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Leachate effluent COD removal using electrocoagulation: a response surface methodology (RSM) optimization and modeling

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ABSTRACT

This study focused on electrocoagulation treatment of leachate effluent using aluminum electrodes in a discontinuous system, the modeling and optimization of which were carried out using the response surface methodology (RSM) basing on the central composite design (CCD). Moreover, individual and interaction effects of principal independent factors (current density (X_1), initial pH (X_2), electrolysis time (X_3), and distance between electrodes (X_4)), on chemical oxygen demand (COD) removal efficiency response, were investigated. The obtained results were in good agreement with the predicted ones with correlation factors $R^2_{\text{Dec}} = 0.94$ and $R^2_{\text{Ajusted}} = 0.88$. At the optimal conditions, maximal removal efficiency was achieved for values of chemical oxygen demand (COD), total organic carbon, total nitrogen, and turbidity of 79.8%, 78%, 45.4%, and 99.9%, respectively. The quite good agreement between the experimental values and the predicted results confirms the reliability of the RSM approach in the modeling and optimizing of the leachate treatment using an electrocoagulation process.

Keywords: COD removal; Leachate treatment; Electrocoagulation; Aluminum electrodes; Response surface methodology (RSM); Central composite design (CCD)

1. Introduction

Generally, landfill-percolated water (leachate) is bacteriologically and chemically (mineral and organic pollutants) heavily loaded. Its composition is difficult to predict as it depends on the waste type, the rainfall amount, and the waste degradation level [1].

Because of the presence of a high proportion of refractory and toxic materials, leachate treatment is generally difficult to accomplish and its discharge standards are difficult to meet.

It constitutes a major source of pollution to the landfill surrounding in general and to water resources in particular [2]. Several techniques have been used for leachate treatment, as reported in the literature, such as reverse osmosis, where it was shown that changes in leachate quality could influence the treatment effectiveness [3], biological treatment [4], advanced oxidation techniques [5], and coagulation–flocculation as a pretreatment using iron-based coagulants. The optimum conditions obtained using the response surface methodology (RSM) with polyferric sulfate as the coagulant

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($8\ g\ L^{-1}$ at pH 6) led to a chemical oxygen demand (COD) and turbidity removal of 56.38% and 89.79%, respectively [6].

Moreover, electrocoagulation (EC) technology was investigated efficiently for the treatment of a wide variety of wastewaters such as tannery wastewaters using aluminum electrodes, with a COD, color, and organic carbon removal efficiencies of 68%, 84.3%, and 55.1%, respectively [7]. Furthermore, landfill leachate treatment using aluminum and iron electrodes was investigated, and the removal efficiencies of COD, total nitrogen (TN), color, and turbidity were respectively 70%, 24%, 56%, and 60% with Al electrodes and 68%, 15%, 28%, and 16% with Fe electrodes [8,9]. Municipal wastewater treatment using EC reduced suspended solid by 98% [10].

This technique is based on the electrochemical dissolution of sacrificial anodes (aluminum or iron) by applying an electrical current that results in the generation, in situ, of coagulants instead of chemical coagulation process [11].

In this process, charged ionic pollution species or others are removed from wastewater due to their reaction with a coagulant metallic ion, having an opposite charge, or with flocs of metallic hydroxides generated within the effluent. When an electrical potential is applied from an external power source, the anode material undergoes an oxidation, while the cathode is subjected to a reduction, The electrochemical reactions with metal M as anode can be as follows [12]:

At the anode:

$$\mathrm{M}_{(s)} \rightarrow \mathrm{M}^{n+}_{(\mathrm{aq})} + n\mathrm{e}^{-} \tag{1}$$

$$2\mathrm{H_2O}_{(l)} \rightarrow 4\mathrm{H}^{+}_{(\mathrm{aq})} + \mathrm{O}_{2(g)} + 4\mathrm{e}^{-} \tag{2}$$

$$2\mathrm{Cl}^{-}_{(\mathrm{aq})} \rightarrow \mathrm{Cl}_{2(g)} + 2\mathrm{e}^{-} \tag{3}$$

At the cathode:

$$2\mathrm{H_2O}_{(l)} + 2\,\mathrm{e}^{-} \rightarrow 2\mathrm{H}_{2(g)} + 2\mathrm{OH}^{-} \tag{4}$$

$$\mathrm{M}^{n+}_{(\mathrm{aq})} + n\mathrm{e}^{-} \rightarrow \mathrm{M}_{(s)} \tag{5}$$

with aq, g, s, M^{n+}, e^{-}, n^{+}, and n denoting aqueous solution, gas, solid, metal ion in aqueous solution, electron, charge of metal ion, and numerical number, respectively.

Cationic species from the anode metal dissolve into the water according to Eq. (1). These cations react with contaminants, creating metal oxides and hydroxides which precipitate. Furthermore, the productions of oxygen gas at the anode by water electrolysis and that of chlorine gas from chloride ions if they are present in the leachate solution are described by Eqs. (2) and (3), respectively.

Simultaneously, reactions take place at the cathode, producing hydrogen gas from water molecules reduction as shown in Eq. (4), resulting in an ascending motion of hydrogen gas bubbles accompanied by that of flocs, hence facilitating their separation from treated water. Another important cathodic reaction results in the reduction of the dissolved metal cations to its elementary state according to Eq. (5) and its deposition on the cathode [13].

In the aluminum case, at first, cationic monomeric species, such as $\mathrm{Al^{3+}}$ and $\mathrm{Al(OH)_2}^{+}$, at low pH, are generated from the dissolution of aluminum anode, which at appropriate pH values are transformed initially into $\mathrm{Al(OH)_3}$ and finally polymerized to $\mathrm{Al_n(OH)_{3n}}$ according to the subsequent reactions [14]:

$$\mathrm{Al} \rightarrow \mathrm{Al}^{3+}{}_{(\mathrm{aq})} + 3\mathrm{e}^{-} \tag{6}$$

$$\mathrm{Al}^{3+}{}_{(\mathrm{aq})} + 3\mathrm{H_2O} \rightarrow \mathrm{Al}\left(\mathrm{OH}\right)_3 + 3\mathrm{H}^{+}{}_{(\mathrm{aq})} \tag{7}$$

$$n\mathrm{Al}\left(\mathrm{OH}\right)_3 \rightarrow \mathrm{Al}_n\left(\mathrm{OH}\right)_{3n} \tag{8}$$

During the EC process and depending on solution pH, monomeric species such as $\mathrm{Al(OH)^{2+}}$, $\mathrm{Al(OH)_2^{2+}}$, $\mathrm{Al_2(OH)_2^{4+}}$, and $\mathrm{Al(OH)^{4-}}$ and polymeric species such as $\mathrm{Al_6(OH)_{15}^{3+}}$, $\mathrm{Al_7(OH)_{17}^{4+}}$, $\mathrm{Al_8(OH)_{20}^{4+}}$, $\mathrm{Al_{13}O_4(OH)_{24}^{7+}}$, and $\mathrm{Al_{13}(OH)_{34}^{5+}}$ are formed, these complexes act as a coagulant. They are adsorbed on the particles and then neutralize colloidal surface charges, similar to chemical coagulation in conventional water treatment [13].

Generally, the electrochemical processes are influenced by the applied current density, the type of electrode used, the distance between electrodes, the electrolysis time, initial solution pH, and the conductivity [15].

The solution conductivity is an important parameter in electrolysis processes in order to ensure good electrical current passage through the solution [16]. Furthermore, increasing solution electrical conductivity optimizes energy consumption and reduces treatment time [8,16]. In the present case, due to the high leachate conductivity ($20\ \mathrm{ms\ cm^{-1}}$ at 25°C), the addition of an electrolyte was not necessary [17].

The study of the effects of various factors affecting the EC process such as current density, initial pH, electrolysis time and distance between electrodes consisted of maintaining all these factors constant but one of them which could vary. However, this approach required a higher number of experiments, which was time-consuming and did not depict the combined effect of all the considered factors. Moreover, the determination of optimal conditions was not reliable [18]. Hence, the application of factorial experimental design of RSM could be used to determine the minimum number of experiments, in order to have significant results, a statistical model relating dependant and independent variables and the optimal conditions to have the maximum pollutant removal (yield) [19–23].

2. Materials and methods

2.1. Experimental design

Experiments were carried out in a batch laboratory scale reactor as shown in Fig. 1. It was used to test EC leachate treatment efficiency using two aluminum plates (the dimensions of both are 150 × 45 × 2 mm) electrodes.

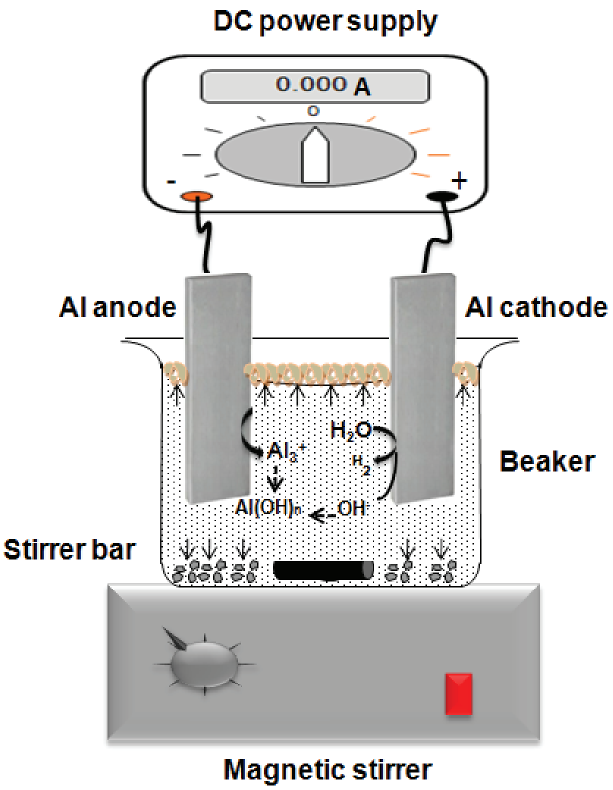

Fig. 1. Electrocoagulation experimental setup with DC power supply, aluminum electrode, and magnetic stirrer.

They were immersed in the batch reactor containing a leachate volume of 500 mL. To obtain uniformity throughout the leachate solution, mixing was carried out using a magnetic stirrer.

A digital D.C. (electrophoresis power supply, EV 202, 0–220 V, 0.0–2.0 A) generator was used to supply electrical current to aluminum electrodes.

To maintain the same experimental conditions, experiments were run under an initial temperature of 25°C. The aluminum electrodes were polished after each experimental use and then rinsed with distilled water before EC experiments.

2.2. Analytical procedures

Leachate samples were obtained from El Haria landfill, receiving Constantine's municipal solid waste. It is the first leachate stabilization pond, and Table 1 shows its main characteristics.

In this study, all parameters were analyzed according to the standard methods [24]. The COD of leachate samples was determined using digestion reactor "Model WTW thermoreactor CR 3000" and spectrophotometer "Model Jasco V-730."

The COD removal efficiency was calculated as follows:

$$\text{COD removel}\left(\%\right)=\frac{\text{COD}_\text{O}-\text{COD}}{\text{COD}_\text{O}}\times 100 \quad (9)$$

Table 1
The properties of raw leachate from Constantine Landfill

Analysis	Value
Color	Brownish
Smell	Fecaloide
pH	7.80–8.26
COD (mg O_2 L^{-1})	5340
Alkalinity (mg $CaCO_3$ L^{-1})	570
TN (mg L^{-1})	1180
Turbidity (NTU)	830
Chloride (mg L^{-1})	1760
Nitrate (mg L^{-1})	320
Conductivity (ms cm^{-1}) at 25°C	20

where COD_0 is the initial COD concentration, COD is the final COD concentration after a treatment duration time t.

For each experiment, the initial pH was adjusted using sodium hydroxide or hydrochloric acid within the range of 5–9, measured by a pH meter model Jenway 3505. The conductivity was measured using "WTW universal meter brand," and turbidity measurements were carried out using "2100P Turbidimeter HACH brand"; total organic carbon (TOC) and TN were measured using the analyzer model "Shimadzu TOC Autosampler ASI-V."

2.3. Statistical analysis and modeling

The purpose of this study was to assess EC effect on COD removal efficiency from leachate using RSM.

The important factors that affect the EC process are current density (X_1), initial pH (X_2), electrolysis time (X_3), and distance between electrodes (X_4) [25].

RSM based on central composite design (CCD) was applied to the present case, in order to optimize EC leachate treatment, consisting of 30 experiments for four variables ($n = 4$) and two levels: low (−) and high (+).

The total number of experiments was determined using the following expression:

$$2^n\ (2^4 = 16\text{: factor points}) + 2n\ (8\text{ axial points}) + 6\ (6\text{ replications center points}) \quad (10)$$

The five different levels used in the codification of the independent variables are represented in Table 2 and are determined according to the following relationship Eq. (11):

$$x_i = \frac{X_i - X_{io}}{\Delta X} \quad (11)$$

where x_i: coded value of the ith independent variable; X_i: natural value of the ith independent variable; X_{io}: natural value of the ith independent variable at the center point; ΔX: the step change value [22].

The CCD aim was to find a mathematical model which allied the response Y (COD removal efficiency) to the independent variables, factors (X_1, X_2… X_i… X_n) used to optimize the process and to find the optimal operating conditions. The mathematical model should be of a second-order polynomial equation (Eq. (12)) which correlates the dependent and independent variables. Moreover, the application of a statistical experimental design reduces the number of experiments to its optimal level and hence the allocated resources (time, reagents, and experimental work).

$$\mathbf{Y}(\%\text{COD removal efficiency}) = a_0 + a_1X_1 + a_2X_2 + a_3X_3 + a_4X_4 + a_{12}X_1X_2 + a_{13}X_1X_3 + a_{23}X_2X_3 + a_{14}X_1X_4 + a_{24}X_2X_4 + a_{34}X_3X_4 + a_{11}X_1^2 + a_{22}X_2^2 + a_{33}X_3^2 + a_{44}X_4^2 \quad (12)$$

To estimate the variable response (% COD removal), the obtained experimental results were treated using MINITAB (16 Minitab Institute, USA) statistical software.

3. Results and discussion

3.1. Experimental design methodology and analysis of variance (ANOVA)

In this study, a CCD was used to determine individual and interactive effects of EC process factors (current density, initial pH and electrolysis time, distance between electrodes) on COD removal efficiency of landfill leachate. The design was studied at five different levels (−2, −1, 0, 1, and +2) for each parameter. Three major steps are involved: carrying out the statistically designed experiments, proposed model coefficients estimation after having realized laboratory experiments, predicting process response, and finally checking the model validity. The coded and noncoded independent variables ranges are represented in Table 2.

The EC experimental results for COD removal and the four-level CCD design matrix are represented in Table 3. It shows the statistical combinations of the independent variables: current density (mA cm^{-2}) (X_1), initial pH (X_2), electrolysis time (min) (X_3), and distance between electrodes (cm) (X_4) with the predicted and experimental COD removal efficiencies (%). It can be noticed that the predicted values were close to the experimental ones.

Fig. 2 represents the plot of the obtained experimental results versus the predicted ones. The data points are closely spread around the first bisectrice indicating a very good fit between the simulated and the experimental results.

Table 2
Range and levels of process factors

Variables	Ranges and levels				
	−2	−1	0	+1	+2
Current density (mA cm^{-2}) (X_1)	13.33	26.66	40	53.33	66.66
Initial pH (X_2)	5	6	7	8	9
electrolysis time (min) (X_3)	30	60	90	120	150
Distance between electrodes (cm) (X_4)	2	2.5	3	3.5	4

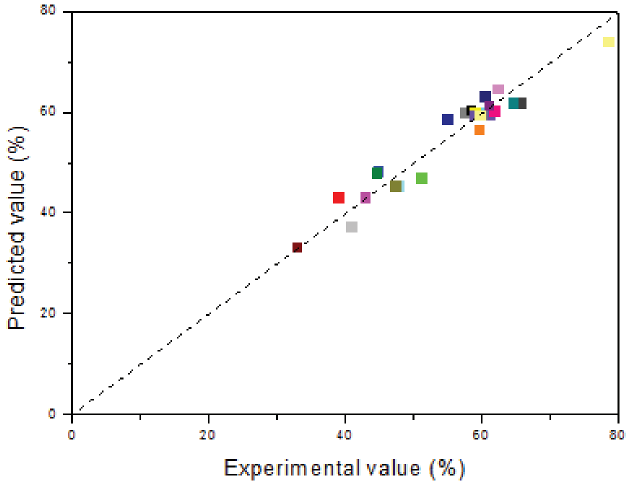

Fig. 2. EC COD removal efficiency of leachate: predicted results versus experimental ones, the dashed line represents the first bisectrice with the data corresponding to the 30 experiments (experimental and predicted) with the correlation coefficient $R^2 = 0.97$.

The model is of the form of a second-order polynomial equation and written as follows (Eq. (13)):

$$\mathbf{Y}(\%\text{COD removal efficiency}) = 59.5483 + 4.44963X_1 - 7.04054X_2 + 3.43496X_3 - 0.518875X_4 + 1.34119X_1X_2 + 3.31731X_1X_3 + 3.41469X_2X_3 - 0.552813X_1X_4 + 2.38331X_2X_4 - 3.57731X_3X_4 - 1.30816X_1^2 - 3.04303X_2^2 - 1.13191X_3^2 - 0.473781X_4^2 \quad (13)$$

Table 4 shows the results of the quadratic response surface model analysis of variance (ANOVA). ANOVA is recommended to examine the efficiency and the significance of the model [26]. The variation of the results is due to the variation associated with the model and the one associated with the experimental error, and the significance of the model is proved or not when the variation is compared with the ones associated with residual error [27].

Fisher variation ratio F-value is the ratio between the mean square of the model and of residual error, which is a statistical measure used to see how well the factors represent the variation in the data with respect to its mean. The model is appropriate and good predictor of the experimental results, when the F-value is greater than the tabulated value of F-distribution for a certain number of degrees of freedom in the model at a level of significance α [8,28].

The F-value obtained (F = 17.35), being greater than the tabular F-value (F_{tabular} = 2.46 at 95% significance), indicates that the model was significant and represented well the variation of COD removal efficiency.

The coefficient of determination R^2 reveals an acceptable fitting of the second-order equation. The R^2-value is always located between 0 and 1. The closer R^2 value to 1, the better the model predicts the response [28]. The R^2-value of 0.94 was obtained (Table 4).

The Student's t-test was involved to determine the significance of the regression coefficient of the parameters.

Table 3
CCD design matrix for the four coded variables with experimental and predicted responses

Exp	Current density (mA cm^{-2})	Initial pH	Electrolysis time (min)	Distance between electrodes (cm)	COD removal efficiency (%)	
					Experimental	Predicted
1	–1	–1	–1	–1	61.001	59.5957
2	+1	–1	–1	–1	61.757	60.2835
3	–1	+1	–1	–1	32.438	31.2302
4	+1	+1	–1	–1	40.858	37.2828
5	–1	–1	+1	–1	57.436	60.1562
6	+1	–1	+1	–1	78.465	74.1133
7	–1	+1	+1	–1	47.652	45.4495
8	+1	+1	+1	–1	62.279	64.7714
9	–1	–1	–1	+1	65.681	62,0455
10	+1	–1	–1	+1	58.284	60.5222
11	–1	+1	–1	+1	38.838	43.2253
12	+1	+1	–1	+1	50.930	47.0667
13	–1	–1	+1	+1	44.686	48.2968
14	+1	–1	+1	+1	59.978	60.0427
15	–1	+1	+1	+1	42.805	43.1354
16	+1	+1	+1	+1	58.805	60.2460
17	–2	0	0	0	47.269	45.4165
18	+2	0	0	0	60.255	63.2150
19	0	–2	0	0	60.895	61.4573
20	0	+2	0	0	32.750	33.2951
21	0	0	–2	0	44.437	48.1508
22	0	0	+2	0	64.497	61.8906
23	0	0	0	–2	54.743	58.6910
24	0	0	0	+2	59.456	56.6155
25	0	0	0	0	58.883	59.5483
26	0	0	0	0	59.619	59.5483
27	0	0	0	0	59.605	59.5483
28	0	0	0	0	59.830	59.5483
29	0	0	0	0	59.783	59.5483
30	0	0	0	0	59.570	59.5483

Table 4
Analysis of variance (ANOVA) for fit of COD removal efficiency from central composite design

Source of variations	Sum of squares	Degree of freedom	Adjusted mean square	F-value
Regression	2932.36	14	209.45	17.35
Residuals	181.05	15	12.07	
Total	3113.41	29		

$R^2 = 0.9418$, Adj-$R^2 = 0.8876$. F-value = 17.35 >>$F_{0.05}$(14. 15) tabular = 2.46

An experimental significance level is calculated from the values known as the Student's coefficient t [29].

The regression coefficients values, standard errors, t-statistics, and significance level p-values are given in Table 5.

To check and confirm the significance of each of the coefficients, it is recommended to use P-values as a tool in order to understand the mutual interaction patterns among the variables. The larger the Student's t-test and the smaller P-value are, the more significant is the corresponding coefficient [28,30]. If the coefficient probability value (P) was greater than 0.05, it can be concluded that the term did not have a significant effect on the predicted response [31].

From the results in Table 5, it can be deduced that current density (mA cm^{-2}) (X_1), initial pH (X_2), and electrolysis time (min) (X_3) have P-values equal to 0.000 which indicates that the terms in the model are significant with 95% confidence level. Otherwise, distance between electrodes (cm) (X_4) had no significant effect since its P-value is equal to 0.476 which is much higher than 0.05. Furthermore, concerning quadratic effects, it can be noticed that the four interactions factors mentioned below are significant compared with others factors.

Current density with electrolysis time (P-value 0.002), initial pH with electrolysis time (P-value 0.001) as well as initial pH with distance between electrodes (P-value 0.015)

Table 5
Estimated regression coefficients and corresponding *t* and significance level

Coefficient	Parameter estimate	Standard error	*t*-Value	*P*-Value
a_0	59.5483	1.4183	41.985	0.000
a_1	4.4496	0.7092	6.275	0.000
a_2	–7.0405	0.7092	–9.928	0.000
a_3	3.4350	0.7092	4.844	0.000
a_4	–0.5189	0.7092	–0.732	0.476
a_{11}	–1.3082	0.6634	–1.972	0.067
a_{22}	–3.0430	0.6634	–4.587	0.000
a_{33}	–1.1319	0.6634	–1.706	0.109
a_{44}	–0.4738	0.6634	–0.714	0.486
a_{12}	1.3412	0.8685	1.544	0.143
a_{13}	3.3173	0.8685	3.819	0.002
a_{14}	–0.5528	0.8685	–0.636	0.534
a_{23}	3.4147	0.8685	3.932	0.001
a_{24}	2.3863	0.8685	2.748	0.015
a_{34}	–3.5773	0.8685	–4.119	0.001

and electrolysis time with distance between electrodes (*P*-value 0.001).

The Pareto analysis calculates the percentage effect (P_i) of each factor from the relationship of Eq. (14) giving more significant information to interpret the results [32].

The Pareto diagram (Fig. 3) confirms the Student's *t*-test by showing the individual and combined effect of factors influencing the COD removal efficiency (%) from leachate.

$$P_i = \frac{a_i^2}{\Sigma a_i^2} \times 100 \qquad i \neq 100 \tag{14}$$

Hence, the most significant parameters among those presented in Table 5 with low *P*-values are shown as well in the Pareto graphic plot of Fig. 3 which are from most to least significant: initial pH, current density, electrolysis time and the interactions between electrolysis time with distance between electrodes, initial pH and electrolysis time, current density with electrolysis time, and then initial pH and distance between electrodes.

3.2. Variables response surface and contour plots

Finding the optimal operating conditions for the COD removal from leachate by EC process is the main objective of the optimization process.

To estimate the difference between the observed and the predicted response values, residual analysis of the response surface design was used and the major diagnostic plots are represented in Fig. 4. The different plots show a good agreement between the two kinds of responses.

Figs. 5(a)–(d) represent the obtained contour plots of the predicted COD removal efficiency, as developed from the polynomial function model, with the independent variables (X_1, X_2, X_3, and X_4). For each plot, two of the independent variables are kept constant, while the two others can vary.

As shown in Fig. 5, the response surface and contour plots represent the results of the interactions between factors which are more significant in EC COD removal from leachate as well as the effect of these factors on the removal efficiency.

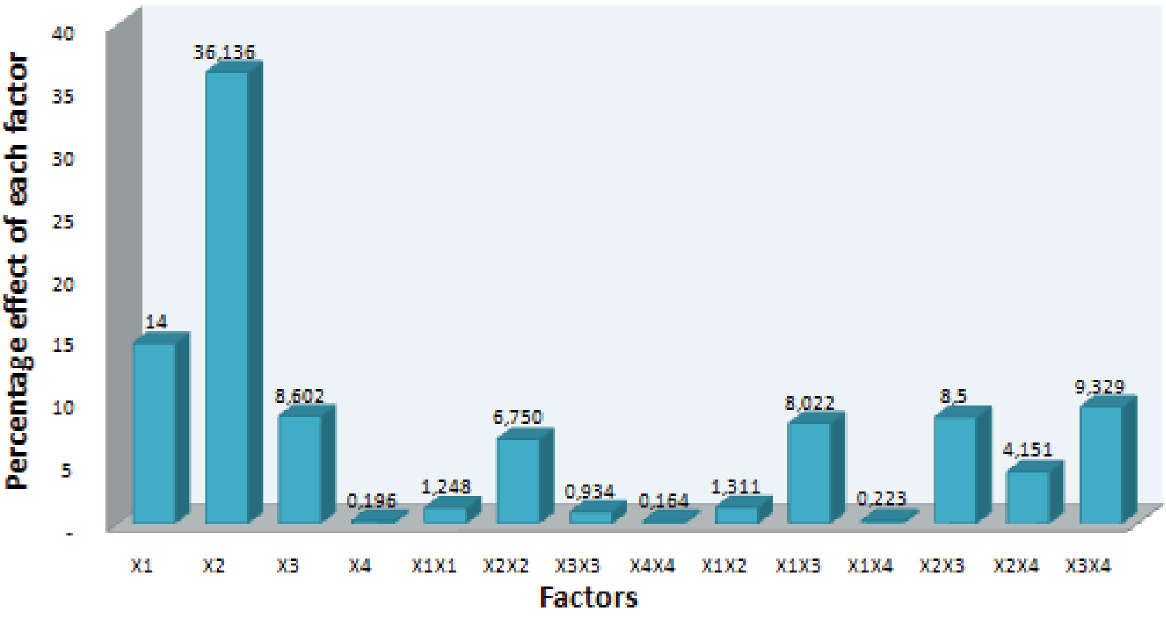

Fig. 3. Pareto graphic analysis (factors: current density (X_1), initial pH (X_2), electrolysis time (min) (X_3), and distance between electrodes (X_4)).

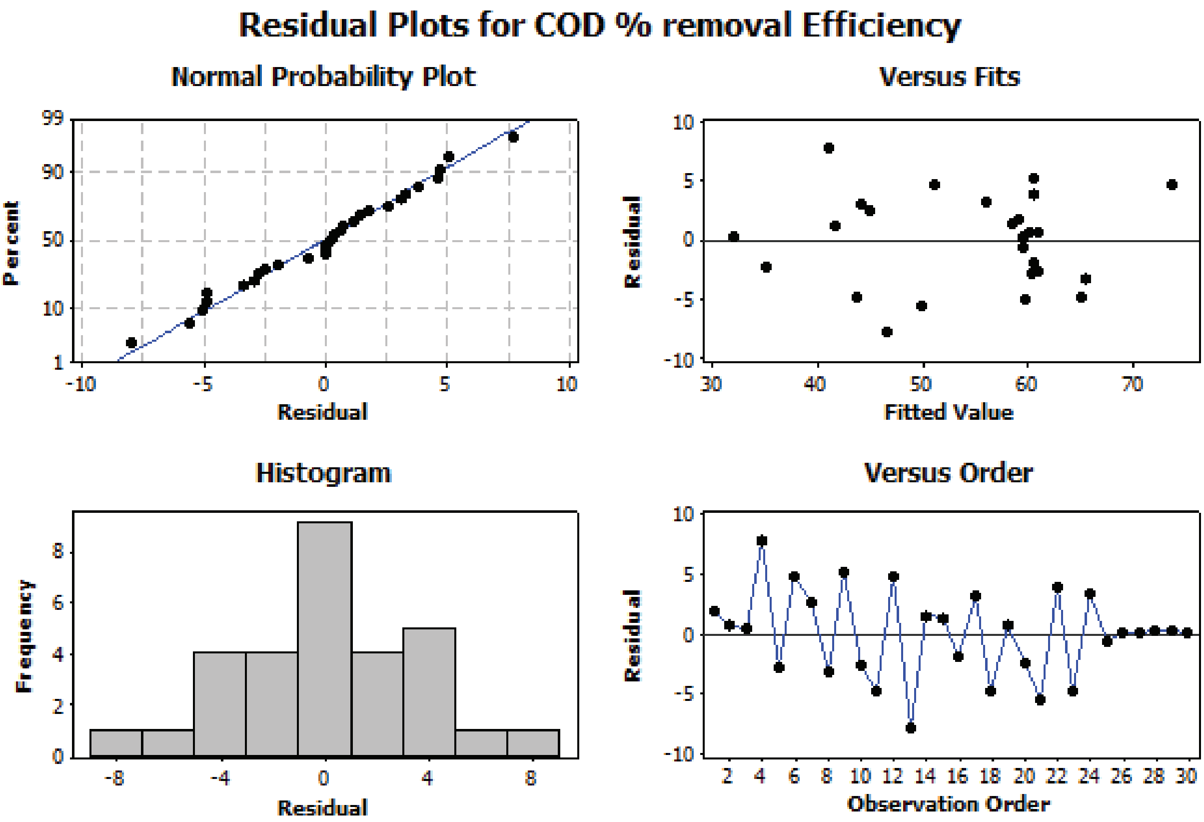

Fig. 4. Residual plots for COD removal efficiency of leachate by electrocoagulation.

The interaction is between (1) current density (mA cm^{-2}) and electrolysis time (min), (2) initial pH and electrolysis time (min), (3) initial pH and distance between electrodes (cm), and (4) electrolysis time (min) and distance between electrodes (cm).

Fig. 5(a) represents the effects of electrolysis time and current density on % COD removal from leachate by EC process for initial pH = 7 and a distance of 3 cm between electrodes.

As can be seen in Fig. 5(a), electrolysis time had a strong positive effect on the % COD removal efficiency when current density was high. In fact, when current density was equal to 66.66 mA cm^{-2} (high), the curve representing the variation of COD removal efficiency increased as electrolysis time increased as well. However, when current density was low 13.33 mA cm^{-2}, it displayed an opposite trend.

As reported in the literature, the most probable reason is that electrolysis time determines anode dissolution rate [1,10]. Furthermore, an increase in current density results in more aluminum dissolution and an increase in bubble generation rate as well [16,34] providing a separation of coagulated leachate pollutants by flotation effect [1]. Indeed, Ilhan et al. [8] and Bouhezila et al. [9] when treating leachate using EC have found that an increase in current density results in a better efficiency of electroflotation, and according to Li et al. as the current density increased, the hydrogen bubbles became denser and smaller in diameter leading to a more efficient flotation [1,35].

Moreover, the EC process using aluminum electrodes results in the release of Al^{3+} cations. However, different species are formed depending on the solution pH and cathodic reduction of water (Eq. (4)) which contributes to the production of hydrogen gas and hydroxide (OH^-) that in turn promotes the formation of aluminum precipitate ($Al(OH)_3$) and contributes to the flocculation process by sweeping, whereas hydrogen gas bubbles promote removal by flotation [35] as already mentioned.

The 3 D plot of COD removal efficiency response surface exhibited a set of maximal values that can be represented by an inclined straight line (see Fig. 5(a)), and the removal efficiency was lower on both sides of this straight line. It should be underlined that when the current density increased above the optimal values more coagulant than what is needed was available in solution resulting in a decrease in removal efficiency behaving as in chemical coagulation [16]. However, as electrolysis time increased, the removal efficiency of COD increased as well. Owing to the presence of aluminum precipitates since pH increased with time during EC, aluminum was then present in solution in excess; therefore, sweeping flocculation could contribute to the COD removal. When current density was lower than the optimal values, it was expected, as the electrolysis time was increased, COD removal efficiency increased as more aluminum cations were present in solution. However, an opposite behavior resulted as can be seen in Fig. 5(a) for current density (13.33 mA cm^{-2}) that could be

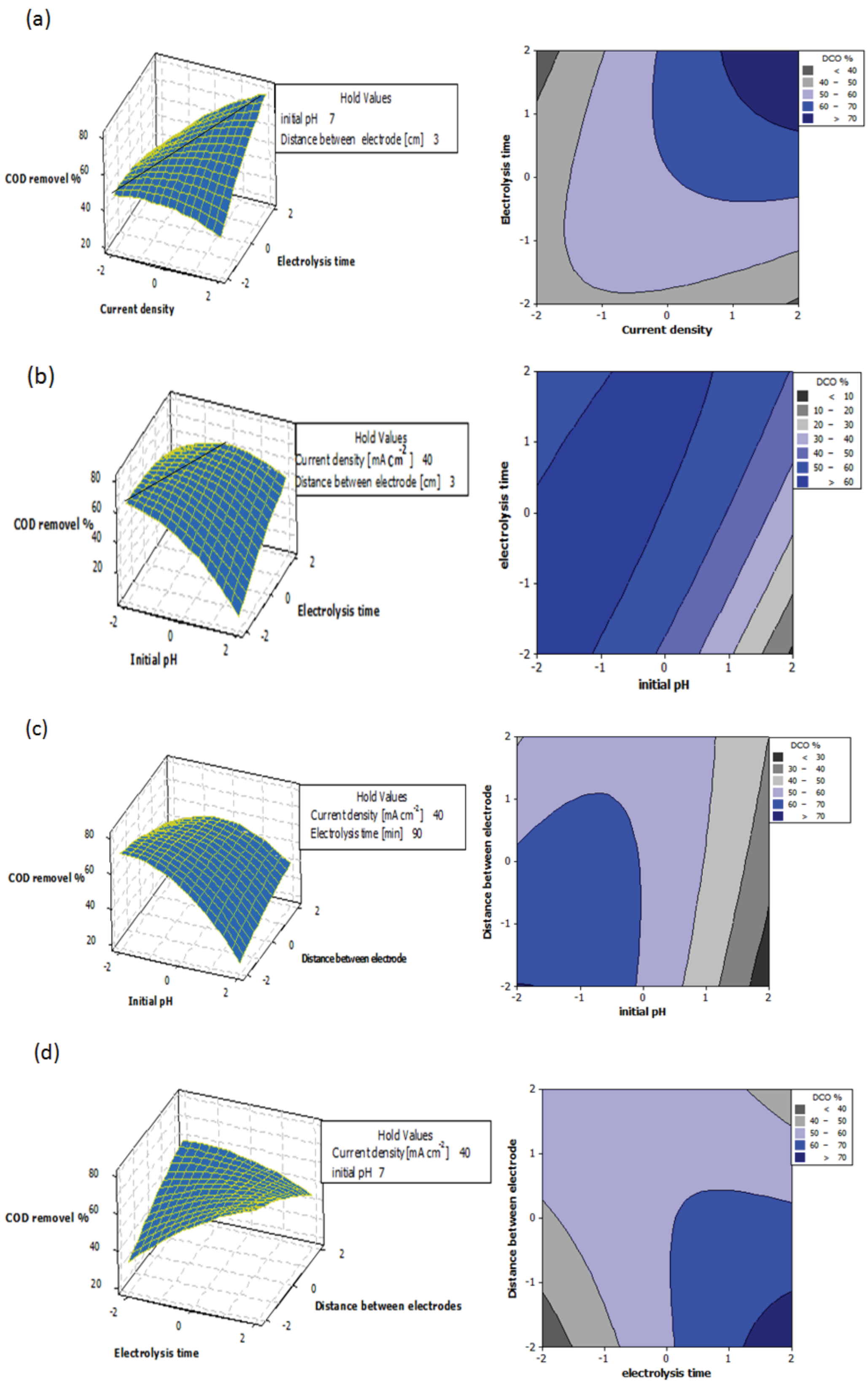

Fig. 5. The response surface and contour plots of % COD removal efficiency from leachate by electrocoagulation as a function of (a) current density (mA cm^{-2}) and electrolysis time (min), (b) initial pH and electrolysis time (min), (c) initial pH and distance between electrodes (cm), and (d) electrolysis time (min) and distance between electrodes (cm).

attributed to an increase in solution pH with time during the EC process [1].

Fig. 5(b) shows the effects of electrolysis time and initial pH on COD removal efficiency for a current density of 40 mA cm^{-2} and a 3 cm distance between electrodes. From the figure, the COD removal efficiency was the highest when both initial pH and electrolysis time were low (pH = 5; time = 30 min). However, if the electrolysis time was increased, while initial pH was kept low (pH = 5), a slight decrease of 10% in COD removal efficiency was noticed contrarily to the case when the pH was kept high (pH = 9) a moderate increase of 30% resulted. Whereas an increase in initial pH, while electrolysis time was kept low (30 min) resulted in a very pronounced decrease of more than 60%, but if electrolysis time was kept high (150 min), the COD variation curve was slightly concave with a maximum at pH = 7; time = 150 min. Furthermore, qualitatively, the maximal removal efficiency seems to be located on a straight line (see Fig. 5(b)).

The pH is an operating factor which strongly influences the performance of an EC process [37,38]. Under the conditions of Fig. 5(b), initial pH seems to have a more pronounced effect on COD removal efficiency than electrolysis time. Indeed, when pH was low (pH = 5), aluminum was under a cationic form $\text{Al}\left(\text{OH}\right)_2^+$ and the coagulation process would take place. However, as the initial pH was increased, the cationic form of aluminum started to decrease, while the anionic form $\text{Al}\left(\text{OH}\right)_4^-$ increased until it exceeded its cationic form at a pH greater than 6.4 (Fig. 6) [38].

Then, the increase in initial pH resulted in a loss of removal efficiency of more than 40% for an electrolysis time of 30 min. On the other hand, this behavior had been greatly attenuated when the electrolysis time was kept at 150 min, with a displacement of the maximal removal to a pH 7, as the initial pH was increased. This could be explained by the fact that at pH 5 the available cationic aluminum complex was most probably greater than the optimal dose; however, as the initial pH increased the available cationic aluminum complex decreased and the removal efficiency increased until pH 7. Over pH 7, the removal efficiency decreased to 48%. The results suggest that as the electrolysis time increased, the effect of initial pH increase was attenuated. In fact, as the electrolysis time increased, more aluminum was present in solution, encouraging, therefore, a sweeping process of the pollution. Moreover, bubbles generation increased as well as electrolysis time increased improving leachate removal [1,11,26,34].

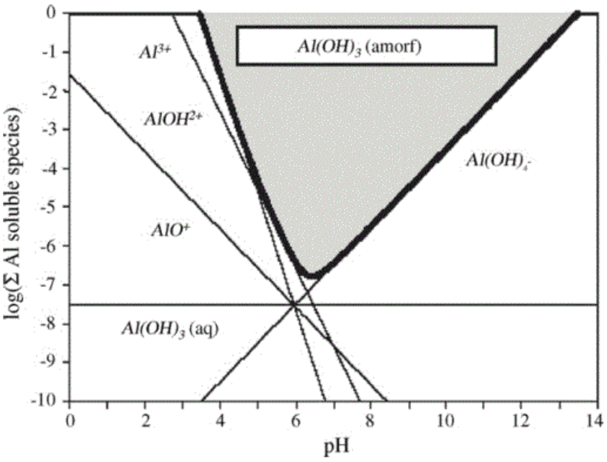

Fig. 6. Diagram of predominance of aluminum species and pH effect.

Moreover, the removal efficiency could be kept at its maximum if both initial pH and electrolysis time were increased. When initial pH was high and electrolysis time was low, the COD removal efficiency was at its lowest value.

Fig. 5(c) shows the effects of distance between electrodes and initial pH for a current density of 40 mA cm^{-2} and electrolysis time of 90 min.

The figure shows that COD removal efficiency was highest when both initial pH and distance between electrodes were at their lowest values.

Moreover, when the initial pH was kept at its lowest value of 5 and distance between electrodes was increased from 2 to 4 cm, this resulted in a slight decrease of 10% in COD removal efficiency. Furthermore, when distance between electrodes was kept at its lowest value of 2 cm and initial pH was increased from 5 to 9, the COD removal efficiency decreased sharply. Therefore, pH had a more important effect on the removal efficiency than distance between electrodes.

At high pH (pH = 9), an increase in the distance between electrodes from 2 to 4 cm led to an increase in COD removal efficiency of 10%. However, at low pH (pH = 5), the same distance variations between the electrodes showed a decrease in COD removal efficiency of 10%. These opposite variations of COD removal efficiency are at the two extremes of pH 5 and 9. The changes in the variation of COD removal efficiency took place progressively as the pH was increased from 5 to 9 as shown in the contour plot of Fig. 5(c), when distance between electrodes was high and initial pH varied between 5 and 9, the resulting curve was concave, as shown on both response surface and contour plots of Fig. 5(c).

In fact, initial pH had a strong influence on COD removal efficiency as shown on Pareto graphic analysis of Fig. 3 where its percentage effect was 36.13% whereas it was insignificantly equal to 0.2% for the distance between electrodes variations. However, when the distance between electrodes was increased beyond 4 cm, depending on initial pH, a decrease in removal efficiency took place. Indeed, as the distance between electrodes was increased, the equivalent resistance of the solution volume between the electrodes increased as well leading to an increase in Ohmic losses which in turn inhibited the rate of anodic oxidation which was accompanied with an increase in solution temperature [9].Therefore, according to the obtained results, the influence of initial pH was determinant for COD removal efficiency.

Depending on contact time, electrode type, and applied electrical power, solution temperature might increase during the EC process [8]. In fact, at a current density of 40 mA cm^{-2}, an increase in distance between electrodes from 2 to 3 cm resulted in a change in temperature from 28°C to 34°C after 90 min of electrolysis time, when using aluminum electrodes on leachate treatment with a conductivity of 20 mS cm^{-1} at 25°C.

Fig. 5(d) shows the effect of distance between electrodes and electrolysis time, for a current density of 40 mA cm^{-2} and an initial pH of 7, on COD removal efficiency. The contour plot shows that electrolysis time had more effect than distance between electrodes, mainly for low distance between electrodes (2 cm) which is confirmed by Pareto results (electrolysis time = 8.6%, distance between electrodes = 1.9%). Moreover, the optimal line follows the diagonal (4 and 150), whereas the maximum was at 150 min and 2 cm. It should be underlined that the COD removal efficiency decreased from its maximum when distance between electrodes increased; however, an opposite behavior could be noticed when electrolysis time was equal to 30 min resulting in an increase in COD removal efficiency when distance between electrodes increased. Bouhezila et al. observed a 10% variation in COD removal efficiency when distance between electrodes increased from 0.5 to 2.8 cm. A high distance between electrodes resulted in an important energy consumption [9].

3.3. EC leachate COD removal efficiency optimal conditions

Eq. (13) represents the polynomial model describing the experimental results of COD removal efficiency as a function of the four independent variables. Upon optimization, a unique solution was found, when using factorial experimental design (RSM), and the optimized results, ensuring the maximum COD removal efficiency, are as follows: a current density (X_1) of 66.66 mA cm^{-2}, an initial pH (X_2) of 6.62, an electrolysis time (X_3) of 150 min, and a distance between the electrodes (X_4) of 2 cm.

The variation of pH with time, under optimal conditions (initial pH of 6.62), during EC, is represented in Fig. 7. It increased from 6.62 to 7.4 in 5 min of electrolysis and continued to do so until it reached a pH of 9.2 at the end of the experiment.

The initial pH of the effluent as mentioned before plays an important role in EC. In fact, it is the most significant parameter as found in this study (Pareto's plot of Fig. 3).

To check the results of the optimization, experiments were carried out using the obtained values for the optimal conditions.

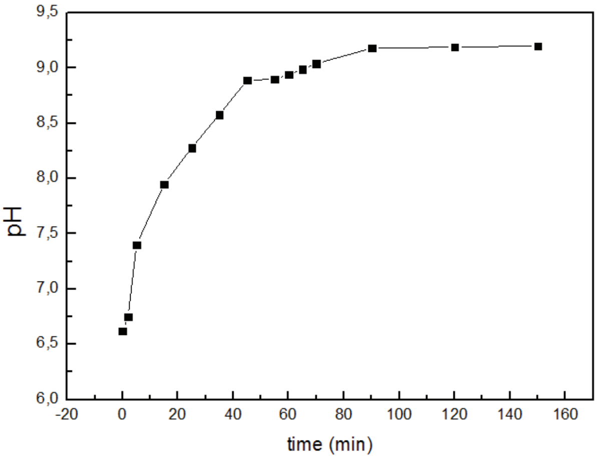

Fig. 7. The influence of initial pH on COD removal efficiency from leachate during electrocoagulation process in the optimal conditions.

The predicted and observed COD removal efficiencies (%) were found to be respectively 80% and 79.8%. These results were in a close agreement, confirming that the RSM could be effectively used to optimize process parameters of leachate treatment by EC using the statistical experimental design.

Moreover, experiments were carried out to check the effectiveness of EC to eliminate TOC, TN and turbidity from leachate under optimal conditions. The results showed an important removal capability of TOC, TN (Fig. 8(a)), and turbidity (Fig. 8(b)) with removal efficiency of 78%, 45.4%, and 99.9%, respectively.

4. Conclusion

Treating leachate by EC, using aluminum electrodes, was carried out in this study, showing its capacity to greatly reduce COD and turbidity. Moreover, the effect of operating

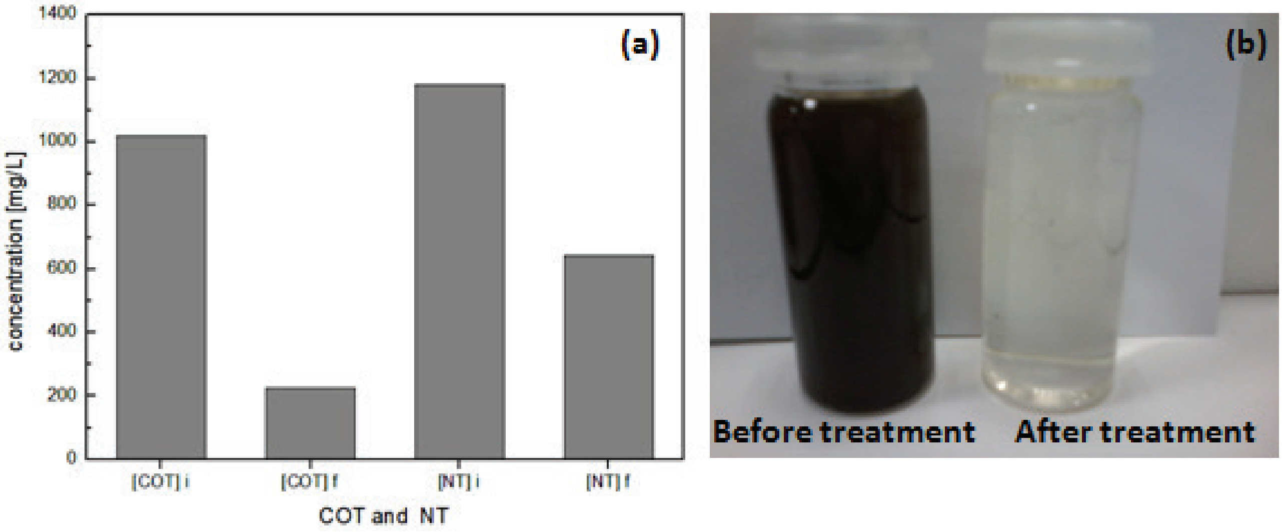

Fig. 8. Effectiveness of electrocoagulation to eliminate: (a) total organic carbon (TOC), total nitrogen (TN), and (b) turbidity.

parameters, such as current density, initial pH, electrolysis time, and distance between the electrodes, on the removal efficiency of COD had been examined covering a wide range of operating conditions.

Statistical optimization method was used in this study and proved to be a powerful tool of optimization in EC process. The experimental data were analyzed using RSM where a four-level of the CCD was applied in the present investigation. The principal objective of RSM was to determine the optimal operational conditions in the treatment of leachate by EC using COD removal efficiency as the response.

The optimized operational parameters found through the application of RSM were for current density (66.66 mA cm^{-2}), initial pH (6.62), electrolysis time (150 min), and distance between the electrodes (2 cm). To confirm these results, experiments were carried out using these same values and the obtained removal efficiency was for COD 79.8% close to the value obtained through RSM (80%) procedure.

The application of RSM classified the operational parameters according to their respective effects on EC and had shown that initial pH was the most determinant one, followed by current density, electrolysis time, and to a less extent by distance between electrodes.

From the results, the optimization using a RSM by a CCD can save time and efforts in estimating optimal conditions.

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References

[1] X. Li, J. Song, J. Guo, Z. Wang, Q. Feng, Landfill leachate treatment using electrocoagulation, Procedia Environ. Sci., 10 (2011) 1159–1164.

[2] S. Renou, J.G. Givaudan, S. Poulain, F. Dirassouyan, P. Moulin, Landfill leachate treatment: review and opportunity, J. Hazard. Mater., 150 (2008) 468–493.

[3] I.A. Talalaj, P. Biedka, Impact of concentrated leachate recirculation on effectiveness of leachate treatment by reverse osmosis, Ecol. Eng., 85 (2015) 185–192.

[4] R. He, X. Wei, B. Tian, Y. Su, Y. Lu, Characterization of a joint recirculation of concentrated leachate and leachate to landfills with a microaerobic bioreactor for leachate treatment, Waste Manage., 46 (2015) 380–388.

[5] F. Isabel, S. Rui, A.R.B. Enric, Electrochemical advanced oxidation processes for sanitary landfill leachate remediation: evaluation of operational variables, Appl. Catal., B, 182 (2015) 161–171.

[6] L. Xian, L. Xiao-Ming, Y. Qi, Y. Xiu, S. Ting-Ting, Z. Wei, L. Kun, S. Yi-Hu, Z. Guang-Ming, Landfill leachate pretreatment by coagulation – flocculation process using iron-based coagulants: optimization by response surface methodology, Chem. Eng. J., 200–202 (2012) 39–51.

[7] R.R. Babu, N.S. Bhadrinarayana, K.M.M.S. Begum, N. Anantharaman, Treatment of tannery wastewater by electrocoagulation, J. Univ. Chem. Technol. Metall., 42 (2007) 201–206.

[8] F. Ilhan, U. Kurt, O. Apaydin, M.T. Gonullu, Treatment of leachate by electrocoagulation using aluminum and iron electrodes, J. Hazard. Mater., 154 (2008) 381–389.

[9] F. Bouhezila, M. Hariti, H. Lounici, N. Mameri, Treatment of the OUED SMAR town land fill leachate by an electrochemical reactor, Desalination, 280 (2011) 347–353.

[10] N.K. Shammas, M.-F. Pouet, A. Grasmick, Flotation Technology, L.K. Wang, N.K. Shammas, W.A. ASelke, D.B. Aulenbach, Eds., Flotation Technology, New York, 2010, pp. 199–220.

[11] E. Bazrafshan, H. Biglari, A.H. Mahvi, Humic acid removal from aqueous environments by electrocoagulation process using iron electrodes, E-J. Chem., 9 (2012) 2453–2461.

[12] A.K. Golder, A.N. Samanta, S. Ray, Removal of Cr^{3+} by electrocoagulation with multiple electrodes: bipolar and monopolar configurations, J. Hazard. Mater., 141 (2007) 653–661.

[13] O.T. Can, M. Bayramoglu, M. Kobya, Decolorization of reactive dye solutions by electrocoagulation using aluminum electrodes, Ind. Eng. Chem. Res., 2 (2003) 3391–3396.

[14] M.Y.A. Mollah, R. Schennach, J.R. Parga, D.L. Cocke, Electrocoagulation (EC) – science and applications, J. Hazard. Mater., 84 (2001) 29–41.

[15] O. Dia, P. Drogui, R. Dubé, Le traitement des lixiviats de sites d ' enfouissement sanitaires – revue de littérature, Rev. des Sci. l'eau, 2017.

[16] V. Khandegar, A.K. Saroha, Electrocoagulation for the treatment of textile industry effluent – a review, J. Environ. Manage., 128 (2013) 949–963.

[17] J. Rosie, I. Shaharin, H. Normala, Electrocoagulation for removal of chemical oxygen demand in sanitary landfill leachate, Int. J. Environ. Sci., 3 (2012) 921–930.

[18] K. Ravikumar, S. Ramalingam, S. Krishnan, K. Balu, Application of response surface methodology to optimize the process variables for Reactive Red and Acid Brown dye removal using a novel adsorbent, Dyes Pigm., 70 (2006) 18–26.

[19] M. Elibol, Response surface methodological approach for inclusion of perfluorocarbon in actinorhodin fermentation medium, Process Biochem., 38 (2002) 667–673.

[20] K. Ravikumar, S. Krishnan, S. Ramalingam, K. Balu, Optimization of process variables by the application of response surface methodology for dye removal using a novel adsorbent, Dyes Pigm., 72 (2007) 66–74.

[21] A.R. Khataee, M. Fathinia, S. Aber, M. Zarei, Optimization of photocatalytic treatment of dye solution on supported TiO_2 nanoparticles by central composite design: intermediates identification, J. Hazard. Mater., 181 (2010) 886–897.

[22] C. Il-hyoung, Z. Kyung-duk, Photocatalytic degradation of azo dye (Reactive Red 120) in TiO_2/UV system: optimization and modeling using a response surface methodology (RSM) based on the central composite design, Dyes Pigm., 75 (2007) 533–543.

[23] M. Berkani, M. Bouhelassa, M.K. Bouchareb, Implementation of a venturi photocatalytic reactor: optimization of photodecolorization of an industrial azo dye, Arabian J. Chem., (in press).

[24] E. Rice, R. Baird, A. Eaton, Standard Methods for the Examination of Water and Wastewater, 22nd ed., American Public Health Association, Washington, 2012.

[25] C. Phalakornkule, S. Polgumhang, W. Tongdaung, Electrocoagulation of blue reactive, red disperse and mixed dyes, and application in treating textile effluent, J. Environ. Manage., 91 (2010) 918–926.

[26] M. Zarei, A. Niaei, D. Salari, A. Khataee, Application of response surface methodology for optimization of peroxi-coagulation of textile dye solution using carbon nanotube – PTFE cathode, J. Hazard. Mater., 173 (2010) 544–551.

[27] A. Aleboyeh, N. Daneshvar, M.B. Kasiri, Optimization of C.I. Acid Red 14 azo dye removal by electrocoagulation batch process with response surface methodology, Chem. Eng. Process., 47 (2008) 827–832.

[28] H. Liu, Y. Chiou, Optimal decolorization efficiency of Reactive Red 239 by UV/TiO_2 photocatalytic process coupled with

response surface methodology, Chem. Eng. J., 112 (2005) 173–179.

[29] A. Alinsafi, M. Khemis, M.N. Pons, J.P. Leclerc, A. Yaacoubi, A. Benhammou, A. Nejmeddine, Electro-coagulation of reactive textile dyes and textile wastewater, Chem. Eng. Process., 44 (2005) 461–470.

[30] A.I. Khuri, C. John, Response Surface: Design and Analysis, Dekker, New York, 1987.

[31] W. Jiang, J.A. Joens, D.D. Dionysiou, K.E.O. Shea, Optimization of photocatalytic performance of TiO_2 coated glass microspheres using response surface methodology and the application for degradation of dimethyl phthalate, J. Photochem. Photobiol., A, 262 (2013) 7–13.

[32] A. Kesraoui, N. Oturan, N. Bellakhal, Experimental design methodology applied to electro-Fenton treatment for degradation of herbicide chlortoluron, Appl. Catal., B, 78 (2008) 334–341.

[33] H. Jafari, A. Hossein, A. Jonidi, Removal of lead and zinc from battery industry wastewater using electrocoagulation process: influence of direct and alternating current by using iron and stainless steel rod electrodes, Sep. Purif. Technol., 135 (2014) 165–175.

[34] S.E. Burns, S. Yiacoumi, C. Tsouris, Microbubble generation for environmental separations and industrial, Sep. Purif. Technol., 11 (2008) 221–232.

[35] P. Drogui, S.K. Brar, H. Benmoussa, Electrochemical removal of pollutants from agro-industry wastewaters, Sep. Purif. Technol., 61 (2008) 301–310.

[36] X. Chen, G. Chen, P.L. Yue, Separation of pollutants from restaurant wastewater by electrocoagulation, Sep. Purif. Technol., 19 (2000) 65–76.

[37] G. Chen, Electrochemical technologies in wastewater treatment, Sep. Purif. Technol., 38 (2004) 11–41.

[38] A.E. Yilmaz, R. Boncukcuo, M.M. Kocakerim, A quantitative comparison between electrocoagulation and chemical coagulation for boron removal from boron-containing solution, J. Hazard. Mater., 149 (2007) 475–481.