Nature Environment and Pollution Technology
An International Quarterly Scientific Journal

ISSN: 0972-6268	Vol. 14	No. 3	pp. 567-572	2015

Original Research Paper

Optimization of Coagulation-Flocculation Process for Automotive Wastewater Treatment using Response Surface Methodology

Abdul Fattah Abu Bakar, Azhar Abdul Halim and Marlia Mohd Hanafiah†
School of Environmental and Natural Resource Sciences, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia
†Corresponding Author: Marlia Mohd Hanafiah

Nat. Env. & Poll. Tech.
Website: www.neptjournal.com

Received: 12-10-2014
Accepted: 23-11-2014

Key Words:
Coagulation-flocculation
Automotive wastewater
Polyaluminium chloride
Anionic polyacrylamide
Response surface methodology

ABSTRACT

This study was conducted to assess the optimization of the coagulation-flocculation process and to investigate the interactive effects of experimental factors in automotive wastewater treatment. Based on the coagulation-flocculation process, an automotive wastewater was treated using polyaluminium chloride as the coagulant and anionic polyacrylamide as the flocculant. Response surface methodology was applied to optimize the operating variables: coagulant dosage, flocculant dosage and pH. We found that the optimum conditions for chemical oxygen demand removal (73.7%) were, a coagulant dosage of 73.3 mg/L, a flocculant dosage of 3.46 mg/L and pH 7.45. The optimum conditions for the removal of heavy metals (Fe, Cr, Cu) were, a coagulant dosage range of 65.26-170.9 mg/L, a flocculant dosage of 5.36 mg/L, and pH 6.13 (with 78.7-99.7% of heavy metals removal). The experimental data and predicted model proved that RSM is a suitable approach for optimizing the coagulation-flocculation process in automotive wastewater treatment.

INTRODUCTION

Heavy metals can be found in environmental elements such as food chains and thus, can cause significant harm to human health. Many treatment processes have been developed to remove heavy metals from wastewater (Gupta & Suhas 2009); and hydroxide precipitation is the most commonly used method, as it is simple and low in cost (Baltpurvins et al. 1996, Macchi et al. 1993, Sanchez et al. 1999). However, this method does not ensure total removal of all metals, as not all metal hydroxides precipitate completely at the same pH. The effective precipitating ability of a particular metal can be reduced by competition brought on by the presence of other metals (Netzer et al. 1974). Moreover, the final concentration of heavy metals after precipitation alone might not meet the standard (EQA 1999). Coagulation-flocculation is a simple, efficient, physicochemical method of treating wastewater. This method is widely used to treat palm oil mill effluent (Ahamad et al. 2005), textile wastewater (Meric et al. 2005), and abattoir wastewater (Amuda & Alade 2006). The removal mechanism used in this process includes, charging to neutralize negatively charged colloids by cationic hydrolysis products and incorporating impurities in an amorphous hydroxide precipitate through flocculation (Duan & Gregory 2003).

The efficiency of the coagulation-flocculation process depends on several factors, such as the type and dosage of the coagulant and flocculant (Hu et al. 2005), pH (Miller et al. 2008), mixing speed and time (Gurses et al. 2003), temperature, and retention time (Howe et al. 2006). Consumption of polymerized forms of metal coagulants, such as polyaluminium chloride (PAC) for wastewater treatment has increased due to their low cost and wide availability, especially in Japan, Europe and North America (Amirtharajah & O'Melia 1990). PAC is commonly used because it has many advantages over conventional coagulants in terms of particulate or organic matter removal and lower sludge production (Sinha et al. 2004).

Response surface methodology (RSM) is a method of designing factorial experiments that help researchers build mathematical models, assess the effects of several factors and obtain optimum conditions for a desirable response, using a limited number of experiments (Ghafari et al. 2009). This method has been applied mostly in the chemical industry, as well as in the physical, engineering, biological, and social sciences (Khuri 2001). The optimum conditions for carrying out the coagulation-flocculation process have been established using RSM. The objective of this study was to optimize the coagulation-flocculation process and investigate the interactions among experimental factors. In this experiment, RSM was used to determine the optimal experimental design of the coagulation-flocculation process. In this study, coagulant dosage, flocculant dosage and pH were the experimental factors that needed to be optimized, while the desired responses were the removal percentages of chemical oxygen demand (COD) and heavy metals (Fe, Cr and Cu). The experiments were conducted to evaluate the efficiency of the treatment process of highly organic and inorganic polluted automotive industry wastewater, using RSM as a tool of experimental design, in coagulation and flocculation process.

MATERIALS AND METHODS

Materials: In this experiment, 10% concentration PAC solution was used and 5% anionic PAM/feedstock solution was prepared using distilled water. Wastewater samples were collected from the primary effluent tank of Oriental Summit Industries (OSI) Sdn Bhd, located in Shah Alam, which produces automotive parts, specifically for cars in Malaysia. Table 1 shows the chemical characteristics of wastewater samples measured based on the standard methods (APHA 2000).

Experimental procedure: The coagulation-flocculation test was carried out using the jar test (VELP-Scientific, Model: JLT6; VELP Scientifica, Usmate, Italy) with 500-mL beakers. The experiment was started by determining the optimum pH. The sample pH was adjusted from pH 5.0 to 9.0 by adding 1.0 mol/L HCl or NaOH solution. In order to obtain the optimum amount of coagulant dosage, PAC was added at dosages varying from nil to 110 mg/L. The optimum flocculant dosage was determined by adding 5% concentration of anionic polymer at dosages varying from nil to 4 mg/L. The sample was immediately stirred at a constant speed of 200 rpm for two minutes, followed by a slow stirring at 40 rpm for ten minutes (Wang et al. 2009). The settlement time was fixed at 30 minutes, according to a preliminary test. Later, samples were taken from the water level around 2 cm below the surface to measure the COD of the treated sample using a HACH spectrophotometer (model DR2010) and a reactor digestion method of 8000 for low range (Hach Company procedure) adapted from APHA (2000). For heavy metal detection, the same sample was also analysed using a Perkin-Elmer inductively coupled plasma-mass spectrometry (model ELAN 6000 ICP-MS).

Experimental design and data analysis: The Minitab version 16 statistical software was used for the statistical design of the experiments and data analysis. The central composite design (CCD), which is the standard RSM, was selected for the optimization of the parameters. Because different variables are usually expressed in different units and have different variation limits, the significance of their effects on response can only be compared after they are coded (Wang et al. 2009). For statistical calculations, variable X_i was coded as x_i according to the following equation:

Table 1: Chemical characteristics of wastewater sample.

Parameter	Range	Mean
Temperature (°C)	25-31	28
pH	8.0-8.5	8.3
COD (mg/L)	580-600	590
Fe (mg/L)	7.1-7.2	7.1
Cr (mg/L)	3.0-3.3	3.1
Cu (mg/L)	0.1-0.2	0.1

Table 2: Ranges and levels of independent variables.

Variables	Range and level				
	-1.68	-1	0	1	1.68
X_1, Flocculant dosage (mg/L)	0	1	2	3	4
X_2, Coagulant dosage (mg/L)	30	50	70	90	110
X_3, pH	5	6	7	8	9

$$X_i = \frac{\mathrm{x_i} - \mathrm{x_{i,0}}}{\delta x_i} \quad ...(1)$$

Where, X_i represents the coded value of independent variable *i*; x_i is the uncoded value of independent variable *i*; $x_{i,0}$ is the median of data array x_i; and δx_i is the step change.

Step change δx_i is defined as follows:

$$\delta x_i = \frac{\max(\mathrm{x_i}) - \min(\mathrm{x_i})}{2} \quad ...(2)$$

Flocculant dosage (x_1), coagulant dosage (x_2) and pH (x_3) were chosen as the three independent variables, their ranges and levels are given in Table 2. COD and heavy metal removal were selected as the dependent variables. The response variable was fitted with a second-order model in the form of a quadratic polynomial equation, as follows:

$$Y_m = b_0 + \sum_{i=1}^{k} b_i X_i + \sum_{i=1}^{k} b_{ii} X_i^2 + \sum_{i}^{i<j} \sum_{j} b_{ij} X_i X_j \quad ...(3)$$

Where, *i* is the linear coefficient, *j* is the quadratic coefficient; *b* is the regression coefficient, and *k* is the number of factors studied and optimized in the experiments. The interactive effects of the independent variables on the dependent variables are illustrated by a two-dimensional contour plot for this experiment.

RESULTS AND DISCUSSION

Optimization of COD removal: The COD removal values

Table 3: Design matrix and results of the central composite design.

Run	Factors			Response (% removal)			
	X_1	X_2	X_3	COD	Fe	Cr	Cu
1	4	130	10	66.66	99.67	99.23	80.32
2	4	10	4	56.66	98.14	78.07	49.18
3	0	130	4	36.66	99.53	83.19	52.45
4	2	170	7	56.66	99.64	93.85	57.37
5	2	70	7	70.00	99.73	99.34	68.85
6	4	130	4	60.00	99.56	84.67	49.18
7	2	70	12	50.00	96.55	96.54	49.18
8	2	70	7	60.00	99.68	98.78	65.57
9	0	10	4	40.00	98.14	76.24	45.90
10	1	70	7	50.00	99.70	99.13	72.13
11	2	70	1	40.00	97.61	46.24	39.34
12	0	10	10	50.00	99.81	98.42	70.49
13	2	70	7	80.00	99.67	98.93	75.40
14	0	130	10	50.00	99.74	99.64	75.40
15	2	70	7	70.00	99.70	99.03	70.49
16	5	70	7	66.66	99.73	98.93	73.77
17	4	10	10	63.33	99.87	99.39	72.13
18	2	70	7	80.00	99.68	93.29	57.37
19	2	30	7	73.33	99.75	98.91	68.85
20	2	70	7	73.33	99.64	98.88	72.13

Key note:
X_1: Flocculant dosage (mg/L)
X_2: Coagulant dosage (mg/L)
X_3: pH

are listed in Table 3 and Quadratic regression models obtained are expressed as follows:

$$Y_{COD} = 72.2938 + 3.9163X_1 - 1.8084X_2 + 7.1781X_3 - 10.0924X_1^2 - 3.0213X_2^2 - 5.3783X_3^2 + 0.4167X_1X_2 - 1.2500X_1X_3 + 1.2500X_2X_3$$
$$R^2 = 0.8601 \quad ...(4)$$

Analysis of variance (ANOVA) was used to analyse the interaction between process variables and responses. The lack of fit (LOF) *F*-test was used to test whether the regression function adequately fits the data. The quadratic regression shows that the model was significant, LOF P value was 0.705 (>0.05), implying a significant model correlation between the variables and responses. The correlation coefficient value ($R^2 = 0.8601$) indicates that only 14% of the total variation could not be explained by the empirical model (Ahamad et al. 2005). Fig. 1 shows that the COD response was obtained by keeping one variable at the central level while the other two variables varied within the experimental range. The two-dimensional contour plot shows that all the contour plots have a considerable curvature. The optimal conditions for COD removal are in the middle of the design boundary, indicating that there are interdependence interactions among these three factors. There were significant interactions between flocculant and coagulant dosages, flocculant dosage and pH and coagulant dosage and pH. The contour plot in Fig. 1(a) shows that at the optimum pH of 7.5, the COD removal was higher when the flocculant and coagulant dosages were in the range of 2-5 mg/L and 20-130 mg/L, respectively. In general, pH 6.0-8.0 is a suitable condition for the formation of amorphous aluminium hydroxide [$Al(OH)_3$] when aluminium ions are used as coagulants. The formation of amorphous $Al(OH)_3$ causes organic matter removal through a sweep floc mechanism by adsorption on the precipitation of $Al(OH)_3$ (Chang et al. 1993). As shown in Fig. 1(b) and Fig. 1(c), a nearly symmetrical contour shape with the maximum response at the centre of the contour indicates that there are significant interactions between flocculant dosage and pH, as well as coagulant dosage and pH. The optimal pH obtained for COD removal was in the range of 6-9, while the optimum dosages for COD removal were obtained as the amount increased to within the 2-5 mg/L range for the flocculant, and 20-120 mg/L for the coagulant. Using eq. (4), the optimal conditions for COD percentage removal were obtained with coagulant dosage of 73.3 mg/L, flocculant dosage of 3.46 mg/L and pH of 7.45. Under optimal conditions, the maximum COD removal was estimated at 73.7%.

Optimisation of heavy metal removal: In this study, the use of anionic PAM, which supplied a negative charge, increased heavy metal removal due to its charge neutralization action and bridging ability (Wang et al. 2009). The addition of flocculant followed by low-sheer mixing during the experiments increased contact between particles, thus allowing particle growth through the sedimentation phenomenon called flocculant settling and enabling the heavy metal removing process. Taking these two factors into account, heavy metal removal was improved significantly as the adsorption bridging ability increased (Wang et al. 2009). The quadratic regression models obtained for iron are as follows:

$$Y_{Fe} = 99.6720 + 0.1416X_1 + 0.1713X_2 + 0.0045X_3 - 0.8098X_1^2 + 0.1169X_2^2 + 0.1219X_3^2 - 0.3833X_1X_2 - 0.0053X_1X_3 - 0.0124X_2X_3$$
$$R^2 = 0.803 \quad ...(5)$$

The results of ($R^2 = 0.803$) for iron removal show that the measured versus predicted plot values for iron were distributed close to a straight line implying that the model fitted the experimental data well. Applying eq. 5, the optimal conditions obtained for iron removal were at a coagulant dosage of 170.9 mg/L, a flocculant dosage of 5.36 mg/L and pH of 6.13. Under optimal conditions (pH 6), maximum iron removal was estimated at 99.7%. The experimental results for chromium removal were represented in the following regression equation:

$$Y_{Cr} = 97.9982 + 11.6513X_1 + 0.4454X_2 + 0.2575X_3 - 9.1119X_1^2 - 0.2730X_2^2 + 0.6602X_3^2 - 1.5609X_1X_2 - 0.3426X_1X_3 - 0.2157X_2X_3$$
$$R^2 = 0.9461 \quad ...(6)$$

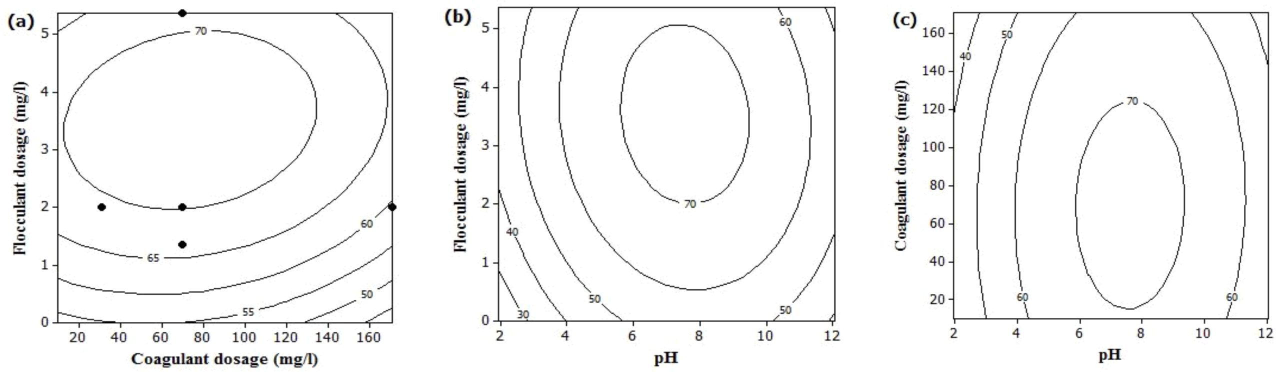

Fig. 1: Contour plot of COD removal showing effects of variables: (a) X_1–X_2, (b) X_1–X_3 and (c) X_2–X_3

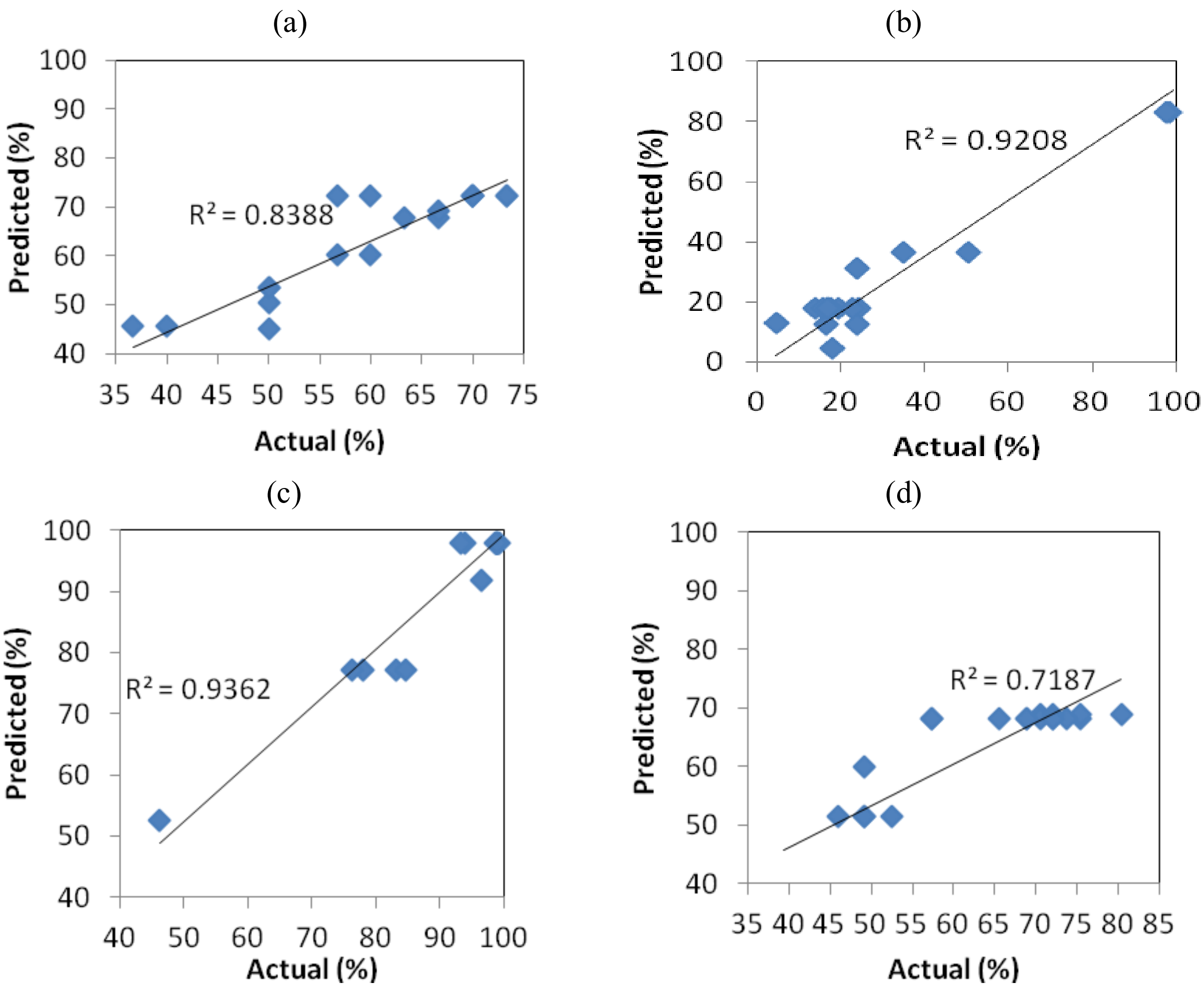

Fig. 2: Predicted versus actual values plot for (a) COD, (b) Fe, (c) Cr, and (d) Cu removal.

The result of LOF *F*-test for Cr was 0.051 (>0.05) and $R^2 = 0.9461$ for chromium percentage removal show that the second-order polynomial model was significant and fit the experimental results well. Fig. 2(c) shows that the measured versus predicted plot values were distributed close to the straight line. The correlation coefficient value ($R^2 = 0.9461$) indicates that only 5.3% of total variation could not be explained by the empirical model. Applying Eq. 6, the optimal conditions obtained for chromium removal were as follows: coagulant dosage of 65.26 mg/L, a flocculant dosage of 5.36 mg/L and pH of 8.88. Under optimal conditions, maximum chromium removal was estimated at 98.7%. Eq. 7 is the result of the regression model for copper removal by coagulation-flocculation test:

$$Y_{Cu} = 68.2326 + 8.6537X_1 + 0.0273X_2 + 0.6820X_3 - 8.0211X_1^2 - 1.3557X_2^2 + 2.1219X_3^2 + 0.8197X_1X_2 + 0.8197X_1X_3 - 0.4098X_2X_3$$

$$R^2 = 0.7618 \quad ...(7)$$

Statistical testing performed using ANOVA shows that the quadratic regression model is significant due to the high LOF P value for Cu removal, i.e., 0.217 (>0.05). The correlation coefficient ($R^2 = 0.7618$) value ensures a satisfactory adjustment of the quadratic model to the experimental data. Applying Eq. 7, the optimal conditions obtained for Cu removal percentage were coagulant dosage of 79.88 mg/L, a flocculant dosage of 5.36 mg/L and pH of 8.88. Under optimal conditions, maximum copper removal was estimated at 78.7%.

CONCLUSION

A coagulation-flocculation test was carried out to treat automotive wastewater, using PAC as the coagulant and aided by anionic PAM as the flocculant. A full factorial central composite design and response surface design were used to optimize the coagulant dosage, flocculant dosage and pH levels. The results show that the optimal conditions for COD removal were at a coagulant dosage of 73.3 mg/L, a flocculant dosage of 3.46 mg/L and pH 7.45, while the optimal conditions for heavy metal (Fe, Cr Cu) removal were in the coagulant dosage range of 65.26-170.9 mg/L, a flocculant dosage of 5.36 mg/L and pH 6.13. The experimental data and predicted model proved that RSM is a suitable approach for optimizing the coagulation-flocculation process in treating automotive wastewater.

ACKNOWLEDGEMENT

The authors would like to acknowledge the Universiti Kebangsaan Malaysia for the financial support under Grant-Industri-2011-021 and the collaboration of Oriental Summit Industries (OSI) Sdn Bhd. Marlia Mohd Hanafiah was supported by the UKM research grants (FRGS/2/2013/STWN01/UKM/03/1 and DLP-2013-034).

REFERENCES

Ahamad, A.L., Ismail, S. and Bhatia, S. 2005. Optimization of coagulation-flocculation process for palm oil mill effluent using response surface methodology. Environmental Science & Technology, 39(8): 2828-2834.

Amirtharajah, A. and O'Melia, C.R. 1990. Coagulation processes: Destabilization, mixing and flocculation. In: Water Quality and Treatment, American Water Works Association, 4th ed., McGraw-Hill, New York.

Amuda, O. S. and Alade, A. 2006. Coagulation/flocculation process in the treatment of abattoir wastewater. Desalination, 19(1-3): 22-31.

APHA. 2000. Standard Methods for the Examination of Water and Wastewater. 20th ed., American Public Health Association, Washington, DC.

Baltpurvins, K.A., Burns, R.C., Lawrance, G.A. and Stuart, A.D. 1996. Use of the solubility domain approach for the modeling of the hydroxide precipitation of heavy metals from wastewater. Environmental Science & Technology, 30: 1493-1499.

Chang, Q., Fu, J.Y. and Li, Z.L. 1993. Principles of flocculation. Lanzhou University Press, Lanzhou, China, pp. 109-110.

Duan, J. and Gregory, J. 2003. Coagulation by hydrolysing metal salts. Advances in Colloid and Interface Science, 100-102: 475-502.

EQA 1974 (Act 127) and Subsidiary Legislation, 1999. International Law Book Services, Kuala Lumpur, Malaysia, pp. 121.

Ghafari, S., Aziz, H.A., Isa, M.H. and Zinatizadeh, A.A. 2009. Application of response surface methodology (RSM) to optimize coagulation-flocculation treatment of leachate using polyaluminum chloride (PAC) and alum. Journal of Hazardous Materials, 163 (2): 650-656.

Gupta, V. K. and Suhas 2009. Application of low-cost adsorbents for dye removal - A review. Journal of Environmental Management, 90(8): 2313-2342.

Gurses, A., Yalcin, M. and Dogar, C. 2003. Removal of Remazol Red RB by using Al (III) as coagulant-flocculant: Effect of some variables on settling velocity. Water Air & Soil Pollution, 146(1-4): 297-318.

Howe, K. J., Marwah, A., Chiu, K. P. and Adham, S. S. 2006. Effect of coagulation on the size of MF and UF membrane foulants. Environmental Science & Technology, 40(24): 7908-7913.

Hu, C. Z., Liu, H. J., Qu, J. H., Wang, D. S. and Ru, J. 2005. Coagulation behavior of aluminum salts in eutrophic water: Significance of Al 13 species and pH control. Environmental Science & Technology, 40(1): 325-331.

Khuri, A. I. 2001. An overview of the use of generalized linear models in response surface methodology. Nonlinear Analysis, 47: 2023-2034.

Macchi, G., Pagano, M., Santori, M. and Tiravanti. G. 1993. Battery industry wastewater: Pb removal and produced sludge. Water Resources, 27(12): 1511-1518.

Meric, S., Selcuk, H. and Belgiorno. V. 2005. Acute toxicity removal in textile finishing wastewater by Fenton's oxidation, ozone and coagulation-flocculation processes. Water Resources, 39(6): 1147-1153.

Miller, S.M., Fugate, E. J., Craver, V.O., Smith, J.A. and Zimmerman, J.B. 2008. Toward understanding the efficacy and mechanism of *Opuntia* spp. as a natural coagulant for potential application in water treatment. Environmental Science & Technology, 42(12): 4274-4279.

Netzer, A., Wilkinson, P. and Beszedits, S. 1974. Removal of trace metals from wastewater by treatment with lime and discarded automotive tires. Water Resources, 8(10): 813-817.

Sanchez, A. G., Ayuso, E. A. and DeBlas O. J. 1999. Sorption of heavy metals from industrial wastewater by low-cost mineral silicates. Clay Minerals, 34(3): 469-477.

Sinha, S., Yoon, Y., Amy, G. and Yoon, J. 2004. Determining the effectiveness of conventional and alternative coagulants through effective characterization schemes. Chemosphere, 57(9): 1115-1122.

Wang, J. P., Chen, Y. Z., Yuan, S. J., Sheng, G. P. and Yu, H. Q. 2009. Synthesis and characterization of a novel cationic chitosan based flocculant with a high water-solubility for pulp mill wastewater treatment. Water Resources, 43(20): 5267-5275.