

Electrocoagulation of Tannery Wastewater using Monopolar Electrodes: Process Optimization by Response Surface Methodology

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ABSTRACT: In the present study, the treatment of tannery wastewater was performed by electrocoagulation method (EC) using aluminium and steel electrodes. Response surface methodology (RSM) with three factors; current density (I), electrolysis time (t) and pH, with each factor at five levels, was used to optimize the factors for higher chemical oxygen demand (COD) and total suspended solids (TSS) removal. Operational parameters I, t and pH were varied between 22–110 mA/cm², 5–45 min and 3–7, respectively. For the optimal parameter values, the removal efficiency of COD and TSS attained respectively 82.2% and 85.5% for aluminium electrodes and 67.4% and 86.2% for steel electrodes. Analysis of variance (ANOVA) showed a high variance coefficient (R^2) value of 0.96 and 0.81, for COD and TSS removal, respectively, thus ensuring a satisfactory adjustment of the second-order regression model with the experimental data. Corresponding energy consumption was found to be 2.92 €/m³ and 8.18 €/m³, for COD removal by using aluminium and steel electrodes, respectively.

Key words: Tannery wastewater, Electrocoagulation, RSM, Optimization, Cost analysis

INTRODUCTION

Considering the large amount and the low biodegradability of chemicals present in the tannery productive cycle, tannery wastewaters represent a serious environmental and technological problem (Di laconi *et al.*, 2002). The removal of toxic organic and inorganic compounds from tannery wastewater by biological processes is generally insufficient, since these compounds are virtually non-biodegradable. In addition, tannery wastewaters are hypersaline effluents with chloride concentrations from 1500 to 28.000 mg/L. As known, high chloride concentrations has been considered as inhibitory for biological wastewater treatment (Costa and Olivi, 2009). Conventional physico-chemical treatment processes are more suitable for the treatment of highly saline wastewaters. Conventional physico-chemical treatment of tannery effluents includes pretreatment, flocculation, sedimentation and sludge handling processes. However, these processes tend to generate large volumes of sludge with a high bound water content slowing down filtration and and to increase the total dissolved solids content of the effluent (Babu *et al.*, 2007). High influent suspended solids concentration of tannery wastewaters constitutes a great problem of applying ion exchange method as the suspended solids may clog

the resin causing inefficient operation. Ion exchangers also require costly regenerants and produce troublesome waste streams (Lefebvre and Moletta, 2006). Electrocoagulation can be considered as an alternative treatment method with many advantages as simple equipment, easy operation and automation, a short retention time, low sludge production and no chemical requirement.

Electrocoagulation can be defined as the process of destabilising suspended, emulsified, or dissolved contaminants in an aqueous medium by introducing an electric current into the medium (Emamjomeh and Sivakumar, 2009; Top *et al.*, 2011) and has attracted great attention in wastewater treatment by the fact that EC has been successfully used in removal of different kinds of pollutants such as organic compounds (Asselin *et al.*, 2008; Abdelwahab *et al.*, 2009; Koparal *et al.*, 2008; Wang *et al.*, 2010), heavy metals (Dermentzis *et al.*, 2011; Zaroual *et al.*, 2009; Nouri *et al.*, 2010) important anions such as nitrate (Emamjomeh *et al.*, 2009), fluoride (Hu *et al.*, 2008; Khatibikamal *et al.*, 2010), phosphate (Irdemez *et al.*, 2006; Vasudevan *et al.*, 2009) and treatment of wastewater such as dairy wastewater (Tchamango *et*

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al., 2010; Kushwaha et al, 2010), textile wastewater (Bayramoglu et al., 2007; Zongo et al., 2009;) biodiesel wastewater (Chavalparit and Ongwandee., 2009), paper industry wastewater (Khansorthong and Hunsom 2009; Katal, and Pahlavanzadeh, 2011), municipal wastewater (Bukhari, 2008; Rogrigo et al., 2010), leachate (Veli et al., 2008; Labanowski et al, 2010; Ilhan et al., 2008), oily wastewater (Tir and Moulai-Mostefa, 2008; Tezcan et al., 2009), petroleum refinery wastewater (El-Naas et al., 2009, Yavuz et al., 2010).

In electrocoagulation process, sacrificial metal anodes (usually aluminum or iron, sometimes steel) are used to produce metal cations that form polymeric metal hydroxide species in solution used in dosing polluted water. After polymeric metal hydroxide species neutralize negatively charged particles, the particles bind together to form aggregates of flocs, resulting in pollutant removal by adsorption of soluble organic compounds and trapping of colloidal particles. Finally, these flocs are removed easily from aqueous medium by sedimentation or flotation. Additionally, electrolytic gas bubbles (mainly hydrogen) causing electroflotation are generated (Holt et al., 2002; Behbahani et al., 2011). In tannery wastewater treatment, electrocoagulation offers inherent advantages: high chloride content of the wastewater leads to a decrease in energy consumption owing to the increase in conductivity and induces in situ electrochemical generation of the chlorine/hypochlorite couple acting as oxidants (Chen, 2004; Feng et al., 2007; Wang et al., 2002).

In this study, the applicability of aluminium and steel electrodes to treat tannery wastewater was investigated. Response surface methodology (RSM) was used to design the experiments, to perform statistical analysis and to determine the optimum conditions. Three factors, namely, the current density (I), the electrolysis time (t) and the pH were selected as variables, whereas, COD and TSS removal efficiencies

were selected as the response. Overall operational cost analyses were also determined.

MATERIALS & METHODS

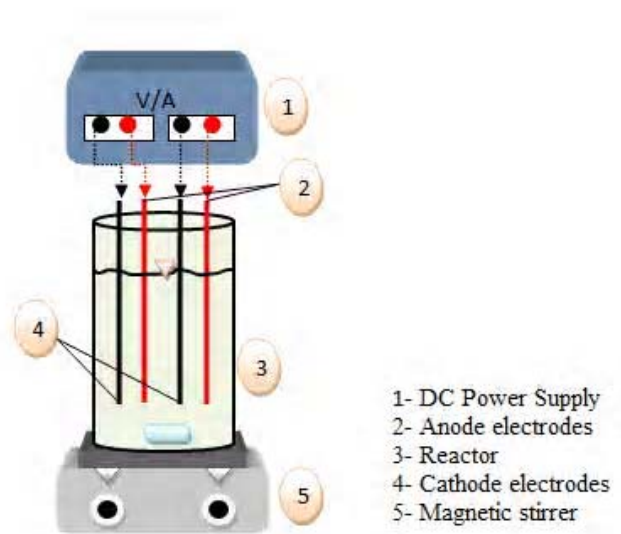
The samples used in the study were obtained from an equalization tank of leather processing factory wastewater. Samples were collected and stored in containers, and kept at 4 °C. The characterization of tannery wastewater is given in Table 1. Before the EC treatments, all tannery effluent samples were preserved and analyzed according to the Standard Methods recommended by the American Public Health Association (APHA, 2005).

The experimental set up used for the electrocoagulation studies is shown in Fig. 1. A laboratory-scale plexiglass EC reactor with 9 cm diameter and 13 cm height was constructed. Electrode sets (two anode and two cathode electrodes) comprised of four monopolar (MP) parallel aluminum plates (6 cm width × 11.5 cm height and 0.1 cm thickness), each having an effective area of 46.2 cm². The electrodes was placed 1.5 cm apart from each other. A valve was installed at the bottom of the reactor to withdraw the precipitated material through a sludge chamber. For each test, 600 mL wastewater sample was used. Electrolyte solution was not used because of high salinity of the wastewater samples. Before each run, electrodes were washed with acetone, and the impurities on the aluminum electrode surfaces were removed by dipping in a solution freshly prepared by mixing 100 cm³ of HCl solution (35%) and 200 cm³ of hexamethylenetetramine aqueous solution (2.80%) for 5 min (Can et al., 2005).

All the chemicals used were of analytical-reagent grade. The electrocoagulation experiments were initiated by using tannery effluent for 45 min with a current density of 22 to 110 mA/cm² which was imposed by means of a DC power supply. At the end of each run, the floated and precipitated materials were

Table 1. Characterization of raw tannery wastewater

Parameter	Value	Parameter	Value
pH	3.93	TSS, (mg/L)	1465
Conductivity, (mS/cm)	43.8	TVS, (mg/L)	1170
COD (mg/L)	3853	TKN, (mg/L)	834
Chloride, (mg/L)	21443	NH ₃ -N, (mg/L)	566
Colour, (Hazen)	700		



1- DC Power Supply
 2- Anode electrodes
 3- Reactor
 4- Cathode electrodes
 5- Magnetic stirrer

Fig. 1. Experimental set-up

withdrawn and the clarified effluent sample was pipetted out from the reactor, and then allowed to settle for a few hours in a polyethylene flask. Finally, the clarified supernatant liquid was collected and preserved according to the standard methods (APHA, 2005) and stored for characterization.

Three analytical steps; adequacy of various models test (sequential model sum of squares and model summary statistics), analysis of variance (ANOVA) and the response surface plotting were performed to establish an optimum condition for the COD and TSS removal from the tannery wastewater. For the statistical design of experiments and data analysis, Statgraphics Centurion XVII.I software programme was used. The three most important operating variables: initial wastewater pH (x_1), current density (x_2) and operating time (x_3) were optimized for tannery wastewater. Their range and levels were shown in Table 2. The ranges and levels of the independent variables were determined from preliminary experiments. In this study, central composite design (CCD), one of the four main types of RSM designs was used for improving and optimizing the process using steel and aluminium electrodes. Central Composite Design (CCD) is an experimental design used by RSM to fit a model by least squares technique. RSM makes it possible to represent independent process parameters in quantitative form as:

$$y = f(x_1, x_2, x_3, \dots, x_n) \pm \varepsilon \quad (1)$$

where y is the response (yield), f is the response function, ε is the experimental error and $x_1, x_2, x_3, \dots, x_n$ are independent parameters. By plotting the expected

response of y , a surface known as the response surface is obtained. A higher order polynomial such as the quadratic model (Eq. (1)) was used in this study. Analysis of variance (ANOVA) was used to obtain the interaction between the process variables and the responses. The quality of the fit polynomial model was expressed by R^2 , and its statistical significance was checked by the Fisher F-test in the same program. Model terms were evaluated by the P value (probability) with 95% confidence level.

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{33} x_3^2 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3 \quad (2)$$

The predicted response (y) (Eq. (2)) is, therefore, correlated to the set of regression coefficients (β): the intercept (β_0), linear $\beta_1, \beta_2, \beta_3$, interaction ($\beta_{12}, \beta_{13}, \beta_{23}$) and quadratic coefficients ($\beta_{11}, \beta_{22}, \beta_{33}$).

RESULTS & DISCUSSION

Initial pH is an important parameter in the determination of the performance of EC process (Do and Chen, 1994; Tir and Mostefa, 2008). It is concluded by the researchers (Daneshvar *et al.*, 2006; Yildiz *et al.*, 2008) that the pH of the reaction solution changes during the electrocoagulation process and the final pH of the effluent actually affects the overall treatment performance. When the initial pH value is less than 4 (acidic), the effluent pH increases, while it tends to decrease when the initial pH value is higher than 8 (basic), and the pH of the effluent changes only slightly when the initial pH value is in the neutral range (around 6–8) (Kabdaşlı *et al.*, 2012). The initial pH value of the

tannery wastewater was determined to be 3.93. During the preliminary experimental study, it was observed that the pH of the processed wastewater increased. This pH increase was attributed to hydrogen evolution at cathodes by Vik et al. (1984). However, Chen (2004) explained this increase in pH by the release of CO₂ from wastewater owing to H₂ bubble disturbance. In addition, the chemical dissolution of aluminium gives rise to the pH increase which could be explained by the excess of hydroxyl ions produced at the cathode and by the liberation of OH⁻ due to the occurrence of a partial exchange of Cl⁻ with OH⁻ in Al(OH)₃ (Feng *et al.*, 2007). In the case of mild steel electrodes, pH value increases gradually during the electrocoagulation process. This may be due to the formation of FeS, which was coincident with the literature (Murugananthan *et al.*, 2004). The pH increase for all the studied current density values can be explained by consequence of continuous OH⁻ formation at the cathode. This is due to the redox reaction of water which being predominant than the anodic water oxidation; or the occurrence of a partial exchange of Cl⁻ with OH⁻ in Al(OH)₃ (Benhadji *et al.*, 2011). It can be concluded from the results that COD and TSS removal is a function of the initial pH.

The current density is defined as the ratio of current input to the electrolytic cell to the surface area of the electrode. The current supplied to the electrochemical reactor is usually expressed in terms of current density (Babu *et al.*, 2007). It has been established that cell current is one of the important parameters to control the reaction rate in the electrochemical processes (Adhoum *et al.*, 2004). For a given time, the removal efficiency increased with the increasing of cell current. At higher cell current values, the amount of metal oxidized increased, resulting in a greater amount of hydroxide flocs for the removal of pollutants. As the cell current increased, the bubble density increased and their size decreased, resulting in a faster removal of pollutants (Hu *et al.*, 2003; Adhoum and Monser,

2004). In addition, Chen et al. (2002) reported that bubble density increases and their size decreases with increasing current density, resulting in a greater upwards flux and a best removal of pollutant and sludge flotation. The obtained results showed that an increase in the current density increased the removal efficiency, which is also stated in literature (Kobyas *et al.*, 2003; Yang, 2007; Tir and Mostefa, 2008).

The effect of current density on the reduction of COD, TSS, TVS and colour were studied by conducting experiments at different current densities (22-110 mA/cm²), and different time intervals (5-45 minute). Overall results of the experimental study for aluminium and steel electrodes were given in Table 3 and Table 4, respectively. Analysis of the results show that removal percentage increased with time. This is due to the oxidation and reduction reactions (Babu *et al.*, 2007). Similar results regarding the effect of treatment time were also reported by Kobyas et al. (2006), Gupta and Babu (2009), Babu et al. (2007), Daneshvar et al. (2006) and Nourouzi et al. (2011).

The COD removal could be attributed to the precipitation of dissolved organics. Since the efficiency of COD removal depended on the quantity of hydroxide flocs, which was bound with time and cell current of electrocoagulation, the concentration of COD decreased rapidly in the first 10 min of the electrocoagulation process. Higher removal efficiencies of COD were observed at longer time periods and higher cell current values (Golder *et al.*, 2005). The lower removal efficiencies at shorter time and low cell current could be explained by the fact that the amount of precipitate formed was not enough and large part of COD in the tannery wastewater was soluble (Song *et al.*, 2004). As seen in Fig. 2 there were no significant differences between mild steel electrodes and aluminum electrodes for the elimination of COD under the same conditions. These results are consistent with the study conducted by Feng et al. (2007).

Table 2. Experimental range and levels of the independent variables

Variables	Symbol	-2	-1	0	1	2
Initial pH	x ₁	3	4	5	6	7
Current density (mA/cm ²)	x ₂	22	44	66	88	110
Electrolysis time (min)	x ₃	5	15	25	35	45

Table 3. Overall results for aluminium plate electrode

Run	X ₁	X ₂	X ₃	COD, mg/L	COD Removal, (%)	TSS, mg/L	TSS Removal, (%)	TVS, mg/L	TVS Removal, (%)	Colour,	
										Hazen	Colour Removal, (%)
1	-1	-1	-1	2530	34	662	55	270	77	492	30
2	1	-1	-1	2133	45	282	81	94	92	318	55
3	-1	1	-1	1608	58	365	75	105	91	309	56
4	1	1	-1	1632	58	380	74	165	86	276	61
5	-1	-1	1	1632	58	372	75	140	88	238	66
6	1	-1	1	1272	67	282	81	117	90	190	73
7	-1	1	1	1080	72	177	88	70	94	244	65
8	1	1	1	1528	60	452	69	215	82	283	60
9	-2	0	0	1821	53	337	77	160	86	351	50
10	2	0	0	1176	69	315	78	190	84	98	86
11	0	-2	0	1808	53	680	54	315	73	414	41
12	0	2	0	984	74	215	85	155	87	116	83
13	0	0	-2	2700	30	145	90	85	93	442	37
14	0	0	2	1192	69	205	86	125	89	93	87
15	0	0	0	1584	59	320	78	155	87	275	61
16	0	0	0	1568	59	315	78	160	86	279	60
17	0	0	0	1520	61	315	78	157	87	280	60
18	0	0	0	1558	60	325	78	162	86	279	60
19	0	0	0	1511	61	317	78	155	87	285	59
20	0	0	0	1511	61	320	78	160	86	282	60

Table 4. Overall results for steel plate electrode

Run	X ₁	X ₂	X ₃	COD Removal,		TSS Removal,		TVS Removal,	
				COD, mg/L	(%)	TSS, mg/L	(%)	TVS, mg/L	(%)
1	-1	-1	-1	2640	31	68	95	65	94
2	1	-1	-1	2520	35	88	94	55	95
3	-1	1	-1	2140	44	333	77	133	89
4	1	1	-1	1920	50	265	82	93	92
5	-1	-1	1	2060	47	157	89	50	96
6	1	-1	1	1780	54	100	93	33	97
7	-1	1	1	1740	55	98	93	30	97
8	1	1	1	1420	63	243	83	57	95
9	-2	0	0	2390	38	287	80	100	91
10	2	0	0	1800	53	260	82	98	92
11	0	-2	0	2780	28	145	90	82	93
12	0	2	0	1900	51	150	90	75	94
13	0	0	-2	2520	35	52	96	67	94
14	0	0	2	1740	55	90	94	60	95
15	0	0	0	2020	48	153	90	75	94
16	0	0	0	2160	44	173	88	78	93
17	0	0	0	2110	45	165	89	75	94
18	0	0	0	2100	45	170	88	77	93
19	0	0	0	2120	45	168	89	76	94
20	0	0	0	2110	45	168	89	75	94

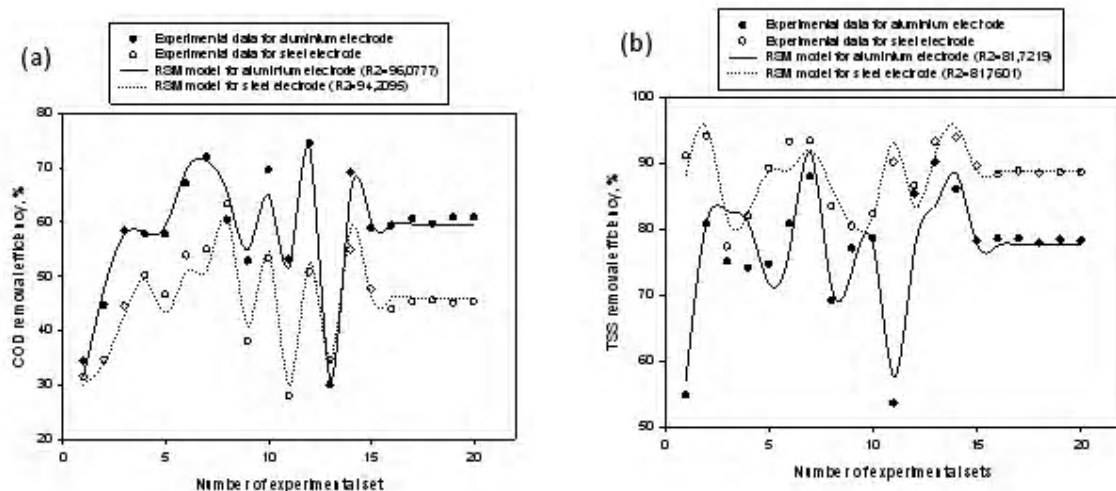


Fig. 2. Comparison of results of aluminium and steel electrodes

The RSM was implemented to establish the optimal operational conditions of the EC process for a maximum COD and TSS removal in treatment of tannery wastewater. A multifactorial experimental design was defined in order to evaluate the influence of several parameters including: the type of the electrodes, the electrolysis time, the initial pH, and the current density. Based on the characteristics of the wastewater and its previous statistical analysis, five different levels (values) were chosen for each parameter. Table 2 presents the variable levels and their codifications. The effects of x_1 , x_2 and x_3 investigated on COD and TSS removal efficiencies were determined using approximating functions.

An adequate fit of the model should be obtained to avoid poor or ambiguous results to ensure the adequacy of the employed model in optimizing a response surface (Myers and Montgomery, 2002; Olmez, 2009). The analysis of variance (ANOVA) of regression parameters of the predicted response surface quadratic model using the experimental results is given in Table 5. The R^2 coefficient gave the proportion of the total variation in the response variable accounted for the predictors (x 's) included in the model. A high R^2 value, close to 1, was desirable and a reasonable agreement with the quadratic model to the experimental data (Table 5). The statistical significance of the model was confirmed by the determination coefficients of the model (R^2 values were determined to be 0.9607 and 0.8172, respectively for COD and TSS removal by using aluminium electrodes and 0.9421 and 0.8176 by using steel electrodes). Higher R^2 values (Table 5) for all responses showed that the model could explain the response successfully. It can be concluded that only 3.93% and 5.79% (COD removal for aluminium and steel

electrodes) and 19.28% and 19.24% (TSS removal for aluminium and steel electrodes) of the variability in the response were not explained by the models. It was suggested that R^2 should be at least 0.80 for a good fit of a model (Joglekar and May, 1987; Olmez, 2009). All the R^2 values obtained in the present study for the response variables were higher than 0.80, indicating that the regression models explained the reaction well. Hence, the response surface model developed in this study for predicting COD and TSS removal efficiency was considered to be satisfactory. Actual values were the measured response data for a particular run, and the predicted values were evaluated from the model and generated by using the approximating functions. Fig. 3 shows that the predicted values of the responses from the models accorded well with the observed values; the data points are distributed relatively close to the straight line ($y = x$). Consequently, the models could be used to navigate the design space. These plots indicate adequate agreement between real data and data obtained from the models. It can be seen from Fig. 3 that the statistical significance of the model was further evident from the fact that the values calculated with the predictive equations were very close to the experimental value. This result indicated that the model was adequate for the prediction of each response. As it can be seen from the Table 5, the F-statistics values were higher for COD removals than that of TSS removals for both electrodes. The large F-values indicated that most of the variation in the response could be explained by the regression model. As seen from Table 5, the Fisher's F-test indicated that the values of Prob > F for three factors was less than 0.05. Generally, the values of Prob > F less than 0.05 implied that the model terms are statistically

Table 5. ANOVA results for response surface quadratic model analysis of variance

	Parameter	Source	Sum of Squares	Degree of Freedom	Mean Square	F-Ratio	P-Value
Aluminium electrode	COD	x ₁	104,397	1	104,397	11,03	0,0077
		x ₂	477,095	1	477,095	50,42	0,0000
		x ₃	1230,78	1	1230,78	130,08	0,0000
		x ₁ x ₁	0,211444	1	0,211444	0,02	0,8841
		x ₁ x ₂	127,281	1	127,281	13,45	0,0043
		x ₁ x ₃	17,8503	1	17,8503	1,89	0,1996
		x ₂ x ₂	14,3968	1	14,3968	1,52	0,2456
		x ₂ x ₃	106,945	1	106,945	11,30	0,0072
		x ₃ x ₃	198,996	1	198,996	21,03	0,0010
		Total error	94,6181	10	9,46181		
		Total (corr.)	2412,3	19			
	R ² =96,0777, Adj. R ² =92,5476						
	TSS	x ₁	14,5924	1	14,5924	0,50	0,4963
		x ₂	387,893	1	387,893	13,25	0,0045
		x ₃	23,8632	1	23,8632	0,82	0,3878
		x ₁ x ₁	5,42324	1	5,42324	0,19	0,6760
		x ₁ x ₂	336,442	1	336,442	11,49	0,0069
		x ₁ x ₃	176,156	1	176,156	6,02	0,0341
		x ₂ x ₂	162,139	1	162,139	5,54	0,0404
x ₂ x ₃		17,6418	1	17,6418	0,60	0,4555	
x ₃ x ₃		112,132	1	112,132	3,83	0,0788	
Total error		292,717	10	29,2717			
Total (corr.)		1601,46	19				
R ² =81,7219, Adj. R ² =65,2716							
Steel electrode	COD	x ₁	189,2	1	189,2	22,14	0,0008
		x ₂	527,621	1	527,621	61,74	0,0000
		x ₃	601,476	1	601,476	70,38	0,0000
		x ₁ x ₁	3,68293	1	3,68293	0,43	0,5263
		x ₁ x ₂	1,6562	1	1,6562	0,19	0,6691
		x ₁ x ₃	5,67845	1	5,67845	0,66	0,4340
		x ₂ x ₂	36,5701	1	36,5701	4,28	0,0654
		x ₂ x ₃	14,8512	1	14,8512	1,74	0,2168
		x ₃ x ₃	0,615626	1	0,615626	0,07	0,7938
		Total error	85,4581	10	8,54581		
		Total (corr.)	1475,82	19			
	R ² =94,2095, Adj. R ² =88,998						
	TSS	x ₁	1,77556	1	1,77556	0,22	0,6474
		x ₂	93,7508	1	93,7508	11,74	0,0065
		x ₃	16,4228	1	16,4228	2,06	0,1821
		x ₁ x ₁	85,2814	1	85,2814	10,68	0,0085
		x ₁ x ₂	18,4528	1	18,4528	2,31	0,1595
		x ₁ x ₃	22,8826	1	22,8826	2,87	0,1214
		x ₂ x ₂	0,229091	1	0,229091	0,03	0,8689
x ₂ x ₃		51,3591	1	51,3591	6,43	0,0296	
x ₃ x ₃		36,9362	1	36,9362	4,63	0,0570	
Total error		79,8579	10	7,98579			
Total (corr.)		437,819	19				
R ² =81,7601, Adj. R ² =65,3441							

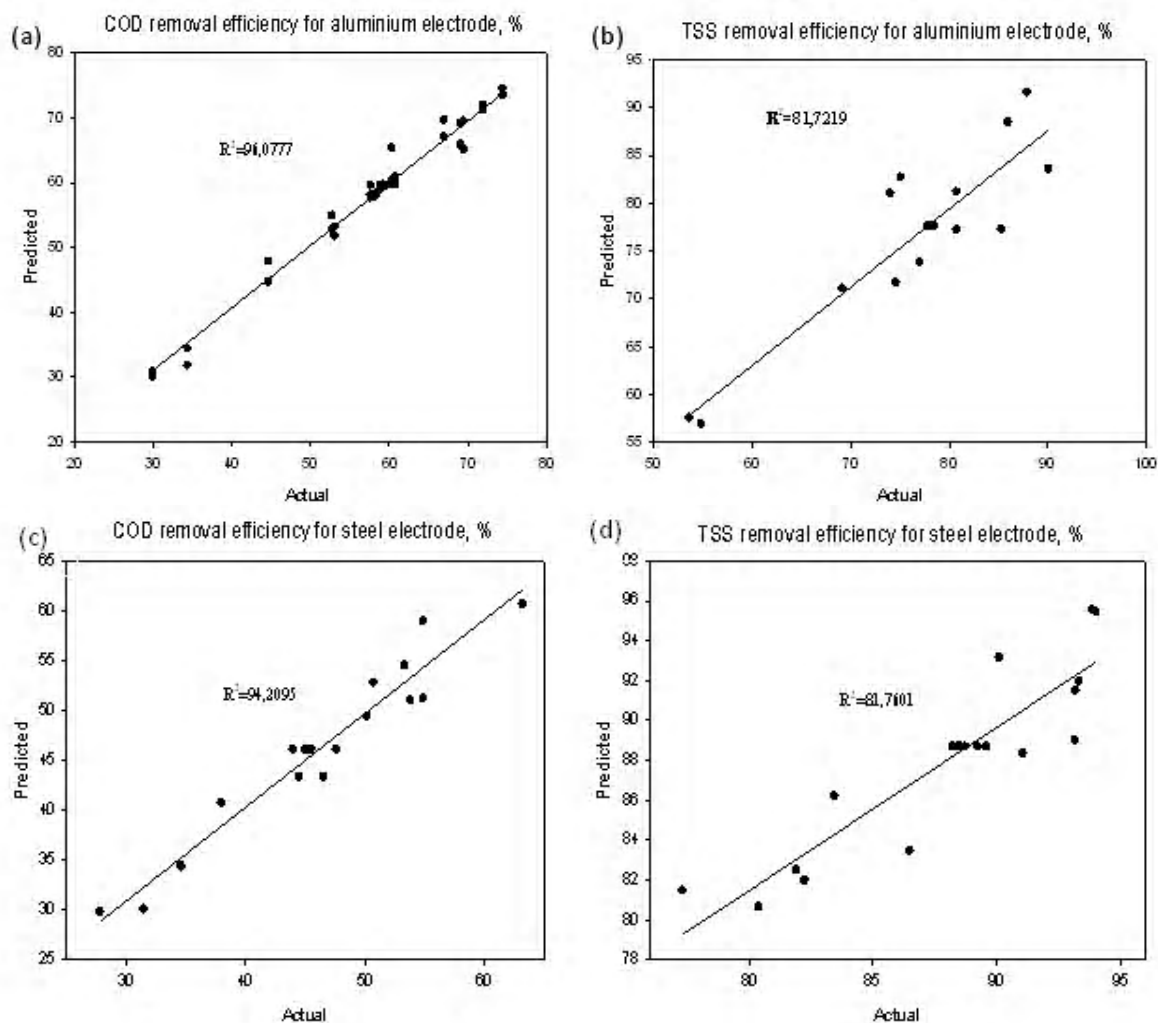


Fig. 3. Predicted versus actual values plot for (a) COD removal for aluminium electrode, (b) TSS removal for aluminium electrode, (c) COD removal for steel electrode and (d) TSS removal for steel electrode

significant, whereas the values greater than 0.1 indicate that the model terms are not significant (Güven *et al.*, 2008; Korbahti and Rauf, 2008; Arslan-Alaton *et al.*, 2009; Zhang *et al.*, 2010). The factors with Prob > F values greater than 0.1 should be excluded from the RSM model. As a result, it can be concluded that none of the factors (x_1 , x_2 , x_3) would be excluded from the RSM model for COD or TSS removal from tannery wastewater by electrocoagulation using aluminium and steel electrodes.

The response surface plots obtained from the software were given in Fig. 4 and Fig. 5. These plots provide a three-dimensional view of the COD and TSS removals surface with different combinations of independent variables. As shown in Figure 4 and 5, all response surface plots have clear peaks. These peaks can be explained as the optimum conditions for

maximum values of the responses attributed to all variables, pH, current density, and electrolysis time in the design space. Moving away from the points shows reduction in removal efficiencies, meaning that neither increase nor decrease in any of the tested variables is desired. It can be seen from Fig. 4 and Fig. 5 that, electrolysis time has a positive effect on COD and TSS removal from tannery wastewater by electrocoagulation. As shown in Fig. 4 that current density has also a positive effect. An increase in the current density improves the removal efficiencies up to an optimum value.

As confirmed by ANOVA results, both COD and TSS removal models validated by using Statgraphics Centurion XVI.I software programme were determined to be linear functions of initial pH (x_1), current density (x_2) and operating time (x_3), and quadratic functions of

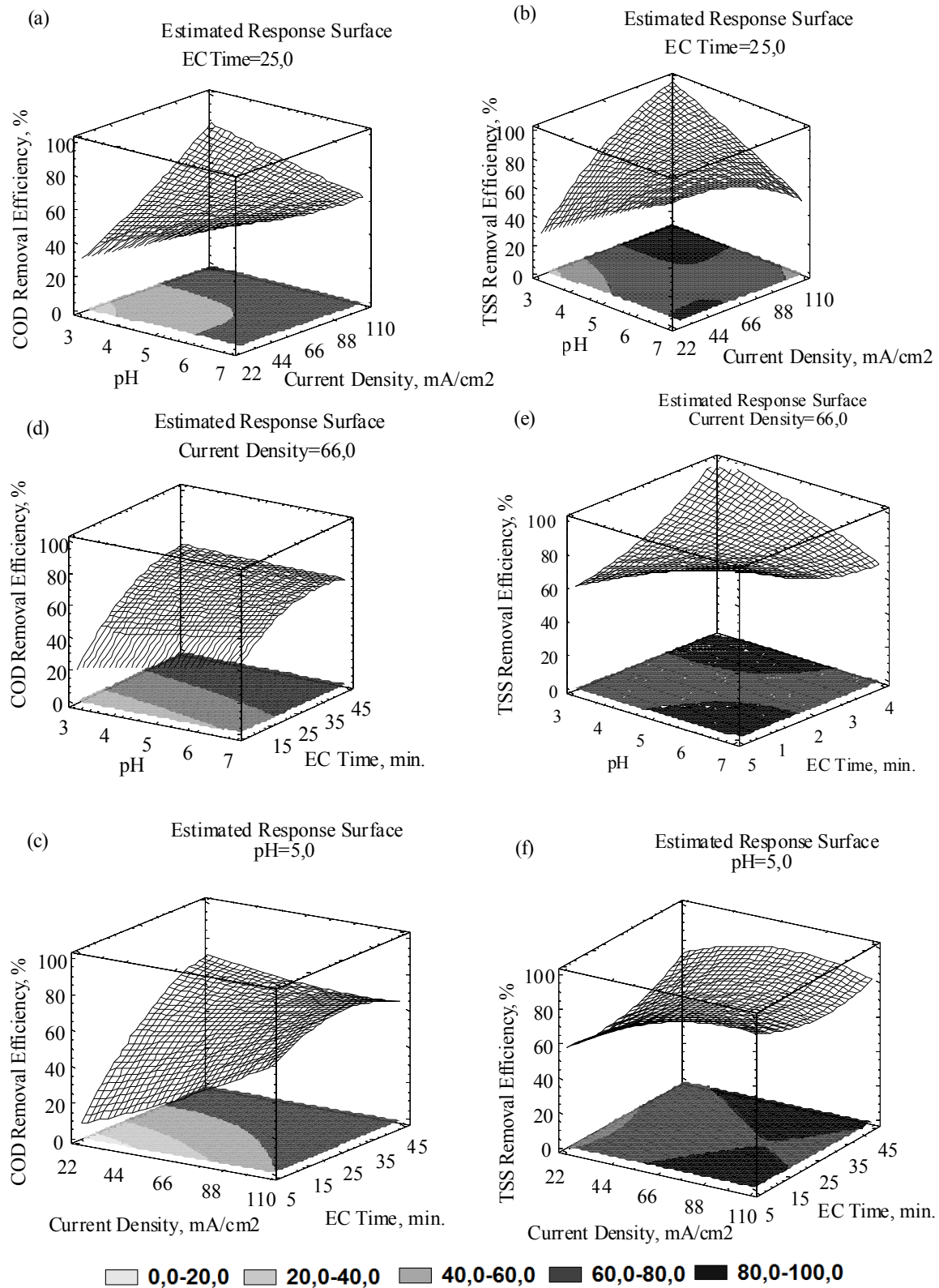


Fig. 3. Effects of the variables on COD and TSS removal efficiencies for aluminium electrodes

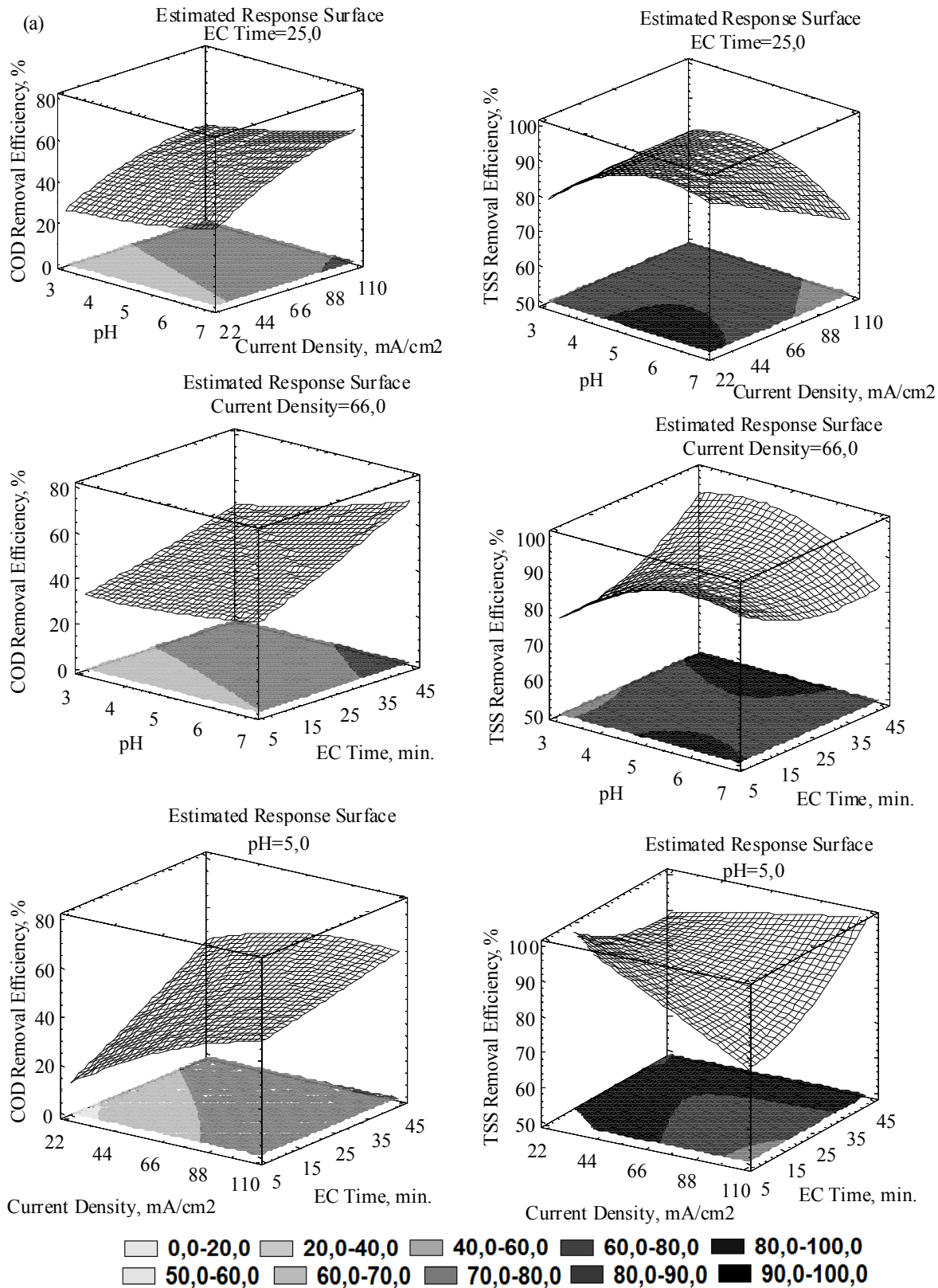


Fig. 4. Effects of the variables on COD and TSS removal efficiencies for steel electrodes

Table 6. Regression coefficients for aluminium and steel electrodes

<i>Coefficient</i>	Aluminium Electrode		Steel Electrode	
	<i>COD</i>	<i>TSS</i>	<i>COD</i>	<i>TSS</i>
	<i>Estimate</i>	<i>Estimate</i>	<i>Estimate</i>	<i>Estimate</i>
constant	-105,892	-133,364	3,15054	27,4924
x ₁	17,338	36,7856	-3,85977	27,5345
x ₂	1,36385	2,55899	0,641358	-0,026751
x ₃	4,12746	1,85797	0,522386	-0,41921
x ₁ x ₁	0,09171	-0,464432	0,382727	-1,8417
x ₁ x ₂	-0,18131	-0,294773	0,0206818	-0,069034
x ₁ x ₃	-0,14937	-0,46925	0,08425	-0,169125
x ₂ x ₂	0,001563	-0,005247	-0,0024918	-0,000197
x ₂ x ₃	-0,01662	-0,00675	-0,0061932	0,011517
x ₃ x ₃	-0,02813	0,021118	0,0015648	0,012121

Table 7. Optimum results for COD and TSS removal for aluminium and steel electrodes

Conditions		Responses removal (%)
Aluminium Electrodes	COD Optimization (x ₁ =3.0; x ₂ =11.0; x ₃ = 32.9)	
	Model prediction results	86.51
	Laboratory results	82.20
	Error	4.31
	Standart deviation	±3.047
	TSS Optimization (x ₁ =3.0; x ₂ =93.1; x ₃ = 45)	
	Model prediction results	100.00
	Laboratory results	85.50
	Error	14.5
	Standart deviation	±10.253
Steel Electrode	COD Optimization (x ₁ =7.0; x ₂ =79.9; x ₃ = 45)	
	Model prediction results	72.74
	Laboratory results	67.40
	Error	5.34
	Standart deviation	±3.775
	TSS Optimization (x ₁ =3.3; x ₂ =109.5; x ₃ = 45)	
	Model prediction results	100.00
	Laboratory results	86.20
	Error	13.8
	Standart deviation	±9.758

Table 8. Results of the operational cost analysis for EC process in optimized conditions

Electrode	COD Removal %	ENC (kWh/m³)	ELC (kg/m³)	OC (€/m³)
Al	82.2	4.56	1.53	2.92
Steel	67.4	4.53	4.72	8.18

the interactions between these three parameters, as represented by Eqs. (3) - (6). The interaction effect between current density and pH, presented the most significant effect on the COD removal by aluminium electrodes ($p=0.043$). As reported in Table 6, the current density and its interaction with pH have the most significant effect on the TSS removal ($p=0.007$). It can be observed that the interaction between pH and electrolysis time has a significant effect ($p=0.0341$) on TSS removal by aluminium electrodes. Electrolysis time affects the production of aluminium ions from aluminium electrode.

$$\text{COD Removal Efficiency for Al Electrode (\%)} = -105,89 + 17,34x_1 + 1,36x_2 + 4,12x_3 + 0,09x_1^2 - 0,18x_1x_2 - 0,15x_1x_3 - 0,02x_2x_3 - 0,03x_3^2 \quad (3)$$

$$\text{TSS Removal Efficiency for Al Electrode (\%)} = -133,364 + 36,78x_1 + 2,55x_2 + 1,85x_3 - 0,46x_1^2 - 0,29x_1x_2 - 0,47x_1x_3 + 0,02x_3^2 \quad (4)$$

$$\text{COD Removal Efficiency for Steel Electrode (\%)} = 3,15 - 3,86x_1 + 0,64x_2 + 0,52x_3 + 0,38x_1^2 + 0,02x_1x_2 + 0,08x_1x_3 \quad (5)$$

$$\text{TSS Removal Efficiency for Steel Electrode (\%)} = 27,49 + 27,53x_1 - 0,03x_2 - 0,42x_3 - 1,84x_1^2 - 0,07x_1x_2 - 0,17x_1x_3 + 0,01x_2x_3 + 0,01x_3^2 \quad (6)$$

Numerical optimization was used to determine the optimum process parameters for maximum COD and TSS removal. Based on response surface and desirability functions, the optimum conditions for COD and TSS removals were obtained. In order to confirm the accuracy of the predicted models and the reliability of the optimum combination, an additional experiment was carried out at optimum conditions. Optimum results for COD and TSS removal for aluminium and steel electrodes were given in Table 7. The removal efficiencies obtained by experimental studies in optimized conditions were found to be very close to the values predicted by the model. COD removal efficiencies achieved in optimized conditions by experimental study were found to be 82.2% and 67.4% using aluminium and steel electrodes, respectively, whereas TSS removal efficiencies were determined to be 85.5% and 86.2% using aluminium and steel electrodes, respectively. The low error in the experimental and predicted values indicated good agreement of the results achieved from models and experiments. These results confirm that RSM is a powerful tool for optimizing the operational conditions of electrocoagulation for COD and TSS removals.

The amount of energy consumption and the amount of electrode material are two important

parameters in the EC process that should be taken into account in order to estimate the EC reactor operational costs (OC) such as € per m^3 of the treated tannery effluent (Eq. 7).

$$OC = aENC + bELC \quad (7)$$

The first term of Eq. 15 evaluates the electrical operational cost, where the electrical energy consumed is calculated in kWh per m^3 of the treated tannery effluent and the electrical energy price (EEP) is calculated in € per kWh. The second term in Eq. 7 estimates the material cost of the EC process, where the maximum possible mass of aluminium and steel, theoretically dissolved from the anode is considered per m^3 of treated tannery effluent and the electrode material price (EMP) is given in € per kg of aluminium and steel.

The prices for electrical energy and electrode material in the Turkish market for July 2012 were 0.088 €/kWh and 1.65 €/kg, respectively. Costs for electrical energy (kWh/ m^3) in Eq. (8) and electrode consumptions (kg/ m^3) were calculated from Faraday's Law in Eq. (9):

$$ENC = \frac{U \cdot i \cdot t_{EC}}{v} \quad (8)$$

$$ELC = \frac{i \cdot t_{EC} \cdot M_w}{z \cdot F \cdot v} \quad (9)$$

where U is cell voltage (V), i is current (A), t_{EC} is operating time (s) and v is volume (m^3) of the wastewater, M_w is molecular mass of aluminium or steel, z is number of electron transferred for aluminium and steel electrodes, respectively and F is Faraday's constant (96487 C/mol) (Gengec *et al.*, 2012). It should be noted that the cost for chemical consumption for pH adjustment was ignored.

The amount of electricity consumption and electrodes mass depletion are compared in Table 8 for both electrodes at optimized conditions. This mass depletion was calculated by subtracting the weight of the electrodes taken at the end of experiment from the weight before the experiments of the same electrodes. As it is shown, the amounts of electrodes mass depletion for steel electrode were higher than that of aluminium electrode in the same operational conditions. In comparison with the operational cost of EC method with steel and aluminium electrodes, EC treatment with steel electrodes is evidently more economical.

CONCLUSION

Electrocoagulation could be assessed as a possible technique for reduction of COD and TSS concentration in the treatment of tannery wastewater. The treatment efficiency was found to be function of the initial pH,

applied current density and electrolysis time. Under optimal values of process parameters, 82.2% COD, 85.5% TSS removal efficiencies for aluminium electrodes and 67.4% COD, 86.2% TSS removal efficiencies for steel electrodes were obtained. Electrocoagulation was strongly enhanced at aluminium surfaces in comparison with steel electrodes in COD removal. But there was no significant difference in TSS removal. In comparison with the operational cost of EC method with steel and aluminium electrodes, EC treatment by using steel electrodes is evidently more economical. The response surface methodology developed in this study showed the presence of a high correlation between experimental and predicted values. Analysis of variance showed a high coefficient of determination value thus ensuring a satisfactory adjustment of the second-order regression model with the experimental data. The effect pH on COD removal by aluminium electrodes is much less important than that of current density and reaction time. The interaction effect on COD removal between current density and pH and current density and time is significant. The interaction effect between the variables on TSS removal was negligible. Consequently; even though aluminium electrodes provide higher COD removal efficiencies, on account of operational cost, steel electrodes should be preferred.

REFERENCES

- Abdelwahab, O., Amin, N. K. and El-Ashtoukhy, E. S. Z. (2009). Electrochemical removal of phenol from oil refinery wastewater. *J. Hazard. Mater.*, **163**, 711–716.
- Adhoum, N. and Monser, L. (2004). Decolourization and removal of phenolic compounds from olive mill wastewater by electrocoagulation. *Chem. Eng. Process.*, **43** (10), 1281–1287.
- Adhoum, N., Monser, L., Bellakhal, N. and Belgaid, J. E. (2004). Treatment of electroplating wastewater containing Cu^{2+} , Zn^{2+} and Cr(VI) by electrocoagulation. *J. Hazard. Mater.*, **112** (3), 207–213.
- APHA, (2005). Standard Methods for the Examination of Water and Wastewater, 21st ed., AWWA, WPCF, Washington DC: American Public Health Association.
- Arslan-Alaton, I., Kobya, M., Akyol, A. and Bayramolu, M. (2009). Electrocoagulation of azo dye production wastewater with iron electrodes: Process evaluation by multi-response central composite design. *Color. Technol.*, **125**, 234–241.
- Asselin, M., Drogui, P., Brar, S.K., Benmoussab, H. and Blais, J. F. (2008). Organics removal in oily bilgewater by electrocoagulation process. *J. Hazard. Mater.*, **151**, 446–455.
- Babu, R., Bhadrinarayana, N. S., Meera Sheriffa Begum K. M. and Anantharaman, N. 2007. Treatment of tannery wastewater by electrocoagulation. *J. Univ. Chem. Technol. Metal.*, **42** (2), 201–206.
- Bayramoglu, M., Eyvaz, M. and Kobya, M. (2007). Treatment of the textile wastewater by electrocoagulation: Economical evaluation. *Chem. Eng. J.*, **128** (2–3), 155–161.
- Behbahani, M., Alavi Moghaddam, M. R. and Arami, M. (2011). A Comparison Between Aluminum and Iron Electrodes on Removal of Phosphate from Aqueous Solutions by Electrocoagulation Process. *Int. J. Environ. Res.*, **5** (2), 403–412.
- Benhadji, R. A., Ahmed, M. T. and Maachi, R. (2011). Electrocoagulation and effect of cathode materials on the removal of pollutants from tannery wastewater. *Desalination*, **277**, 128–134.
- Bukhari, A. A. (2008). Investigation of the electrocoagulation treatment process for the removal of total suspended solids and turbidity from municipal wastewater. *Bioresour. Technol.*, **99**, 914–921.
- Chavalparit, O. and Ongwandee, M. (2009). Optimizing electrocoagulation process for the treatment of biodiesel wastewater using response surface methodology. *J. Environ. Sci.*, **21**, 1491–1496.
- Chen, G. H. (2004). Electrochemical technologies in wastewater treatment. *Sep. Purif. Technol.*, **38**, 11–41.
- Chen, X., Chen, G. and Yue, P. L. (2002). Novel electrode system for electroflotation wastewater. *Environ. Sci. Technol.*, **36**, 778–783.
- Costa, C. R. and Olivi, P. (2009). Effect of chloride concentration on the electrochemical treatment of a synthetic tannery wastewater. *Electrochim. Acta*, **54**, 2046–2052.
- Daneshvar, N., Oladegaragoze, A. and Djafarzadeh, N. (2006). Decolorization of basic dye solutions by electrocoagulation: an investigation of the effect of operational parameters. *J. Hazard. Mater.*, **129**, 116–122.
- Dermentzis, K., Christoforidis, A. and Valsamidou, E. (2011). Removal of nickel, copper, zinc and chromium from synthetic and industrial wastewater by electrocoagulation. *I. J. Environ. Sci.*, **1** (5), 697–710.
- Di Iaconi, C., Lopez, A., Ramadori, R., Di Pinto, A. C. and Passino, R. (2002). Combined chemical and biological degradation of tannery wastewater by a periodic submerged filter (SBBR). *Water Res.*, **36**, 2205–2214.
- Do, J. S. and Chen, M. L. (1994). Decolorization of dye-containing solutions by electrocoagulation. *J. Appl. Electrochem.*, **24**, 785–790.
- El-Naas, M. H., Al-Zuhair, S., Al-Lobaney, A. and Makhlof, S. (2009). Assessment of electrocoagulation for the treatment of petroleum refinery wastewater. *J. Environ. Manage.*, **91**, 180–185.
- Emamjomeh, M. M. and Sivakumar, M. (2009). Review of pollutants removed by electrocoagulation and electrocoagulation/flotation processes. *J. Environ. Manage.*, **90**, 1663–1679.

- Feng, J. W., Sun, Y. B., Zheng, Z., Zhang, J. B., Li, S. and Tian, Y. C. (2007). Treatment of tannery wastewater by electrocoagulation. *J. Environ. Sci.*, **19**, 1409–1415.
- Gengec, E., Kobya, M., Demirbas, E., Akyol, A. and Oktor, K. (2012). Optimization of baker's yeast wastewater using response surface methodology by electrocoagulation. *Desalination*, **286**, 200–209.
- Golder, A. K., Hridaya, N., Samanta, A. N. and Ray, S. (2005). Electrocoagulation of methylene blue and eosin yellowish using mild steel electrodes. *J. Hazard. Mater.*, **127 (1-3)**, 134–140.
- Gupta, S. and Babu, B. V. (2009). Removal of toxic metal Cr (VI) from aqueous solutions using sawdust as adsorbent: Equilibrium, kinetics and regeneration studies. *Chem. Eng. J.*, **150**, 352–365.
- Güven, G., Perendeci, A. and Tanyolac, A. (2008). Electrochemical treatment of deproteinated whey wastewater and optimization of treatment conditions with response surface methodology. *J. Hazard. Mater.*, **157**, 69–78.
- Holt, P. K., Barton, G. W., Wark, M. and Mitchell, C. A. (2002). A quantitative comparison between chemical dosing and electrocoagulation. *Colloid. Surface A.*, **211 (2-3)**, 233–248.
- Hu, C., Lo, S., Kuan, W. and Lee, Y. (2008). Treatment of high fluoride-content wastewater by continuous electrocoagulation–flotation system with bipolar aluminum electrodes. *Separ. Purif. Tech.*, **60**, 1–5.
- Hu, C. Y., Lo, S. L. and Kuan, W. H. (2003). Effect of co-existing anions on fluoride removal in electrocoagulation (EC) process using aluminum electrodes. *Water Res.*, **37**, 4513–4523.
- Ilhan, F., Kurt, U., Apaydin, O. and Gonullu, M. T. (2008). Treatment of leachate by electrocoagulation using aluminum and iron electrodes. *Environ. Eng. Sci.*, **154**, 381–389.
- Irdemez, S., Demircioğlu, N. and Yildiz, Y. S. (2006). The effects of pH on phosphate removal from wastewater by electrocoagulation with iron plate electrodes. *J. Hazard. Mater.*, **137 (2)**, 1231–1235.
- Joglekar, A. M. and May, A. T. (1987). Product excellence through design of experiments. *Cereal Foods World*, **32**, 857–868.
- Kabdaply, I., Arslan-Alaton, I., Ölmez-Hancı, T. and Tünay, O. (2012). Electrocoagulation applications for industrial wastewaters: a critical review. *Environ. Technol. Reviews*, **1 (1)**, 2–45.
- Katal, R. and Pahlavanzadeh, H. (2011). Influence of different combinations of aluminum and iron electrode on electrocoagulation efficiency: Application to the treatment of paper mill wastewater. *Desalination*, **265**, 199–205.
- Khansorthong, S. and Hunsom, M. (2009). Remediation of wastewater from pulp and paper mill industry by the electrochemical technique. *Chem. Eng. J.*, **151**, 228–234.
- Khatibikamal, V., Torabian, A., Janpoor, F. and Hoshyaripour, G. (2010). Fluoride removal from industrial wastewater using electrocoagulation and its adsorption kinetics. *J. Hazard. Mater.*, **179**, 276–280.
- Kobya, M., Can, O. T. and Bayramoglu, M. (2003). Treatment of textile wastewaters by electrocoagulation using iron and aluminum electrodes. *J. Hazard. Mater.*, **100**, 163–178.
- Kobya, M., Hiz, H., Senturk, E., Aydinler, C. and Demirbas, E. (2006). Treatment of potato chips manufacturing wastewater by electrocoagulation. *Desalination*, **190**, 201–211.
- Koparal, A. S., Yildiz, Y. Ş., Keskinler, B. and Demircioğlu, N. (2008). Effect of initial pH on the removal of humic substances from wastewater by electrocoagulation. *Separ. Purif. Tech.*, **59**, 175–182.
- Korbahti, B. K. and Rauf, M. A. (2008). Response surface methodology (RSM) analysis of photoinduced decoloration of toluidine blue. *Chem. Eng. J.*, **136 (1)**, 25–30.
- Kushwaha, J. P., Srivastava, V. C. and Mall, I. D. (2010). Organics removal from dairy wastewater by electrochemical treatment and residue disposal. *Sep. Purif. Technol.*, **76**, 198–205.
- Labanowska, J., Pallier, V. and Feuillade-Cathalifaud, G. (2010). Study of organic matter during coagulation and electrocoagulation processes: Application to a stabilized landfill leachate. *J. Hazard. Mater.*, **179**, 166–172.
- Lefebvre, O. and Moletta, R. (2006). Treatment of organic pollution in industrial saline wastewater: A literature review. *Water Res.*, **40 (20)**, 3671–3682.
- Muruganathan, M., Raju G. B. and Prabhakar, S. (2004). Removal of sulfide, sulfate and sulfite ions by electro coagulation. *J. Hazard. Mater.*, **109 (1-3)**, 37–44.
- Myers, R. H. and Montgomery D. C. (2002). *Response Surface Methodology: Process and Product Optimization using Designed Experiments*. (USA: John Wiley & Sons)
- Nouri, J., Mahvi, A.H. and Bazrafshan, E. (2010). Application of electrocoagulation process in removal of zinc and copper from aqueous solutions by aluminum electrodes. *Int. J. Environ. Res.*, **4**, 201–208.
- Nourouzi, M. M., Chuah, T. G. and Choong, T. S. Y. (2011). Optimisation of reactive dye removal by sequential electrocoagulation–flocculation method: Comparing ANN and RSM prediction. *Water Sci. Technol.*, **63 (5)**, 984–994.
- Ölmez, T. (2009). The optimization of Cr(VI) reduction and removal by electrocoagulation using response surface methodology. *J. Hazard. Mater.*, **162**, 1371–1378.
- Rodrigo, M. A., Cañizares, P., Buitrón, C. and Sáez, C. (2010). Electrochemical technologies for the regeneration of urban wastewaters. *Electrochim. Acta*, **55**, 8160–8164.

- Song, Z., Williams, C. J. and Edyvean, R. G. J. (2004). Treatment of tannery wastewater by chemical coagulation. *Desalination*, **164** (3), 249–259.
- Tchamango, S., Nansou-Njiki, C. P., Ngameni, E., Hadjiev, D. and Darchen, A. (2010). Treatment of dairy effluents by electrocoagulation using aluminium electrodes. *Sci. Total Environ.*, **408**, 947-952.
- Tezcan, U. U., Koparal, A. S. and Bakir Ogutveren, U. (2009). Electrocoagulation of vegetable oil refinery wastewater using aluminum electrodes. *J. Environ. Manage.*, **90**, 428-433.
- Tir, M. and Moulai-Mostefa, N. (2008). Optimization of oil removal from oily wastewater by electrocoagulation using response surface method. *J. Hazard. Mater.*, **158**, 107–115.
- Top, S., Sekman, E., Hoşver, S. and Bilgili, M. S. (2011). Characterization and electrocoagulative treatment of nanofiltration concentrate of a full-scale landfill leachate treatment plant. *Desalination*, **268**, 158–162.
- Vasudevan, S., Lakshmi, J., Jayaraj, J. and Sozhan, G. (2009). Remediation of phosphate- contaminated water by electrocoagulation with aluminium, aluminium alloy and mild steel anodes. *J. Hazard. Mater.*, **164** (2-3), 1480-1486.
- Veli, S., Ozturk, T. and Dimoglo, A. (2008). Treatment of municipal solid wastes leachate by means of chemical- and electro-coagulation. *Sep. Purif. Technol.*, **61**, 82–88.
- Vik, E. A., Carlson, D. A., Eikum, A. S. and Gjessing, E. T. (1984). Electrocoagulation of potable water. *Water Res.*, **18**, 1355–1360.
- Wang, C. T., Chou, W. L. and Huang, K. Y. (2010). Treatment of polyvinyl alcohol from aqueous solution via electrocoagulation. *Sep. Sci. Technol.*, **45** (2), 212-220.
- Wang, H. M., Shang, C., Cheung, Y. K. and Chen, G. (2002). Chloride Assisted Electrochemical Disinfection, paper presented at the Eighth Mainland-Taiwan Environmental Protection Conference, Tsin Chu, Taiwan.
- Yang, C. L. (2007). Electrochemical coagulation for oily water demulsification. *Sep. Purif. Technol.*, **54**, 388–395.
- Yavuz, Y., Koparal, A. S. and Ogutveren, U. B. (2010). Treatment of petroleum refinery wastewater by electrochemical methods. *Desalination*, **258**, 201–205.
- Yýlđýz, Y. S., Koparal, A. S. and Keskinler, B. (2008). Effect of initial pH and supporting electrolyte on the treatment of water containing high concentration of humic substances by electrocoagulation. *Chem. Eng. J.*, **138**, 63–72.
- Zaroual, Z., Chaair, H., Essadki, A. H., El Ass, K. and Azzi, M. (2009). Optimizing the removal of trivalent chromium by electrocoagulation using experimental design. *Chem. Eng. J.*, **148** (2-3), 488-495.
- Zhang, H., Li, Y., Wu, X., Zhang, Y. and Zhang, D. (2010). Application of response surface methodology to the treatment landfill leachate in a three-dimensional electrochemical reactor. *Waste Manage.*, **30**, 2096–2102.