

OPTIMIZATION OF COAGULATION PRETREATMENT OF A REAL DAIRY EFFLUENT USING A RESPONSE SURFACE METHOD

Radia Madjdoub*¹ and Nadji Moulai-Mostefa²

¹ Department of Process Engineering, University of Blida, Route de Soumaa, 09000 Blida, Algeria

² Materials and Environmental Laboratory University of Medea, Ain D'Heb, 26001 Medea, Algeria

Received 15 September 2018; received in revised form 16 May 2019; accepted 18 May 2019

Abstract:

This paper proposes a pretreatment of a real dairy effluent by coagulation and decantation using two types of coagulants, aluminum sulfate ($Al_2(SO_4)_3$) and ferric chloride ($FeCl_3$). In order to optimize the best coagulation conditions leading to maximums of COD and turbidity removals, response surface method (RSM) was employed. The analysis of variance showed that the values of the correlation coefficients (R^2) for the reduction of turbidity and COD were found equal respectively to 0.959 and 0.840, which gives an idea about the validity of the quadratic developed models and their predictive qualities. The results predicted by the models were 98.18 and 77.06% of turbidity and COD removals, at $Al_2(SO_4)_3$ concentration of 1200 mg/L and time of treatment of 38.57min. These results are in agreement with those obtained experimentally.

Keywords:

Dairy effluent, Coagulation, DCO, Turbidity, Optimization, RSM

© 2019 Journal of Urban and Environmental Engineering (JUEE). All rights reserved.

* Correspondence to: Nadji Moulai-Mostefa. E-mail: moulai_nadj@yahoo.fr

INTRODUCTION

Dairy industry, as most food industries produces large quantities of wastewater emulsions (oil-in-water), difficult to treat because of their complex behavior. These emulsions contain carbohydrates, proteins and milk fat (Tikariha & Sahu, 2014). They have a high biological oxygen demand (BOD) and chemical oxygen demand (COD) in addition to nitrogen and phosphorus. Thus dairy wastewaters must be treated by three water rinsing steps before being discharged in the environment (Singh *et al.*, 2014; Bharati & Shinkar, 2013).

Several processes may be used for treating these effluents. They aim at recovering proteins and lactose, or degrading substances which may alter river water quality (Vidal *et al.*, 2000). It is efficient to use treatments which eliminate pollutants, and decrease BOD and COD (Singh *et al.*, 2014).

Main techniques are aerobic purification (Tocchi *et al.*, 2012; Harush *et al.*, 2011) and anaerobic processes (Passeggi *et al.*, 2009; Vlyssides *et al.*, 2012), in addition to membranes processes (Balannec *et al.*, 2002; Gong *et al.*, 2012; Suarez *et al.*, 2014) and membranes bioreactors (Andrade *et al.*, 2013).

Coagulation is mainly used in wastewater treatment (Ayeche, 2012; Birjandi *et al.*, 2013; Silva *et al.*, 2009) as it permits elimination and destabilization of colloidal particles by addition of an electrolyte. They aggregate as larger particles, and precipitate as hydroxides (Everet, 1988).

Coagulation and flocculation facilitate elimination of suspended matter and colloids by gathering them as flocks whose separation is done by decantation, flotation and/or filtration. It permits to eliminate a part of pollutants such as organic matters and heavy metal, micropollutants and colloidal macromolecules (Xiong *et al.*, 2017).

The most used coagulants are in general iron and aluminum ions (Fe^{3+} and Al^{3+}), which polymerize under different forms according to pH (Cathalifaud *et al.*, 1998).

The objective of this work is to develop a pretreatment process of a dairy effluent. The process combines coagulation and decantation by using two types of chemical coagulants, aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3$) and ferric chloride (FeCl_3). Experiments were conducted following a modeling by surface responses (RSM).

MATERIALS AND METHODS

Dairy effluents

Wastewater samples were collected from a dairy unit near Blida (Algeria). This unit is connected to the dairy effluent, consisting of process water, washing waters

and cleaning waters. 10 L of fluid were collected and kept at 4 °C to avoid degradation of dairy products.

Table 1 presents results of physiochemical characteristics of effluent rejected by the dairy plant. COD, turbidity, pH and temperature values exceed by far the limits relative to rejected liquids. The analyzed organic charge averaged 2678.4 mg of O_2/L for COD, 264 NTU for turbidity and 450 mg/L for suspended matters. Such values correspond to this type of rejects (Tikariha & Sahu, 2014; Singh *et al.*, 2014).

MATERIALS

Ferric chloride (FeCl_3), aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3$), sodium chloride (NaCl), sodium hydroxide (NaOH), chlorhydric acid (HCl), sulfuric acid (H_2SO_4), potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$), silver sulfate (Ag_2SO_4) were supplied by Panreac (Spain).

Analytic methods

Turbidity was measured with a turbidimeter from Eutech Instruments (TN-100). Effluent pH was measured according to AFNOR NFT 90-008 method, using a pH-meter Jenway 3505 permitting to measure simultaneously temperature (± 0.1 °C) and pH. COD was measured according to AFNOR NFT 90-101 norm and was expressed in oxygen (mg/L) of solution.

Device and experimental protocol

The various coagulation-sedimentation tests were conducted on dairy effluent at room temperature (24 ± 2 °C) according to the well-known protocol of Jar Test and using a flocculator (Stuart-flocculator model, SW6). Each coagulant test was performed in six one-liter beakers containing 500 mL of solution to be treated. Coagulant solution volumes were introduced within six beakers at escalating doses of 200 to 1200 mg/L for a short period of agitation (3 min), but with rapid stirring speed (180 rpm) to ensure a good distribution of additives and good chemical destabilization of colloids. This phase was followed by a slow agitation (30 rpm) for 10, 20, 30 and 40 min in order to promote bringing into contact of the continuous particles and avoid breaking the formed flocks. Finally, these flocks were kept undisturbed for 120 min. After settling, a sample was analyzed.

Table 1. Physical and chemical characteristics of dairy effluent

| Properties | Sample | Standards |
|-------------------------|--------|-----------|
| pH | 10.43 | 5.5–8.5 |
| Temperature (°C) | 34 | 30 |
| Turbidity (NTU) | 264 | - |
| COD (mg/L) | 2678.4 | 125 |
| Suspended matter (mg/L) | 450 | 30-100 |

Experimental design

Response surface methodology (RSM) and in particular a D-optimal design was employed to evaluate the influence of experimental parameters and their interactions on the reduction of COD and turbidity. D-optimal design is useful for the estimation of parameters because it minimizes the generalized variance. Many environmental applications have used this design for optimization and predictions (Grčić *et al.*, 2010; Hasan *et al.*, 2012; Kermet-Said & Moulai-Mostefa, 2015).

The selected (independent) variables were the coagulant concentration (X_1), stirring time (X_2) and type of coagulant (X_3), where the percentage of removal of turbidity (Y_1) and the percentage of removal of COD (Y_2) were selected as responses. Using the obtained data from experiments, regression analysis was made.

Table 2 summarizes the initial levels for the process factors. The range of valid values for these factors was deduced from preliminary tests. Experiments were performed in duplicate. The relationship between responses and independent variables was calculated by a second order polynomial equation (**Eq. 1**):

$$Y = b_0 + \sum b_i + \sum b_{ii}X_i^2 + \sum \sum b_{ij}X_iX_j \quad (1)$$

where Y is the expected response and, X_i are the input variables. The regression coefficients (b_0 , b_i , b_{ii} and b_{ij}) were calculated and analyzed in terms of statistical significance (Bas & Boyaci, 2007).

The construction of the D-optimal design and its analysis were performed using statistical software Modde-6 (Umetrics).

RESULTS AND DISCUSSION

D-Optimal experiments

The modalities of D-Optimal design include 17 coagulation experiments (**Table 3**) with four replicates to calculate the pure error (center point).

The study of the factor effects allowed giving various settings in order to optimize the operating variables leading to better efficacy of treatment of dairy effluent. The obtained experimental results were analyzed by a regression procedure of response surface and were evaluated in the form of a polynomial equation of the second order. The quadratic regression models for the removal of turbidity (Y_{1A} , Y_{1B}) and COD (Y_{2A} , Y_{2B}) are as follows:

Table 2. Independent variables and corresponding levels in the experimental field

| Symbol | Designation | Field |
|--------|---|----------|
| X_1 | Concentration of coagulant (mg/L) | 200–1200 |
| X_2 | Coagulation time (min) | 10–40 |
| X_3 | Coagulant nature (A: FeCl ₃ ; B: Al ₂ (SO ₄) ₃) | A or B |

Table 3. Coagulation experimental matrix

| Exp | X_1 | X_2 | X_3 | Y_1 | Y_2 |
|-----|-------|-------|---|-------|-------|
| 1 | 200 | 10 | FeCl ₃ | 74.10 | 64.14 |
| 2 | 1200 | 10 | FeCl ₃ | 94.66 | 50.95 |
| 3 | 1200 | 40 | FeCl ₃ | 51.90 | 55.08 |
| 4 | 200 | 30 | FeCl ₃ | 86.90 | 72.76 |
| 5 | 1200 | 20 | FeCl ₃ | 96.16 | 70.53 |
| 6 | 533 | 10 | FeCl ₃ | 77.54 | 50.22 |
| 7 | 867 | 40 | FeCl ₃ | 40.07 | 28.31 |
| 8 | 200 | 10 | Al ₂ (SO ₄) ₃ | 52.27 | 74.44 |
| 9 | 1200 | 10 | Al ₂ (SO ₄) ₃ | 95.32 | 71.62 |
| 10 | 1200 | 40 | Al ₂ (SO ₄) ₃ | 99.30 | 75.18 |
| 11 | 1200 | 30 | Al ₂ (SO ₄) ₃ | 99.26 | 73.68 |
| 12 | 533 | 40 | Al ₂ (SO ₄) ₃ | 77.95 | 66.81 |
| 13 | 700 | 25 | Al ₂ (SO ₄) ₃ | 71.89 | 43.58 |
| 14 | 700 | 25 | Al ₂ (SO ₄) ₃ | 72.43 | 45.60 |
| 15 | 700 | 25 | Al ₂ (SO ₄) ₃ | 70.32 | 48.90 |
| 16 | 700 | 25 | Al ₂ (SO ₄) ₃ | 71.17 | 51.10 |

$$Y_{1A} = 70.435 + 8.114X_1 - 3.782X_2 - 3.734X_3 + 16.419X_1^2 - 10.236X_2^2 - 6.575X_1X_2 - 5.144X_1X_3 - 13.361X_2X_3 \quad (2)$$

$$Y_{1B} = 70.435 + 8.114X_1 - 3.782X_2 + 3.734X_3 + 16.419X_1^2 - 10.236X_2^2 - 6.575X_1X_2 + 5.144X_1X_3 + 13.361X_2X_3 \quad (3)$$

$$Y_{2A} = 43.686 - 2.885X_1 - 0.331X_2 - 7.218X_3 + 26.854X_1^2 - 3.525X_2^2 + 1.399X_1X_2 + 0.867X_1X_3 - 5.497X_2X_3 \quad (4)$$

$$Y_{2B} = 43.686 - 2.885X_1 - 0.331X_2 + 7.218X_3 + 26.854X_1^2 - 3.525X_2^2 + 1.399X_1X_2 - 0.867X_1X_3 + 5.497X_2X_3 \quad (5)$$

The second order regression models obtained for the operating variables of the removal of turbidity and COD are quite satisfactory as shown in Fig. 1 presenting the predicted values by the models and values obtained experimentally. A comparison of estimated and experimental values confirms the quality of the modeling and the absence of the curvature effect.

The quality of these models and their predictive powers are related to the coefficient of determination (R^2). A high value of R^2 near 1 is desirable and expected R^2 (predicted) must be in reasonable agreement with the adjusted R^2 for a significant model. In addition, the values of R^2 for removal of turbidity and COD are in the order of 0.959 and 0.840, respectively. Adjusted R^2 values are 0.911 and 0.658 for turbidity and COD removals.

The descriptive quality of the models was confirmed. However a second analysis of variance (ANOVA) is used to check this conclusion (Bezerrara *et al.*, 2008). The statistical significance of the models was tested with Fisher's statistical test. The results of ANOVA for the selected responses are given in **Table 4**.

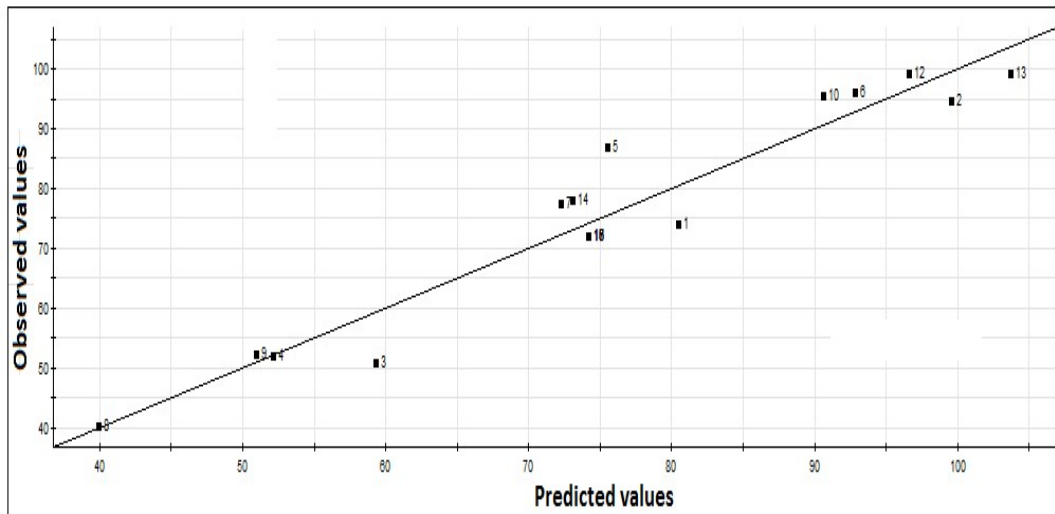


Fig. 1 Graphic test adequacy of the model (Removal of turbidity)

Table 4. Analysis of variance (ANOVA) for the RSM responses

| Source | Sum of squares | Degree of freedom | Mean square | F-value | P |
|--|----------------|-------------------|-------------|---------|-------|
| Turbidity, Y_1 (a) | | | | | |
| Model (regression) | 4644,82 | 8 | 580.602 | 20.2195 | 0.000 |
| Residual | 201.004 | 7 | 28.715 | | |
| Lack of fit | 198.456 | 4 | 49.614 | 58.3997 | 0.004 |
| Pure error | 2.5486 | 3 | 0.8495 | | |
| COD, Y_2 (b) | | | | | |
| Model (regression) | 2491.55 | 8 | 311.444 | 4.60021 | 0.029 |
| Residual | 473.914 | 7 | 67.702 | | |
| Lack of fit | 440.186 | 4 | 110.046 | 9.78821 | 0.045 |
| Pure error | 33.7283 | 3 | 11.2428 | | |

It was noticed from these results that both models are statistically significant if we take into account the value of F ($F_{\text{model (Turbidity)}} = 20.2195$ and $F_{\text{model (COD)}} = 4.6002$) and a probability value ($P = 0.000$ and 0.029 for turbidity and COD, respectively).

Specific effect of factors on system responses

Before proceeding to the evaluation of the effectiveness of the treatment process, we could theoretically establish the specific effect of each factor on selected responses, as shown in Fig. 2.

Examination of this figure shows for turbidity that the linear effect of the coagulant concentration (X1), the quadratic contribution X12 and, the interaction term between the coagulant nature and coagulation time ($X_2X_3(B)$) have the positive and important effect on turbidity removal, while the quadratic contribution (X_{22}) and, the interaction term ($X_2X_3(A)$) have the negative effect; the others do not affect significantly the turbidity removal.

However for the removal of COD, it was noticed that the linear effects of the nature of coagulant (X3(B)), the quadratic contribution (X12) and, the term of interaction

($X_2X_3(B)$) have the important effect on COD. The nature of coagulant (X3(A)) and the term of interaction ($X_2X_3(A)$) were found to have a negative effect on COD. Other factors were found to be negligible.

From the analysis of these graphics, it can be concluded that the coagulant nature and its concentration are always the most important factors for their remarkable effects on the reduction of turbidity and COD.

Optimization of operating conditions

The experimental field was selected from the variation of three factors; so it is difficult to reproduce in a simple way the variation of the responses. Therefore we have to use sections of projections which involve fixing a given level to certain factors. The response surface representation spaces are defined from the variation of two factors.

The graphical representation of the pre-established models in the variable space allows obtaining iso-response curves. These curves constitute a response surface projection in the horizontal plane (Fig. 3 and Fig. 4).

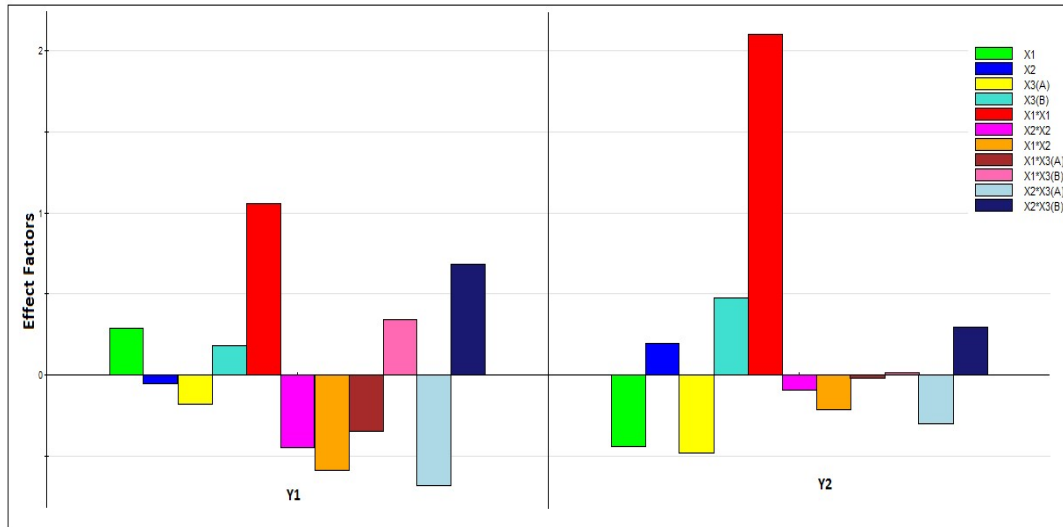


Fig. 2 Specific effects of operational factors on turbidity (Y₁) and COD (Y₂)

They are interpreted as contour lines on which are projected the value of the response. Beyond two factors, it is necessary to maintain at a constant level factors whose variations are not described in the horizontal plane. By putting the values predicted by the models as iso-response curves, we can analyze the effect of factors on the responses.

Figures 3 and 4 regroup iso-response curves for the percentages of removal of turbidity and COD according to the concentration of the coagulant agent and coagulation time maintaining X3 (coagulant nature) fixed. From Fig. 3, it was noted that the maximum of percentage of removal of turbidity and COD are achieved in the intervals [1000-1200] and [200-300] mg/L of coagulant (FeCl₃), respectively. While, the coagulation time was between 10 and 20 min. In Fig. 4, the optimum concentration of Al₂(SO₄)₃ was between 1100 and 1200 mg/L, and the optimal time was between 10 and 40 min for COD removal. For turbidity removal, the optimum concentration of Al₂(SO₄)₃ was observed between 1000 and 1200mg/L, and the optimal time was between 22 and 40 min. From this figure, it was observed that the increasing of the concentration of the coagulant agent (Al₂(SO₄)₃) leads to an increase of the percentage of removal of turbidity and COD, which is the case of FeCl₃ in Fig. 3. Therefore, the concentration of the coagulant agent has a positive effect on both responses. Indeed coagulation time has a negative effect on the response, which results in the decrease of the percentage of removal of turbidity and COD with time. The aim of this optimization is to find the best operating variables leading to the desired responses. After the analysis of the system response modeling based on various factors, the optimum may be localized by the method of route of the response surface and iso-response curves (Birjandi *et al.*, 2013). Considering previous results that show the positive effects of the

coagulant concentration and its nature on the responses, we can firstly visualize and analyze the effects of significant factors and seeking the most favorable conditions to obtaining better treatment of this effluent. The main objective is to determine the optimum factors to obtain the maximum of COD and turbidity removals in the coagulation process.

Based on such criteria, the software provides the optimal values of operating factors and predicted responses. The best local maximums were found to be at coagulant concentration of 1200 mg/L, time of treatment of 38.57 min and (Al₂(SO₄)₃) as coagulant. The corresponding optimal values of turbidity and COD removals were 98.18 and 77.06 %, respectively. These predicted results are in agreement with those obtained experimentally when (Al₂(SO₄)₃) was used. In these conditions, the values of experimental values are 99.30 and 75.18 % for turbidity and COD removals, respectively.

CONCLUSION

The objective of this work was to evaluate the effectiveness of chemical process and in particular coagulation-decantation for the treatment of dairy effluents. The physicochemical characterization showed that the selected effluent has two main features. The first is its wealth of readily biodegradable organic matter. High variations in flow, temperature, pH and pollution load are the second feature.

Chemical coagulation treatment tests showed that the two used coagulants contribute to the reduction of turbidity and organic load of the dairy effluent. Based on the D-Optimal design, the number of experiments was reduced and the operating factors leading to the best conditions of treatment were optimized. The analysis of variance showed that the value of the

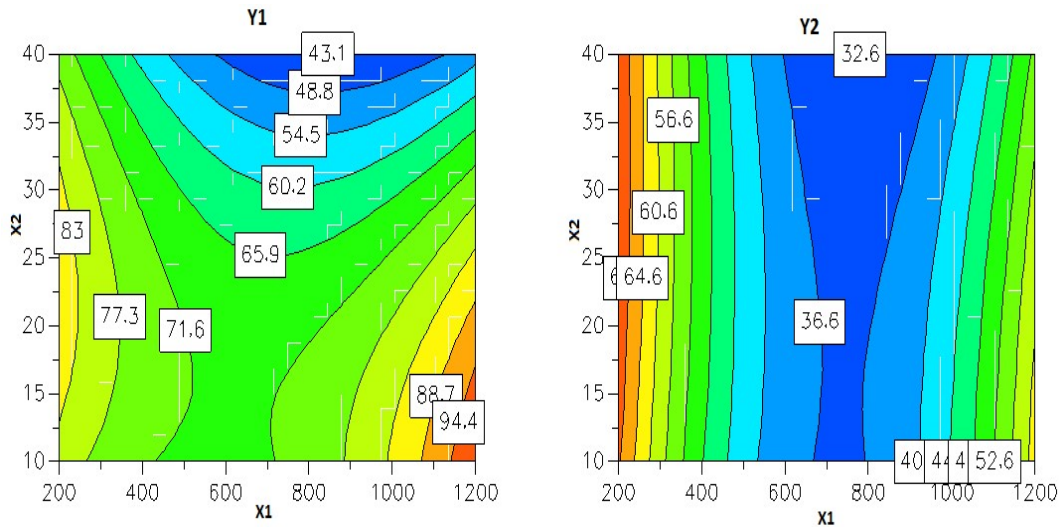


Fig. 3 Iso-response curves for the reduction of turbidity (Y₁) and COD (Y₂) of the effluent as a function of the concentration of coagulant and coagulation time, X₃ = FeCl₃

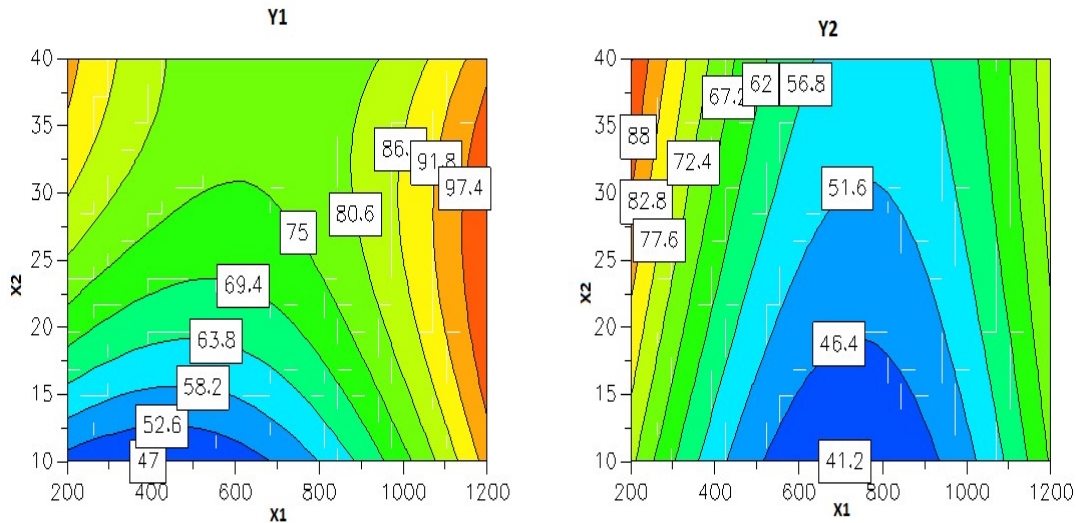


Fig. 4 Iso-response curves for the reduction of turbidity (Y₁) and COD (Y₂) of the effluent as a function of the concentration of coagulant and coagulation time, X₃ = Al₂(SO₄)₃

correlation coefficient R², for the reduction of turbidity and COD was 0.959 and 0.840 respectively, which gives an idea about the validity of the quadratic developed models and their predictive qualities. The optimal conditions (1200 mg/L of Al₂(SO₄)₃ and, time of treatment of 38.575min) leading to the removal efficiencies (98% for turbidity and 77% for COD) are in agreement with those obtained experimentally.

Acknowledgment The authors thank Professor M.Y. Jaffrin from the University of Compiegne (France) for his thorough reading of the manuscript.

REFERENCES

Andrade, H., Motta, G.E., Amaral, M.C.S. (2013) Treatment of dairy wastewater with a membrane bioreactor. *Braz. J. Chem. Eng.*, 30, 759-770.

Ayeche, R. (2012) Treatment by coagulation-flocculation of dairy wastewater with the residual lime of national algerian industrial gases company (NIGC-Annaba). *Energy Procedia*, 18, 147-156.
 Balanec, B., Gésan-Guiziu, G., Chaufer, B., Baudry, M.R., Daufin, G. (2002) Treatment of dairy process waters by membrane operations for water reuse and milk constituents concentration. *Desalination*, 147, 89-94.
 Bezerraa, M.A., Santelli, R.E., Oliveira, E.P., Villar, L.S., Escalera, L.A. (2008) Response surface methodology (RSM) as a tool for optimization in analytical chemistry. *Talanta*, 76, 965-977.
 Bharati, S. Shinkar, N.P. (2013) Comparative study of various treatments for dairy industry wastewater. *J. Eng.* 3, 42-47.
 Birjandi, N., Younesi, H., Bahramifar, N., Ghafari, S., Zinatizadeh, A.A., Sethupathi, S. (2013) Optimization of coagulation-flocculation treatment on paper-recycling wastewater: Application of response surface methodology. *J. Environ. Sci. Health A*, 48, 1573-1582.
 Cathalifaud, Ayele, J., Mazet, M. (1998) Etude de la complexation des ions aluminium par des molécules organiques: constantes et stœchiométrie des complexes. Application en traitement de potabilisation des eaux. *Wat. Res.*, 32, 2325-2334.

- Everet, H. (1988) Basic principles of colloid science. Piccadilly, London: The Royal Society of Chemistry, Burlington house, UK.
- Gong, Y.W., Zhang, H.X., Cheng, X.N. (2012) Treatment of dairy wastewater by two-stage membrane operation with ultrafiltration and nanofiltration. *Wat. Sci. Technol.*, 65, 915-919.
- Grčić, I., Vujević, D., Koprivanac, N. (2010) The use of D-optimal design to model the effects of process parameters on mineralization and discoloration kinetics of Fenton-type oxidation. *Chem. Eng. J.* 157, 408-419.
- Harush, D.P., Hampannavar, U.S., Mallikarjunaswami, M.E. (2011) Treatment of dairy wastewater using aerobic biodegradation and coagulation treatment of dairy wastewater using aerobic biodegradation and coagulation. *Int. J. Environ. Sci. Res.*, 1, 23-26.
- Hasan, D.B., AbdulAziz, A.R., Daud, W.M. (2012) Using D-optimal experimental design to optimize remazol black B mineralisation by Fenton-like peroxidation. *Environ. Technol.*, 33, 1111-1121.
- Kermet-Said, H., Moulai-Mostefa, N. (2015) Optimization of turbidity and COD removal from pharmaceutical wastewater by electrocoagulation: Isotherm modeling and cost analysis. *Polish J. Environ. Stud.*, 24, 1049-1061.
- Silva, A.G.M., Hornes, M.O., Mitterer, M.L., Queiroz, M.I. (2009) Application of coagulants in pretreatment of fish wastewater using factorial Design. *Desalination Wat. Treat.*, 1, 208-214.
- Singh, N.B., Singh, R., Imam, M.M. (2014) Wastewater management in dairy industry: pollution abatement and preventive attitudes. *Int. J. Sci. Environ. Technol.*, 3, 672-683.
- Suárez, A., Fidalgo, T., Riera, F.A. (2014) Recovery of dairy industry wastewaters by reverse osmosis. Production of boiler water. *Sep. Purif. Technol.*, 133, 204-211.
- Tikariha, A., Sahu, O. (2014) Study of characteristics and treatments of dairy industry wastewater. *J. Appl. Environ. Microbiol.*, 2, 16-22.
- Tocchi, C., Federici, E., Fidati, L., Manzi, R., Vinciguerra, V., Petruccioli, M. (2012) Aerobic treatment of dairy wastewater in an industrial three-reactor plant: Effect of aeration regime on performances and on protozoan and bacterial communities. *Wat. Res.*, 46, 3334-344.
- Vidal, G., Carvalho, A., Mendez, R., Lema, J.M. (2000) Influence of the content in fats and proteins on the anaerobic biodegradability of dairy wastewaters. *Bioresour. Technol.*, 74, 231-239.
- Xiong, Z., Cao, J., Yang, D., Lai, B., Yang, P. (2017) Coagulation-flocculation as pre-treatment for micro-scale Fe/Cu/O₃ process (CF-mFe/Cu/O₃) treatment of the coating wastewater from automobile manufacturing. *Chemosphere*, 166, 343-351.