Journal of Hazardous Materials 163 (2009) 650–656

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Application of response surface methodology (RSM) to optimize coagulation–flocculation treatment of leachate using poly-aluminum chloride (PAC) and alum

Shahin Ghafari[a], Hamidi Abdul Aziz[b,*], Mohamed Hasnain Isa[c], Ali Akbar Zinatizadeh[d]

[a] *Department of Chemical Engineering, Faculty of Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia*
[b] *School of Civil Engineering, Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia*
[c] *Civil Engineering Department, Universiti Teknologi PETRONAS, 31750 Tronoh, Perak, Malaysia*
[d] *Civil Engineering Department, Engineering Faculty, University of Razi, Kermanshah, Iran*

ARTICLE INFO

Article history:
Received 5 March 2007
Received in revised form 1 April 2008
Accepted 4 July 2008
Available online 26 July 2008

Keywords:
Coagulation–flocculation
Leachate
Poly-aluminum chloride (PAC)
Response surface methodology (RSM)
Central composite design (CCD)
Analysis of variances (ANOVA)

ABSTRACT

Coagulation–flocculation is a relatively simple physical–chemical technique in treatment of old and stabilized leachate which has been practiced using a variety of conventional coagulants. Polymeric forms of metal coagulants which are increasingly applied in water treatment are not well documented in leachate treatment. In this research, capability of poly-aluminum chloride (PAC) in the treatment of stabilized leachate from Pulau Burung Landfill Site (PBLS), Penang, Malaysia was studied. The removal efficiencies for chemical oxygen demand (COD), turbidity, color and total suspended solid (TSS) obtained using PAC were compared with those obtained using alum as a conventional coagulant. Central composite design (CCD) and response surface method (RSM) were applied to optimize the operating variables viz. coagulant dosage and pH. Quadratic models developed for the four responses (COD, turbidity, color and TSS) studied indicated the optimum conditions to be PAC dosage of 2 g/L at pH 7.5 and alum dosage of 9.5 g/L at pH 7. The experimental data and model predictions agreed well. COD, turbidity, color and TSS removal efficiencies of 43.1, 94.0, 90.7, and 92.2% for PAC, and 62.8, 88.4, 86.4, and 90.1% for alum were demonstrated.

1. Introduction

Sanitary landfill leachate, a highly polluted industrial wastewater, has been a cause for significant concern with landfilling being the most common technique in solid waste disposal [1]. The implementation of the most suitable technique for the treatment of leachate is directly governed by the characteristics of the leachate. Leachates from different landfills vary considerably in their chemical compositions due to factors such as the type of solid wastes deposited, hydrogeology of the landfill site, specific climate conditions, moisture routing through the landfill, landfill age as well as design and operation of the landfill [2–5]. Biological treatment processes are effective for young or freshly produced leachate, but are ineffective for leachate from older landfills (>10 years old). In contrast, physical–chemical methods which are not favored for young leachate treatment, are advised for older leachate [6].

Coagulation–flocculation is a relatively simple physical–chemical technique commonly used for water and wastewater treatment. The removal mechanism of this process mainly consists of charge neutralization of negatively charged colloids by cationic hydrolysis products, followed by incorporation of impurities in an amorphous hydroxide precipitate through flocculation [7]. This technique has been employed successfully for the treatment of old landfill leachates [8]. The method is mainly proposed for pretreatment of fresh leachates, or for post-treatment of partially stabilized leachates with low biodegradability, i.e. low BOD_5/COD ratio [4].

Inorganic metal salts such as aluminum (alum) sulfate, ferrous sulfate, ferric chloride and ferric chloro-sulfate are generally used in coagulation–flocculation. Among these inorganic coagulants, iron salts are often more efficient than aluminum ones [8]. In recent years, there has been a rise in the use of polymerized forms of metal coagulants such as poly-aluminum chloride (PAC) for water treatment in Europe, Japan and North America due to their reduced cost and wider availability [9,10]. Such products are claimed to be more advantageous over conventional coagulants because of their higher removal of particulate and/or organic matters as well as natural advantages of lower alkalinity consumption and lesser sludge production [10]. Amokrane et al. [8] reported that conventional coagulants generally remove 10–25% COD from young leachates and 50–65% COD from stabilized leachates or biologically pretreated leachates. However, application of polymerized

---

* Corresponding author. Tel.: +60 4 5996215; fax: +60 4 5941009.
E-mail address: cehamidi@eng.usm.my (H.A. Aziz).

0304-3894/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2008.07.090

forms of metal coagulants in leachate treatment is not well documented.

The appropriate implementation of this method depends upon how precisely coagulant dosage and pH are chosen. Therefore, trial and error has been conventionally practiced to optimize these variables. These studies were conducted using “changing one factor at a time” method, i.e. a single factor is varied while all other factors are kept unchanged for a particular set of experiments. Likewise, other variables would be individually optimized through the single-dimensional searches which are time consuming and incapable of reaching the true optimum as interaction among variables is not taken into consideration [11]. As a solution, the statistical method of response surface methodology (RSM) has been proposed to include the influences of individual factors as well as their interactive influences. RSM which is a technique for designing experiment helps researchers to build models, evaluate the effects of several factors and achieve the optimum conditions for desirable responses in addition to reducing the number of experiments [12]. Analysis of variance (ANOVA) provides the statistical results and diagnostic checking tests which enables researchers to evaluate adequacy of the models.

The present study investigates the comparative suitability of PAC and alum as coagulants for leachate treatment. Central composite design (CCD) and RSM was used to design the experiments, build models and determine the optimum conditions. Removal of COD, turbidity, color and TSS were monitored throughout the experiments. Thus, the statistical design was based on two factors (coagulant dosage and pH) and four responses (COD, turbidity, color and TSS).

2. Materials and methods

2.1. Leachate sampling and characterization

Leachate samples were taken from Pulau Burung Landfill Site (PBLS) located in Byram Forest Reserve in Penang, Malaysia. This site receives 1500 tonnes of solid waste daily. PBLS has an area of 23.7 ha and is equipped with a natural marine clay liner and three leachate collection ponds [13]. This landfill has been developed semi-aerobically employing a controlled tipping technique in 1991 and leachate recirculation system in 2001 [14–16].

Samples were collected from one of the ponds, six times at 2-week intervals, within about 3 months from January to March 2005. Sample collection and preservation were done in accordance with the Standard Methods for the Examination of Water and Wastewater [17]. The collected samples were stored at 4 °C. Characterization was carried out immediately after samples arrived in the laboratory. Table 1 shows the characteristics of samples determined according to the Standard Methods [17].

Table 1
Characteristics of raw leachate from PBLS

Parameters	Range[a]	Mean[b]
Temperature (°C)	25–31	27
pH	8.2–8.5	8.4
COD (mg/L)	1794–2094	1925
TSS (mg/L)	38–96	80
NH_4-N (mg/L)	1070–1300	1184
Color (Pt. Co.)	3640–4100	3869
Turbidity (FAU)	268–502	347
Alkalinity (mg/L as $CaCO_3$)	4260–5510	5093

[a] The values are average of three measurements. The differences between the measurements for each were less than 1%.

[b] Average of six samples taken from January to March 2005.

Table 2
Range of critical parameters obtained from literature

Critical parameter	Range	Reference
Speed of rapid mixing (rpm)	100–250	[10,19]
Duration of rapid mixing (min)	1–5	[10,23]
Speed of slow mixing (rpm)	30–60	[4,22]
Duration of slow mixing (min)	10–55	[4,21]
Settling time (min)	30–120	[8,19]

Aghamohammadi et al. [13] reported low BOD_5/COD ratio (0.17) and high ammoniacal nitrogen concentration (1225 mg/L) for this leachate which implies that it is highly stabilized and has low biodegradability.

2.2. Coagulation–flocculation

In this study two coagulants were applied; alum as a metal salt and poly-aluminum chloride (PAC) as a pre-hydrolyzed metal salt. The alum used in this study was in powder form with the formula $Al_2(SO_4)_3{\cdot}18H_2O$ ($M = 666.42$ g/mol, 51–59% $Al_2(SO_4)_3$, pH 2.5–4) and supplied by Merck, Germany. A hydrolyzed solution of PAC with the formula $Al(OH)_xCl_y$ (where x is in the range 1.35–1.65, and $y = 3 - x$) with the usual acid character (pH 2.3–2.9) due to the presence of hydrochloric acid, was supplied by Idaman Bersih Sdn. Bhd., Malaysia. An 18% solution of PAC was used as stock solution throughout the experiments. Coagulation–flocculation experiments were carried out using a conventional jar-test apparatus (VELP-Scientifica, Model: JLT6, Italy) with impellers equipped with 2.5 cm × 7.5 cm rectangular blades. The time and speed for rapid and slow mixing were set with an automatic controller.

Table 2 shows a summary of test conditions for leachate treatment obtained from studies conducted by different researchers. Accordingly, for this research, the operating parameters were adopted as rapid mixing speed 80 rpm, slow mixing speed 30 rpm, rapid mixing time 1 min, slow mixing time 15 min, and settling time 30 min.

2.3. Experimental design and data analysis

The Design Expert Software (version 7.0) was used for the statistical design of experiments and data analysis. In this study, the central composite design (CCD) and response surface methodology (RSM) were applied to optimize the two most important operating variables: coagulant dosage and pH. Experiments were initiated as a preliminary study for determining a narrower range of coagulant dosage and pH prior to designing the experimental runs. Accordingly, coagulant dosages from 0.1 g/L were tried and the increments continued until appreciable reductions were observed in the process responses (COD, turbidity, color, and TSS). Likewise, a wide pH range of 2–12 was examined to search for a narrower and more effective range. As a result the study ranges were chosen as coagulant dosage 1–3 g/L and pH 6.5–8.5 for PAC, and coagulant dosage 9–10 g/L and pH 6–8 for alum. Table 3 shows the CCD in the form of a 3^2 full factorial design with four additional experimental trials (run numbers 10–13) as replicates of the central point and obtained experimental results at each assay. In this table the independent variables levels are presented in terms of the original unit of measurement (g/L) in addition to coded levels (in parentheses). The coded values for coagulant dosage (A) and pH (B) were set at five levels: −1 (minimum), −0.5, 0 (central), +0.5, and +1 (maximum). Experimental results are shown as percent removal of COD, turbidity, color and TSS.

In order to obtain the optimum dosage and pH, four dependent parameters were analyzed as responses; COD removal, turbidity

Table 3
CCD for the study of two experimental variables for both coagulants (PAC and alum) and obtained results

Run no.	PAC						Alum					
	Experimental design		Results (removal (%))				Experimental design		Results (removal (%))			
	A: dosage[a] (code)	B: pH (code)	COD	Turbidity	Color	TSS	A: dosage[a] (code)	B: pH (code)	COD	Turbidity	Color	TSS
1	1.00 (−1)	6.50 (−1)	26.7	47.0	46.8	44.8	9.00 (−1)	6.0 (−1)	42.7	72.3	56.1	80.2
2	3.00 (+1)	6.50 (−1)	28.5	50.4	42.3	48.7	10.00 (+1)	6.0 (−1)	63.5	92.9	87.8	90.3
3	1.00 (−1)	8.50 (+1)	17.8	53.8	49.2	65.1	9.00 (−1)	8.0 (+1)	57.8	76.0	70.8	88.6
4	3.00 (+1)	8.50 (+1)	19.6	64.2	32.0	56.1	10.00 (+1)	8.0 (+1)	40.3	79.3	69.2	81.2
5	1.50 (−0.5)	7.50 (0)	34.8	81.5	80.0	77.3	9.25 (−0.5)	7.0 (0)	55.7	85.3	79.9	87.5
6	2.50 (+0.5)	7.50 (0)	32.9	85.1	87.6	82.3	9.75 (+0.5)	7.0 (0)	56.7	85.3	86.0	86.0
7	2.00 (0)	7.00 (−0.5)	37.2	82.3	80.0	79.7	9.50 (0)	6.5 (−0.5)	65.3	85.9	82.2	94.1
8	2.00 (0)	8.00 (+0.5)	32.6	89.7	78.6	89.7	9.50 (0)	7.5 (+0.5)	42.3	78.6	67.5	82.5
9	2.00 (0)	7.50 (0)	43.4	96.3	91.6	90.6	9.50 (0)	7.0 (0)	63.3	88.5	86.9	88.0
10	2.00 (0)	7.50 (0)	42.1	93.0	87.2	96.7	9.50 (0)	7.0 (0)	31.2	65.8	54.3	79.3
11	2.00 (0)	7.50 (0)	46.7	98.4	94.0	95.6	9.50 (0)	7.0 (0)	65.8	94.7	92.6	94.5
12	2.00 (0)	7.50 (0)	48.3	97.2	95.2	89.3	9.50 (0)	7.0 (0)	69.4	89.6	88.1	89.9
13	2.00 (0)	7.50 (0)	51.5	95.0	94.6	94.9	9.50 (0)	7.0 (0)	52.0	75.7	72.9	86.3

[a] Unit of dosage: g/L.

removal, color removal, and TSS removal. The quadratic equation model for predicting the optimal conditions can be expressed according to Eq. (1):

$$Y=\beta_0+\sum_{i=1}^{k}\beta_i\cdot X_i+\sum_{i=1}^{k}\beta_{ii}\cdot X_i^2+\sum_{i_{\leq j}}^{k}\sum_{j}^{k}\beta_{ij}\cdot X_i\cdot X_j+\cdots+e \qquad (1)$$

where i is the linear coefficient, j is the quadratic coefficient, β is the regression coefficient, k is the number of factors studied and optimized in the experiment and e is the random error.

Analysis of variance (ANOVA) was used for graphical analyses of the data to obtain the interaction between the process variables and the responses. The quality of the fit polynomial model was expressed by the coefficient of determination R^2, and its statistical significance was checked by the Fisher's F-test in the same program. Model terms were evaluated by the P-value (probability) with 95% confidence level. Three-dimensional plots and their respective contour plots were obtained for both coagulants (PAC and alum) based on effects of the two factors (coagulant dosage and pH) at five levels. Furthermore, the optimum region was identified based on the main parameters in the overlay plot.

3. Results and discussion

3.1. Statistical analysis

The relationship between the two variables (coagulant dosage and pH) and the four important process responses (COD, turbidity, color, and TSS removal efficiencies) for the coagulation–flocculation process was analyzed using response surface methodology (RSM). Significant model terms are desired to obtain a good fit in a particular model. The CCD shown in Table 3 allowed the development of mathematical equations where predicted results (Y) were assessed as a function of coagulant dosage (A) and pH (B) and calculated as the sum of a constant, two first-order effects (terms in A and B), one interaction effect (AB) and two second-order effects (A^2 and B^2) according to Eq. (1). The results obtained were then analyzed by ANOVA to assess the "goodness of fit". Equations from the first ANOVA analysis were modified by eliminating the terms found statistically insignificant. Table 4 illustrates the reduced quadratic models in terms of coded factors and also shows other statistical parameters. Data given in this table demonstrates that all the models were significant at the 5% confidence level since P values were less than 0.05.

The lack of fit (LOF) F-test describes the variation of the data around the fitted model. If the model does not fit the data well, this will be significant. The large P values for lack of fit (>0.05) presented in Table 4 (PLOF) show that the F-statistic was insignificant, implying significant model correlation between the variables and process responses.

The R^2 coefficient gives the proportion of the total variation in the response predicted by the model, indicating ratio of sum of squares due to regression (SSR) to total sum of squares (SST). A high R^2 value, close to 1, is desirable and a reasonable agreement with adjusted R^2 is necessary [20]. A high R^2 coefficient ensures a satisfactory adjustment of the quadratic model to the experimental data.

Adequate precision (AP) compares the range of the predicted values at the design points to the average prediction error. Ratios greater than 4 indicate adequate model discrimination

Table 4
ANOVA results for response parameters

Response	Final equation in terms of code factors	P	PLOF	R^2	Adj. R^2	AP	S.D.	CV	PRESS
PAC									
COD	$42.48+0.57A-4.47B-12.07A^2-8.02B^2$	0.0060	0.1172	0.8061	0.7091	7.120	5.75	16.18	559.34
Turbidity	$93.37+3.45A+5.40B-25.52A^2-14.50B^2$	<0.0001	0.0532	0.9717	0.9576	20.146	3.91	4.92	369.42
Color	$90.47-3.97A-1.93B-15.11A^2-33.15B^2-3.17AB$	<0.0001	0.1035	0.9720	0.9520	17.012	4.96	6.73	3009.65
TSS	$90.74-0.57A+7.28B-26.61A^2-8.93B^2$	<0.0001	0.1153	0.9499	0.9248	15.083	5.00	6.43	796.75
Alum									
COD	$62.59+2.52A+1.81B-18.73A^2-5.25B^2-3.38AB$	0.0011	0.0550	0.9186	0.8604	10.558	4.42	8.14	764.88
Turbidity	$87.00+2.66A+5.42B-7.09A^2-6.51B^2$	0.0226	0.1063	0.7240	0.5859	6.712	5.47	6.64	622.68
Color	$84.54+1.58A+7.54B-15.61A^2-7.67B^2-0.042AB$	0.0040	0.1040	0.8801	0.7945	8.968	5.63	7.36	2426.59
TSS	$90.09+0.07A+0.64B-5.52A^2-4.02B^2-0.55AB$	0.0242	0.4274	0.7926	0.6445	5.408	2.94	3.39	392.18

P: probability of error; PLOF: probability of lack of fit; AP: adequate precision; S.D.: standard deviation; CV: coefficient of variance; PRESS: predicted residual error sum of squares.

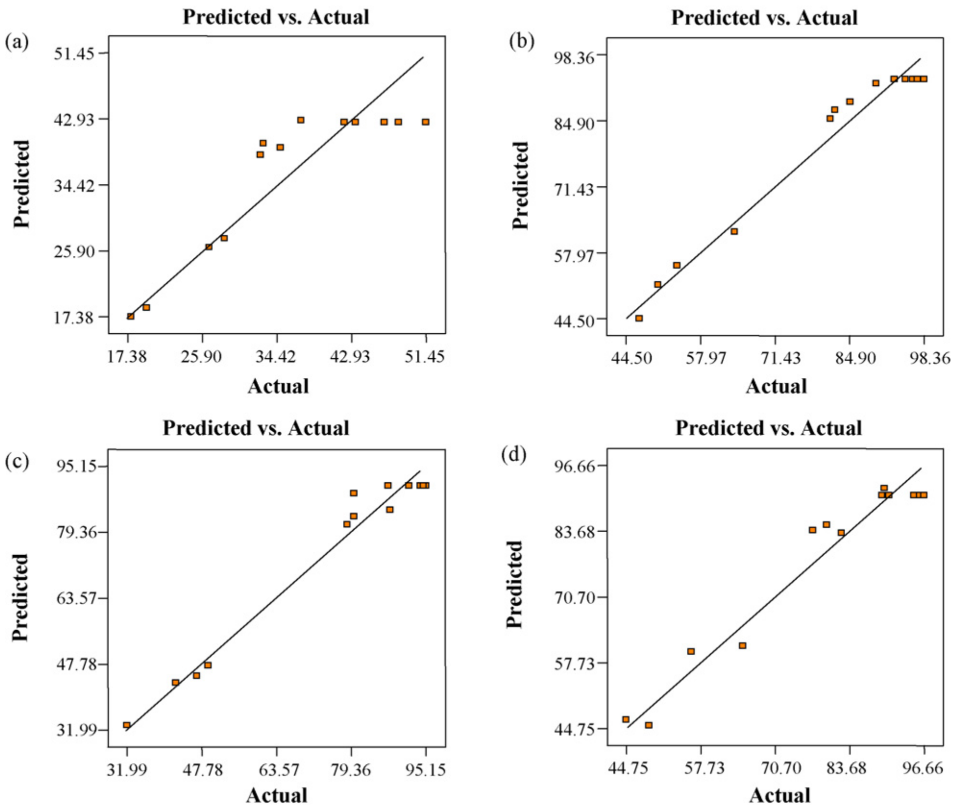

Fig. 1. Design-expert plot; predicted vs. actual values plot for (a) COD removal, (b) turbidity removal, (c) color removal, and (d) TSS removal using PAC.

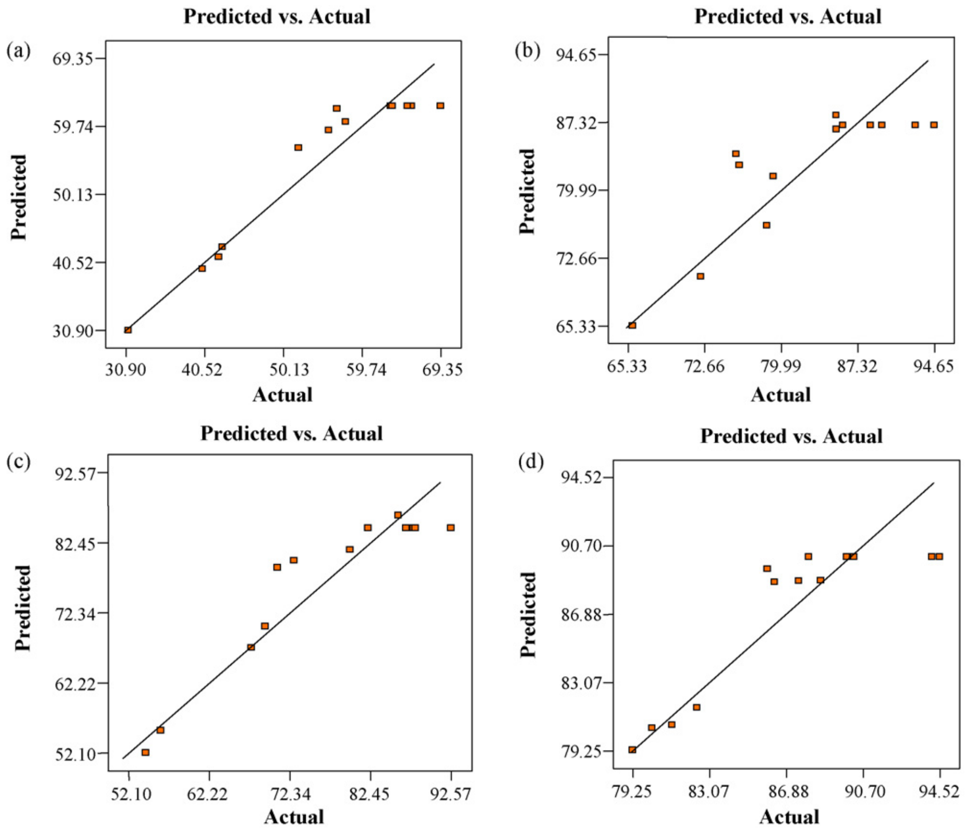

Fig. 2. Design-expert plot; predicted vs. actual values plot for (a) COD removal, (b) turbidity removal, (c) color removal, and (d) TSS removal using alum.

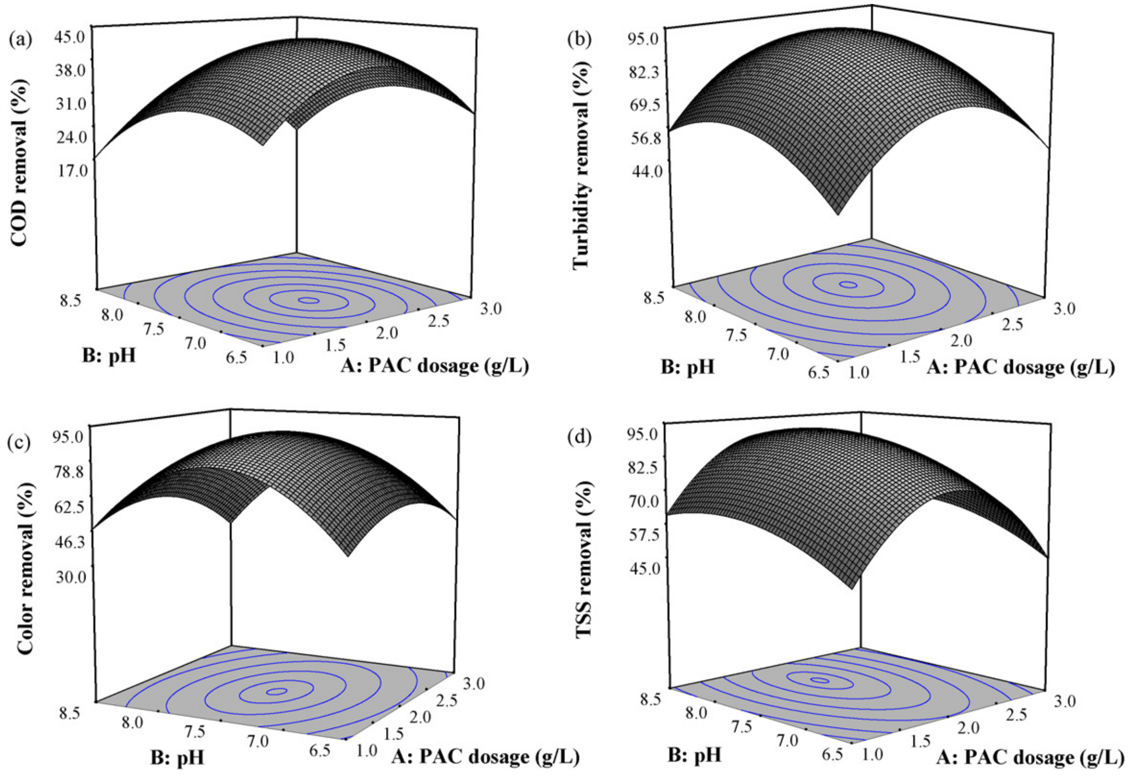

Fig. 3. Design-expert plot; response surface plot for (a) COD removal, (b) turbidity removal, (c) color removal, and (d) TSS removal using PAC.

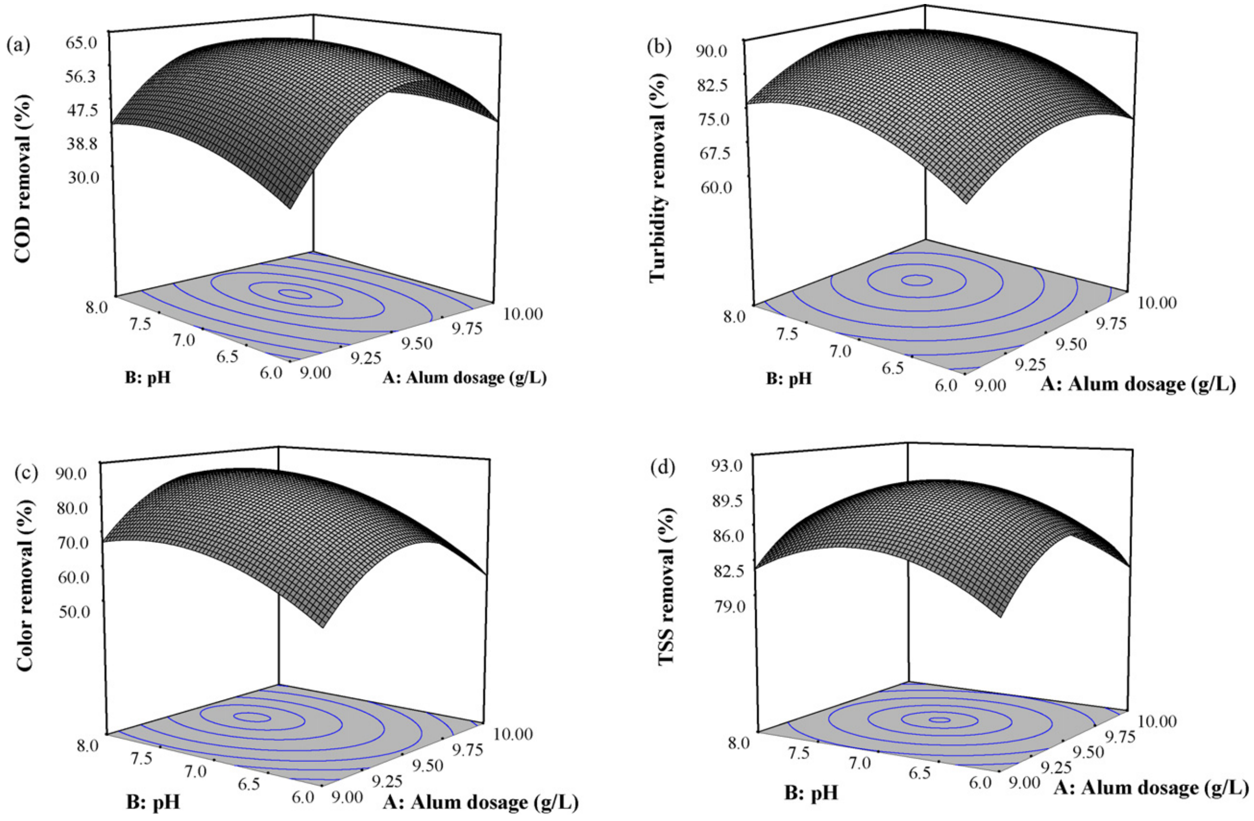

Fig. 4. Design-expert plot; response surface plot for (a) COD removal, (b) turbidity removal, (c) color removal, and (d) TSS removal using alum.

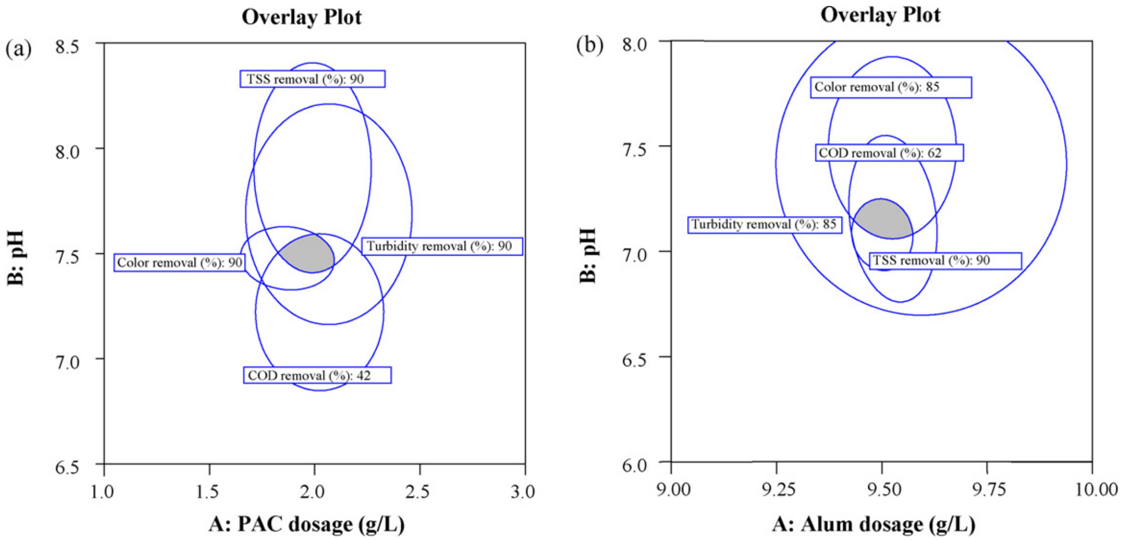

Fig. 5. Design-expert plot; overlay plot for optimal region using (a) PAC and (b) alum.

[11,18]. Diagnostic plots such as the predicted versus actual values (Figs. 1 and 2) help us judge the model satisfactoriness. The predicted versus actual values plots of parameters removal are presented in Figs. 1 and 2 for PAC and alum, respectively. These plots indicate an adequate agreement between real data and the ones obtained from the models. Besides, AP values higher than four (Table 4) for all the responses confirm that all predicted models can be used to navigate the design space defined by the CCD.

The coefficient of variance (CV) as the ratio of the standard error of estimate to the mean value of the observed response defines reproducibility of the model. A model normally can be considered reproducible if its CV is not greater than 10% [18]. According to Table 4, the only model which falls short in terms of reproducibility is the model for COD removal using PAC (CV = 16.18).

3.2. *Process analysis*

The response surface plots for PAC and alum are shown in Figs. 3 and 4, respectively. The plots are approximately symmetrical in shape with circular contours. All response plots show clear peaks, implying that the optimum conditions for maximum values of the responses are attributed to pH and dosage in the design space. The two-dimensional representation of the responses on the dosage—pH plane (contour plot) show concentrically closed curves whose centers represent the optimum conditions. Response surface plots in Fig. 3 indicate optimum points to be at about pH 7.5 and dosage 2 g/L for PAC. Likewise, Fig. 4 demonstrates that the optimum removal occurred at around pH 7 and dosage 9.5 g/L for alum. Removal efficiencies are found to reduce when moving away from these points, meaning that either increase or decrease in any of the tested variables results in decline of the responses.

The COD removal response surfaces in Fig. 4a indicate 62.8% removal efficiency which agrees with findings of Amokrane et al. [8] using conventional coagulants for stabilized leachate. A comparison with Fig. 3a shows lower COD removal (43.1%) using PAC. Furthermore, the response surfaces in Figs. 3 and 4 show turbidity, color and TSS removal efficiencies were respectively 94.0, 90.7, and 92.2% for PAC and 88.4, 86.4, and 90.1% for alum at optimum conditions. In other words, PAC resulted in higher removal of turbidity, color and TSS, but yield lower COD removal compared to alum. The higher efficiency in improving physical characteristics of leachate reveals why PAC is recommended for treatment of moderate—COD wastewaters.

Table 5
The minimum permissible values of responses for identifying optimum condition

Coagulant	Minimum removal			
	COD (%)	Turbidity (%)	Color (%)	TSS (%)
PAC	42	90	90	90
Alum	62	85	85	90

3.3. *Process optimization*

With multiple responses, the optimum condition where all parameters simultaneously meet the desirable removal criteria could be visualized graphically by superimposing the contours of the response surfaces in an overlay plot. Graphical optimization displays the area of feasible response values in the factor space and the regions that do fit the optimization criteria would be shaded [11]. Table 5 shows the chosen response limits for each parameter as the minimum permissible values. These minimum constraints were chosen relatively close to the acquired maximum removal efficiencies in order to obtain a moderately precise optimum zone. The shaded areas in Fig. 5(a) and (b) show the optimum conditions for PAC and alum, respectively. The optimum removal was obtained at pH 7.5 and dosage 2 g/L (corresponding to 0.5 g/L as aluminum) with PAC as coagulant and at pH 7 and dosage 9.5 g/L

Table 6
Verification experiments at optimum conditions

Conditions	Responses (removal (%))			
	COD	Turbidity	Color	TSS
PAC (2 g/L at pH 7.5)				
Experimental value	46.7	94.4	92.0	92.6
Model response	42.8	93.4	90.5	90.7
Error	3.9	1.0	1.5	1.9
Standard deviation	±2.76	±0.70	±1.05	±1.32
Alum (9.5 g/L at pH 7)				
Experimental value	60.8	88.9	83.2	92.5
Model response	62.6	87.0	84.5	90.1
Error	−1.8	1.9	−1.3	2.4
Standard deviation	±1.26	±1.32	±0.93	±1.67

(corresponding to 0.76 g/L as aluminum) with alum as coagulant. The results showed that in comparable amounts of aluminum, alum showed higher COD removal whereas higher turbidity, color and TSS removal efficiencies were achieved with PAC due to its bridging ability.

Two additional experiments were conducted applying the optimum conditions to confirm the agreement of the results achieved from models and experiments for both PAC and alum. As shown in Table 6, the removal efficiencies for all response parameters obtained from the experiments and as estimated by models were in close agreement.

4. Conclusions

Physical–chemical methods are advised for old and stabilized leachate treatment; among which coagulation–flocculation is one of the simple and common methods. Although, there are many types of coagulants available to treat water and wastewater, opting the most effective coagulant for a particular wastewater still largely depends on the outcome of laboratory jar testing. PAC, a known coagulant for water treatment, but uncommon in leachate treatment, was investigated for leachate treatment in the present study. Alum as a conventional coagulant was also applied to the same leachate for performance comparison. The optimum conditions obtained were 2 g/L PAC at pH 7.5 and 9.5 g/L alum at pH 7. The results showed good agreement between experimental and model predictions.

At optimum conditions, 62.8% COD removal was achieved using alum, whereas removal using PAC was 43.1%. Thus, the relatively low COD removal efficiencies using either PAC or alum substantiates the idea that coagulation–flocculation should be used as a pre/post treatment for leachate treatment. In contrast, higher removal efficiencies for turbidity (94.0%), color (90.7%), and TSS (92.2%) were achieved using PAC than those using alum (88.4%, 86.4%, and 90.1%) even though the alum dosage was almost fivefold of the PAC dosage. Therefore, this study reveals that PAC is more efficient in improving physical characteristics of leachate rather than removing COD; for this reason, PAC is recommended for wastewater treatment in which COD is not a significant concern.

References

[1] S. Ghafari, H.A. Aziz, M.H. Isa, Coagulation process for semi-aerobic leachate treatment using poly-aluminum chloride, in: The AEESEAP International Conference "Engineering a Better Environment for Mankind", Kuala Lumpur, Malaysia, June 7–9, 2005.

[2] L.M. Chu, K.C. Cheung, M.H. Wong, Variations in the chemical properties of landfill leachate, Environ. Manage. 18 (1) (1994) 105–117.

[3] A.A. Tatsi, A.I. Zouboulis, A field investigation of the quantity and quality of leachate from a municipal solid waste landfill in a Mediterranean climate (Thessaloniki, Greece), Adv. Environ. Res. 6 (2002) 207–219.

[4] A.A. Tatsi, A.I. Zouboulis, K.A. Matis, P. Samaras, Coagulation–flocculation pretreatment of sanitary landfill leachates, Chemosphere 53 (2003) 737–744.

[5] H.A. Aziz, M.S. Yusuff, M.N. Adlan, N.H. Adnan, S. Alias, Physico-chemical removal of iron from semi-aerobic landfill leachate by limestone filter, Waste Manage. 24 (2004) 353–358.

[6] D.J.L. Forgie, Selection of the most appropriate leachate treatment methods. Part 2. A review of recirculation, irrigation and potential physical–chemical treatment methods, Water Pollut. Res. J. Canada 23 (1988) 329–340.

[7] J. Duan, J. Gregory, Coagulation by hydrolyzing metal salts, Adv. Colloid Interface Sci. 100–102 (2003) 475–502.

[8] A. Amokrane, C. Comel, J. Veron, Landfill leachates pretreatment by coagulation–flocculation, Water Res. 31 (1997) 2775–2782.

[9] A. Amirtharajah, C.R. O'Melia, Coagulation Processes: Destabilization, Mixing and Flocculation, Water Quality and Treatment, American Water Works Association, fourth ed., McGraw Hill, 1990.

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

[11] R.L. Mason, R.F. Gunst, J.L. Hess, Statistical Design and Analysis of Experiments, Eighth Applications to Engineering and Science, second ed., Wiley, New York, 2003.

[12] A.I. Khuri, J.A. Cornell, Response Surfaces, Design and Analyses, 2nd ed., Marcel Dekker Inc., New York, 1996.

[13] N. Aghamohammadi, H.A. Aziz, M.H. Isa, A.A. Zinatizadeh, Powdered activated carbon augmented activated sludge process for treatment of semi-aerobic landfill leachate using response surface methodology, Bioresource Technol. 98 (2007) 3570–3578.

[14] H.A. Aziz, N. Othman, M.S. Yusuff, D.R.H. Basri, F.A.H. Ashaari, M.N. Adlan, F. Othman, M. Johari, M. Perwira, Removal of copper from water using limestone filtration technique. Determination of mechanism of removal, Environ. Int. 26 (2001) 395–399.

[15] H.A. Aziz, M.N. Adlan, M.S.M. Zahari, S. Alias, Removal of ammoniacal nitrogen (NH_4-N) from municipal solid waste leachate by using activated carbon and limestone, Waste Manage. 22 (2004) 371–375.

[16] D.R.H. Basri, A.A.K. Mohamed, H.A. Azizi, F.A.H. Assari, The effectiveness of cockle shells in treating leachate organic pollutants, in: ISWA International Symposium and Exhibition on Waste Management in Asian Cities, Hong Kong Convention and Exhibition Centre, October 2000, pp. 23–25.

[17] APHA, WPCF, AWWA, Standard Methods for the Examination of Water and Wastewater, 19th ed., American Public Health Association (APHA), Washington, DC, 1992.

[18] Q. Beg, V. Sahai, R. Gupta, Statistical media optimization and alkaline protease production from *Bacillus mojavensis* in a bioreactor, Process Biochem. 39 (2003) 203–209.

[19] R. Connolly, Y. Zhao, G. Sun, S. Allen, Removal of ammoniacal-nitrogen from an artificial landfill leachate in downflow reed beds, Process Biochem. 39 (2004) 1971–1976.

[20] 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.

[21] I.M. Ramirez, M.T.O. Velasquez, Removal and transformation of recalcitrant organic matter from stabilized saline landfill leachates by coagulation–ozonation coupling processes, Water Res. 38 (2004) 2359–2367.

[22] A.I. Zouboulis, X.L. Chai, I.A. Katsoyiannis, The application of bioflocculant for the removal of humic acids from stabilized landfill leachates, J. Environ. Manage. 70 (2004) 35–41.

[23] A.C. Silva, M. Dezotti, G.L. Sant'Anna Jr., Treatment and detoxification of a sanitary landfill leachate, Chemosphere 55 (2004) 207–214.