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The optimization and modeling of PCP wastewater using response surface methodology by electrocoagulation process

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ABSTRACT

In this study, electrocoagulation process was performed using Al and Fe electrodes for personal care product (PCP) industry wastewater treatment. Response surface methodology approach using Central Composite Design was applied to develop a mathematical model and optimize process parameters (initial pH, current density and electrolysis time) for chemical oxygen demand (COD) and total suspended solids (TSS). The predicted values of models obtained using RSM were in good agreement with experimental data. The optimum conditions for the COD removal were found to be pH of 8.03, current density of 58 mA/cm^2, electrolysis time of 33 with Al electrodes, whereas the optimum conditions were pH of 5.9, current density of 75 mA/cm^2, electrolysis time of 45 min with Fe electrodes. Under optimum conditions, 97.09% COD removal was obtained using Al electrodes and 98.76% COD removal was obtained using Fe electrodes. The operating costs for the COD removal from PCP wastewater by electrocoagulation process using Al and Fe electrodes at optimized conditions were calculated to be 3.75 and 3.86 €/m^3, respectively. Additionally, the sludge samples formed in the process was characterized by Fourier transform infrared spectroscopy (FT-IR) analysis. According to FT-IR results, pollutants in PCP wastewater were linked to $Al(OH)_3$ and $Fe(OH)_3$ compounds.

Keywords: PCP wastewater; Electrocoagulation; RSM; Cost analysis; Sludge characterization

1. Introduction

During last decades, the focus of environment and health research has partly turned from conventional pollutants (e.g., aromatic hydrocarbons) to so-called emerging pollutants, among which personal care products (PCPs) are particularly one of the most important groups [1]. PCP industry includes various manufactured products (shampoo, shower gel, body lotion etc.). Therefore, PCP wastewater is characterized by high levels of COD content, dissolved and suspended solids, oil/grease, and phosphates [2,3]. Additionally, PCP wastewater contains compounds that are not easily biodegradable (e.g., galaxolide, tonalide, ketone and xylene) and these are partially removed in conventional biological wastewater treatment plants [2]. PCP wastewater has a low BOD_5/COD ratio [2], thus physical and chemical treatment processes such as coagulation/flocculation, fenton, electrocoagulation, electro-fenton are frequently used to remove organic pollutants in this type of wastewater [2,4,5]. Furthermore, several studies have identified PCP wastewater as a pollutant for surface water and groundwater resources [6].

Electrocoagulation (EC) is a novel technique used for wastewater treatment [7–10] due to its advantages in comparison to conventional treatment processes. The EC process is easy and feasible, and in addition to having short operation time, no additional reagent, low sludge production and operation cost [11]. Thus, this process is also preferred in treatment of wastewater with different characteristics. In addition to low operational cost, installation and materials used in the EC process are also cost effective.

An electric current is applied to the anode and the cathode in a reactor for the EC process. In this process, electrodes (Al or Fe) are dissolved by electrolysis, while forming a range of coagulant species and metal hydroxides, which destabilize

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and aggregate the colloidal particles, as well as adsorb dissolved pollutants [12]. During treatment of wastewater by the EC process, three successful reactions occur;

- During the electrolytic reactions of electrodes (Al or Fe), coagulants are formed;

  $$Al \rightarrow Al^{+3} + 3e^{-} \tag{1}$$

  In addition, electrolysis of water occurs on the anode and the cathode;

  $$2H_2O + 2e^{-} \rightarrow H_2 + 2OH^{-} \text{ cathodic reaction} \tag{2}$$

  $$2H_2O + 4H^{+} + O_2 + 4e^{-} \text{ anodic reaction} \tag{3}$$

- Destabilization of pollutants, particle suspensions and emulsions;

  $$Al^{+3} + 3e^{-} \rightarrow 3Al \tag{4}$$

  $$Al^{+3} + 3OH^{-} \rightarrow 3Al(OH)_3 \tag{5}$$

- Aggregation of destabilized phase for the formation of flocs.

To optimize wastewater treatment processes, various multivariate statistical models have been used in recent years. Among these multivariate statistical models, RSM is a useful and highly preferred technique to minimize the amount of time needed and the cost of experimental sets. This mathematical model is a technique that utilizes modeling and analysis of a problem that is dependent on numerous variables, provides estimated answers to this problem, and checks the accuracy of the model [13]. RSM designs an optimum multi factor model for EC processes by evaluating the interactions between multiple explanatory variables and one or more response variables, thus reducing the experimental set numbers [14]. CCD is the most commonly used sub-design model of RSM. CCD is a flexible method demonstrating the interaction between variables using a minimized experimental set.

In this study, electrocoagulation experiments were performed for PCP wastewater treatment, using aluminum and iron electrodes. The main objective of the study is to investigate and optimize EC variable parameters such as pH, current density and electrolysis time in removal of chemical oxygen demand (COD) and total suspended solid (TSS) from PCP wastewater via RSM. The EC process' operational cost analyses were also conducted under optimum experimental conditions.

2. Experimental method

2.1. Materials

Real wastewater from a PCP production factory was used in this study. Table 1 shows the characteristics of influent PCP wastewater. Before the EC process, the PCP effluents were preserved and analyzed in accordance with the Standard Methods recommended by the American Public Health Association (APHA) [15].

Table 1
Characterization of influent PCP wastewater

Parameter	Influent values	Analytical method/apparatus
pH	6.44	pH meter Eutech pH 510
COD (mg/L)	13,950	APHA (2005) 5220-D
Chloride (mg/L)	3,650	APHA (2005) 4500-Cl-
Conductivity (mS/cm)	11.45	Conductivity meter Eutech CON 510
TSS (mg/L)	300	APHA (2005) 2540-D

2.2. Experimental setup and procedure

Fig. 1 shows the schematic representation of the experimental EC process apparatus. A laboratory-scale plexiglass EC reactor with 9 cm diameter and 13 cm height was used. Electrode sets (two anodes and two cathodes) with four monopolar (MP) parallel aluminum and iron plates (6 cm width × 11.5 cm length, and 0.1 cm thickness) were conducted. Electrodes having an effective area of 46.2 cm^2 were 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. A 600 mL sample of wastewater was used for each test. Since the salinity of the wastewater samples was found to be sufficient, electrolyte solution was not used. Before each run, electrodes were cleaned according to the method reported by Gengec et al. [16]. All chemicals used in the study were of analytical-reagent grade. Current density in the range of 11–75 mA/cm^2 were applied to the effluent for 45 min. by means of a DC power supply. The clarified effluent sample was pipetted out of the reactor, allowed to settle for a few hours in a polyethylene flask at the end of each set, and then the supernatant liquid was preserved in accordance with the Standard Methods and stored for analysis. Fourier Transform Infrared Spectroscopy (FT-IR, Schimadzu 8900) was used to analyze the sludge formed at the bottom of the flask.

2.3. Experimental design and model development

In this study, the Statgraphics Centurion XVII software programme was used for the statistical design of experiments and data analysis. Adequacy of various model tests (sequential model sum of squares and model summary statistics), analysis of variance (ANOVA), and response surface plotting were performed to establish optimum conditions. The full-factorial CCD based on RSM consisting of 20 experiments was used to optimize and investigate the influence of operating parameters on EC process using iron and aluminum electrodes. The three following operational parameters; were taken as input parameters: (X_1) pH: 5–9, (X_2) J: 11–75 mA/cm^2, and (X_3) t_{EC}: 5–45 min. were taken as input parameters while COD and TSS removal ratios were taken as responses of the system (Y). Coded and actual values of variables of the experimental design matrix are given in Table 2, whereas experimental data for the process are shown in Table 3. Table 4 represents final pH values and sludge volume formed at the end of the experimental sets.

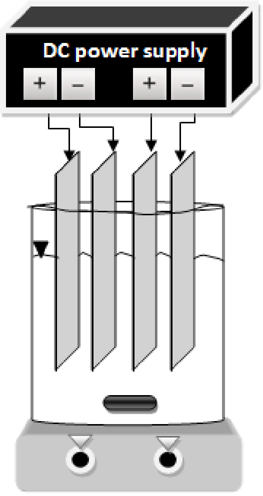

Fig. 1. Schematic diagram of the EC process apparatus.

Table 2
Coded and actual values of variables of the experimental design matrix for electrocoagulation

Factors	Original factor (X)	Coded factors				
		–2	–1	0	+1	+2
pH	X_1	5	6	7	8	9
Current Density (mA/cm^2)	X_2	11	27	43	59	75
Time (min)	X_3	5	15	25	35	45

The ranges and values of the independent variables were determined from the preliminary experiments. For statistical calculations, the operating parameters (X_1, X_2 and X_3) were coded as X_i according to the following relationship:

$$y = f(X_1, X_2, ..., X_n) \pm \varepsilon \tag{6}$$

where y is the response in coded units, f is the response function, X_1, X_2, …, X_n are the independent variables, and ε is the experimental error. RSM-based CCD works with the coded value for process variables. The relation between the coded form and the actual value may be given below:

$$X_i = \frac{X_i - X_{avg}}{\Delta X} \tag{7}$$

where X_i is the actual value of the ith factor in the actual units, X_{avg} is the average of the low and high values for the ith factor, and ΔX represents the step change. To correlate the relationship between independent variables and responses, the second-order polynominal model was selected for further analysis. The generalized mathematical form of second-order polynomial equation is shown below:

$$\begin{aligned} Y = {} & \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{11} X_1^2 + \beta_{22} X_2^2 \\ & + \beta_{33} X_3^2 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 \end{aligned} \tag{8}$$

Table 3
CCD experimental design matrix for the electrocoagulation using Fe and Al electrodes

Run	X_1	X_2	X_3	X_1	X_2	X_3
1	−1	−1	−1	6	27	15
2	1	−1	−1	8	27	15
3	−1	1	−1	6	59	15
4	1	1	−1	8	59	15
5	−1	−1	1	6	27	35
6	1	−1	1	8	27	35
7	−1	1	1	6	59	35
8	1	1	1	8	59	35
9	–2	0	0	5	43	25
10	2	0	0	9	43	25
11	0	–2	0	7	11	25
12	0	2	0	7	75	25
13	0	0	–2	7	43	5
14	0	0	2	7	43	45
15	0	0	0	7	43	25
16	0	0	0	7	43	25
17	0	0	0	7	43	25
18	0	0	0	7	43	25
19	0	0	0	7	43	25
20	0	0	0	7	43	25

Table 4
Experimental data for the electrocoagulation by Fe and Al electrodes

Run	Sludge volume mL/ 0.6 m^3 of wastewater		Final pH	
	Al electrodes	Fe electrodes	Al electrodes	Fe electrodes
1	95	11	8.97	10.9
2	45	22	9.15	12.02
3	135	35	7.2	12.9
4	56	30	9.21	12.71
5	289	40	10.07	12.45
6	127	50	9	12.98
7	187	200	7.91	11.02
8	50	160	9.73	10.95
9	275	200	9.35	11.21
10	50	180	10.23	11.32
11	78	15	9.6	10.62
12	65	80	9.92	9.4
13	40	15	8.16	10.44
14	88	85	9.64	12.72
15	97	30	8.48	12.98
16	156	25	9.64	12.8
17	130	25	9.65	12.85
18	124	27	9.6	12.78
19	140	25	9.59	12.82
20	135	28	9.65	12.82

where Y is the response in coded units, β_0 is a constant, and (β_1, β_2, β_3), (β_{12}, β_{13}, β_{23}), and (β_{11}, β_{22}, β_{33}) are the linear, interactive, and quadratic coefficients, respectively. ANOVA was used to check the adequacy of the developed mathematical model and the determination co-efficient (R^2) was used to express the quality of the fit of the model. Additionally, Fisher F-test was used to express statistical significance of the polynomial model. Model terms were evaluated by the p-value and the F-value.

3. Results and discussion

3.1. Regression analysis and optimization of operating parameters

3.1.1. Electrocoagulation using Al electrodes

A second-order polynomial response surface model was applied to fit the experimental results obtained by CCD. The regression equations obtained for the COD and TSS removal by electrocoagulation using Al electrodes can be presented as follows:

$$\text{COD removal, \%} = -134.458 + 11.2671 \times X_1 + 2.01854 \times X_2 + 7.67718 \times X_3 - 0.717134 \times X_1^2 + 0.159805 \times X_1 \times X_2 - 0.271363 \times X_1 \times X_3 - 0.0293445 \times X_2^2 + 0.00319386 \times X_2 \times X_3 - 0.0854229 \times X_3^2 \quad (9)$$

$$\text{TSS removal, \%} = -20.7938 + 42.2088 \times X_1 - 1.96918 \times X_2 - 0.757733 \times X_3 - 4.49216 \times X_1^2 + 0.322969 \times X_1 \times X_2 + 0.11675 \times X_1 \times X_3 + 0.00605602 \times X_2^2 - 0.0171875 \times X_2 \times X_3 + 0.0263409 \times X_3^2 \quad (10)$$

The results of the ANOVA tests showed that the models were highly significant with low p-values and high F-values [17]. The F-values and corresponding p-values obtained from the model show that the quadratic model is significant for the COD and TSS removal by electrocoagulation using Al electrodes.

It has been reported [18] that positive values of the coefficients of variables in equations indicate the synergistic effect, while negative values indicate antagonistic effect. As it can be seen from the equations, the individual operating variables, such as the initial pH of the solution, the current density and electrolysis time have a net positive effect on COD removal, whereas the current density and electrolysis time have a net negative effect on TSS removal. It was observed that the value of individual operating parameters that have positive coefficients increase by the increase in COD and TSS removal efficiencies, whereas the value of parameters having negative coefficients decrease by the decrease in COD and TSS removal efficiencies. The adequacy of quadratic models was evaluated by constructing diagnostic plots such as predicted vs. actual ones for the experimental data, and the graph is given in Fig. 2. As seen in Fig. 2, the data points lie close to the diagonal line for all graphs, which indicates a good agreement between actual and predicted data. The agreement between the actual and the predicted values of the COD and TSS removal was found to be satisfactory and in accordance with the statistical significance of the quadratic model.

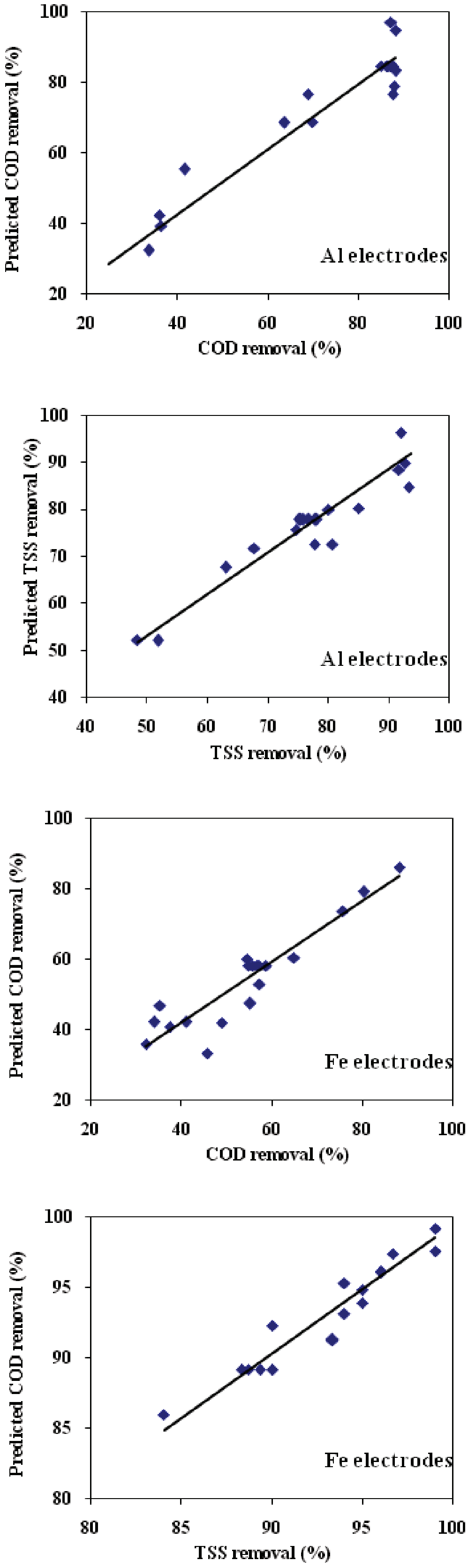

Fig. 2. Predicted vs. actual plots for the removal of COD and TSS.

Significance of the predicted response surface quadratic model for COD and TSS removal by EC process using Al electrodes was analyzed using ANOVA and the results of all experiments performed are shown in Table 5. The higher *F*-values and lower *p*-values ($p < 0.05$) confirm that the developed model is statistically significant [19]. Moreover, the *p*-value (Prob > *F*) related to the *F*-value could be used to determine whether the *F*-value is high enough or not. It is noted [20] that the significance of the variable increases with the increase in the sum of squares (SS) value. Moreover, the *p*-value lower than 0.0001 for the second-order polynomial fitting demonstrated that the model is highly significant and model terms are significant at 95% probability level.

ANOVA results of the response surface quadratic model of the COD and TSS removal are given in Tables 6 and 7, respectively. Model *F*-value is found to be 13.248 with corresponding *p*-value of 0.000188 and high SS value indicating that the model is highly significant and can explain the relationship between response and independent variables for COD removal. It can be concluded that the quadratic and interacting coefficients are not as significant as the linear coefficients. The ANOVA indicated that electrolysis time has the most significant effect on COD removal, followed by current density. However, pH of the solution had an insignificant effect on COD removal. The COD equation adequately represented the relationships among the responses and significant variables. According to the ANOVA results given in Table 6, the quadratic coefficients of electrolysis time and current density had significant effects, whereas the quadratic coefficient of pH has an insignificant effect on COD removal.

Table 5
ANOVA results of regression parameters of the predicted response surface quadratic model

Model	R^2	Adjusted R^2	Sum of squares	Mean square	*F*-value	Prob > F
Al electrodes						
COD	0.92	0.85	9,175.92	1,019.55	13.248	0.000188
TSS	0.88	0.78	2,719.62	302.18	8.528	0.001223
Fe electrodes						
COD	0.85	0.73	3,675.69	408.41	6.818	0.002996
TSS	0.91	0.83	904.18	100.46	3.741	0.025827

Table 6
ANOVA results of the response surface quadratic model of COD removal

Source	Al electrodes						Fe electrodes					
	Sum of squares	*Df*	Mean square	*F*-ratio	*P*-value	Remark	Sum of squares	*Df*	Mean square	*F*-ratio	*P*-value	Remark
Model	9,175.92	9	1,019.55	13.248	0.000188	Significant	3,675.69	9	408.41	6.818	0.002996	Significant
X_1	27.6557	1	27.6557	0.35	0.5651	Not significant	0.0000617809	1	0.0000617809	0.00	0.9992	Not significant
X_2	1,969.36	1	1,969.36	25.20	0.0005	Significant	1,539.93	1	1,539.93	25.71	0.0005	Significant
X_3	4,323.5	1	4,323.5	55.32	<0.0001	Highly significant	587.545	1	587.545	9.81	0.0107	Significant
X_1X_1	12.9305	1	12.9305	0.17	0.6928	Not significant	403.665	1	403.665	6.74	0.0267	Significant
X_1X_2	52.3011	1	52.3011	0.67	0.4324	Not significant	311.513	1	311.513	5.20	0.0457	Significant
X_1X_3	58.9104	1	58.9104	0.75	0.4056	Not significant	99.4708	1	99.4708	1.66	0.2265	Not significant
X_2X_2	1418.89	1	1418.89	18.16	0.0017	Significant	106.484	1	106.484	1.78	0.2120	Not significant
X_2X_3	2.08911	1	2.08911	0.03	0.8734	Not significant	376.662	1	376.662	6.29	0.0310	Significant
X_3X_3	1,834.69	1	1,834.69	23.48	0.0007	Significant	163.881	1	163.881	2.74	0.1291	Not significant
Total error	781.513	10	78.1513				598.967	10	59.8967			
Total (corr.)	1,0022.5	19					4,274.67	19				
R^2	92.2%						R^2	85.98%				

Table 7
ANOVA results of the response surface quadratic model of TSS removal

Source	Al electrodes						Fe electrodes					
	Sum of squares	*Df*	Mean square	*F*-ratio	*P*-value	Remark	Sum of squares	*Df*	Mean square	*F*-ratio	*P*-value	Remark
Model	2,719.62	9	302.18	8.528	0.001223	Significant	904.18	9	100.46	3.741	0.025827	Significant
X_1	240.25	1	240.25	6.78	0.0263	Significant	9.0	1	9.0	3.09	0.1091	Not significant
X_2	600.005	1	600.005	16.93	0.0021	Significant	1.0	1	1.0	0.34	0.5707	Not significant
X_3	650.25	1	650.25	18.35	0.0016	Significant	42.25	1	42.25	14.52	0.0034	Significant
X_1X_1	507.37	1	507.37	14.32	0.0036	Significant	112.328	1	112.328	38.61	0.0001	Significant
X_1X_2	213.624	1	213.624	6.03	0.0339	Significant	29.3914	1	29.3914	10.10	0.0098	Significant
X_1X_3	10.9044	1	10.9044	0.31	0.5913	Not significant	32.0	1	32.0	11.00	0.0078	Significant
X_2X_2	60.4323	1	60.4323	1.71	0.2208	Not significant	10.7966	1	10.7966	3.71	0.0829	Not significant
X_2X_3	60.5	1	60.5	1.71	0.2206	Not significant	16.0574	1	16.0574	5.52	0.0407	Significant
X_3X_3	174.452	1	174.452	4.92	0.0508	Not significant	99.4352	1	99.4352	34.18	0.0002	Significant
Total error	354.346	10	35.4346				29.0933	10	2.90933			
Total (corr.)	3,074.11	19					333.402	19				
R^2	88.47%						R^2	91.27%				

However, the interaction effects between pH and current density, between pH and electrolysis time, and between current density and electrolysis time were insignificant on COD removal. These results confirmed high probability ((Prob > *F*) > 0.1) by means of ANOVA.

As it can be seen from Table 7, ANOVA of the TSS removal by EC process with Al electrodes showed an *F*-value of 8.528 and *p*-value of 0.001223 implying that the model was significant. The ANOVA table obtained from the response surface quadratic model shows that current density and electrolysis time had the most significant effects, whereas the pH of the solution had comparatively less significant effect on TSS removal. ANOVA study also shows that X_1X_1 in quadratic coefficients and X_1X_2 in interaction coefficients had significant effects, whereas X_1X_3 and X_2X_3 in interaction coefficients, and X_2X_2 and X_3X_3 in quadratic coefficients had insignificant effects on the TSS removal.

The model R^2-values should be at least 0.80 to explain good agreement of quadratic fits to navigate the design space [21]. As it can be seen from Table 5, R^2-values of the models obtained from COD and TSS removal by Al electrodes were found to be 0.92 and 0.88, respectively. This indicates that only 8% (COD removal) and 12% (TSS removal) of total variations could not be explained by the model. The results obtained from the EC process with Al electrodes suggested that the mathematical models express the reaction well due to the R^2-values >0.80 for COD and TSS removal.

In this study, a numerical optimization technique was carried out using response surface and desirability functions. According to the CCD results, optimum operating conditions to reach the maximum removal of COD and TSS by EC process using Al and Fe electrodes are given in Table 8. The experimental values were found to be consistent with the predicted ones. Under these conditions, the predicted removal efficiency of COD and TSS for Al and Fe electrodes was determined to be 97.09%, 99.45% and 98.76%, 99.89%, respectively.

Table 8
Optimum operating conditions of the process variables

	Al electrodes		Fe electrodes	
Factor	COD	TSS	COD	TSS
pH	8.03	5.68	5.90	9.0
Current density	58	11	75	75
Time	33	45	45	6.6

3.1.2. Electrocoagulation using Fe electrodes

The regression equations obtained for the COD and TSS removal by electrocoagulation process using Fe electrodes can be presented as follows:

$$\text{COD removal, \%} = -190.471 + 64.0489 \times X_1 + 1.57973 \times X_2 - 2.42989 \times X_3 - 4.00685 \times X_1^2 - 0.390008 \times X_1 \times X_2 + 0.352617 \times X_1 \times X_3 + 0.00803888 \times X_2^2 + 0.0428855 \times X_2 \times X_3 - 0.0255303 \times X_3^2 \quad (11)$$

$$\text{TSS removal, \%} = 229.094 - 30.4927 \times X_1 - 1.26446 \times X_2 - 0.137587 \times X_3 + 2.11367 \times X_1^2 + 0.119797 \times X_1 \times X_2 - 0.2 \times X_1 \times X_3 + 0.00255975 \times X_2^2 + 0.00885469 \times X_2 \times X_3 + 0.0198867 \times X_3^2 \quad (12)$$

ANOVA results indicated that the models were highly significant with low *p*-values and high *F*-values. The *F*-values and corresponding *p*-values obtained from the model show that the quadratic model is significant for COD and TSS removal by electrocoagulation process using Fe electrodes.

Individual operating variables such as initial pH of the solution and current density had a net positive effect, whereas electrolysis time had a net negative effect on COD removal. Furthermore, three operating variables had a net negative effect on TSS removal.

As it can be seen in Tables 6 and 7, the ANOVA of COD and TSS removal by Fe electrodes showed *F*-values of 6.818 and 3.741, respectively. Corresponding *p*-values were determined to be 0.002996 and 0.025827 respectively, implying that the model is significant. Current density and electrolysis time had significant effects on COD removal whereas pH had an insignificant effect. The ANOVA study showed that X_1X_1 in quadratic coefficients, X_1X_2 and X_2X_3 in interaction coefficients had significant effects, whereas X_1X_3 in interaction coefficients and X_2X_2, X_3X_3 in quadratic coefficients had insignificant effects on COD removal. The ANOVA study of TSS removal by Fe electrodes showed that pH and current density had insignificant effects, whereas electrolysis time had a significant effect on TSS removal. It can be concluded from Table 7 that only the quadratic coefficients X_2X_2 have insignificant effects, whereas the other quadratic coefficients and all interactions coefficients have significant effects on TSS removal.

The surface response and contour plots of the quadratic model is given in Figs. 3 and 4. In Figs. 3 and 4, the response surface and the contour plot were developed as a function of two variables within the experimental ranges, while one variable was kept constant.

*R*²-values of the models for COD and TSS removal using Fe electrodes were determined to be 0.85 and 0.91, respectively. This indicated that only 15% (COD removal) and 9% (TSS removal) of total variations could not be explained by the model. The results obtained from the EC process with Fe electrodes suggested that the mathematical models developed in this study for predicting the COD and TSS removal efficiencies may be considered satisfactory.

The high correlation between experimental results and model (predicted) results indicates the reliability of CCD incorporate desirability function method and the function could be effectively used to optimize the operating variables of EC for COD and TSS removal. Table 8 shows the optimized conditions under the specified constraints determined for the highest desirability.

3.2. Sludge characterization by FT-IR

Under the optimum conditions in COD removal, the characteristics of the sludge were analyzed by FT-IR scanning method and the graph of this analysis is given in Fig. 5. FT-IR spectrum gives information about surface chemistry and the functional groups on the sample surface, while the absorption bands and peaks provide evidence for the presence of some surface functional groups. In FT-IR spectra of sludge samples peaks observed at 3,352.14 and 3,334.87 cm^{-1} bands correspond to O-H stretching vibrations [22]. Peaks at 2,853.28 and 2,850.39 cm^{-1} correspond to C-H stretching mode of saturated C-C bonds, representing the presence of hydrocarbons in the sludge [23]. The band at 1,737.75 cm^{-1} in FT-IR spectra of sludge formed at the end of the electrocoagulation process using Fe electrodes probably corresponds to the Na-F bounding [22]. The peaks at 1,595.97 and 1,628.09 bands are

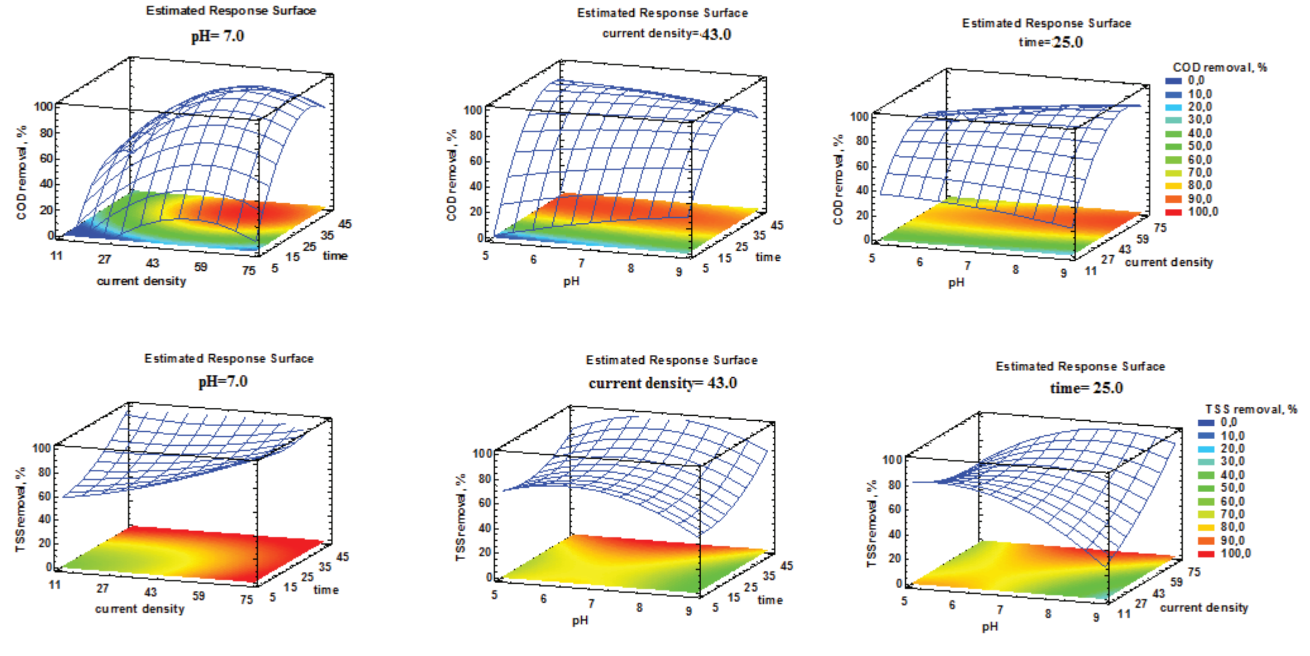

Fig. 3. Three-dimensional response surface graphs for the effects of variables on the COD and TSS removals (Al electrodes).

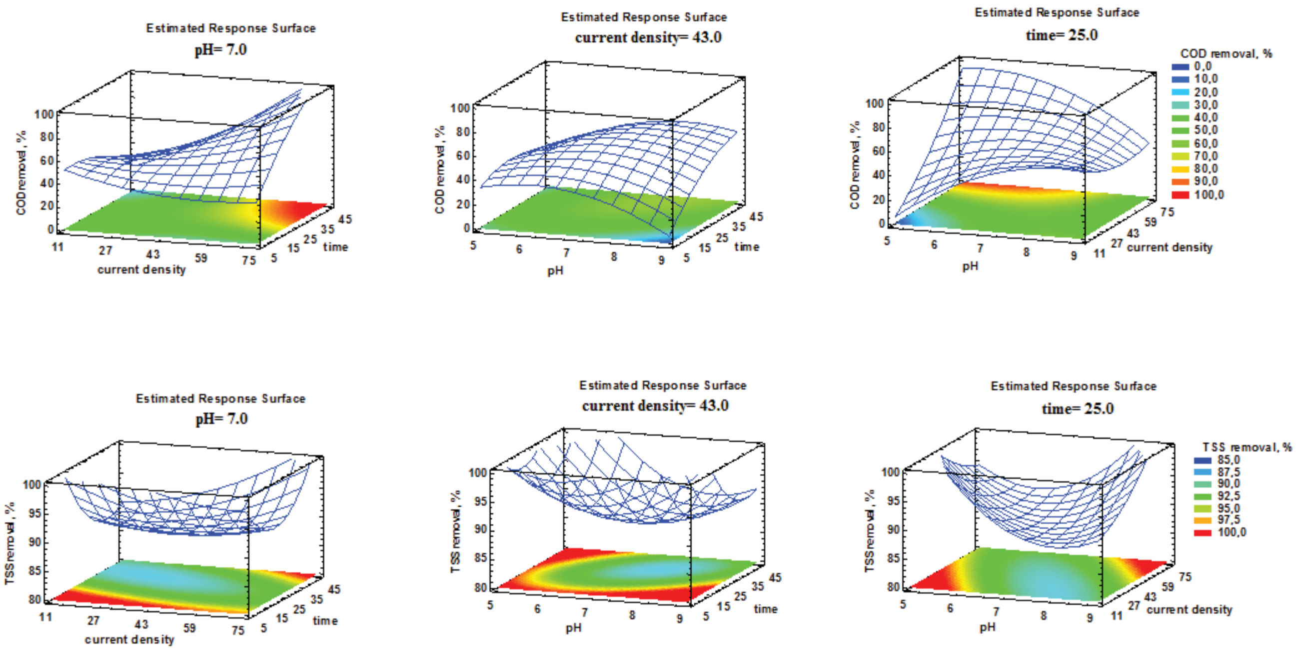

Fig. 4. Three-dimensional response surface graphs for the effects of variables on the COD and TSS removals (Fe electrodes).

likely to be attributed to O-H bending whereas 1,465.50 and 1,455.64 cm^{-1} bands can be assigned to Al-O-H bending vibrations [24]. Carbonyl groups were represented by the peaks of 1,066.43 cm^{-1}, 1,208.82; 1,070.31 and 1,021.98 cm^{-1} [25]. The peak observed at 922.94 cm^{-1} can be attributed to Si-O stretching for sludge generated at the process using Fe electrodes. The bands at 719.54, 719.68 and 782.58 cm^{-1} may be ascribed to the stretching of aromatic C=C [26] for the generated sludge. Peaks of 3,352.14 and 3,334.87 cm^{-1} show presence of M(OH) groups. The obtained FT-IR results highlighted that pollutants in PCP industry wastewater were linked to aluminum hydroxide and iron hydroxide compounds.

3.3. Cost analysis

The amount of energy consumption and the amount of electrode material are two important parameters in the operational cost analysis of the EC process. The operational cost (OC) at optimum conditions was calculated by the following equation:

$$\mathrm{OC} = \mathrm{aENC} + \mathrm{bELC} \tag{13}$$

where aENC (kWh/m^3) denotes the electrical energy consumed, bELC(kg/m^3) estimates the material cost. The electrical energy consumption was calculated using the following equation [16]:

$$\mathrm{ENC} = \frac{U \times i \times t_{\mathrm{EC}}}{v} \tag{14}$$

where U is the applied voltage (V), i is the current (A), t_{EC} is the operating time (s) and v is the volume (m^3) of the wastewater.

Electrode material consumption was calculated using the following equation:

$$\mathrm{ENC} = \frac{i \times t_{\mathrm{EC}} \times M_w}{z \times F \times v} \tag{15}$$

where i is the current (A), t_{EC} is the operating time (s) and v is the volume (m^3) of the wastewater, M_w is the molecular mass of aluminum (26.98 g/mol) or iron (55.84 g/mol), z is the number of electrons transferred ($z = 3$ for aluminum and iron electrodes) and F is the Faraday's constant (96,487 C/mol). Cost of chemicals for adjustment of a desired pH was ignored.

In the optimum conditions in COD removal, operational cost of the EC process using Al and Fe electrodes was found to be 3.75 and 3.86 €/m^3, respectively. It can be concluded that no significant difference was obtained in operational cost of electrocoagulation process by using Al or Fe electrodes.

4. Conclusion

In this study, the performance of the EC process on PCP wastewater was evaluated focusing on the effects of operating parameters such as pH, current density and electrolysis time using Response Surface Methodology coupled with Central Composite Design. The response surface models in the study showed a high correlation between actual and predicted values. The ANOVA showed high determination of coefficient values ($R^2 > 0.80$) ensuring a satisfactory adjustment of the second-order regression models with the experimental data. The optimal values of process parameters (pH: 8.03, current density: 58 mA/cm^2, electrolysis time: 33 min) resulted in 97.09% COD removal using Al electrodes, whereas the optimal values of process parameters (pH: 5.9, current density: 75 mA/cm^2, electrolysis time: 45 min) resulted in 98.76% COD removal using Fe electrodes. No significant difference was obtained in the operational cost of the process when carried out by using Al or Fe electrodes at optimum conditions. The results of this study indicate that an EC process by Al and Fe electrodes is

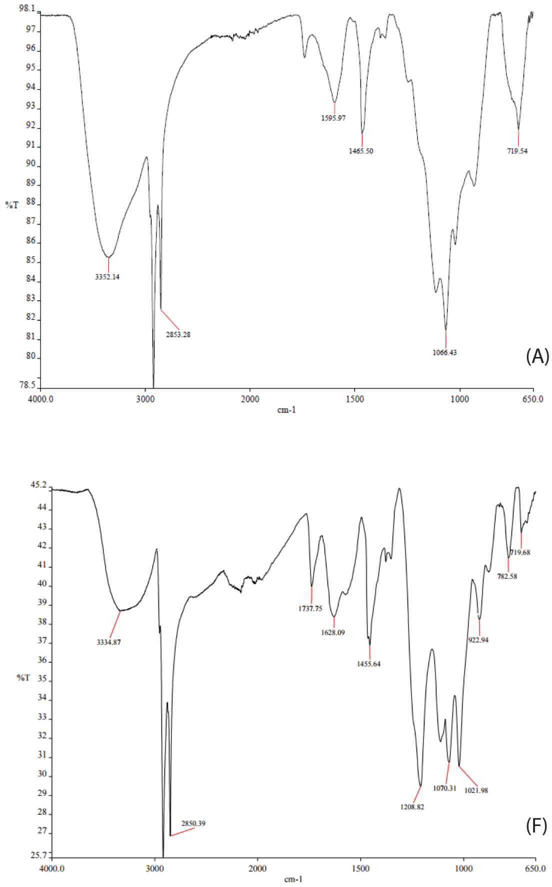

Fig. 5. FT-IR spectrum of the sludge generated in the EC process using Al (A) and Fe (F) electrodes.

applicable as a powerful technique for removal of COD and TSS from PCP wastewater under operating conditions.

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