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Optimization of electrocoagulation operating parameters for COD removal from olive mill wastewater: application of Box–Behnken design

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Abstract: Box–Behnken response surface design was successfully employed to optimize and study the olive mill wastewater (OMW) treatment by electrocoagulation (EC) process. The influence of four decisive factors were modelled and optimized to increase the removal of chemical oxygen demand (COD). The Box–Behnken design (BBD) results were analyzed and the second-order polynomial model was developed using multiple regression analysis. The model developed from the experimental design was predictive and a good fit with the experimental data with a high coefficient of determination (R^2) value (more than 0.98). The optimal operating conditions based on Derringer's desired function methodology are found to be; initial pH of 4.4, a current density of 27.6 mA/cm^2, electrolysis time of 14.1 min, and chloride concentration of 3.2 g/L. Under these conditions, the predicted COD removal efficiency was found to be 67.14% with a desirability value of 0.94. These experimental results were confirmed by validation experiments and proved that Box–Behnken design and response surface methodology could efficiently be applied for modelling of COD removal from OMW.

Keywords: Olive mill wastewater, electrocoagulation, Box–Behnken design, response surface methodology.

1. Introduction

Olive oil production is one of the most traditional agricultural industries with great economic importance in most of the Mediterranean countries. The Mediterranean region alone provides 98% of the total surface for olive tree cultivation and 97% of the world total olive oil production, which has been estimated at 2.74 million tons in the last six years [1]. However, the extraction process generates a considerable amount of olive mill wastewater (OMW), a highly polluted effluent with the volume reaches more than 30 million m^3 per year [2].

The extraction of olive oil generates vast quantities of wastes that may have a high impact on land and water environments because of their high phytotoxicity. Due to their high load of organic matter, a series of hazards of these effluents related to the contamination of soil, hindrance of plants growth, leaks to the underground aquifers, pollution of water bodies, inhibition of auto purification processes, as well as phytotoxic impacts to aquatic fauna and to ecological equilibria and intense odour nuisance have been reported so far [2-5].

Olive mill wastewaters (OMW) composition is highly variable and depends, in particular, by variety, ripeness and type of the oil extraction technology. The olive oil extraction systems could be classified in two main categories: traditional pressing process, used for many centuries with minor modifications, and centrifugal processes, including two centrifugation systems, called three- and two-phase systems. Generally, OMW is a foul-smelling acidic wastewater composed of water (83–92%), organic matter (4–16%) and minerals (1–2%) [6]. The organic load reflected in the high biological oxygen demand (up to 100 g l^{-1}) and chemical oxygen demand (up to 200 g l^{-1}) concentrations [7,8] comprises sugars, nitrogenous compounds, fatty acids, polyalcohols, polyphenols, pectin and fats [9,10]. Phenolic fraction characterized by its great variety and complexity is regarded as the most embarrassing part of OMW [11,12]. This fraction, which resists biological degradation, causes harmful effects on the flora and fauna of disposed of areas [4].

OMW also exhibit significant saline toxicity levels, confirmed by high electroconductivity (EC) values. Inorganic compounds including chloride, sulphate

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and phosphoric salts of potassium, calcium, iron, magnesium, sodium and traces of other elements [13].

The difficulty in treating OMW resides in its high content in recalcitrant organic compounds, most of which are resistant to conventional processes [12].

Nowadays, the most common method for eliminating OMW is through evaporation in storage ponds, owing to the low investment required and the climate conditions in Mediterranean countries [14]. However, this operating method has several important disadvantages, such as bad odour, infiltration and insect proliferation [15].

Several physicochemical, biological and combined processes have been examined for the treatment of OMW, resulting in considerable organic load and toxicity abatement, such as biological processes, aerobic and anaerobic [16-18], advanced oxidation processes, owing to the strong oxidation potential of the agents used [8], chemical precipitation using lime [19], adsorption using different mineral substrates as adsorbents [20-22], nanofiltration and reverse osmosis membranes [5,23,24]. However, these processes suffer from serious inconveniences such as high cost, low efficiency and sludge disposal problems.

In recent years there has been growing interest in electro-chemical oxidation processes for the treatment of industrial effluents and therefore for the treatment of olive mill wastewater as well. Gotsi et al. [25] applied electrochemical oxidation of OMW with a titanium-tantalum-platinum-iridium anode. Almost complete degradation of phenols was achieved, but relatively low COD removal (40%) even after long operation times. Subsequently, Tezcan Ün et al. [26] investigated the electrochemical oxidation of three-phase technology OMW using Ti/RuO2 anode. The treated OMW effluent presented a final COD around 167 mg/L (99.6% removal efficiency) and almost complete abatement of phenolic compounds. Recently, Flores et al. [27] reported the treatment of OMW by electrochemical oxidation with a BDD anode and an air-diffusion cathode for the generation of H_2O_2, electro-Fenton and photo electro-Fenton, and the latter one yielded a maximum efficiency of up to 80% mineralization.

The electrocoagulation (EC) process is one of the most useful electrochemical processes. This technique has been the subject of several studies over the last decade and remains a very active field of research [28-30]; unfortunately, relatively few studies report the use of this technology to treat the OMW. Inan et al. [31] applied electrocoagulation for the treatment of OMW. For this purpose, aluminum and iron were used in the reactor simultaneously as materials for the electrodes. Similarly, Hanafi et al. [32] examined a coupled treatment process for OMW comprising electrocoagulation using an aluminum electrode and then a biological process. Other than these studies, OMW electrocoagulation was found capable of reducing the phenolic compounds as well as oil-grease and turbidity [33, 34].

To date, most of the studies on the optimization of wastewater treatment process have focused on the traditional one-factor-at-a time approach. However, this approach, which does not take into account the cross effects from the factors considered, is time-consuming and has in poor optimization results. Response surface methodology (RSM) is an efficient way to achieve such an optimization by analyzing and modelling the effects of multiple variables and their responses and finally optimizing the process [35,36]. RSM also generates a mathematical model that can be used to predict the response of a system to any new condition.

Although this method has been used for the optimization of various processes conditions that provide enhanced treatment of different wastewaters [5,36-38], it has not been well exploited to optimize COD removal in OMW by electrocoagulation.

In this study, the objective of the present study was to assess the electrocoagulation treatment of OMW. Box–Behnken statistical experiment design (BBD) and response surface methodology (RSM) were used to statistically develop model and to study and evaluate main effects, interaction effects and quadratic effects of the process parameters (initial pH, current density, electrolysis time and NaCl concentration) on Chemical oxygen demand (COD) removal efficiency.

2. Materials and methods

2.1. OMW characterization

OMW was obtained from an olive oil continuous processing plant located

Fresh olive mill wastewater (OMW) used in this study was obtained from the homogenization tank of an olive oil semi-modern press plant located in Beni-Mellal (Morocco). OMW was collected in a closed plastic container and stored at 4°C. The main characteristics of OMW were analyzed as per the procedures of Standard Methods [39,] and average values are given in Table 1.

2.2. Experimental procedure

Electrocoagulation (EC) combines the functions and advantages of conventional coagulation, flotation and electrochemistry in water and wastewater treatment [30,40,41]. Upon the application of direct current, the coagulant is generated in situ by electrolytic oxidation of an appropriate anode material that leads, at appropriate pH, to firstly destabilize small colloidal particles, and secondly, to fulfil simultaneous coagulation and flotation with less production of sludge [42,43].

Table 1. Characterization of olive mill wastewater.

Parameter	Unit	Value (mean ± SD)
pH		4.90 ± 0.30
Conductivity	mS/cm	18.50 ± 1.12
Chemical oxygen demand (COD)	g/L	98.21 ± 6.70
Biological oxygen demand (BOD)	g/L	37.40 ± 3.30
Total suspended solids (TSS)	g/L	5.76 ± 0.52
Total polyphenols	g/L	6.80 ± 0.73
Total Kjeldhl nitrogen (TKN)	g/L	1.63 ± 0.05

The proposed mechanism of chemical reactions occurring in the EC process is shown by the following main reactions at the aluminium electrodes [29,30]:

Anode : $Al_{(s)} \leftrightarrow Al^{3+}_{(aq)} + 3e^-$

Cathode : $3H_2O_{(aq)} + 3e^- \leftrightarrow 3/2H_{2(g)} + 3OH^-_{(aq)}$

The hydroxyl ions produced at the cathode increase the pH in the electrolyte and we have a reaction in the aqueous solution between Al^{3+} and OH^- ions to form aluminium hydroxide.

In bulk : $Al^{3+}_{(aq)} + 3OH^-_{(aq)} \leftrightarrow Al(OH)_{3(s)}$

The generated Al^{3+} ions would immediately undergo further spontaneous reactions to produce corresponding hydroxides and/or poly-hydroxides in a wide pH range. These hydroxides/poly-hydroxides/poly-hydroxy metallic compounds such as $Al_6(OH)_{15}^{3+}$, $Al_7(OH)_{17}^{4+}$, $Al_8(OH)_{20}^{4+}$, $Al_{13}O_4(OH)_{24}^{7+}$, $Al_{13}(OH)_{34}^{5+}$, which transform finally into $Al(OH)_3$ according to complex precipitation kinetics, have a strong affinity with dispersed/dissolved ions as well as the counter ions to cause coagulation/adsorption [31,44].

The electrocoagulation experiments were conducted in a home-made Plexiglas cell (Figure 1). Parallel rectangular aluminium sheets (30 mm x 80 mm) used as electrodes were disposed vertically in the cell at a distance of 2 cm from each other and there was a 3 cm distance between the electrodes and the bottom of the cell which allowed easy stirring. The polarity of current was reversed at regular intervals in order to minimize the deposition on electrodes. In each run, 0.25 L of wastewater was placed into the reactor, and all the runs were performed for a constant temperature (19–20°C). The range of current density variations was 10–30 mA/cm^2, pH values were taken as 4, 5, and 6 units, and duration of coagulation process varied in the limits of 10–20 min.

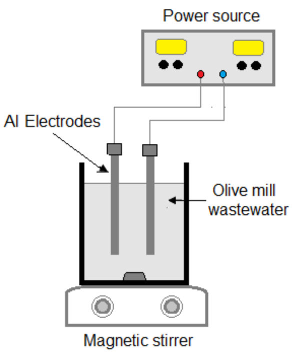

Figure 1. Schematic of the electrocoagulation cell

The treated effluents were collected, filtered and used for the determination of the COD. All experiments were performed in triplicate, and the average values were recorded. The removal efficiency (R in %) was calculated using the following equation:

$$R(\%) = \frac{Y_0 - Y}{Y} \times 100$$

where Y_0 and Y represent the initial and final value of COD.

2.3. Experimental design

Response surface methodology (RSM) is a useful statistical tool for the optimization of different processes and widely used for experimental design. In this study, Box-Behnken statistical screening design was used to statistically develop a model and to study and evaluate main effects, interaction effects and quadratic effects of the process parameters on the removal efficiency of COD. The effects of the four independent variables (initial pH (X_1), current density (X_2), electrolysis time (X_3) and chloride concentration (X_4)) on the response (COD removal) were investigated to determine the effective electrocoagulation operating conditions, which was validated by conducting additional experiments.

Table 2. Coded and actual values of the variables of the design of experiments for the overall electro-coagulation optimization.

Factor	Variables	Coded levels of variables		
		-1	**0**	**+1**
X_1	pH	4	5	6
X_2	Current density (mA cm^{-2})	10	20	30
X_3	Electrolysis time (min)	10	15	20
X_4	NaCl concentration (g l^{-1})	1	3	5

Table 3. Experimental design matrix and response based on the experimental runs and predicted values on COD removal (%) proposed by BBD design.

Run	Independent variables				COD Removal (%)	
	X_1 pH	X_2 Current density (mA/cm^2)	X_3 Electrolysis time (min)	X_4 [NaCl] (g/L)	Experimental	Predicted
1	5(0)	30(1)	20(1)	3(0)	67,12	67,26
2	5(0)	20(0)	15(0)	3(0)	62,75	62,75
3	4(-1)	20(0)	15(0)	1(-1)	60,33	59,81
4	5(0)	20(0)	10(-1)	5(1)	56,15	56,43
5	5(0)	10(-1)	10(-1)	3(0)	56,63	56,77
6	5(0)	20(0)	20(1)	5(1)	58,05	57,38
7	6(0)	10(-1)	15(0)	3(0)	49,14	48,14
8	4(-1)	20(0)	15(0)	5(1)	60,8	60,28
9	5(0)	20(0)	10(-1)	1(-1)	54,87	55,65
10	5(0)	20(0)	15(0)	3(0)	62,75	62,75
11	5(0)	20(0)	20(1)	1(-1)	59,21	59,05
12	5(0)	30(1)	15(0)	5(1)	63,07	63,11
13	6(1)	20(0)	15(0)	5(1)	46,96	47,77
14	6(1)	20(0)	10(-1)	3(0)	49,35	49,05
15	5(0)	20(0)	15(0)	3(0)	62,75	62,75
16	5(0)	10(-1)	15(0)	1(-1)	55,65	55,24
17	5(0)	30(1)	10(-1)	3(0)	63,66	63,91
18	5(0)	10(-1)	15(0)	5(1)	55,14	55,22
19	5(0)	30(1)	15(0)	1(-1)	64,45	63,98
20	4(-1)	20(0)	10(-1)	3(0)	62,49	61,36
21	6(1)	20(0)	20(1)	3(0)	51,19	51,94
22	4(-1)	10(-1)	15(0)	3(0)	59,48	60,65
23	4(-1)	30(1)	15(0)	3(0)	66,93	68,04
24	4(-1)	20(0)	20(1)	3(0)	62,9	62,81
25	6(1)	30(1)	15(0)	3(0)	58,42	57,37
26	6(1)	20(0)	15(0)	1(-1)	48,32	49,13
27	5(0)	10(-1)	20(1)	3(0)	57,73	57,77

The Box-Behnken design (BBD) was specifically selected since it requires fewer runs than a central composite design (CCD) in cases of three or four variables. Each independent variable was coded at three levels between +1 and –1 (Table 2). A total number of 27 experiments, including three centre points were carried out, and the experimental conditions and corresponding results (responses) are presented in Table 3. A second-order polynomial model corresponding to the BBD was fitted to correlate the relationship between the independent variables and the response and also to identify the relevant model terms using statistical software (Design Expert 11). Considering all the linear terms, square terms and interaction items, the quadratic response model can be described as:

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{i=1}^{k} . \sum_{j=1}^{k} \beta_{ij} X_i X_j + \varepsilon$$

where Y is the response (COD removal efficiency, %); β_0, β_i *(i* = 1, 2, 3, 4*)* and β_{ij} *(i* = 1, 2, 3, 4*; j* = 1, 2, 3, 4*)* are the model coefficients and X_i and X_j the coded independent variables.; and ε is the error [45].

The quality of the fit of the polynomial model equation was expressed by the coefficient of determination R^2 and the values of adjusted-R^2. The significance of each term in the equation is to estimate the goodness of fit in each case. The adequacy of the model was further justified through analysis of variance (ANOVA) and ANOVA tables were generated. The regression coefficients of the linear, quadratic and the interaction involved in the model and their effects were analyzed by the *F*-test and *P*-value.

In order to visualize the relationship between the response and experimental levels of each factor, the regression coefficients were used to make a statistical calculation to generate 3D surface plots from the fitted polynomial equation. These graphs are drawn by maintaining two factors constant (in turn at its middle level) and varying the other two factors in order to understand their primary and interactive effects on the dependent variables.

3. Results and discussion

3.1. Response analysis and interpretation by Box–Behnken design (BBD)

In order to study the combined effect of independent variables (initial pH, current density, electrolysis time, and chloride concentration) on the COD removal efficiency, experiments were performed for different combinations of the parameters using statistically designed experiments and the results are shown in Table 3, that includes the design and the experimental and predicted values. Model adequacy checking was performed on the experimental data to determine whether the approximating model would give poor or misleading results.

Table 4. The sequential model sum of squares and model summary statistics tested for response.

	Sequential Model Sum of Squares					Model Summary Statistics				Remarks
Source	SS[(a)]	DF[(b)]	MS[(c)]	F-value[(d)]	p-value[(e)]	SD[(f)]	R^2	Adj. R^2	Pred. R^2	
Mean	42569,5	1	42569,5							
Linear	189,90	4	47,47	5,80	0,0024	3,06	0,5134	0,4250	0,2366	
2FI	41,45	6	6,91	0,7980	0,5853	3,54	0,6255	0,3914	-0,2369	
Quadratic	**131,79**	**4**	**32,95**	**58,79**	**<0.0001**	**0,9211**	**0,9818**	**0,9606**	**0,8970**	**Suggested**
Cubic	5,97	8	0,7464	3,96	0,0999	0,3489	0,9980	0,9867	0,7771	Aliased
Residual	0,7545	4	0,1886							
Total	42939,3	27	1590,3							

[(a)] Sum of Squares.
[(b)] Degrees of Freedom of variance source.
[(c)] Mean of Squares (=SS/DF).
[(d)] F-value of variance source = MS/MSres;
[(e)] Probability of error to be significant.
[(f)] Standard Deviation

Fitting of the data to various models (linear, interactive, quadratic and cubic models) was carried out to obtain the regression equation. In general, exploration of a fitted response surface may produce poor or misleading results, unless the model exhibits a good fit, which makes checking of the model adequacy essential [46]. To decide about the adequacy of model among various models, two different tests namely the sequential model sum of squares and model summary statistics were carried out in the present study, and the results are given in Table 4.
A quadratic model was found to be the most suitable model for COD removal. The model was found to have maximum R^2, adjusted R^2, predicted R^2 and also exhibited low p-values (p-value < 0.0001). Predicted R^2 is a measure of how good the model predicts a response value. The adjusted R^2 and predicted R^2 should be within approximately 0.20 of each other to be in reasonable agreement. If they are not, there may be a problem with either the data or the model. In our case, the predicted R^2 of 0.897 is in reasonable agreement with the adjusted R^2 of 0.9606. The adequacy of the model was further justified through analysis of variance (ANOVA).

3.2. Fitting of second-order polynomial equation

An empirical relationship expressed by a second-order polynomial equation was fitted between obtained experimental results on the basis of the Box–Behnken experimental design model and the input variables. The equation in terms of coded factors can be used to make predictions about the response for given levels of each factor. The final equation obtained in terms of coded factors is given below:

$$\text{COD removal (\%)} = 62{,}75 - 5{,}8X_1 + 4{,}16X_2 + 1{,}09X_3 - 0{,}22X_4 + 0{,}45X_1X_2 + 0{,}35X_1X_3 - 0{,}45X_1X_3 + 0{,}59X_2X_3 - 0{,}61X_3X_4 - 4{,}67X_1^2 + 0{,}46X_2^2 - 1{,}79X_3^2 - 3{,}84X_4^2 \quad \text{Eq (1)}$$

3.3. Statistical analysis

The quality of the model was evaluated based on the coefficient of determination in addition to the ANOVA statistical analysis. The significance of each coefficient was determined using p-value, which is used as a tool to check the significance of each coefficient and is necessary to understand a pattern of mutual interactions between the process variables. If the p-value is the smaller, it is the more significant significance of the corresponding coefficient and P-values lower than 0.05 indicates that the model is statistically significant [47]. The regression coefficients and p-value for the second-order polynomial equation are presented in Table 5 and it could be concluded that three linear effects of (X_1, X_2 and X_3) and three quadratic effects of (X_1^2, X_3^2 and X_4^2) were significant and indicate the pattern of the interactions between the variables.

The significance of the F-value depends on the number of degrees of freedom (DF) in the model. In general, the effects lower than 0.05 are significant. The ANOVA result for the COD removal shows F-value of 69.14, which implies that the developed quadratic model has a significant effect on the response. The large value of F-value indicates that most of the variation in the response can be explained by the regression model.

Table 5. Analysis of variance (ANOVA) variables fitted to quadratic polynomial model.

Source	**CE**	**SS**	**DF**	**MS**	**F-value**	**p-value**	Remarks
Model	62,75	821,27	14	58,66	69,14	< 0.0001	**significant**
X_1	-5,80	403,10	1	403,10	475,11	< 0.0001	
X_2	4,16	207,33	1	207,33	244,37	< 0.0001	
X_3	1,09	14,19	1	14,19	16,73	0,0015	
X_4	-0,22	0,5896	1	0,5896	0,6950	0,4208	
X_1X_2	0,45	0,8372	1	0,8372	0,9868	0,3401	
X_1X_3	0,35	0,5112	1	0,5112	0,6026	0,4526	
X_1X_4	-0,45	0,8372	1	0,8372	0,9868	0,3401	
X_2X_3	0,59	1,39	1	1,39	1,64	0,2244	
X_2X_4	-0,21	0,1892	1	0,1892	0,2230	0,6452	
X_3X_4	-0,61	1,49	1	1,49	1,75	0,2100	
X_1^2	-4,67	116,38	1	116,38	137,17	< 0.0001	
X_2^2	0,46	1,17	1	1,17	1,37	0,2639	
X_3^2	-1,79	17,11	1	17,11	20,17	0,0007	
X_4^2	-3,84	78,44	1	78,44	92,45	< 0.0001	

CE: Coefficient estimate

Model adequacy checking was performed to determine whether the approximating model would give poor or misleading results. Figure 2 shows the residual and the influence plots for the experimental data obtained from this study. The predicted values obtained were quite close to the experimental values, and the points of all predicted and experimental response values fall very close to the 45° line (Figure 2a), indicating that the model developed was successful in capturing the correlation between the process variables on the response. Figure 2b shows the standard % probability plot of residuals for a response was normally distributed, as they lie reasonably close on a straight line and shows no deviation of the variance.

3.4. Effect of variables on COD removal efficiency

In order to gain a better understanding of the interaction between the independent variables and estimate the COD removal efficiency over the independent variables, three-dimensional (3D) response surface plots for the measured response were constructed from the regression equation. These representations describe the relative effects of any two variables on COD removal efficiency when the remaining variables were kept constant.

Figures 3a, 3b and 3c show the combined effects of initial pH correspond with current density, electrolysis time and NaCl concentration, respectively. As can be seen from the figures, when initial pH was adjusted in the range 4–5, high removals of COD was achieved. This behaviour is by the amphoteric character of aluminium hydroxide that does not precipitate at pH less than 2. In alkaline medium, a slight drop is recorded due to the consumption of the OH^- ion and the formation of $Al(OH)_4^-$ which is useless for water treatment [31]. The results are in agreement with Adhoum and Monser [33] and Hanafi et al. [32], who concluded that the highest COD removal efficiency has been obtained in acidic medium.

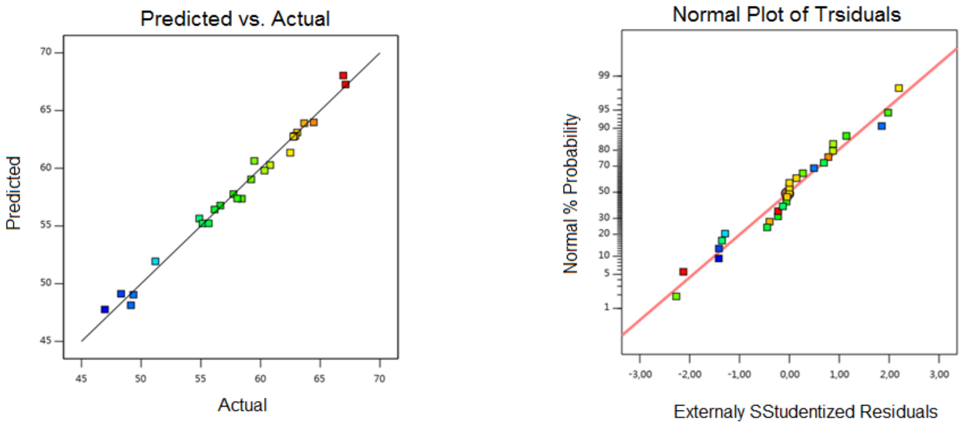

Figure 2. (**a**) predicted response versus actual response, (**b**) Normal % probability versus residual error

This result is entirely meaningful in the application of electrocoagulation to OMW treatment since the typical pH of OMW is between 4.5 and 5.5, which allows it to be directly treated by electrocoagulation without further pH adjustment.

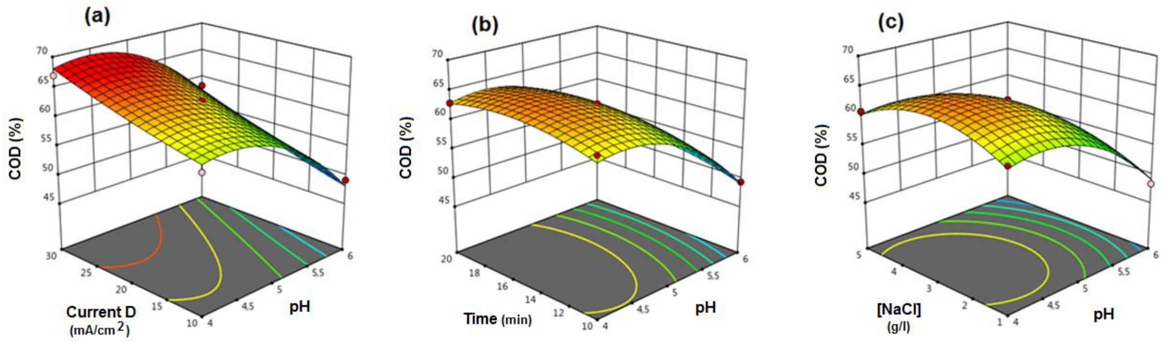

Figure 3. Effects of **(a)** initial pH and current density **(b)** initial pH and electrolysis time **(c)** initial pH and NaCl concentration, on COD removal efficiency

Current density directly determines both coagulant dosage and bubble generation rates, as well as strongly influencing both solution mixing and mass transfer at the electrodes. The effects of current density correspond with initial pH, electrolysis time and NaCl concentration, are presented in Figures 3a, 4a and 4b, respectively. These figures clearly show that the COD removal efficiency increase when the current density increased from 10 to 30 mA/cm^2. A similar observation was previously observed by Holt et al. [48] and was explained by the fact that, at higher currents, Al^{3+} ions undergo hydrolysis, and the resulting aluminium hydroxides produce more sludge with consequent significant removal of COD. Also, by increasing the current density of the cell, the number of hydrogen bubbles at the cathode increased, resulting in a higher upward flux and faster removal of COD [48,49].

The effect of electrolysis time and initial pH and the effect of electrolysis time and current density as an estimate of per cent COD removal are shown in Figures 3b and 4a, respectively.

It can be depicted from the response graphs that percentage of COD removal increases slightly with increasing electrolysis time from 10 to 20 min.

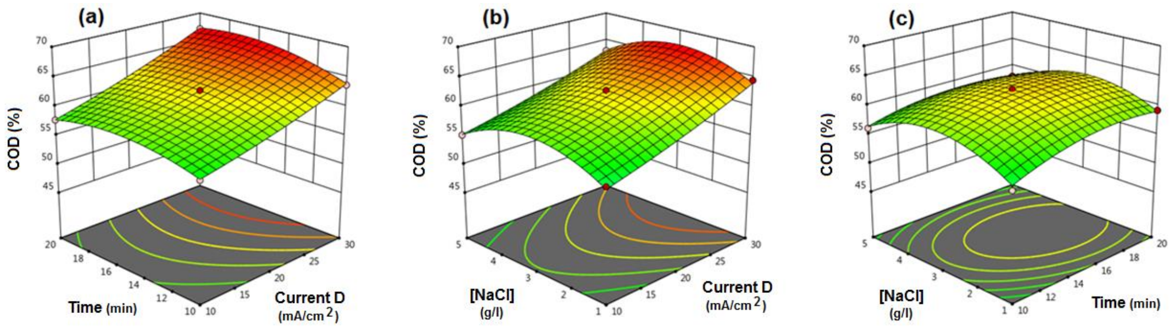

Figure 4. Effects of **(a)** current density and electrolysis time **(b)** current density and NaCl concentration **(c)** electrolysis time and NaCl concentration, on COD removal efficienc

The surface plots for COD removal efficiency presented in Figures 3c, 4b and 4c show the combined effects of NaCl concentration with initial pH, electrolysis time and current density, respectively. The response surface of mutual interactions between the variables was found to be elliptical, and the maximum COD removal efficiency was obtained in when increasing NaCl concentration to 3 g l^{-1}. Similar results were reported by Moussa et al.[50] and Khandegar and Saroha [51]. In addition to the coagulation process, when anode potential is sufficiently high, secondary reactions may also occur, such as indirect oxidation if the solution contains Cl^-, the following reactions may take place in the EC cell [33,52,53]:

$$2Cl^- \rightarrow Cl_2 + 2e^-$$

$$Cl_2 + H_2O \rightarrow HOCl + Cl^- + H^+$$

$$HOCl \rightarrow OCl^- + H^+$$

The formation of active chlorine species (Cl_2, HOCl, OCl^-) enhances the performance of the EC reactor through oxidation reactions.

Whereas the further increase in NaCl concentration decreased the COD removal efficiency. This demonstrates that an excess amount of Cl^- in the solution is detrimental to the coagulation of the pollutants. Indeed, the presence of the Cl^- ions in the solution containing $Al(OH)_3$ forms some transitory compounds, such as $Al(OH)_2Cl$, $Al(OH)Cl_2$ and $AlCl_3$. The transitory compounds finally dissolve in the solution with excess Cl^-, as a form of $AlCl_4^-$ [32, 54]. Thus, the amount of $Al(OH)_3$ coagulants decreases, resulting in a decrease of the removal efficiency.

3.5. Optimization and validation

In order to determine the optimum process parameters for the maximum COD removal efficiency, Derringer's desired function methodology optimization was used in this present study. This function searches for a combination of factor levels that simultaneously satisfies the requirements for each response in the design [36]. According to the BBD results, the optimal operating conditions for the maximum COD removal based on Derringer's desired function methodology are found to be the initial pH (X_1) of 4.4, current density (X_2) of 27.6 mA cm^{-2}, electrolysis time (X_3) of 14.1 min, and NaCl concentration (X_4) of 3.2 g/L. Under these conditions, the predicted removal efficiency of COD is found to be 67.14% with a desirability value of 0.94. This set of optimum conditions are used to validated experimentally. Triplicate experiments carried out under the optimized conditions, and the average COD removal was 67.03 ± 0.12%. The results are closely related with the data obtained from optimization analysis using desirability functions, indicating Box–Behnken design incorporate with desirability functions could be effectively used to optimize the operational parameters for the COD removal efficiency.

The efficiency of removal of COD (67,03%) obtained under optimal operating conditions is better than those found by Inan et al. [34] when they applied electrocoagulation for the treatment of OMW (52% COD was removed by the aluminum anode) and by Hanafi et al. [35] when they examined a coupled treatment process for OMW comprising electrocoagulation using an aluminum electrode and then a biological process (after electrocoagulation, the COD of OMW descended approximately 60.7%).

4. Conclusion

The main objective of the present study was to investigate the efficiency of the electrocoagulation process to treat olive mill wastewater. The performance of aluminium electrodes for removal of chemical oxygen demand was modelled and optimized using response surface methodology. The effects of four important operational parameters, including initial pH current density, electrolysis time, and chloride concentration, were evaluated by the response surface plots. Model summary statistics showed that the developed model was adequate and precise with the experimental data. Analysis of variance showed a high coefficient of determination value (R^2) of 0.98 for ensuring a satisfactory fit of the developed second-order polynomial regression model with the experimental data. The simultaneous optimization of the multi-response system by desirability function indicated that 67.14 % removal of COD can be possible by using the optimal conditions of initial pH (X_1) of 4.4, current density (X_2) of 27.6 mA/cm^2, electrolysis time (X_3) of 14.1 min, and NaCl concentration (X_4) of 3.2 g/L^1. The excellent agreement between the predicted and the experimental results verified the validity of the model and the existence of an optimal point. This indicated that the RSM was a powerful tool for determining the exact optimal values of the individual factors.

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