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Coagulation of landfill leachate by FeCl₃: process optimization using Box–Behnken design (RSM)

Smita S. Kumar[1] · Narsi R. Bishnoi[1]

Abstract FeCl₃ coagulation was used to achieve maximum reduction of COD, phosphate, sulfate and color and process optimization (FeCl₃ dosage, pH, reaction time) was done by BBD-RSM. Responses were recorded in terms of EC, COD, phosphate, color and sulfate removal. Variables A (pH) and B (reaction time) were negatively related to removal of COD and phosphate, whereas, C (FeCl₃ dosage) was positive in case of COD removal and negative for phosphate removal. pH and coagulant dosage had negative relationship with color removal; however, reaction time showed positive relationship. In case of percent sulfate removal, variable A (pH) demonstrated negative relationship whereas B (reaction time) and C (FeCl₃ dosage) were found to be positively related. Numerical optimization of the model revealed a maximum reduction of 71, 93, 86 and 99.6 % COD, phosphate, color and sulfate at optimal FeCl₃ dosage = 3 g/l, pH 8, and reaction time = 95 min.

Keywords Landfill leachate · Ferric chloride · Response surface methodology · Box–Behnken design · Coagulation · Optimization · COD · Decolorization · Phosphate removal · Sulfate removal

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Introduction

Growing urbanization and rapid industrialization have further worsened the problem of solid waste management in almost each and every part of the world. Approximately 95 % of solid waste generated worldwide is disposed off in landfills (Kurniawan et al. 2006). Percolation of rainwater and/or the moisture content of the waste itself gives rise to the generation of dark-colored concentrated mixture that leaches from the waste in the form of 'garbage juice' (Sari et al. 2013; Zhao et al. 2013a, b). On an average, 1 ton of MSW in a landfill site produces 0.2 m³ of leachate (Kurniawan and Lo 2009). Landfill leachate is characterized by the presence of high pH, suspended solids (SS), chemical oxygen demand (COD), color and alkalinity which can significantly contaminate the receiving water bodies (Kjeldsen et al. 2002; Adlan et al. 2011; Zhao et al. 2013a, b; De Torres-Socías et al. 2014). Therefore, landfill leachate treatment has always been a subject of considerable interest (Oller et al. 2011; Sari et al. 2013).

On the basis of chemical constituents and the ambient conditions, several physical, chemical and biological methods are being employed solely and/or in integration for the removal of unwanted constituents from landfill leachate (Castrillón et al. 2010; Xiao et al. 2013; Zhao et al. 2013a, b; Anfruns et al. 2013; Wang et al. 2014a, b). The presence of refractory compounds and large variations in type and concentration of pollutants render biological methods inapplicable for the purpose in spite of being cost-effective, reliable, simple and economical (Kurniawan et al. 2006; Abbas et al. 2009; Wang et al. 2012; Wu et al. 2014). For old, stabilizing leachates mostly physico-chemical techniques are recommended (Ghafari et al. 2010).

Coagulation/flocculation is a widely employed and oldest treatment methods in landfill leachate treatment

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(Nair and Ahammed 2013; Kamaruddin et al. 2014). Selection of the coagulant type and dosages critically determine the success of as well as efficiency of treatment achieved. Generally, coagulation for landfill leachate treatment involves the addition of ferric/alum salts (Ayoub et al. 2001). However, it has been established that iron salts are more efficient than aluminium ones (Renou et al. 2008). Therefore, in the present study we have chosen $FeCl_3$ as a coagulant. Other factors which affect the efficiency of coagulation and hence need optimization are pH, mixing, temperature and retention time etc. (Wang et al. 2007).

Conventionally, multi-factor optimization is done by one-factor at-a-time approach while keeping the others constant at a specific set of conditions. It is easy to design and implement but one-factor at a time approach is time-consuming and do not take into account the interactions between factors. Consequently, it cannot be used to find the optimum conditions with greater accuracy (Wang et al. 2014a, b). To overcome these limitations, statistical experimental designs [including response surface methodology (RSM)] were proposed. Applicability of RSM lies in the measurement of responses for multiple variables influencing the system (Jin et al. 2014). RSM together with Box–Behnken design (RSM-BBD) was chosen for the current study to quantitatively investigate the effects of different operating conditions and their interactions on landfill leachate treatment efficiency while using $FeCl_3$ as a coagulant. The main objective of this work was to optimize the coagulation process by BBD of RSM. Percent reduction in COD, color, phosphate and sulfate and EC were chosen as the dependent output variables. $FeCl_3$ dosage, initial pH and reaction time were chosen as the influence factors. Generally phosphate and sulfate removal are not studied as responses while treating landfill leachate. However, as now-a-days combined and sequential processes are increasingly being employed for the treatment of landfill leachate employing physicochemical pre or post treatments. While using $FeCl_3$ coagulation as a pre-treatment method followed by any biological treatment; we are also concerned with the concentration of phosphate and sulfate present in the wastewater and an external supply is needed to maintain the required concentrations. EC was chosen as a response to observe the variation on the electrical conductivity of the resulting effluent and can be a useful parameter in electrochemical treatments as well as novel treatment methods such as MFC.

Materials and methods

Sample collection and characterization

The leachate samples were collected from a landfill site located in Bhalaswa, NW Delhi, India (28°44′26″N

77°9′26″E). The site has been operational since 1993. The site occupies 21.06 acres of land and receives about 2200 tons of waste per day (Mor et al. 2006). 50 l leachate samples were obtained from a nearby drain to which all the leachate flows and were stored at 4 °C before being used and analyzed. All samples used in the present work were collected from a single point source at single site on different times. However, general trend is a subject of subsequent papers and beyond the scope of the present work.

Experimental methodology

Coagulation experiments were carried out in seventeen 250 ml Erlenmeyer flasks. Each flask was filled with 100 ml of the raw leachate and was continuously mixed at 140 rpm in an orbital shaker. Stepwise coagulation process was carried out in the following manner: (1) 100 ml leachate sample was taken in a flask (250 ml); (2) pre-decided quantities of solid $FeCl_3 \cdot 6H_2O$ were added to the flasks in a single step (2, 2.5 and 3 g/l); (3) its pH was adjusted (to 8, 10 and 12) in accordance with the experimental design using NaOH after adding the coagulant; (4) the mixture was stirred for the specified time (30, 90 and 150 min) at 140 rpm velocity; (5) allowed to settle for 1 h; (6)and supernatant was analyzed for COD, color, phosphate, EC, TDS and Salt concentrations and percent removal were calculated where needed. All the runs were carried out at room temperature (Table 1).

Experimental design and data analysis

Box–Behnken design has specific positioning of design points and always has three levels for each factor coded as −1, 0, and +1. It has been created for estimating a quadratic model and provides strong coefficient estimates near the center of the design space (where the presumed optimum is), but weaker at the corners of the cube (where there are no design points). It is a rotatable quadratic design

Table 1 Characteristics of raw landfill leachate

Chemical oxygen demand (mg/l)	9600
Sulphate(mg/l)	474
Phosphate (mg/l)	15.27
pH	8.68
Conductivity (mS/cm)	2.65
Color	Blackish-brown
Volatile suspended solid (VSS)	550
Volatile fatty acids (VFA)	3912
Total Kjeldahl nitrogen (TKN)	1932
Ni (ppm)	0.3
Fe (ppm)	0.203

Table 2 Operating conditions for coagulation process

Factor	Value (actual)	Axis low	Axis high
pH	10	8	12
Reaction time (min)	90	30	150
Concentration of co-agulant (g/l)	2.5	2	3

where factor combinations are at the midpoints of the edges and at the centre (Bezerra et al. 2008; Ferreira et al. 2007). A Box–Behnken statistical experimental design with the RSM was used to investigate the effects of the three independent variables namely $FeCl_3$ dosage, initial pH and reaction time on coagulation. % COD, phosphate, sulfate and color removals were chosen as the response parameters. EC, TDS and Salt concentrations were also observed in the resulting effluent. BBD was chosen because of its economical and efficient nature. Table 2 presents the details of operating conditions for coagulation process. To evaluate the contribution of the three variables, experimental data were analyzed and fitted to the following second-order polynomial model using Design Expert 9.0 software:

$$Y = \beta 0 + \sum_{i=1}^{k} \beta i X i + \sum_{i=1}^{k} \beta i i X i 2 + \sum_{i=1}^{k=1} \sum_{j=i+1}^{k} \beta i j X i X j + \varepsilon \tag{1}$$

where Y represents the predicted response; Xi and Xj are the independent variables, β_0, βi, βii and βij are regression coefficients for intercept, linear, quadratic and interaction coefficients respectively, ε is the error and k is the number of variables studied (Nair and Ahammed 2013). The significance of the model equation and model terms was evaluated by F test (Jadhav et al. 2013). The quality of the quadratic model equation was expressed by the determination coefficient R^2 and adjusted R^2 (Jadhav et al. 2013). Analysis of variance (ANOVA) was applied to evaluate the statistical significance of the model (Jadhav et al. 2013). The optimal values were obtained by solving the regression equation and contour plots were used for analyzing the interactive effect of each variable (Jadhav et al. 2013, 2014).

Analytical methods

The COD of the samples were analyzed in accordance with the Standard Methods using the closed reflux titrimetric method (APHA 1998). pH, TDS, Salt concentrations and EC were measured digitally by multi response meter after proper calibration (Eutech pH meter Model PC-510 from Eutech Instruments). Phosphate was measured with the ammonium molybdate method using a UV visible spectrophotometer (at 690 nm). Color was also measured using UV–Vis spectrophotometer (390 nm). Sulfate was measured with barium chloride method taking absorbance at 420 nm. All experiments were done at room temperature and were repeated at least thrice to ensure statistical accuracy.

Calculations

Percent removals of the responses (COD, phosphate, color and sulfate) from leachate were calculated as follows:

$$\% \, Removal = \left\{ \frac{C_i - C_f}{C_i} \right\} \times 100 \tag{2}$$

where C_i and C_f are the initial and final concentrations of the respective parameters.

Results and discussion

Validation of response surface models and statistical analysis

The physicochemical characteristics of the raw leachate are summarized in Table 1. A total of 17 set of experiments were run according to BBD. BBD matrix for experimental design (real and coded values of the three factors, i.e. pH, coagulant dosage and reaction time) and observed and predicted responses for percent removal of COD, phosphate, color and sulfate have been summarized in Table 3. Second-order polynomial equations were used to draw relationship between independent variables and responses. The regression equation coefficients were calculated and data was fitted to a second-order polynomial equation for removal of COD, phosphate, color and sulfate from landfill leachate using $FeCl_3$ as a coagulant.

As is obvious from the results, the obtained values were reasonably close to the predicted experimental values, specifying the efficiency of developed model to describing the correlation between the controlling parameters on treatment efficiency of landfill leachate. Within the chosen range of the experiment, observed percent removal efficiencies varied between 57.4 and 71.3 % for COD (average being 64.38); 87–94 % for phosphate (average 90 %); 73–86 % for color (average 79) and 92–99.6 % (average 97.7) for sulfate. Table 4 provides the ANOVA of variables fitted to quadratic polynomial models as well as other statistical parameters for COD, phosphate, color and sulfate removals and EC.

A closer analysis of the table reveals that all the models were significant at the 5 % confidence level and in most of the cases P values were less than 0.05. Values obtained for

Table 3 Box–Behnken design matrix for experimental design, observed and predicted response for removal of COD, phosphate and color

Run order	Real (coded) values			Response (Y (%))							
	A	B	C	COD		Phosphate		Color		Sulfate	
	pH	Reaction time (min)	Coagulant dosage (g/l)	O	P	O	P	O	P	O	P
1	8 (−1)	150 (+1)	2.5 (0)	58.3	58.03	92.67	92.69	96.1	96.15	99.60	99.68
2	10 (0)	30 (−1)	3 (+1)	69	68.59	91.14	90.98	79.9	80.05	99.50	99.52
3	10 (0)	90 (0)	2.5 (0)	69.8	69.8	87.81	87.83	78.75	78.68	98.50	98.64
4	10 (0)	30 (−1)	2 (−1)	73.3	73.14	92.21	92.39	77.2	77.05	98.30	98.25
5	8 (−1)	90 (0)	3 (+1)	56.4	56.51	93.12	93.28	97.86	97.66	99.50	99.37
6	12 (+1)	90 (0)	2 (−1)	63.3	63.19	90.24	90.08	78.88	79.08	97.25	97.39
7	10 (0)	90 (0)	2.5 (0)	70.8	69.8	87.98	87.83	78.84	78.68	98.50	98.64
8	12 (+1)	30 (−1)	2.5 (0)	70	70.28	90.16	90.14	74.81	74.76	98.16	98.08
9	8 (−1)	90 (0)	2 (−1)	54	53.86	94.46	94.28	95.76	95.86	97.00	96.93
10	12 (+1)	150 (+1)	2.5 (0)	62.6	62.3	88.9	88.9	75.98	75.93	92.00	91.88
11	10 (0)	150 (+1)	3 (+1)	70	70.16	90.4	90.22	75.7	75.86	98.94	98.99
12	12 (+1)	90 (0)	3 (+1)	63	63.14	89.39	89.57	73.39	73.29	96.00	96.07
13	10 (0)	90 (0)	2.5 (0)	70.8	69.8	87.96	87.83	78.31	78.68	98.73	98.64
14	10 (0)	150 (+1)	2 (−1)	62.6	63.01	90.15	90.32	83.01	82.86	99.16	99.14
15	10 (0)	90 (0)	2.5 (0)	68.6	69.8	87.46	87.83	78.62	78.68	98.73	98.64
16	10 (0)	90 (0)	2.5 (0)	69	69.8	87.92	87.83	78.9	78.68	98.73	98.64
17	8 (−1)	30 (−1)	2.5 (0)	58.3	58.6	94.26	94.26	95.64	95.69	93.00	93.12

O observed, *P* predicted

Table 4 SD, Mean, CV, PRESS, AP and R2 for all the responses

	COD	Phosphate	Color	Sulfate	EC
SD	0.83	0.25	0.25	0.15	0.17
Mean	65.28	90.37	82.21	97.74	8.29
CV (%)	1.28	0.27	0.3	0.15	1.99
PRESS	18.98	4.06	3.64	1.6	2.56
R^2	0.982	0.9871	0.9907	0.998	0.9953
Adjusted R^2	0.9588	0.9705	0.9788	0.9953	0.9892
Predicted R^2	0.932	0.9187	0.9014	0.9792	0.9366
Adequate precision	20.134	21.741	27.784	67.917	45.5

correlation coefficient ($R^2 = 0.9820$–0.9980) in the present study for COD, Phosphate, color, sulfate and EC were higher than 0.80. Correlation coefficient needs to be at a minimum of 0.80 for a good fit of model (Abu Amr et al. 2014). A high R^2 value (closer to 1) demonstrates good accordance between the calculated and observed results within the range of experiment and shows that a desirable and reasonable agreement with adjusted R^2 is necessary (Nordin et al. 2004; Abu Amr et al. 2014). The range in predicted response relative to its associated error can be measured by adequate precision. The "Adequate Precision" ratio should be higher than 4 so that the predicted models can be used to navigate the space (Kousha et al. 2012). For the present model, AP values models lie

between 20.13 and 67.91; which is an adequate signal for the model and suggests that the data obtained through predicted quadratic model is reliable and can be used to navigate the design space. Based on the results, the response surface models constructed for predicting percent COD, phosphate, color, sulfate removal efficiency and EC concentrations were considered reasonable.

Optimization of variables for COD, phosphate, color and sulfate removal

The effect of factors, i.e. pH, reaction time and coagulant dosage on the responses, i.e. percent removal of COD, phosphate, color and sulfate was analyzed on the basis of

quadratic polynomial equations derived on the basis of RSM (Eqs. 3–6). A (pH) was a vital factor ($P > 0.0001$) and had a negative effect on all the responses, i.e. percent removal of COD, phosphate, color and sulfate (Eqs. 3–6) from landfill leachate thus suggesting decreased removal with increase in pH. B, reaction time (min) ($P > 0.0001$) considerably affects the removal efficiency of the selected parameters by determining the extent of completion of the reaction. Independent variable time had a negative effect on COD and phosphate (Eqs. 3, 4) and positive effect on color and sulfate removal (Eqs. 5, 6). C, coagulant dosage ($P > 0.0001$) has considerable effect on the removal efficiency and plays an important role in enhanced removal. Within the chosen range, coagulant dose had positive effect on COD and sulfate removal and negative effect on phosphate and color removal (Eqs. 3–6). COD and sulfate removal increased as the initial concentration of coagulant increased because at higher concentration more coagulant molecules or ions (Fe^{2+} and Cl^-) were available for binding with the impurities thus resulting in better removal. However, phosphate and color removal efficiencies decreased with increase in coagulant dosage. As seen from the equations; elevated parameter estimation values of variables A, B, C, AB, AC, BC, A^2, B^2, C^2 demonstrated high significance and hence summit the magnitude of these variables in the coagulation process. The variables A (pH) and B (reaction time) were negatively related to removal of COD and phosphate, whereas C ($FeCl_3$ dosage) was positive in case of COD removal and negative for phosphate removal. pH and coagulant dosage had negative relationship with color removal; however, reaction time showed positive relationship. In case of percent sulfate removal, variable A (pH) demonstrated negative relationship whereas B (reaction time) and C ($FeCl_3$ dosage) gave us an idea about its positive relationship.

Percent COD removal

The Model F value of 42.33 implies the model is significant. Values of "Prob $> F$" <0.0500 indicate model terms are significant. In this case A, B, C, AC, BC, A^2, B^2 and C^2 were significant model terms. Values >0.1000 indicate the model terms are not significant. The "Lack of Fit F value" of 0.24 implies the Lack of Fit is not significant relative to the pure error. Non-significant lack of fit is good and we want the model to fit. The "Pred R^2" of 0.9320 is in reasonable agreement with the "Adj R^2" of 0.9588, i.e. the difference is <0.2.

$$\% \, COD \, removal \, (Y1) = 68.54 - 1.60 \times A - 0.79 \times B \, 2.29$$
$$\times C - 1.03 \times AB - 3.28 \times AC$$
$$- 3.35 \times BC - 2.75 \times A^2$$
$$- 4.32 \times B^2 - 1.77 \times C^2 \qquad (3)$$

The interaction of two factors while keeping the third one constant on the percent removal efficiency of COD, phosphate, color and sulfate has been illustrated in 3D response surface plots (Figs. 2, 3, 4, 5a–c). Figure 2a–c demonstrates the interactive effect of two variables, i.e. (a) reaction time and pH at constant coagulant dose of 2.5 g/l, (b) pH and coagulant dose at constant reaction time of 90 min, and (c) % COD removal and reaction time at constant reaction pH (10) on percent COD removal efficiency. In Fig. 1a, COD removal increased with increase of pH from 8.0 to 10.0 and reaction time from 30 to 90 min and the exhibited a decreasing trend with any further increase in pH and time. COD removal was highest (68 %) around a pH of 8, reaction time around 90 min at a constant coagulant dosage of 2.5 g/l. COD removal increased with both, i.e. coagulant dosage as well as pH. A Maximum removal of 71.21 % COD was observed at a dosage of 3 g/l, pH 8.2 and reaction time 90 min (Fig. 1b). In a recent study, Liu et al. (2012) reported an optimum pH of 8 and dose 10 g/l for 68.65 % reduction in COD. It was observed that coagulant dosage had a far significant effect on COD removal within the chosen range as compared to that of pH and reaction time. At low concentration of $FeCl_3$, COD removal was found to be lower (60 % at 2 g/l and pH 8) which might be due to non availability of the coagulant to neutralize all the impurities present. Higher coagulant dosage had enough species to react with all of the impurities. COD removal also increased with increase in pH from 60 to approximately 64.8 % around a pH value of 10.7, coagulant dose of 2 g/l and constant reaction time of 90 min. In Fig. 1c, at a constant pH of 10, COD removal increased with increasing concentration of $FeCl_3$ and reaction time. A maximum removal of around 70 % was observed at 3 g/l coagulation dose, pH 10 after 58 min of the reaction. Adlan et al. (2011) combined $FeCl_3$ coagulation and dissolved air flotation (DAF) for the maximum removal of COD and color from semiaerobic landfill leachate using CCD of RSM and reported respective removal efficiencies of 75 and 93 %. Boumechhour et al. (2013) reported 64.18 % COD removal at the optimum dosage of 1.2 g/l of $FeCl_3$ at pH 6. Moradi and Ghanbari (2014) using RSM, employed ferric chloride coagulation as a pre-treatment process for landfill leachate treatment prior to Fenton oxidation and achieved approximately 65, 79 and 95 % removals of COD, color and TSS respectively (pH 7 and 1500 mg/l $FeCl_3$). Rivas et al. (2004) combined a sequential coagulation–flocculation and Fenton oxidation process in their study to achieve maximum removal of colloidal particles present in the leachate. About 90 % COD removal was achieved with an initial concentration of 7400 mg/l at pH 8.5 by using 0.8 g/l of $FeCl_3$. Amokrane et al. (1997) reported that $FeCl_3$ when used as coagulant was able to remove 55 % COD. A combination of coagulation
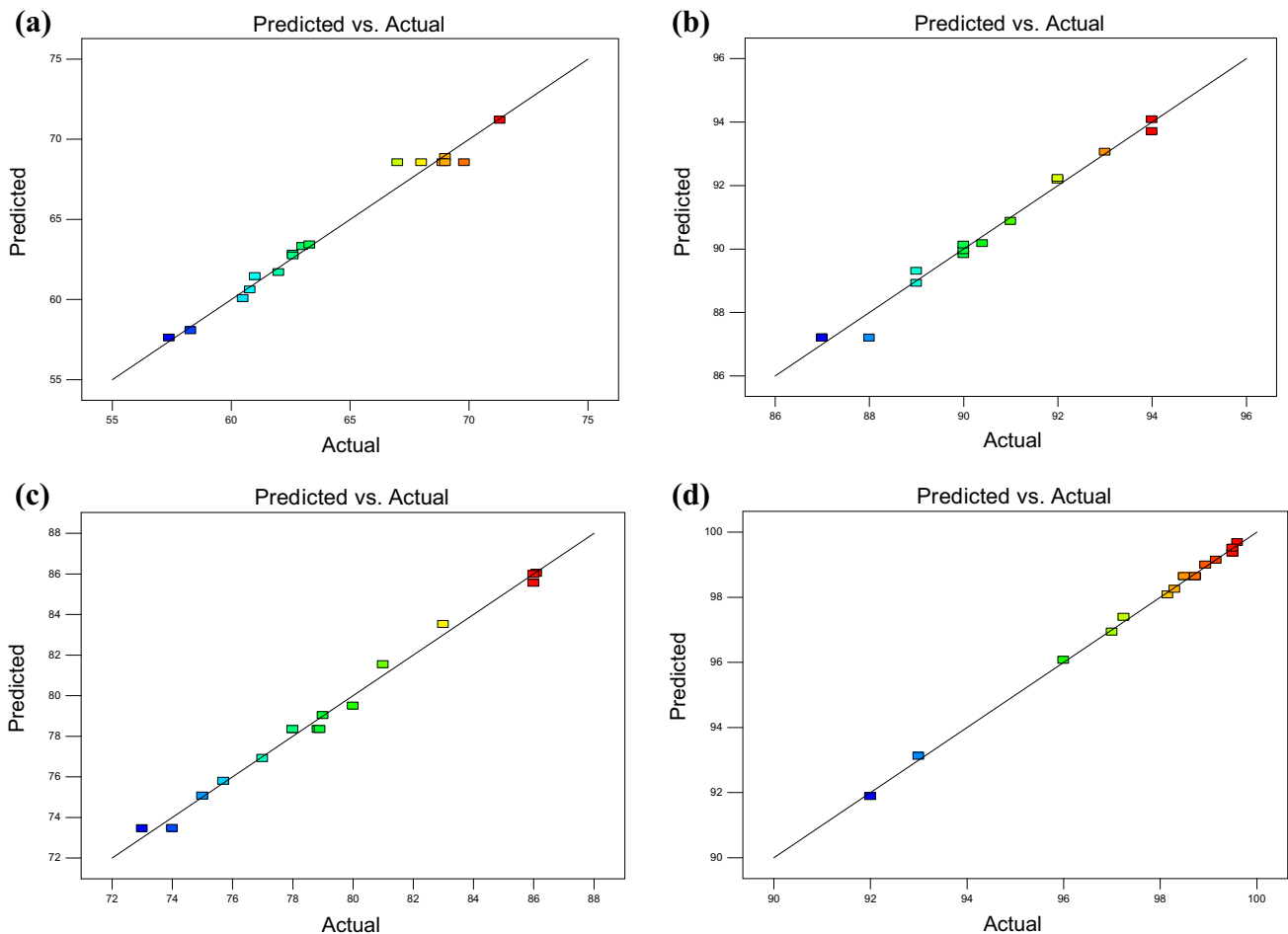
(a)

(b)

(c)

(d)

Fig. 1 Plots for correlation of predicted versus actual percent removal efficiency for **a** COD, **b** phosphate, **c** color, **d** sulfate

and Fenton oxidation with FeCl$_3$ as a coagulant reduced COD by up to 90 % (US Environmental Protection Agency 2002).

Percent phosphate removal

The Model F value of 59.45 implies the model is significant. In this case A, B, A^2, B^2, C^2 are significant model terms. The "Lack of Fit F value" of 0.65 implies the Lack of Fit is not significant relative to the pure error. "Pred R^2" of 0.9187 is in reasonable agreement with the "Adj R^2" of 0.9705, i.e. the difference is <0.2.

$$\% \text{Phosphate removal}\,(Y2) = 87.20 - 1.88 \times A - 0.70$$
$$\times B - 0.33 \times C\,0.25 \times AB\,0.00 \times AC\,0.35$$
$$\times BC\,2.35 \times A^2\,1.70 \times B^2\,1.95 \times C^2 \qquad (4)$$

Figure 3a–c shows the response surface plots for combined effect two variables (keeping the third constant) on percent Phosphate removal efficiency. Optimal conditions for phosphate removal were exactly located inside the design boundary as is obvious from the

figure which shows an obvious trough in the response surfaces. Interactive effects between reaction time and pH, coagulant dose and pH and coagulant dose and reaction time were significant on phosphate removal. As can be seen from Fig. 3a, at a constant coagulant dose of 2.5 g/l, phosphate removal was highest at the central values and decreased with increase in reaction time and pH, and then again increased with further increase in reaction time and pH values. Plot of reaction time versus pH showed optimum region from pH range 9.3 to slightly above 12 and reaction timings from 49 to 150 min. Figure 3b, c, coagulant dose versus pH and coagulant dosage versus reaction time confirmed that the optimal conditions for phosphate removal were located in the region, where pH, coagulation dosage and reaction time ranged from 9.3 to above 12, 2.2–2.87 g/l and 60–154 min respectively.

Color removal

The Model F value of 83 implies the model is significant. A, B, C, AB, AC, BC, A^2, B^2, C^2 are significant model terms. The "Lack of Fit F value" of 2.25 implies the Lack
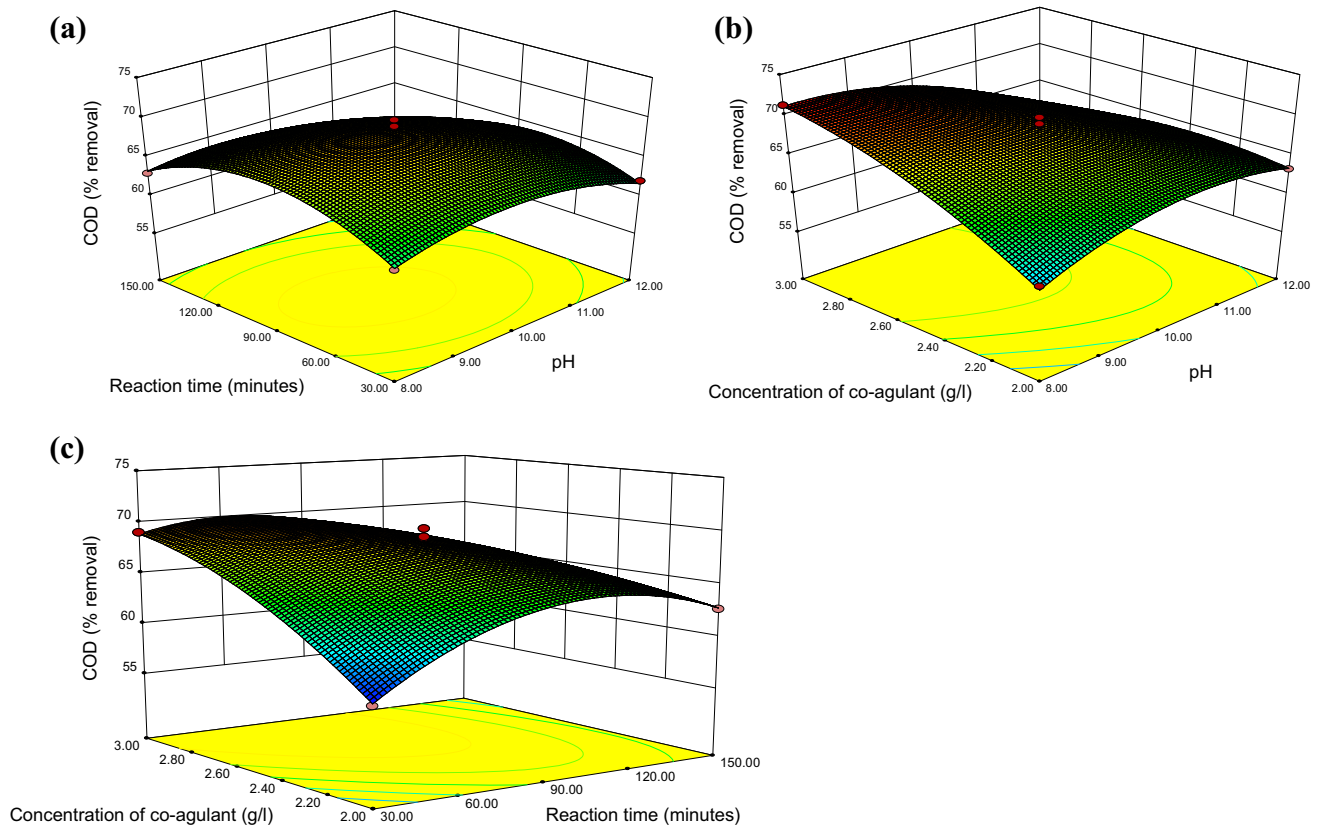
(a)

(b)

(c)

Fig. 2 Response surface plots for combined effect of **a** reaction time and pH at constant coagulant dose of 2.5 g/l, **b** pH and coagulant dose at constant reaction time of 90 min, and **c** percent COD removal and reaction time at constant reaction pH (10) on percent COD removal efficiency

of Fit is not significant relative to the pure error. The "Pred R^2" of 0.9014 is in reasonable agreement with the "Adj R^2" of 0.9788, i.e. the difference is <0.2.

$$\% \text{ Color removal} (Y3) = 78.35 - 4.76 \times A \ 0.73 \times B$$
$$- 1.29 \times C - 1.53 \times AB$$
$$- 1.50 \times AC - 2.58 \times BC \ 1.38$$
$$\times A^2 - 0.70 \times B^2 \ 1.28 \times C^2$$
$$(5)$$

Figure 4a with change in reaction time and pH at constant coagulant dose of 2.5 g/l color removal shows a gradual but constant increase from 81 % (at pH 8 and time 30 min) to 86 % (pH 8 and 150 min) with increase in time, whereas, color removal exhibited gradual decrease with increase in pH and then became almost stable after pH 10 (76 % at pH 11.74 and time 30 min). As can be seen from Fig. 4b illustrating 3D plot of coagulant dose and pH at constant reaction time of 90 min, color removal showed a slight increase with increasing coagulant dose from 85 % (at pH 8 and conc. 2 g/l) to 86 % (pH 8 and concentration of coagulant = 3 g/l). However, from an initial removal of 85 % at pH 8, color removal decreased gradually to 79 % (at pH 12 and coagulant dosage of 2 g/l). The results were in accordance with some of the previous studies, e.g. Liu

and co-workers reported an optimum pH of 8 and dose 10 g/l for 93.31 % reduction in color. Figure 4c plots the 3D interaction of coagulant dose and reaction time at constant reaction pH (10) on percent Color removal efficiency. After 30 min of reaction time, at pH 10 around 77 % of color was removed with FeCl$_3$ and it increased with increase in FeCl$_3$ dosage to approximately 80 % (with 3 g/l). With increasing retention time, color removal increased from 77 to 83 %. Researchers have conducted many studies using iron based coagulants for the treatment of landfill leachate. Zamora et al. (2000) reported a 50–70 % color reduction by a combined treatment employing activated carbon and coagulation. Aziz et al. (2007) investigated CF using four kinds of coagulant viz. alum, ferric(III) chloride, ferrous(II) sulphate and ferric (III) sulphate and recommended ferric chloride as a practicable coagulant to deal with decolorization of landfill leachate (achieved 94 % color removal at 800 mg/l of FeCl$_3$ and pH 4). Jamali et al. (2009) reported 70 % color removal.

Sulfate removal

The Model F value of 380.19 implies the model is significant. A, C, AB, AC, BC, A^2, B^2, C^2 are significant

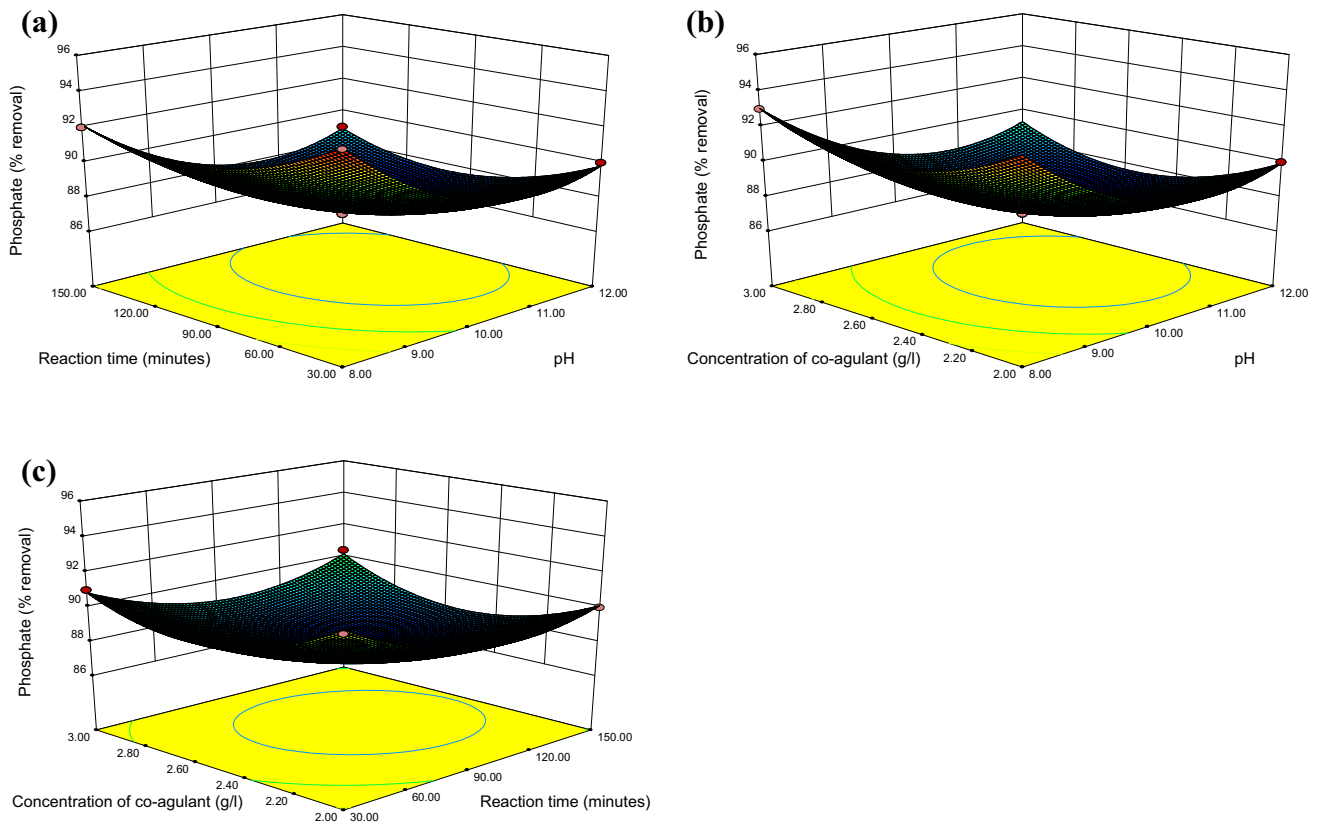**(a)**

(b)

(c)

Fig. 3 Response surface plots for combined effect of **a** reaction time and pH at constant coagulant dose of 2.5 g/l, **b** coagulant dose and pH at constant reaction time of 90 min, and **c** coagulant dose and reaction time at constant reaction pH (10) on percent phosphate removal efficiency

model terms. The "Lack of Fit *F* value" of 1.97 implies the Lack of Fit is not significant relative to the pure error. The "Pred R^2" of 0.9792 is in reasonable agreement with the "Adj R^2" of 0.953, i.e. the difference is <0.2.

$$\% \, \text{Sulfate removal} \, (Y4) = 98.64 - 0.71 \times A \, 0.09$$
$$\times B \, 0.28 \times C - 3.19 \times AB$$
$$- 0.94 \times AC - 0.36 \times BC$$
$$- 2.24 \times A^2 - 0.71 \times B^2 \, 1.04 \times C^2$$

(6)

Response surface plots for combined effect of reaction time and pH at constant coagulant dose of 2.5 g/l on sulfate removal from landfill leachate has been shown in Fig. 5a. As is obvious from the figure, sulfate removal showed a sharp increase with increase in pH as well as retention time. With increasing pH, it increased from 93 % (at 8) to 98.5 % (at 10.58 after 30 min of retention time) whereas, increase in retention time up to 150 min led to the removal of almost 99.5 % of sulfate from the Leachate sample. Sulfate removal gradually increased with increase in FeCl₃ dose (Fig. 5b) from 97 % (at pH 8 and dose 2 g/l) to 99 % (at pH 8; 3 g/l). However, with increase in pH, removal efficiency exhibited an initial increase from 97 %, attained

a maximum of 99 % (at pH 10) and then again decreased with any further increase in pH (97 % at pH 12). With increasing coagulant dose and retention time (Fig. 5c), sulfate removal efficiency improved slightly from 98 to 99 %. The results of the optimization study have been illustrated in Fig. 6a, b showing the contour plot numerical optimization and the overlay plot showing graphical optimization within the chosen criteria having the factors within range and maximized responses (COD, phosphate and color). Numerical optimization of the model revealed that the maximum reduction of 71, 93, 86 and 99.6 % COD, phosphate, color and sulfate could be achieved respectively at optimal FeCl₃ dosage = 3 g/l, pH 8, and reaction time = 95 min; whereas the average EC (mS/cm), TDS (ppt) and salt (ppt) concentration in the effluent were 8.29, 6.35 and 4.35.

Conclusions

The objective of this study was to explore the optimum process conditions, using RSM, required while using FeCl₃ as a coagulant to remove COD, phosphate and color from landfill leachate as well as to study the effect of FeCl₃
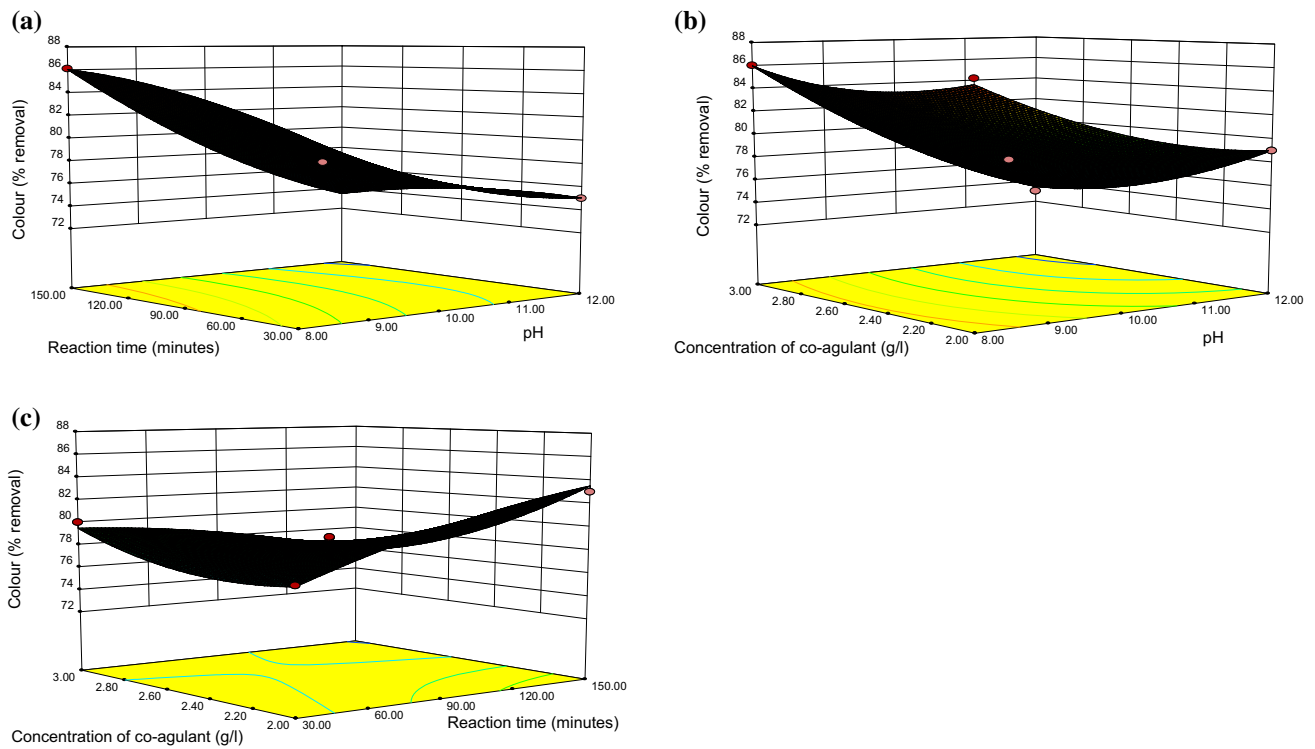
Fig. 4 Response surface plots for combined effect of **a** reaction time and pH at constant coagulant dose of 2.5 g/l, **b** coagulant dose and pH at constant reaction time of 90 min, and **c** coagulant dose and reaction time at constant reaction pH (10) on percent color removal efficiency
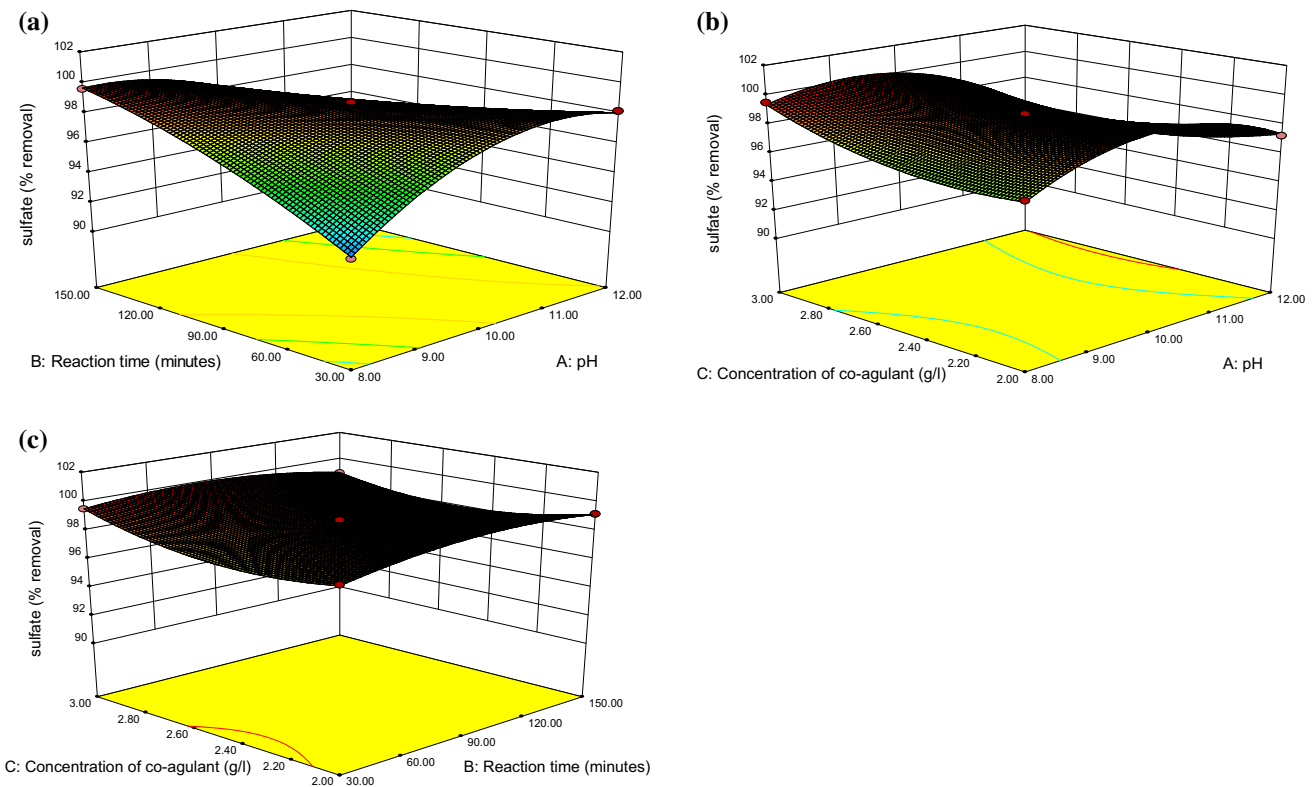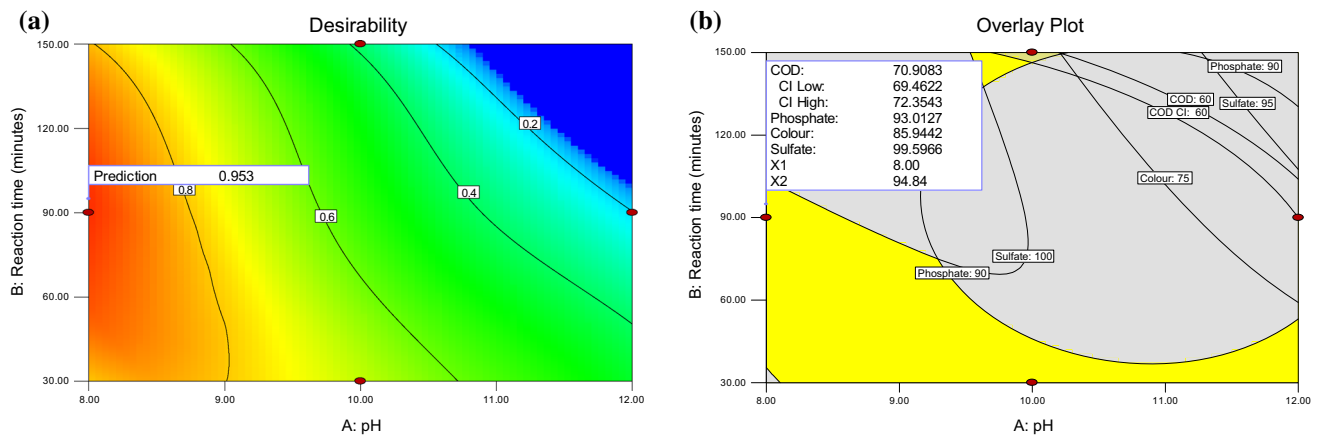

Fig. 5 Response surface plots for combined effect of **a** reaction time and pH at constant coagulant dose of 2.5 g/l, **b** coagulant dose and pH at constant reaction time of 90 min, and **c** coagulant dose and reaction time at constant reaction pH (10) on percent sulfate removal efficiency

(a)

(b)

Fig. 6 a Contour plot showing results of numerical optimization, b overlay plot showing graphical optimization within the chosen criteria

addition on EC resulting from the treatment. Using BBD, on the basis of RSM, it was established that amalgamation of pH, coagulant dosage and reaction time has considerable effect on removal of the selected parameters. Maximum removal of COD was observed 71.3 % at pH 8.0, coagulant dose of 3 g/l and reaction time of 90 min. Maximum phosphate removal of 94 % was achieved at pH 8 after 30 min at a coagulant dosage of 2.5 g/l and after 90 min at a coagulant dosage of 2 g/l. Color removal of 86.1 was observed at pH 8 with 2.5 g/l of $FeCl_3$ after 150 min of the reaction whereas 86 % of color was removed with 2 g/l of the coagulant after 90 min of the reaction. Almost complete removal (99.6 %) of sulfate was observed at pH 8 with 2.5 g/l of $FeCl_3$ after 150 min of the reaction. As was obvious from "Prob > F" values <0.0500 model terms have important effect on removal using $FeCl_3$ as a coagulant. $FeCl_3$ can be significantly employed as a coagulant for pre-treatment or post-treatment of landfill leachate having high concentration of recalcitrant compounds rendering biological processes inefficient.

However, as is obvious from the study and earlier reports as well, the extent of removal may vary depending on the composition of the solid waste in the dumpsite and landfill leachate constituent compounds so that a preliminary study needs to be done so as to achieve higher removal efficiencies.

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