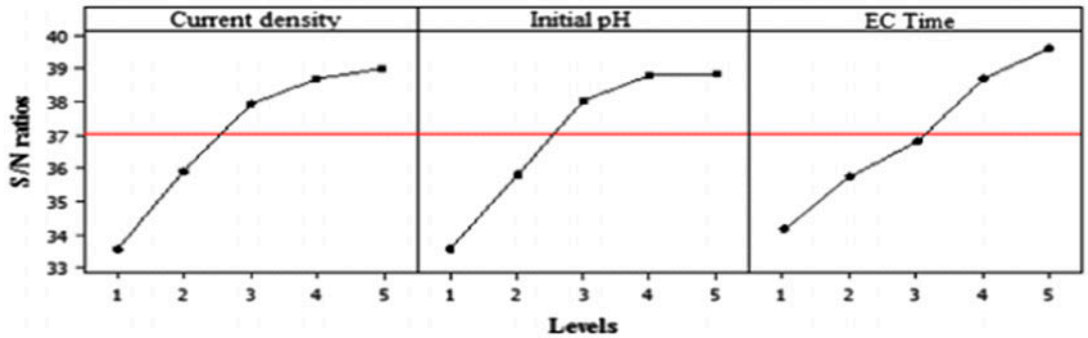

Fig. 3b. The effect of each parameter on chrome removal efficiency for aluminum electrode. On the left side, it shows the current density with different currents (10–50 mA/cm^2). In the middle, it presents different initial pH values from 3 to 7. On the right side, it explains EC time with different intervals from 5 to 25 min.

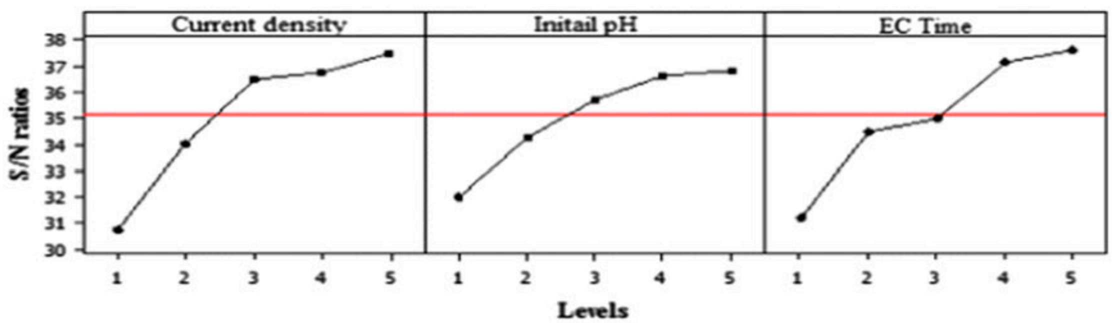

Fig. 3c. The effect of each parameter on color removal efficiency for aluminum electrode. On the left side, it shows the current density with different currents (10–50 mA/cm^2). In the middle, it presents different initial pH values from 3 to 7. On the right side, it explains EC time with different intervals from 5 to 25 min.

case of aluminum electrode. It can be seen that the optimum pH was 7 (fifth parametric level).

3.5. Effect of electrolysis time on EC process

There is a strong relationship between electrolysis time and formation of metal hydroxide which is responsible for removal of pollutants, and some parameters are time dependent. In this study, electrolysis time was given at the range of 5–25 min. The two cases of iron and aluminum electrodes, Figs. 2a, 2b, 2c, and Figs. 3a, 3b, 3c show the effect of electrolysis time on removal efficiency of pollutants. It can be concluded that the removal efficiency of COD, total chrome, and color increased with an increasing operation time. And the highest removal efficiency for all responses parameters was at the fifth level (25 min).

3.6. Statistical analysis

Analysis of variance (ANOVA) was performed to examine the effective parameters and their confidence levels on the COD, total chrome, and color removal efficiencies. The function of the ANOVA is to explore which process parameters significantly affect the process responses. Table 4 (panel a, b and c) illustrates the results of the ANOVA test for COD, total chrome, and color in iron and aluminum electrodes, respectively. According to S/N ratio analysis, it can be noticed from Table 4 (panel a, b and c) that the factors can be classified according to their significance as follows: in the case of iron electrode, current density > electrolysis time > initial pH for the COD, total chrome, and color removal efficiencies. Whereas the result of aluminum electrode was: initial pH > current density > time of COD, and total chrome removal efficiencies, while as, current density > time > pH for color removal efficiency.

In Taguchi's method, the confirmation test is important to verify the experimental results. The confirmation experiment is performed. In this study, after determining the optimum conditions and predicting the response under these conditions, a new experiment was designed and carried out with the optimum

Table 4
Results of the ANOVA test and contribution percentage

	DOF		SS		MS		F		P		C%[a]	
Variables	I	II	I	II	I	II	I	II	I	II	I	II
a: for COD removal performance												
A: CD mA/cm^2	4	4	62.011	49.323	15.5028	12.3307	54.70	52.73	0.000	0.000	61.6	33.8
B: pH	4	4	6.280	51.459	1.5700	12.8648	5.54	55.01	0.009	0.000	6.3	35.3
C: Time (min)	4	4	29.015	42.205	7.253	10.5512	25.59	45.12	0.000	0.000	29	29
Error	12	12	3.401	2.806	0.2834	0.2339					3.1	1.9
Total	24	24	100.708	145.794								
b: for total chrome removal performance												
A: CD mA/cm^2	4	4	21.511	105.31	5.3776	26.327	6.39	11.66	0.005	0.000	42.4	31.5
B: pH	4	4	8.156	105.26	2.0391	26.316	2.42	11.65	0.105	0.000	16.0	31.4
C: Time (min)	4	4	10.986	97.16	2.7464	24.291	3.26	10.76	0.05	0.001	21.6	29.0
Error	12	12	10.097	27.10	0.8415	2.258					20.0	8.1
Total	24	24	50.750	334.83								
c: for color removal performance												
A: CD mA/cm^2	4	4	221.7	153.94	55.42	38.486	3.25	11.57	0.050	0.000	32.5	38.0
B: pH	4	4	113.3	79.62	28.32	19.906	1.66	5.98	0.223	0.007	16.6	19.6
C: Time (min)	4	4	143.7	132.05	35.92	33.011	2.11	9.92	0.143	0.001	21.0	32.6
Error	12	12	204.5	39.93	17.04	3.328					29.9	9.8
Total	24	24	683.1	405.54								

Notes: SS: sum of squares; DOF: degree of freedom; C%: contribution percentage.
[a]Contribution is defined as 100 x (Sum of squares/Total sum of squares).

Table 5
Optimum experimental conditions predicted and observed removal efficiency values (iron and aluminum electrode)

	CD		pH_i		ET				
Perform criteria	level	value	level	value	level	value	Observed %	Predicted %	C.L %
For iron electrode									
COD	5	50	4	7	5	25	63.3	58.3	50.2–66
Total chrome	3	30	5	8	5	25	99.7	99.9	99.9–100
Color	5	50	4	7	5	25	82.0	92.0	48–99.3
For aluminum electrode									
COD	5	50	5	7	5	25	64.4	60.0	52.7–66.9
Total chrome	5	50	5	7	5	25	99.0	99.7	92.2–99.9
Color	5	50	5	7	5	25	88.0	92.0	79.0–97.3

Notes: CD: current density; ET: electrolysis time; C.L: confidence limit.

levels of EC parameters. Table 5(a and b) shows the optimum working conditions. Thus, the equation omega transformation (Eq. (15)) was applied to evaluate the predicted value in order to clarify as percentage value of the result offered in Table 5. In addition, the percentage contribution of each factor effecting COD, total chrome, and color removal was calculated as illustrated in Table 4 using the following equation (Eq. (17)) [39]:

$$C\% = 100 \times \frac{\text{Sum of squares}}{\text{Total sum of squares}} \quad (17)$$

It can be noticed that the current density had the highest contributions to the variability of the experimental results for iron electrode. Contribution percentage on COD, total chrome, and color were attained as 61.6, 42.4, and 32.5, respectively. In the case of aluminum electrode, the initial pH was the highest contribution percentage for COD and total chrome as 35.3 and 31.4, moreover, for color was the lowest as 19.6.

3.7. Operating costs

The operating cost is considered a vital parameter that affects the implementation of any method of wastewater treatment. In this paper, the operating costs have been calculated for EC process under optimum conditions. Generally, the operating cost includes material (mainly electrodes) cost, electrical energy cost, as well as labor, maintenance, and other costs. However, in this study, the operating costs were calculated as energy consumption and electrode material where as consumption quantities per m^3 of wastewater treated. Unit prices, given as Turkish market, 2015, are as follows: electrical energy price 0.1 $/kWh, electrode material price 0.2 $/kg, for iron and for aluminum 1.5 $/kg. The electrode and energy consumptions in the EC process were calculated via the following equations (Eqs. (18) and (19)):

$$\text{Energy}_{\text{consumption}} = \frac{I \times V \times t}{v} \quad (18)$$

where $\text{Energy}_{\text{consumption}}$ is the energy consumption (kWh/m^3), V is the voltage (Volts), I is the current (Amperes), t is the EC time (hour), and v is the volume of the treated wastewater (m^3). Besides, electrode consumption was evaluated according to Faraday's law as the following equation (Eq. (19)):

$$\text{Electrode}_{\text{consumption}} = \frac{(I \times t \times M_w)}{(z \times F \times v)} \quad (19)$$

where F is the Faraday's constant (96,485 C/mol), M_w is the molar mass of electrode type as in iron (56 g/mol), aluminum (27 g/mol), and z is the number of electron transfer (zFe:2) and (zAl:3).

In this paper, in the case of iron electrodes, operating costs for both of COD and color removals were calculated as 0.88 $\$/m^3$, besides, for chrome removal was 0.70 $\$/m^3$. However, in the case of aluminum electrode, operating costs for COD, chrome, and color removals were evaluated as 0.94 $\$/m^3$. Ultimately, EC process is an effective costs method for treating tannery wastewater compared with other methods [40].

4. Conclusion

In this study, Taguchi design experiment (L_{25}) was carried out to optimize the effective parameters on the removal efficiency of tannery wastewater pollutants by EC process. The larger-the-better S/N ratio was used to analyze the result experiments. A confirmation experiment within the optimal process parameters was conducted to assess the usefulness of the Taguchi optimization design technique. In view of our results, the conclusion can be given as follow:

(1) For iron electrode: current density was the most significant parameter on COD, total chrome, color, and its percentage value was 61.6, 42.4, and 32.5%, respectively. Together with, the second important factor for COD, total chrome and color was electrolysis time and its percentage contribution value was 29, 21.6, and 21%, respectively. Finally, the slightest factor was the initial pH. According to the result statistical analysis, for COD removal, the optimum condition was achieved as: current density 50 mA/cm^2, initial pH 7, and electrolysis time 25 min, for total chrome removal: current density 30 mA/cm^2, initial pH 8, and electrolysis time 25 min, and for color removal: current density 50 mA/cm^2, initial pH 7, and electrolysis time 25 min. In addition, the operating costs for both of COD and color removals were computed as 0.88 $\$/m^3$, besides, for chrome removal was 0.70 $\$/m^3$.

(2) For aluminum electrode: the initial pH was significant parameter on COD and its percentage contribution value was 35.3%, hence both current density and initial pH have the same effect on total chrome and their percentage values were 31.5 and 31.4%, respectively. With regard to color, current density was the most factor and its percentage contribution value was 38%. The second important parameter on COD was the current density with percentage value 33.8%. On the contrary, for color the second important factor was electrolysis time and its percentage value was 32.6%, and also, it can be concluded that the color is independent on the change of initial pH and its percentage value was 19.6%. Electrolysis time for COD and total chrome was the slightest parameter with the same percentage contribution value 29%. As said by the results statistical analysis, the set of optimum condition for COD, total chrome, and color removal was current density 50 mA/cm^2, initial pH 7, and electrolysis time 25 min, whereas operating costs for COD, chrome, and color removals were evaluated as 0.94 $\$/m^3$.

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