Assessment of coagulation pretreatment of leachate by response surface methodology

Ridha Lessoued, Fatiha Souahi and Leonor Castrillon Pelaez

ABSTRACT

Coagulation-flocculation is a relatively simple technique that can be used successfully for the treatment of old leachate by poly-aluminum chloride (PAC). The main objectives of this study are to design the experiments, build models and optimize the operating parameters, dosage m and pH, using the central composite design and response surface method. Developed for chemical organic matter (COD) and turbidity responses, the quadratic polynomial model is suitable for prediction within the range of simulated variables as it showed that the optimum conditions were m of 5.55 g/L at pH 7.05, with a determination coefficient R^2 at 99.33%, 99.92% and adjusted R^2 at 98.85% and 99.86% for both COD and turbidity. We confirm that the initial pH and PAC dosage have significant effects on COD and turbidity removal. The experimental data and model predictions agreed well and the removal efficiency of COD, turbidity, Fe, Pb and Cu reached respectively 61%, 96.4%, 97.1%, 99% and 100%.

Key words | central composite design (CCD), characterization, coagulation–flocculation, landfill leachate, modelling, poly-aluminum chloride (PAC)

Ridha Lessoued (corresponding author)
Fatiha Souahi
Département de Génie Chimique,
École Nationale Polytechnique,
Av. Hassen Badi, El-harrach,
Alger 16200,
Algérie
E-mail: *redha.lessoued@g.enp.edu.dz*; *rlessoued@yahoo.fr*

Leonor Castrillon Pelaez
Chemical Engineering and Environmental Technology Department,
University Technology Institute of Asturias,
University of Oviedo,
Gijón,
Spain

INTRODUCTION

The leachate is a dark aqueous effluent generated as a consequence of rainwater percolation, inherent moisture content of then solid wastes, water production due to chemical and biochemical processes and ground water entering into the waste (Rasool *et al.* 2016). The composition of leachate depends on landfill age, percolation, precipitation and the type of solid waste. Complex quality and the presence of hazardous and toxic materials in landfill leachate along with low BOD_5:chemical organic matter (COD) ratio limit the application of biological processes (Tatsi *et al.* 2003; Ghanbari 2014).

Among the various physical-chemical technologies, coagulation-flocculation is widely used in pre-treatment of leachate for prior biological or for other physico-chemical process (Tatsi *et al.* 2003; Wang *et al.* 2009; Verma & Kumar 2016). Factors such as pH, coagulant dose and coagulant type play important roles in the coagulation-flocculation process (Liu *et al.* 2012). Coagulation-flocculation can reduce COD, turbidity, colour and metals with a high effectiveness that depends on contaminant and the coagulant/flocculant type (Marañón *et al.* 2010; Boumechhour *et al.* 2012; Verma & Kumar 2016). This technique has been employed successfully for the treatment of old landfill leachates (Ghafari *et al.* 2009). Indeed, it has been reported that conventional coagulants are efficient for removing COD; it reaches a rate of 10% to 25% from young leachates and 50% to 65% from old leachates (Nurfarahim *et al.* 2015; Nofriady *et al.* 2017). In recent years, the use of polymerized forms of metal coagulants, such as poly-aluminum chloride (PAC) for water treatment, has increased. The widespread use of the latter coagulants when compared to the conventional ones, especially in Europe, Japan and North America, is due to their reduced cost as well as higher efficiency and wider availability (Ghafari *et al.* 2009; Zhe *et al.* 2016).

Municipal solid waste (MSW) generated in the Principality of Asturias (Spain) is deposited in a central landfill which started operating in January 1986. This landfill is managed by the Consortium for the Management of Solid Waste, COGERSA. The landfill occupies a surface area of 250 ha and it receives approximately 550,000 tonnes of MSW per year, with about 38% content of organic matter (Marañón *et al.* 2008).

Usually used for optimization of chemical processes in wastewater treatment, response surface method (RSM) is a

doi: 10.2166/wst.2017.397

statistical tool that evaluates relative significance of independent variables. Moreover, the parameters optimization with RSM can be performed even for a limited number of experiments and RSM offers also an empirical model for the responses (Liu 2005; Ghanbari 2014). Analysis of variance (ANOVA) provides the statistical results and diagnostic checking tests which enables researchers to evaluate adequacy of the models (Ghafari *et al.* 2009). The aim of the present work is to optimize the coagulation-flocculation process for leachate treatment with PAC using central composite design (CCD) and RSM. This study details the individual and interactive influences of two independent variables (i.e. coagulant dose and pH) on the removal of COD and turbidity from landfill leachate.

METHODS

Coagulation–flocculation

Five leachate samples ($n = 5$) were collected from the central landfill in 20-L plastic containers, transported to the laboratory and stored at 4 °C. Physicochemical analyzes were performed in triplicate over the following 2 days. pH, conductivity and turbidity were measured using a CRISON pH 25 00514, CRISON CM 35 91313 (CRISON Instruments, Spain), and an EUTECH INSTRUMENTS TN-100 497281(Singapore), respectively. DBO_5 was measured by the method of Warburg. COD was determined following the Method 5220 D (closed reflux, colorimetric method) of *Standard Methods for the Examination of Water and Wastewater* (APHA/AWWA/WEF 1998) using a Perkin Elmer (Waltham, MA, USA) Lambda 35 Visible-UV system. Metals (Fe, Cu and Pb) were determined using a PerkinElmer, PinAAcle 900F, Atomic Absorption Spectrophotometer after acid microwave digestion with HNO_3 and H_2O_2.

Coagulation-flocculation studies were performed in a conventional jar-test apparatus equipped with 6 × 500-mL volume beakers. The experimental process consisted of three successive stages: an initial rapid mixing stage that took place for 3 min at 180 rpm, followed by a slow mixing stage for 17 min at 40 rpm, then, after a settling period of 60 min, the supernatant was withdrawn from the beaker and analyzed. Mother solutions containing 18% of PAC were prepared for the coagulation experiments. The variables studied were pH and reagent dose (m). The pH values of samples were adjusted to the desired levels by the addition of an appropriate amount of HCl solution. The doses of PAC studied were 5 to 6 g/L and the analyzed pH varied between 6.7 and 7.5.

Experimental design and data analysis

The coagulant dosage and pH were optimized for maximum reduction in the two factors (COD and turbidity) as main factors in coagulation process using CCD. The latter was selected for the present study because of its very efficient design tool for fitting the second-order models (Ghanbari 2014). The experiments were performed using the Minitab Software Trial (version 16). The range of the selected pH values and the dosages, pH = 6.7 to 7.5 and m = 5 to 6 g/L, are chosen according to the references (Ghafari *et al.* 2009; Marañón *et al.* 2010) as well as according to a large number of experiments. The carried out CCD contains 13 experiments with four cube points (±1), four axial points ($\alpha \pm 1.414$), and five replicates at the center points (0). Denoting α for the distance of each axial point (also called star point) from the center in a CCD, the experimental levels of the independent variables (factors) are presented in Table 1.

Second-order polynomial response model for predicting the optimal conditions and revealing the interaction between the two factors, can be expressed according to expression (1) (Ghanbari 2014).

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \sum_{j=i+1}^{k} \beta_{ij} x_i x_j + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \varepsilon \qquad (1)$$

where β_0 is the constant coefficient; β_i, β_{ij} and β_{ii} are the regression coefficients of linear, interaction, and quadratic term, respectively; k the number of factors; Y is the predicted response; x_i and x_j are independent factors in coded units and ε is the error term (Chattoraj *et al.* 2014; Pooja 2014). The quality of the fitted polynomial model was quantified by the coefficient of determination R^2 and its statistical significance was checked by the Fisher's F-test in the same program (Ghafari *et al.* 2009). The R^2 value measures how

Table 1 | Coded and actual levels of independent variables

Coded levels					
Independent variable	−1.414	−1	0	+1	+1.414
Actual levels					
pH	6.7	6.8	7.1	7.4	7.5
Coagulant dose (g/L)	5	5.2	5.5	5.8	6

much variability in the observed response values can be explained by the experimental variables and their interactions. The closer the R^2 value is to 1, the better the model predicts the response (Liu 2005; Smaoui *et al.* 2016). Adjusted R^2 measures to which extent the model fits well the data when the number of predictors in the model is adjusted. Moreover, adjusted R^2 is also considered in the lack-of-fit test for the degrees of freedom, which should be an approximate value of R^2 (Thuy & Lim 2011). The *P*-value is used as a tool to check the significance of each factor and interaction between factors with 95% confidence level. For small *P*-value, the corresponding model and the individual coefficient get more significant (Thuy & Lim 2011). Three-dimensional plots and their respective contour plots were established and the optimum region was identified based on the main factors in the overlay plot. Response optimizer in Figure 4 is an optimization plot that shows the affect of each factor (columns) on the responses or composite desirability (rows). The vertical red lines on the graph represent the current factor settings. The numbers displayed at the top of a column show the current factor level settings (m and pH). The horizontal blue lines and numbers represent the responses for the current factor level (COD and turbidity). Finally, confirmatory experiments were performed in triplicate using the optimized conditions obtained from numerical optimization to validate the model. The average values of the experiments were compared with the predicted values by the model in order to quantify the accuracy and suitability of the model (Pooja 2014).

RESULTS AND DISCUSSION

Physico-chemical characteristics

Physicochemical characteristics of leachate are summarized in Table 2. Leachate had a pH of about 8.6. Biodegradable organic matter (BOD_5) reached values of up to 1,100 mg/L, whereas high concentrations of COD were measured around of 4,539.4 mgO_2/L. On the other hand, leachate presented a relatively low biodegradability ratio BOD_5:COD of 0.24 and high levels of heavy metal contents. According to its characteristics, the effluent was classified as an 'old leachate' (Boumechhour *et al.* 2012).

Statistical analysis

The relationship between the two variables (coagulant dosage and pH) and the two responses (COD Y_1 and turbidity Y_2 removal efficiency) for the coagulation-flocculation process was analyzed using response surface methodology (RSM). Significant model terms are required to obtain a suitable fit in a particular model. The CCD shown in Table 3 allowed the development of mathematical equations where predicted results COD and turbidity were assessed as a function of coagulant dosage (x_1) and pH (x_2). The equations of the models (2, 3) in terms of coded factors are given below:

Table 2 | Landfill leachate characterization

Parameters	Unit	Mean
pH	–	8.6
Temperature	°C	10.6
Conductivity	mS/cm	23.4
Turbidity	NTU	65.3
COD	mg/L	4,539.4
BOD_5	mg/L	1,100
BOD_5/COD	–	0.24
Fe	mg/L	40.4
Pb	mg/L	34.21
Cu	mg/L	1.87

$$Y_1(\%) = -4654.6 + 630.9x_1 + 839.8x_2 - 40.8x_1^2 - 49.9x_2^2 - 24.7x_1x_2 \quad (2)$$

$$Y_2(\%) = -4780.6 + 271.2x_1 + 1170.9x_2 - 41.4x_1^2 - 93.1x_2^2 + 26x_1x_2 \quad (3)$$

According to ANOVA results presented in Table 4, a quadratic polynomial model was statistically significant to represent the real relationship between the COD and turbidity removal efficiency of the coagulant and the variables, with a very a high R^2 of 99.33 and 99.92 and adjusted R^2 of 98.85 and 99.86 for COD and turbidity, respectively (Rasool *et al.* 2016). In other words, when R^2 and adjusted R^2 are considerably different, there is a chance that insignificant terms have been included in the model (Myers & Montgomery 2002). Since both values were close in this study, the above possibility was proved to be invalid. Furthermore, it is possible for models with high R^2 coefficient to yield poor predictions of new observations. As an indicator of predictive capability of regression model, R^2 prediction has been proposed and is calculated from the prediction of the residual error sum of squares (PRESS) (Myers & Montgomery 2002; Montgomery 2009). R^2 prediction should be in a reasonable agreement with the adjusted R^2 (Yuyang

Table 3 | Results of the CCD for two responses

	Experimental design coded		Response removals (%)					
			COD			Turbidity		
Run no.	m (x_1)	pH (x_2)	Experimental	Predicted	Residual	Experimental	Predicted	Residual
1	−1	−1	47.5	48.1	−0.6	88.3	88.3	0.0
2	1	−1	57.4	57.8	−0.4	84	83.63	0.37
3	−1	1	49.4	49.8	−0.4	78.6	78.69	−0.01
4	1	1	49.4	49.7	−0.3	84.7	84.42	0.28
5	−1.414	0	47.5	46.9	0.6	85.8	85.67	0.13
6	1.414	0	54	53.7	0.3	86	86.4	−0.4
7	0	−1.414	55.3	54.7	0.6	84.4	84.6	−0.2
8	0	1.414	50.6	50.2	0.4	78.3	78.37	−0.07
9	0	0	61	60.48	0.52	96.4	96.38	0.02
10	0	0	60.3	60.48	−0.18	96.4	96.38	0.02
11	0	0	60.5	60.48	0.02	96.4	96.38	0.02
12	0	0	60.6	60.48	0.12	96.3	96.38	−0.08
13	0	0	60	60.48	−0.48	96.4	96.38	0.02

Table 4 | ANOVA results for response parameters

Responses	Regression	LOF	*P*-value	R^2	$R^2_{adjusted}$	$R^2_{predicted}$	PRESS
COD	0.000	0.093	0	99.33	98.85	96.1	13.736
Turbidity	0.000	0.001	0	99.92	99.86	99.44	3.258

et al. 2017). Obtained value of R^2 prediction expected the proposed model to explain about of 96.1% and 99.44% for Y_1 and Y_2, respectively, of variability in predicting new observations. The overall predictability based on this criterion seems quite satisfactory when compared to previous results presented in Li *et al.* (2010), Wu *et al.* (2010a) and Ghanbarzadeh *et al.* (2012), where predicted R^2 values were calculated independently by the authors from available PRESS amounts. The lack of fit (LOF) F-test describes the variation of the data around the fitted model. If the model did not fit the data well, the latter would be large enough. The *P*-values for LOF presented in Table 4 show that the F-statistic was insignificant, indicating significant model correlation between the factors and process responses.

The predicted versus actual values plots of parameters removal are shown in Figure 1(a) and 1(b). These plots indicate a good agreement between experimental data and the fitted models. Correlation coefficient of 0.993 and 0.999 reveal the high validity of the obtained models for COD and turbidity removals.

Process analysis and optimization

The response surface plots shown in Figure 2(a) and 2(b) indicated that the optimum removal was found at about pH 7.05 and dosage 5.55 g/L. Clear peaks for both response plots are presented which means that the optimum conditions for maximum values of the responses are attributed to pH and dosage in the design space. At this condition, the response surfaces suggested that coagulant dosage and pH had a significant effect on the COD and turbidity removal. Indeed, the removal of COD and turbidity showed, respectively, 60.95% and 96.38% efficiency that agree with findings of Mohd *et al.* (2011) and Marañón *et al.* (2010) for an old leachate. Figure 3(a) shows how PAC dose and pH affect the COD removal efficiency. It can be deduced that COD removal increases when pH decreases and PAC dose increases at the same time. As illustrated in the contour plot in Figure 3(b), it was observed that turbidity removal increases as we move from the corners toward the center of the plot. The

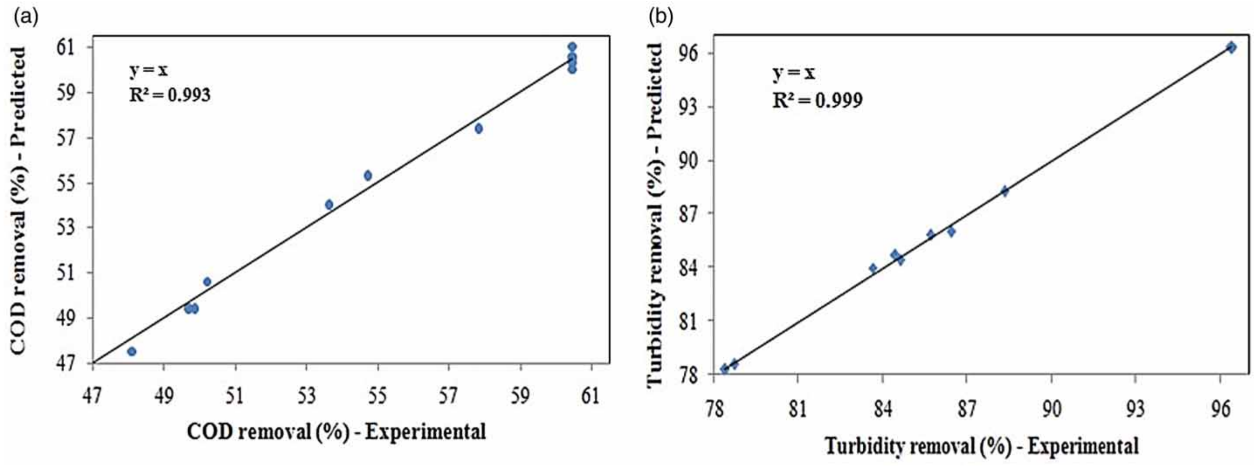

Figure 1 | Experimental vs. predicted values plot for (a) COD removal and (b) turbidity.

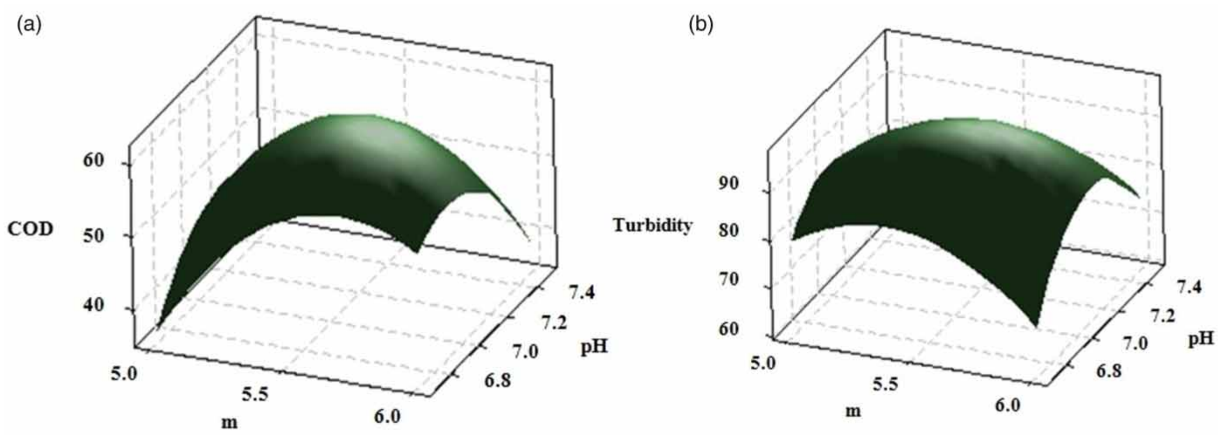

Figure 2 | 3D surface contour plots for (a) COD and (b) turbidity removal.

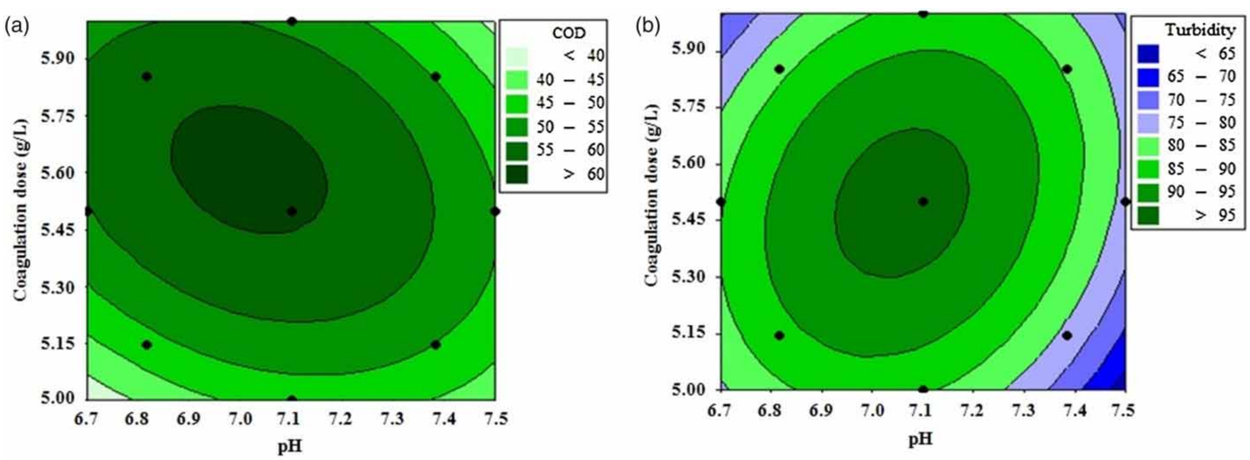

Figure 3 | 2D surface contour plots for (a) COD and (b) turbidity removal.

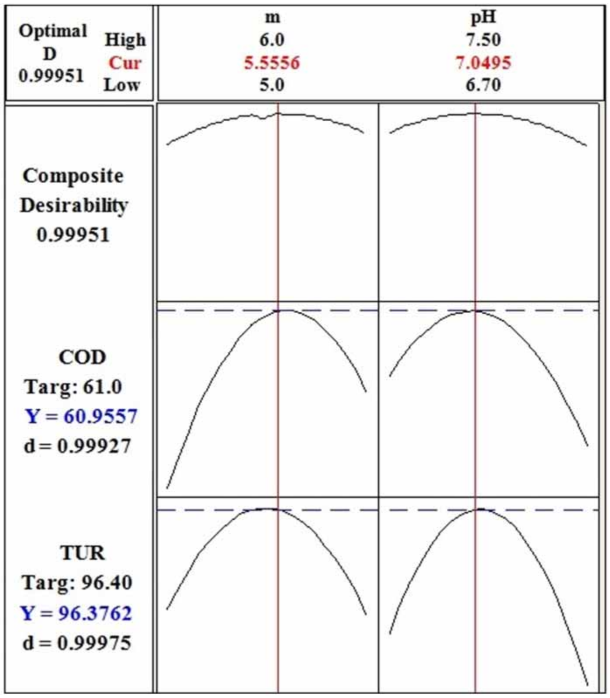

Figure 4 | Optimizing graph for COD and turbidity (TUR) removal efficiency.

contour levels reveal a peak centered at pH 7.05 and coagulant dose 5.55 g/L.

Response optimizer is applied in order to optimize the coagulation conditions. The goal is to target (Targ) COD and turbidity at 100%. As shown in Figure 4, the optimum condition obtained was pH = 7.049 and coagulant dose = 5.55 g/L. The predicted values are 60.96 and 96.37% for COD and turbidity, respectively.

Desirability ranges between one for the ideal case and zero when responses are outside their acceptable limits. The individual desirability d of both COD and turbidity is 0.999. Therefore, the composite desirability D of these two variables is 1.0. As shown in Figure 5, the optimum conditions of COD and turbidity responses can be also identified by superimposing their contours in an overlay plot in which the optimum area is clearly noted in blank against the green area that did not meet the criteria.

Triplicate experiments are conducted applying the optimum conditions (pH = 7.05 and PAC dosage 5.55 g/L). Table 5 demonstrates that the removal effectiveness, for both responses, from experiment results which agree well with the model predictions. Removal efficiencies and standard deviations of responses are respectively 60.4% and 0.39 and 97.7% and 0.93 for COD and turbidity. In addition, high removal percentages of about **97.1%**, **99%** and **100%** are found for **Fe**, **Pb** and **Cu** heavy metals, respectively. As foreseen, these results confirm the good reproducibility of the proposed models in the design range.

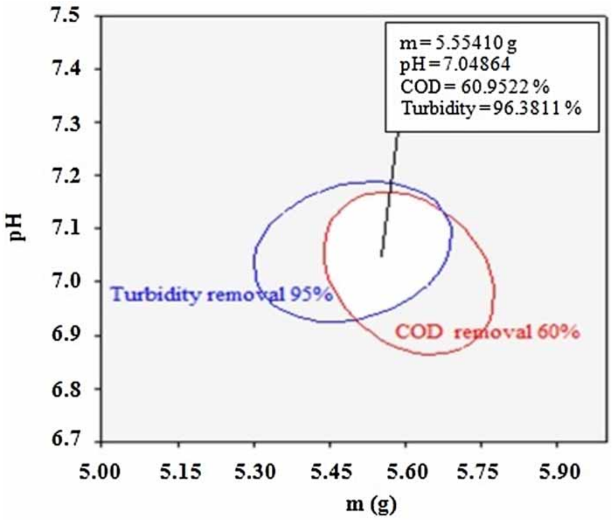

Figure 5 | Overlay contour plots of COD and turbidity removal.

Table 5 | Confirmation experiments at optimum conditions (pH = 7.05 and m = 5.55 g/L)

	Predicted value	**Experimental value**	**Error**	**Standard deviation**
Turbidity (NTU)	96.38%	97.7%	1.38	0.93
COD (mg/L)	60.96%	60.4%	0.56	0.39

CONCLUSION

RSM using CCD was investigated to examine the effects of pH and coagulant dose on the productiveness of PAC coagulation-flocculation process. The optimum conditions obtained were 5.55 g/L at pH 7.05. The results showed suitable agreement between experimental and model predictions. At optimum conditions, 61%, 96.4%, 97.1%, 99% and 100% for COD, turbidity, Fe, Pb and Cu removal were achieved. Therefore, this study showed that PAC is an efficient coagulant in improving physico-chemical characteristics of leachate. For this reason, it can be used as an appropriate pretreatment of old landfill leachate.

REFERENCES

APHA/AWWA/WEF 1998 *Standard Methods for the Examination of Water and Wastewater*. 20th edn, American Public Health

Association/American Water Works Association/Water Environment Federation, Washington, DC, USA.

Boumechhour, F., Rabah, K., Lamine, C. & Said, B. M. 2012 Treatment of landfill leachate using Fenton process and coagulation-flocculation. *Water Environ, J.* **27**, 114–119.

Chattoraj, S., Mondal, N. K., Das, B., Roy, P. & Sadhukhan, B. 2014 Biosorption of carbaryl from aqueous solution onto Pistia stratiotes biomass. *Appl. Water Sci.* **4**, 79–88.

Ghafari, S., Aziz, H. A., Isa, M. H. & Zinatizadeh, A. 2009 Application of response surface methodology (RSM) to optimize coagulation-flocculation treatment of leachate using poly-aluminum chloride (PAC) and alum. *J. Hazard. Mater.* **163**, 650–656.

Ghanbari, F. & Moradia, M. 2014 Application of response surface method for coagulation process in leachate treatment as pretreatment for Fenton process: biodegradability improvement. *J. Water Process Eng.* **4**, 67–73.

Ghanbarzadeh, L., Sabour, M., Amiri, A. & Rabbani, O. 2012 Application of quadratic regression model for Fenton treatment of municipal landfill leachate. *Waste Manage.* **32**, 1895–1902.

Li, W., Hua, T., Zhou, Q., Zhang, S. & Li, F. 2010 Treatment of stabilized landfill leachate by the combined process of coagulation/flocculation and powder activated carbon adsorption. *Desalination* **264**, 56–62.

Liu, H. L. & Chiou, Y. R. 2005 Optimal decolorization efficiency of reactive Red 239 by UV/TiO_2 photocatalytic process coupled with response surface methodology. *Chem. Eng. J.* **112**, 173–179.

Liu, X., Li, X. M., Yang, Q., Yue, X., Shen, T. T., Zheng, W., Luo, K., Sun, Y. H. & Zeng, G. M. 2012 Landfill leachate pretreatment by coagulation-flocculation process using iron based coagulants: optimization by response surface methodology. *Chem. Eng. J.* **202**, 39–51.

Maranon, E., Castrillon, L., Fernandez-Nava, Y., Fernandez-Mendez, A. & Fernandez-Sanchez, A. 2008 Coagulation-flocculation as a pretreatment process at landfill leachate nitrification denitrification plant. *J. Hazard. Mater.* **156**, 539–544.

Marañón, E., Castrillón, L., Fernández-Nava, Y. & Fernández-Méndez, A. 2010 Colour, turbidity and COD removal from old landfill leachate by coagulation-flocculation treatment. *Waste Manage. Res.* **28**, 731–737.

Mohd, N. A., Puganeshwary, P. & Hamidi, A. A. 2011 Optimization of coagulation and dissolved airflotation (DAF) treatment of semi-aerobic landfill leachate using response surface methodology (RSM). *Desalination* **277**, 74–82.

Montgomery, D. C. 2009 *Design and Analysis of Experiments*, 7th edn, John Wiley & Sons (Asia), Singapore.

Myers, R. H. & Montgomery, D. C. 2002 *Response Surface Methodology: Process and Product Optimization Using Designed Experiments*, 2nd edn, John Wiley & Sons, New York, NY, USA.

Nofriady, A., Nuradam, E. & Kris, T. B. 2017 Comparison of poly aluminium chloride (PAC) and aluminium sulphate coagulants efficiency in waste water treatment plant. *Inovasi Teknik Kimia* **2**, 24–31.

Nurfarahim, R., Hamidi, A. A. & Mohd, O. F. 2015 Potential use of polyaluminium chloride and tobacco leaf as coagulant and coagulant aid in post-treatment of landfill leachate. *Avicenna J. Environ. Health. Eng.* **2**, e5836.

Pooja, G. S. & Indu, S. T. 2014 Enhanced removal of COD and color from landfill leachate in a sequential bioreactor. *Bioresour. Technol.* **170**, 10–19.

Rasool, M. A., Babak, T., Naz, C., Pendashteh, A. R. & Sadat, A. M. 2016 Use of a plant-based coagulant in coagulation-ozonation combined treatment of leachate from a waste dumping site Mirroshandel. *Ecol. Eng.* **90**, 431–437.

Smaoui, Y., Chaabouni, M., Sayadi, S. & Bouzid, J. 2016 Coagulation flocculation process for leachate pretreatment and optimization with response surface methodology. *Desalin. Water Treat.* **57** (31), 14488–14495.

Tatsi, A. A., Zouboulis, A. I., Matis, K. A. & Samaras, P. 2003 Coagulation-flocculation pretreatment of sanitary landfill leachates. *Chemosphere* **53**, 737–744.

Thuy, K. & Lim, K. 2011 Response surface methodological approach to optimize the coagulation-flocculation process in drinking water treatment. *Chem. Eng. Res. Des.* **89**, 1126–1113.

Verma, M. & Kumar, R. N. 2016 Can coagulation-flocculation be an effective pre-treatment option for landfill leachate and municipal wastewater co-treatment? *Perspect. Sci.* **8**, 492–494.

Wang, X. J., Chen, S. L., Gu, X. Y. & Wang, K. Y. 2009 Pilot study on the advanced treatment of landfill leachate using a combined coagulation, Fenton oxidation and biological aerated filter process. *Waste Manag.* **29**, 1354–1358.

Wu, Y., Zhou, S., Qin, F., Ye, X. & Zheng, K. 2010a Modeling physical and oxidative removal properties of Fenton process for treatment of landfill leachate using response surface methodology (RSM). *J. Hazard. Mater.* **180**, 456–465.

Yuyang, L., Jing, X., Dongsheng, S. & Yao, D. 2017 Huajun feng effective removal of contaminants in landfill leachate membrane concentrates by coagulation. *Chemosphere* **167**, 512–519.

Zhe, L., Yongjun, L., Peter, K., Jiaxuan, W., Yi, C. & Xiaochang, W. 2016 Poly aluminum chloride (PAC) enhanced formation of aerobic granules: coupling process between physicochemical–biochemical effects. *Chem. Eng. J.* **284**, 1127–1135.

First received 21 December 2016; accepted in revised form 19 June 2017. Available online 7 July 2017