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Optimization of operational parameters in the pretreatment of surface water by electrocoagulation using a response surface method

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ABSTRACT

The objectives of this work were to investigate the use of electrocoagulation (EC) as a pretreatment for surface water prior to its purification. To minimize the number of experiments, an experimental design was proposed for the control of experiments and the knowledge of the parameter effects on the effectiveness of this operation. For a best approach, a response surface method (RSM) was used in order to evaluate the influence of operational parameters on water quality. The influence of varying parameters was studied using in particular a D-optimal design. The models of surface responses developed in this study to predict the effectiveness of the pretreatment process were regarded as sufficiently applicable. The results obtained by polynomial simulation are in agreement with those obtained during the preliminary experiments.

Keywords: Surface water; Pretreatment; Electrocoagulation; Optimization; RSM

1. Introduction

The goal of water pretreatment prior to its purification by membrane separation is to provide a consistent and high quality feed water to mitigate the flux decline of membranes [1].

Pretreatment technologies have advanced from conventional coagulation and multimedia filtration, to microfiltration and ultrafiltration. While coagulation generally has little effect on scaling, coagulation pretreatment can be effective for the removal of microorganisms, colloids, and organics [2]. However, the chemical methods of pretreatment are less effective because sulphate present in water forms deposits and can reduce the effectiveness of water purification essentially when membranes are used [3].

Recent research has demonstrated that electrochemical techniques which offer attractive alternatives to the aforementioned traditional methods for treating wastewaters [4,5]. Electrocoagulation (EC), which is one of these techniques, is the electrochemical production of destabilization agents that brings about charge neutralization for pollutant removal, and it has been widely used for water or wastewater treatment [6,7].

EC is a process consisting of creating a floc of metallic hydroxide within the effluent to be treated by electro-dissolution of a soluble anode. The coagulant in this technique is mentioned *in situ* by dissolution of a sacrificial anode and it involves three main processes [8]: electrolytic reaction at electrode surface,

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formation of coagulants by electrolytic oxidation in aqueous phase and adsorption of colloidal particles on coagulant, and removal by sedimentation or flotation.

It must be noted that, the reported studies on pretreatment of surface water by chemical or electrochemical processes deal with the conventional method of experimentation, which involves changing one of the independent parameters maintaining the others at fixed levels. This classical or conventional method involves many experimental runs, which are time-consuming; ignores interaction effects between the considered operating parameters of the process, and leads to a low efficiency in optimization. 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 [9,10].

The objectives of this research were to investigate the use of EC as a pretreatment for surface water prior to its purification. To minimize the number of experiments, an experimental design was used for the control of experiments and the knowledge of the parameter effects on the effectiveness of these operations. For a best approach, an RSM was used in order to optimize the operational parameters leading to a best quality of water quantified by turbidity measurements.

2. Materials and methods

2.1. Experimental device

The experimental device is depicted in Fig. 1. As can be seen, a laboratory scale reactor consisted of an undivided EC cell made of organic glass with parallel plates and rectangular aluminum electrodes. The gap between the anode and cathode was fixed at a distance of 1.5 cm. The anode and cathode were connected to an electric generator.

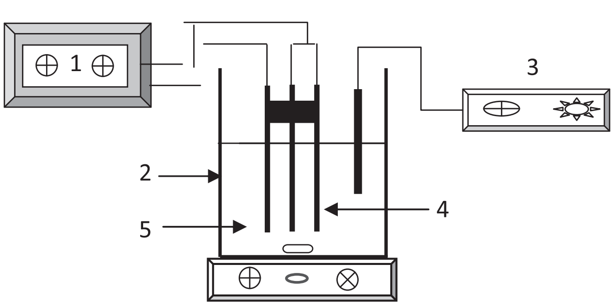

Fig. 1. Pilot plant EC cell (1. DC power supply; 2. EC cell; 3. pH-meter and thermometer; 4. Cathode; and 5. Anode).

2.2. Materials

Samples used in the present study were collected from the alimentation of a pharmaceutical unit of production. The characteristics of the water before treatment are given in Table 1. Sodium chloride (NaCl) used for the improvement of conductivity was purchased from Fluka.

2.3. Analysis

Standard methods were adopted for quantitative estimation of turbidity. The pH was measured using a pH-meter (digtal Inolab, pH level 1, model 60027).

2.4. Experimental design

The statistical design of experiments is a structured and systematized method of experimentation in which all factors varied simultaneously over a set of experimental runs in order to determine the relationship between the factors affecting the output responses. RSM was applied to evaluate and determine the optimum operating conditions. In order to evaluate the pretreatment efficiency and the effect of operating conditions on the EC performance, a D-optimal design was applied.

The D-optimal method is relatively a new technique, related to RSM, used for carrying out the design of experiments, the analysis of variance, and the empirical modeling [11]. The D-optimal design is a computer aided design which contains the best subset of all possible experiments. A design is defined to be D-optimal if it maximizes the determinant of the information matrix [12]. This design allowed studying multiple factors with varying levels using a minimal number of experiments. It also maximizes the information in the selected set of experimental runs with respect to a stated model.

Table 1
Water characteristics before treatment

Features	Initial conditions
Turbidity	2–5 NTU
Total hardness	510–550 ppm
pH	7–8
NaCl concentration	1 g/L

Table 2
Factors and their levels

Factor	Specification	Experimental field	Unity
X_1	Current density	0.1−0.5	mA/cm^2
X_2	pH	5–9	–
X_3	Electrolyze time	1–10	min

In this work, the effects of three independent factors were investigated using D-optimal design. Coded and original levels for the process factors are shown in Table 2. The coding of variables was done per the equation:

$$X_i = (x_i - x_{cp})/\Delta x_i \quad (1)$$

where X_i is the coded level, x_i is the real value, x_{cp} is the real value of the centred point, and Δx_i is the value of variable change step.

The suggested mathematical model takes into account all the double interactions between the factors and the nonmonotonous effects. Thus the model, noted Y and representing the response, is of polynomial quadratic type (Eq. (2)):

$$Y = a_0 + a_1X_1 + a_2X_2 + a_3X_3 + a_{11}X_1^2 + a_{22}X_2^2 + a_{33}X_3^2 + a_{12}X_1X_2 + a_{13}X_1X_3 + a_{23}X_2X_3 \quad (2)$$

where Y is the response and X_1, X_2, and X_3 are the factors.

To estimate the coefficients of this model, a set of experiments well spread in the domain that is a design of experiments optimal for a second-order polynomial model are needed. Indeed, the quality of the coefficient estimation and the quality of the prevision only depend on the choice of the experimental points. For a studied response (Y), the estimates (a_i, a_{ii}, and a_{ij}) were calculated using a multilinear regression.

Some experiments were replicated in order to estimate the variance of the experimental results. Then, to minimize the effect of systemic errors, experiments were carried out in a random fashion.

3. Results and discussion

3.1. Statistical analysis

The arrangements of D-optimal experiments include 17 sets of EC experiments including three repetitions for the calculation of the pure error.

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.

By using multiple regression analysis, the response (turbidity) was correlated with the three design factors using the second-order polynomial (Eq. 2). The quadratic regression model for turbidity (Y, NTU) in terms of coded factors is given by Eq. (3):

$$Y = 0.2395 + 0.0213X_1 + 0.0310X_2 + 0.0519X_3 + 0.0751X_1^2 + 0.1599X_2^2 + 0.0547X_3^2 - 0.1819X_1X_2 + 0.0840X_1X_3 + 0.0183X_2X_3 \quad (3)$$

Fig. 2 shows the representation of the observed value (*experimental*) according to the predicted values (*calculated*).

The quality of this model and its power of prediction, are related to the variance coefficient, R^2. 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 a value of 0.923. This value confirms that the equation of the model is highly reliable. This also indicates that the model terms are significant. The model is also reproducible; the value of reproducibility is close to 1.

The statistical significance of the ratio of mean square variation due to regression and mean square

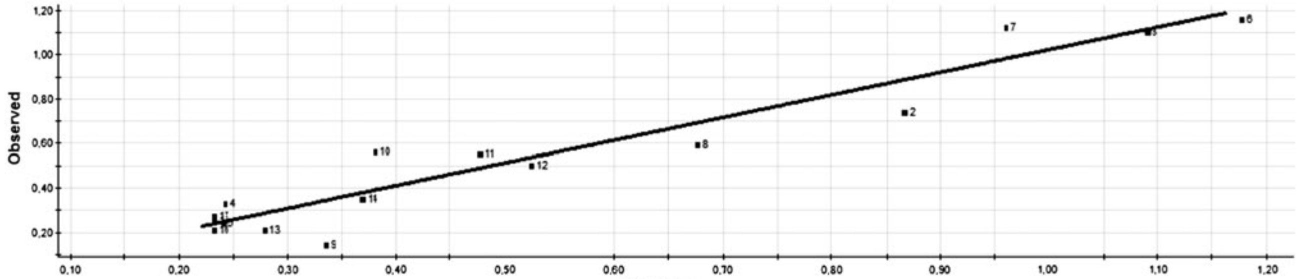

Fig. 2. Relation between experimental and predicted turbidity.

Table 3
Analysis of variance (ANOVA) for the RSM model of turbidity

Source	Sum of squares	Degrees of freedom	Mean square	*F*-value	*P*
Model (Regression)	1.7776	9	0.1818	7.7308	0.011
Residual	0.1411	6	0.0235		
Lack of fit	0.1392	4	0.0348	37.302	0.026
Pure error	0.0018	2	0.0009		

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 [13].

Table 3 shows ANOVA results for turbidity response (Y). The F-ratio shown is used to determine the statistical significance of the extraction–elution process. The F-value is a ratio of two independent estimates of experimental error. Associated with this ratio, a P-value which quantifies the probability of making an error by associating an effect with a given factor. The P-value also provides the exact level of significance of a hypothesis test. The R-square values indicate the percentage of variation of the response that is explained by the deliberate variation of the factors in the case of experiment. The ANOVA of these responses demonstrated that the model is highly significant as is evident from the value of $F_{\text{statistic}}$ (the ratio of mean square due to regression to mean square to real error) ($F_{\text{model}} = 7.7308$) and a very low probability value ($p = 0.011$). The low value of probability indicates that the model is considered statistically significant [14].

3.2. *Effect of variables on turbidity removal*

The own effect of the main factors and their interactions on the response can be deduced by simulation. The iso-response curves were used to determine the best compromise in the experimental domain. Fig. 3 shows the effects of pretreatment factors and their interactions on turbidity. These effects represent the coefficients in the surface response model Eq. (3).

With regard to these effects, pretreatment time has the most significant influence. This statistical interpretation is in agreement with what would physically take place in the electrochemical process. The longer time of pretreatment is, the more of suspended matter is evacuated towards the surface by the bubbles produced by electrolysis. However, it seems that interactions pH–pH have a positive effect on turbidity whereas the interactions current density-pH have a negative effect. Indeed, in the electrochemical processes, the most important factors are the current density and the initial pH. These two parameters are responsible for the performance of this process [15]. It is thus very significant to control these two factors simultaneously in order to be able to determine the optimum conditions for pretreatment. In addition, it seems according to these results that the interactions between current density and electrolysis time have also a considerable effect on the effectiveness of pretreatment.

3.3. *Optimization of the pretreatment factors*

Using experimental design, the combined effects of the three variables can be predicted which are difficult

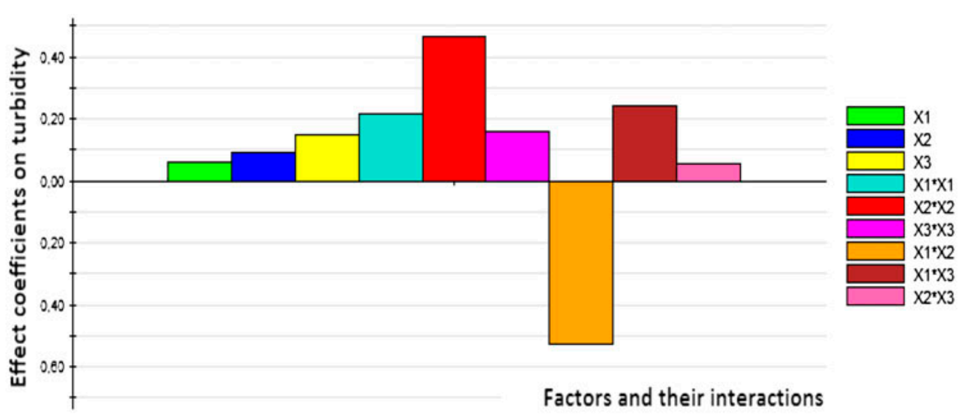

Fig. 3. Effects of the operating factors and their interactions on the turbidity of the treated solution.

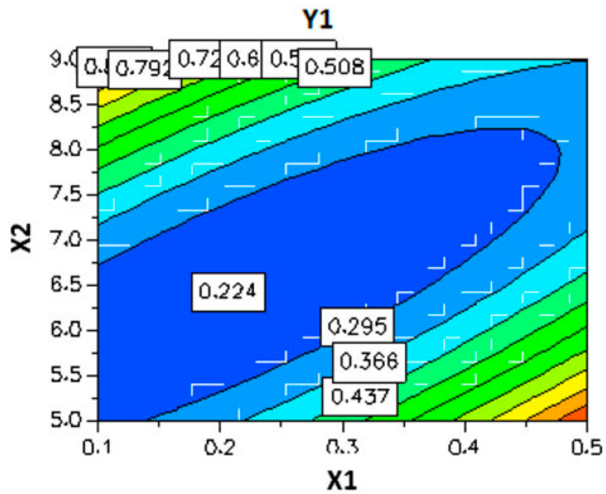

Fig. 4. Contour plots of turbidity removal vs. current density and pH.

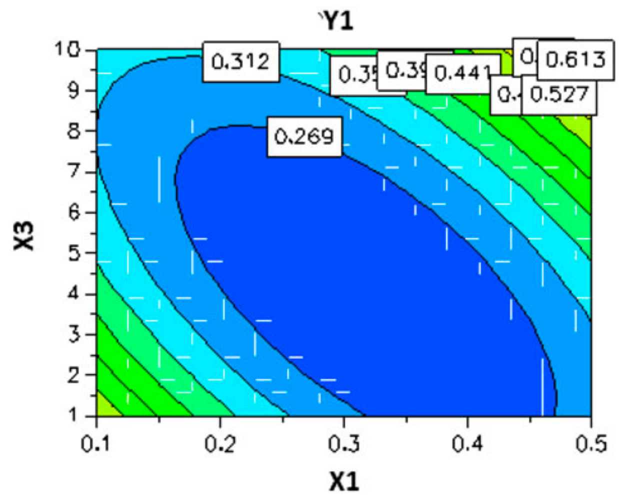

Fig. 5. Contour plots of turbidity removal vs. current density and electrolyze time.

to observe in conventional methods. The effects of variables on turbidity removal are shown in Figs. 4–6, respectively.

Fig. 4 shows the contour plots of interactions between varying current density (X1) and pH (X2) on the removal turbidity (Y1), where the time (X3) is kept at a constant value (medium value). In the batch EC process, current density is a critical parameter, as it is the only operational parameter that can be directly controlled; it was suggested that current density determines both coagulant dosage and bubble generation rates [16]. From this figure, it was noted that the increase in current density and pH improve the elimination of the suspended matter. The removal turbidity gradually increased with increasing pH from a value of 7.5 at any current density. For values of pH > 8, the effectiveness of elimination falls gradually. A minimal turbidity of 0.224 NTU is reached when the pH is between 6.5 and 7.5 and the current density is about 0.3 mA/cm^2, owing to the fact that these two factors contribute to the increase in water quality, the turbidity reaches a minimum value. These values can be considered as optimal values leading to the best operation of pretreatment.

Fig. 5 shows the combined effects of current density (X1) and electrolysis time (X3) on turbidity. The corresponding two-dimensional contours show a considerable curvature in contour curves, implying that these two factors are interdependent. 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 vs. treatment time shows that the optimal conditions for removal turbidity were located

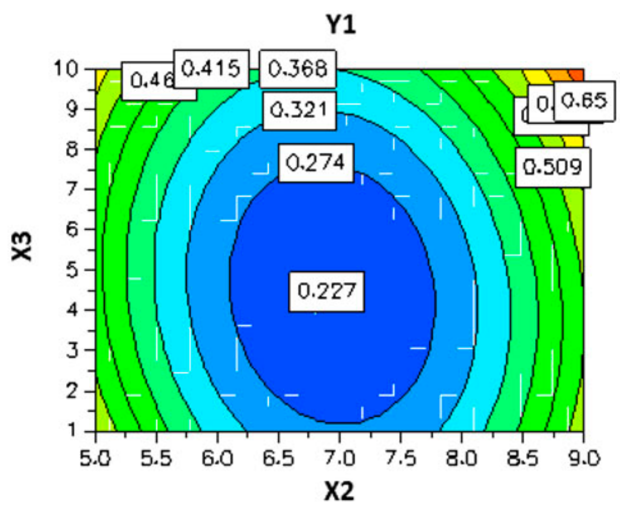

Fig. 6. Contour plots of turbidity removal vs. pH and electrolyze time.

in the region, where current density ranged from 0.3 to 0.45 mA/cm^2 and treatment time of 2–7 min. When the electrolyze time is higher than 08 min, the water turbidity increases. This can be explained by the fact that more the processing time increases, the release of ions $Al3^+$ increases causing an increases in water turbidity. 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.

From Fig. 6, illustrating the combined effects of pH (X2) and electrolyze time (X3) on turbidity (Y1), it was noted the presence of an optimal region where the turbidity is at its minimum value of 0.227. For a value of pH of 7 and electrolyze time of 5 min, the turbidity is minimal. This proves that the optimal conditions have been met and the pretreatment process is effective.

The optimal values of the process variables for the minimum turbidity can be obtained from the contour plots realized for the three independent factors. It was found that the optimal values are: current density of $0.3\,\mathrm{mA/cm^2}$, pH = 7, and electrolyze time of 05 min. At these conditions the turbidity is about 0.22.

4. Conclusion

In the present study, the performance of an electrochemical method as EC used for the pretreatment of water prior to reverse osmosis treatment was evaluated using an experimental design. The quadratic model developed in this study shows the presence of a high correlation between experimental and predicted values. Analysis of variance showed a high coefficient of determination value, thus ensuring a satisfactory adjustment of the second-order regression model with the experimental data. Under optimal values of process parameters obtained by simulation (current density = $0.3\,\mathrm{mA/cm^2}$, pH = 7, electrolyze time = 05 min) the efficiency of the pretreatment by EC was demonstrated where the turbidity was about 0.22 NTU.

References

[1] H.-F. Zhang, B.-S. Sun, X.-H. Zhao, J.-M. Sun, Membrane fouling caused by soluble microbial products in an activated sludge system under starvation, Desalin. Water Treat. 1 (2009) 180–185.

[2] A. Bagga, S. Chellam, D. Clifford, Evaluation of iron chemical coagulation and electrocoagulation pretreatment for surface water microfiltration, J. Membr. Sci. 309 (2008) 82–93.

[3] K. Jones, C. O'Melia, Ultrafiltration of protein and humic substances: Effect of solution chemistry on fouling and flux decline, J. Membr. Sci. 193 (2001) 163–173.

[4] M. Mollah, R. Schennach, J. Parga, D. Cocke, Electrocoagulation-science and applications, J. Hazard. Mater. 84 (2001) 29–41.

[5] Y. Yildiz, A. Koparal, S. Irdemez, B. Keskinler, Electrocoagulation of synthetically prepared waters containing high concentration of NOM using iron cast electrodes, J. Hazard. Mater. 139 (2007) 373–380.

[6] P. Canizares, C. Jimenez, F. Martinez, C. Saez, M. Rodrigo, Study of the electrocoagulation process using aluminumand iron electrodes, Ind. Eng. Chem. Res. 46 (2007) 6189–6195.

[7] T.C. Timmes, H.-C. Kim, B.A. Dempsey, Electrocoagulation pretreatment of seawater prior to ultrafiltration: Bench-scale applications for military water purification systems, Desalination 249 (2009) 895–901.

[8] M.Y.A. Mollah, P. Morkovsky, J.A.G. Gomes, M. Kesmez, J. Parga, D.L. Cocke, Fundamentals, present and future perspectives of electrocoagulation, J. Hazard. Mater. 114 (2004) 199–210.

[9] S. Morgenthaler, M.M. Schumacher, Robust analysis of a response surface design, Chemom. Intell. Lab. Syst. 47 (1999) 127–141.

[10] M.Y. Nordin, V.C. Venkatesh, S. Sharif, S. Elting, A. Abdullah, Application of response surface methodology in describing the performance of coated carbide tools when turning AISI 104 steel, J. Mater. Process. Technol. 145 (2004) 46–58.

[11] R.H. Myers, D.C. Montgomery, Response Surface Methodology: Process and Product Optimization Using Designed Experiments, second ed., John Wiley and Sons, New York, NY, 2002.

[12] R. Schwabe, W. Wierich, D-optimal designs of experiments with non-interacting factors, J. Statist. Plann. Inference 44 (1995) 371–384.

[13] L. Huiping, Z. Guoqun, N. Shanting, L. Yiguo, Technologic parameter optimization of gas quenching process using response surface method, Comput. Mater. Sci. 38 (2007) 561–570.

[14] M.S. Phadke, Quality Engineering Using Robust Design, Prentice Hall, New Jersey, 1989.

[15] M. Tir, N. Moulai-Mostefa, Electrochemical treatment of metal working emulsions using Box-Behnken design, Desalin. Water Treat. 7 (2009) 214–219.

[16] M. Khemis, J.P. Leclerc, G. Tanguy, G. Valentin, F. Lapicque, Treatment of industrial liquid wastes by electrocoagulation. Experimental investigations and an interpretation model, Chem. Eng. Sci. 61 (2006) 3602–3609.