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Electrochemical treatment of metal working emulsions using Box-Behnken design

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ABSTRACT

In this study an experimental design was employed to investigate the effects of different operating conditions on the removal of oil by electrocoagulation with aluminum electrodes. Box-Behnken design was then used to optimize the electrocoagulation process and to evaluate the effects and interactions of variables: current density, initial pH and treatment time on the turbidity removal. A sample of metal working emulsion (5% in wt.) with a high turbidity was used in the experimental study. The test results indicated that electrocoagulation was very efficient and able to achieve 99% turbidity removal. Analysis of variance (ANOVA) showed a high coefficient of determination (R^2) value of 0.993, thus ensuring a satisfactory adjustment of the second-order regression model with the experimental data.

Keywords: Metal working emulsion; Turbidity; Electrocoagulation; Box-Behnken design; Optimization

1. Introduction

Metal working emulsions (MWE) are extensively used in metal working industries, such as rolling mills, forge and metal workshops, because these fluids provide the combined cooling and lubrication required by different metal working operations. Metal working emulsions are also used to increase tool life, wash away removed metal, protect the tool from corrosion, reduce friction and improve the overall finish of the work piece [1].

The main problem with MWE is that they become contaminated with use and lose their properties and effectiveness. Consequently, they must be replaced by new ones, thus yielding waste metal working emulsions which are generally high in COD and turbidity. The amount of MWE generated from metal working operations increases every year, constituting a serious danger to the environment due to their high surface-active and organic pollutant loads [2]. Appropriate treatment of these wastewaters is necessary in order to reduce the impact of their discharge. Various treatment methods are used to treat MWE, as chemical coagulation [3], ultrafiltration [1,4], and distillation [5].

To separate this type of emulsion out of hydrocarbon and water, the interfacial film must be destroyed to make it possible the finely-sized oil droplets to form larger droplets through coalescence [6]. For this purpose, electrocoagulation has a more prominent role in the treatment of MWE because it provides some significant advantages compared to the other techniques such as: no chemical additive is added to destabilize the emulsion, simple equipment, easy operation, low cost of exploitation capital, and weak quantity of residual rejections [7].

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Electrocoagulation is a technique of industrial processing liquid waste. It proceeds by creation of an electric field between soluble anodes, usually made of iron or aluminum and supports coagulation by increasing the probability of meeting of the loads present in the effluent. The cations such as Fe^{3+} and Al^{3+} produced by anodic dissolution play the part of coagulants by gathering the colloidal particles in the form of flocs [8].

In conventional multifactor experiments, optimization is usually carried out by varying a single factor while keeping all other factors fixed at a specific set of conditions. Moreover, this approach is time consuming and ignores the combined interactions between physicochemical parameters [9]. To solve this problem, response surface methodology (RSM) can be employed as an interesting strategy to implement process conditions which drive to optimal response by performing a minimum number of experiments. RSM is a combination of mathematical and statistical techniques used for developing, improving and optimizing the processes and used to evaluate the relative significance of several affecting factors even in the presence of complex interactions. Recently, this method has been used to determine optimum parameters in different processes [10,11].

In the present work, an attempt has been made to employ Box-Behnken design using response surface methodology for optimizing the key influencing parameters (i.e. current density, initial pH, and treatment time) on turbidity removal using electrocoagulation technique in a batch system.

2. Experimental technique

2.1. Material and methods

Metal working emulsions (oil-in-water emulsions) were prepared from a cutting mineral oil Tasfalout B22 supplied by Naftal (Algeria) and currently used for drilling and machining operations. The emulsions were diluted in deionized water to form very stable emulsion with mean the zeta potential equal to – 83.1 mV. All experiments were carried out with emulsions containing 5% (in wt.) of oil, corresponding to high turbidity (29,700 NTU). The zeta potential was measured using a Zetasizer (Malvern Instrument 500208). The turbidity of the solution was measured using a turbidimeter HACH, model 18900-10.

2.2. Experimental apparatus

The electrocoagulation experimental apparatus consists of an electrolytic cell which was a Plexiglas reactor in witch two aluminum electrodes plates were connected to a digital DC power supply (0–30 V, 2.5 A) in monopolar mode. The electrodes were situated vertically in the cell at a 1 cm apart from each other. The volume of the oil/water emulsion treated was 400 cm^3 and the total effective electrode area was 40 cm^2. The pH was adjusted to a desirable value using NaOH or H_2SO_4 and in all the experiments; sodium sulphate Na_2SO_4 at 5 gL^{-1} concentration was added for sufficient electrical conductivity of the emulsion to be treated.

2.3. Box–Behnken design

The Box–Behnken design is used in order to optimize the number of experiments to be carried out to ascertain the possible interactions between the studied parameters and their effects on the oil removal. Box–Behnken design is a spherical, revolving design; it consists of a central point and the middle points of the edges of the cube circumscribed on the sphere [12]. It is a three level fractional factorial design consisting of a full 2^2 factorial seeded into a balanced incomplete block design. It consists of three interlocking 2^2 factorial designs having points, all lying on the surface of a sphere surrounding the center of the design. It has been applied for optimization of several chemical and physical processes; and the number of experiments are decided accordingly [13].

In the present study, the Box–Behnken experimental design is applied to investigate and validate the treatment process parameters affecting the removal of oil by electrocoagulation. Current density (X_1), pH (X_2) and treatment time (X_3) are input variable parameters, while oil concentration was kept as a constant input parameter. The interval of the allowed values for these factors was deduced from the preliminary tests carried out (Table 1). The factor levels were coded as –1 (low), 0 (central point or middle) and 1 (high).

The rate of oil elimination, Y (%) was designed as a response of the studied system and it was calculated by the following equation:

$$Y(\%) = \left[\frac{(\mathrm{Tur})_i - (\mathrm{Tur})_f}{(\mathrm{Tur})_i} \right] \times 100 \tag{1}$$

where $(\mathrm{Tur})_i$ and $(\mathrm{Tur})_f$ are turbidities of the emulsion in an initial and final state respectively.

For this response (Y), a polynomial model of the second degree is established to quantify the influence of the variables.

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

Table 1
Experimental design levels of chosen variables

Variables	Levels in Box–Behnken design		
Coded level	Low (–1)	Middle (0)	High (+1)
Current density, mA/cm^2	5	20	35
pH	5	8	11
Treatment time, min	6	18	30

where X_1, X_2 and X_3 are the independent variables representing current density, pH and time of electrolysis respectively; β_0 is a constant; β_1, β_2 and β_3 are the coefficients translating the linear weight of X_1, X_2 and X_3 respectively; β_{12}, β_{13} and β_{23} are the coefficients translating the interactions between the variables; β_{11}, β_{22} and β_{33} of the coefficients translating the quadratic influence of X_1, X_2 and X_3. Linear and second order polynomials were fitted to the experimental data to obtain the regression equations.

3. Results and discussion

3.1. Statistical analysis

In this work the combined effects of current density, pH, and treatment time at various levels for oil removal were monitored. Table 2 shows the data resulting from the experiments of the effect of the three variables on the treatment of metal working emulsions. The experimental results were analyzed through a RSM design to obtain an empirical model for the best response. The predicted results by the model are shown in Table 2.

The estimated response seems to have a functional relationship only in a local region or near the central points of the model. The quadratic model was used to explain the mathematical relationship between the independent variables and dependent responses.

The coefficients values of Eq. (2) were calculated and tested for their significance using Design-MODDE 6 and are listed in Table 3. The *P* values are used as a tool to check the significance of each coefficient, which in turn may indicate the pattern of the interactions between the variables. The smaller the value of *P*, the more significant is the corresponding coefficient. It can be seen from this table that the linear coefficients (X_1, X_2), a quadratic term coefficient (X_3^2) were highly significant ($P = 0.002$). A linear coefficient (X_3) and a quadratic coefficient (X_1^2, X_2^2) may be slightly significant ($P = 0.06$). The other term coefficients (X_1X_2, X_1X_3 and X_2X_3) are not significant.

Table 3
Test of significance for regression coefficients

Coefficient	Coefficient value	Standard error	Significance level (P)
β_0	96.7667	2.5470	0.0021
β_1	12.9488	1.5597	0.0004
β_2	–9.5050	1.5597	0.0017
β_3	29.9912	1.5597	0.0173
β_{11}	–26.8046	2.2958	0.0539
β_{22}	–26.5321	2.2958	0.0573
β_{33}	–14.0696	2.2958	0.0016
β_{12}	–3.4500	2.2057	0.1785
β_{13}	–0.5525	2.2057	0.8121
β_{23}	–3.8950	2.2057	0.1376

The mathematical expression of relationship of the turbidity removal with the three variables (X_1, X_2 and X_3) is shown below as in terms of coded factors. This equation makes it possible to predict the rate of oil removal emulsion.

$$Y = 96.767 + 12.949\ X_1 - 9.505\ X_2 + 29.991\ X_3 - 26.804\ X_1^2 - 26.532\ X_2^2 - 14.069\ X_3^2 \quad (3)$$

Table 2
Box-Behnken design consisting of experiments for the study of three experimental factors in coded and actual levels with experimental and predicted values for turbidity removal, *Y* (%)

Test number	Coded level of variables			Actual level of variables			Turbidity removal *Y*, %	
	X_1	X_2	X_3	*i*, mA/cm²	pH	t_E, min	Observed	Predicted
1	–1	–1	0	5	5	18	34.63	36.54
2	1	–1	0	35	5	18	72.32	69.33
3	–1	1	0	5	11	18	21.44	24.43
4	1	1	0	35	11	18	45.33	43.42
5	–1	0	–1	5	8	6	12.55	12.40
6	1	0	–1	35	8	6	34.66	39.40
7	–1	0	1	5	8	30	78.23	73.49
8	1	0	1	35	8	30	98.13	98.28
9	0	–1	–1	20	5	6	33.54	31.78
10	0	1	–1	20	5	6	23.40	20.56
11	0	–1	1	20	5	30	96.72	99.55
12	0	1	1	20	11	30	71.00	72.75
13	0	0	0	20	8	18	98.44	96.76
14	0	0	0	20	8	18	96.53	96.77
15	0	0	0	20	8	18	95.33	96.76

Fig. 1 shows the representation of the observed value (experimental) according to the predicted values (calculated).

The good correlation between the measured values and those predicted by the model confirms the quality of this model. In addition, the model gives R^2 value of 0.993 and an adjusted R^2 value of 0.982. These values confirm that the equation of the model is highly reliable. This indicates also that the model terms are significant at 95% of probability level.

The statistical significance of the ratio of mean square variation due to regression and mean square residual error was tested using the analysis of variance (ANOVA). ANOVA is a statistical technique that subdivides the total variation in a set of data into component parts associated with specific sources of variation for the purpose of testing hypotheses on the parameters of the model [14].

According to analysis of variance (Table 4), it was shown that the predictability of the model is at 95% confidence interval. The ANOVA of these responses demonstrated that the model is highly significant as is evident from the value of $F_{statistic}$ (the ratio of mean square due to regression to mean square to real error), (F_{model} = 83.579) and a very low probability value (P = 0.0001). The value of probability $P < 0.01$ indicates that the model is considered statistically significant [15].

Fig. 2 shows the studentized residuals vs. predicted turbidity removal plot. The general impression is that the plot should be a random scatter, suggesting that the variance of original observations is constant for all values of the response. Generally, it is important to confirm the fitted model to make sure that it gives sufficient approximation to the actual test.

3.2. Effect of variables on turbidity removal

Using experimental design, the combined effects of the three variables can be predicted which is difficult to observe in conventional methods. The effects of variables on turbidity removal are shown in Fig. 3. This figure shows the 3-D response surface plots of interactions between varying current density and pH on removal turbidity where the time is kept at a constant value (30 mn). The semi-spherical response surface of removal turbidity

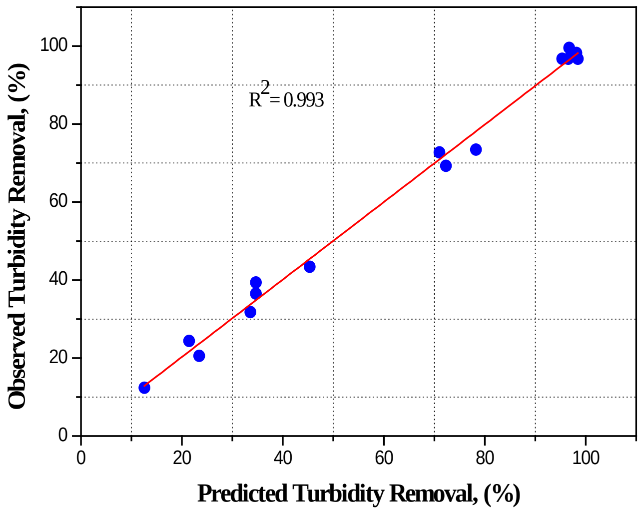

Fig. 1. Relation between experimental and predicted turbidity removal using Eq. (3).

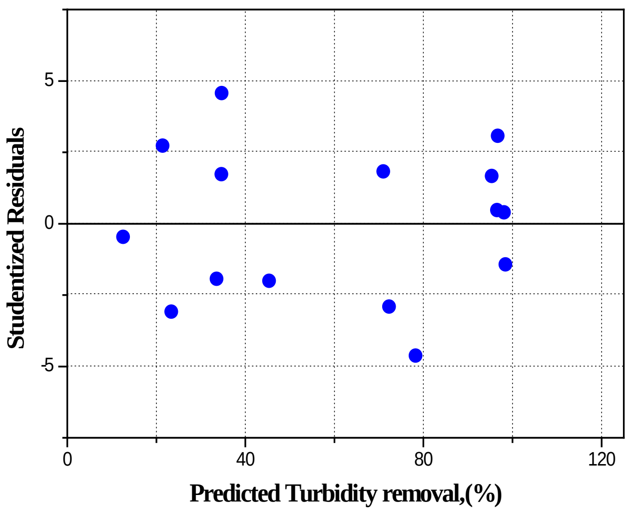

Fig. 2. Predicted turbidity removal and studentized residual plots.

Table 4
ANOVA results for the quadratic equation for turbidity removal of MWE

Source	Degree of freedom	Sum of squares	Mean square	*F* value	*P*
Model	9	14639.40	1626.60	83.579	0.0001
Residual	5	97.31	19.46	__	__
Lack of fit	3	92.39	30.79	12.518	0.0750
Pure error	2	4.92	2.46	__	__
Total	14	14736.71	1659.85	__	__

R^2 = 0.993; R^2_{adj} = 0.982

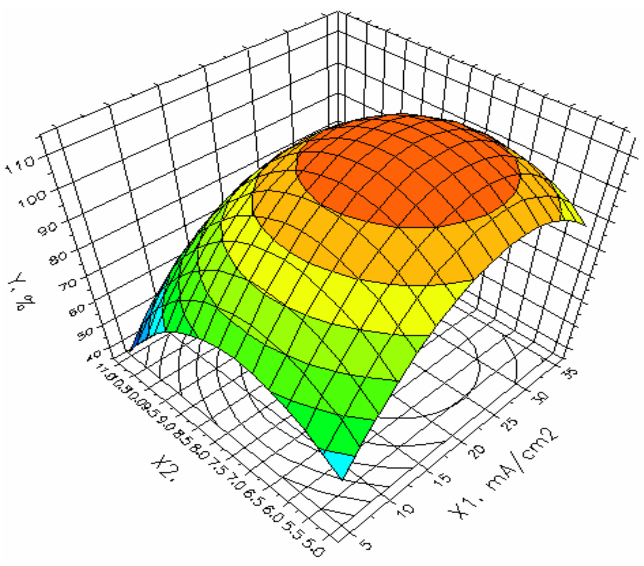

Fig. 3. 3D response surface plots for turbidity removal vs. current density and pH, MWE 5% (in wt.), pH = 7.

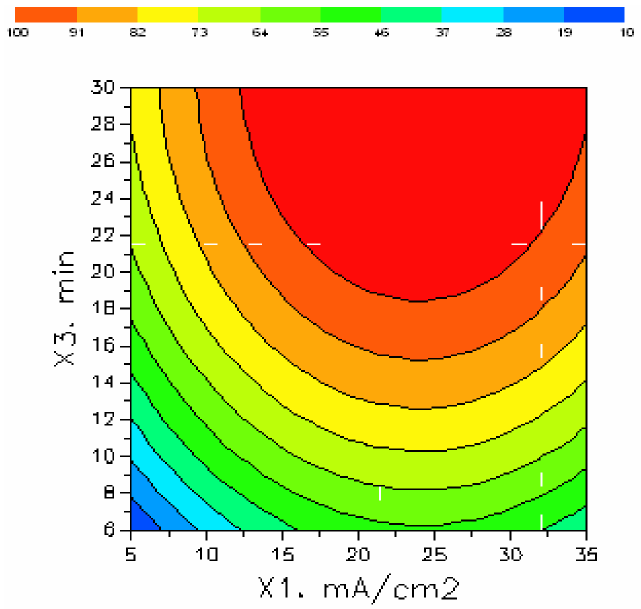

Fig. 4. Contour plots of turbidity removal vs. current density and treatment time, MWE 5% (in wt.), pH = 7.

gradually increased with increasing pH (from 5 to 7) at any current density, and again gradually decreased above pH = 7. For values of pH > 8, the effectiveness of elimination falls gradually. The maximum removal turbidity was observed at neutral pH (6–7). This is in agreement with many works related to oil/water emulsion treatment by electrocoagulation process [16,17].

The surface plot shows the increase in removal turbidity with an increase in current density. In the scope of operational cost, the optimum pH value and current density are 7 and 20 mA/cm^2, respectively, for optimum removal turbidity percentage.

Fig. 4 illustrates the two-dimensional contour plots of the quadratic model. The corresponding two-dimensional contours show a considerable curvature in contour curves, implying that these two factors were interdependent (Fig. 4). It can be deduced from these observations that there are significant interactive effects on turbidity removal between current density and treatment time. The contour plot of current density versus treatment time shows that the optimal conditions for removal turbidity were located in the region, where current density ranged from 20 to 25 mA/cm^2 and treatment time 20–30 min (Fig. 4).

According to Faraday's law, since the current density increases, the efficiency of ion production on the anode and cathode increases. Therefore, there is an increase in flocs production in the solution and hence an improvement in the efficiency of turbidity removal. Additionally, bubble generation rate increases and bubble size decreases with increasing current density. These effects are both beneficial for high pollutant removal by H_2 flotation [18]. Moreover as shown by Khemis et al. [19], higher production rates of hydrogen allowed by higher currents, favors the flotation of the flocculated matter.

The optimization of the operating conditions was obtained by optimizing the model of Eq. (3). These values were also experimentally validated. The optimum values of the process variables for the maximum turbidity removal efficiency are shown in Table 5. It was found that the optimal current density is 23.59 mA/cm^2, at which the predicted turbidity removal is 99.33%. As we can see, these results closely agree with the experimental results,

Table 5
Optimum and confirmative values of the process parameters for maximum removal efficiency

Processes parameters	Optimized values (predicted values)	Confirmation values (mean actual values)
Turbidity removal *Y*, %	99.33	98.85
Current density *i*, mA/cm^2	23.59	23.59
pH	7.17	7.17
Treatment time t_E (min)	20	20

confirming that the Box-Behnken design could be effectively used to optimize the process parameters in complex processes using the statistical design of experiments.

4. Conclusion

In the present study, the performance of electrochemical treatment of metal working emulsion was studied focusing on the influence of operating parameters such as current density, pH and treatment time by using a response surface method and in particular a Box-Benhken design. The results obtained from the present study revealed that RSM was a suitable method to optimize the operating conditions of electrocoagulation. The response surface models developed in this study for predicting turbidity removal efficiency were considered to be adequately applicable. Analysis of variance showed a high coefficient of determination value (R^2 = 0.993) ensuring a satisfactory adjustment of the second-order regression model with the experimental data. Interestingly, 3-dimension response surfaces plots can be a good way for visualizing parameter interactions. The results of this study indicate that electrocoagulation is an effective method for turbidity removal.

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