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Optimization of Coagulation–Flocculation Process for Mature Landfill Leachate Treatment Using Response Surface Methodology (RSM).

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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 landfill leachate treatment. In this research, capability of poly-aluminum chloride (PACl) in the treatment of stabilized leachate from Qazvin Landfill Site, Iran was studied. The removal efficiencies for chemical oxygen demand (COD), turbidity, color and total suspended solid (TSS) obtained using PACl 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 including coagulant dosage and pH. Quadratic models were developed for the four responses (COD, turbidity, color and TSS). The results of this study indicated that the optimum conditions were PACl 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 39.95, 90, 87.9, and 87.3% for PACl, and 62, 78.8, 82.4, and 85.1% for alum were demonstrated. Results from this study showed that alum and PACl can be used as pretreatment of leachate for COD removal. Removal efficiency of PACl for turbidity, color and TSS is more than alum and alum usage is 5 times greater than PACl therefore it is concluded that PACl is better coagulant for enhancement of leachate characteristics than alum.

Keywords: Coagulation- Flocculation, Landfill leachate, Poly Aluminium Chloride (PACl), Response surface methodology(RSM), Analysis of variances(ANOVA)

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INTRODUCTION

In recent decade municipal and industrial solid waste production has been increased. It is generally caused by increasing population and urbanization coupled by change of consumption pattern and overuse of resources. Nowadays high production of solid waste is a global crisis (1,2).

One of the most common methods for solid waste disposal is sanitary landfill. Sanitary landfills have been used for about 95% of municipal solid waste in developing countries because it is an economical and environmentally accepted method for municipal solid waste disposal (3,4).

Naturally landfill site is a complex physical, chemical and biological system and landfill leachate is one of the most important products of this system from environmental point of view (5,6). Leachate generated from landfills can be defined as a high strength organic wastewater which contains the high concentration of recalcitrant organics and toxic mineral matter such as heavy metals. When untreated leachate discharged directly in to the environment, it may cause many environmental and health adverse effects (7). Management of all types of wastewater can play an important role in the protection of public health and the environment (8).

There are many important effective factors on the quality and quantity of leachate that include: seasonal changes, type of landfill method, method of compacting, characteristics of solid waste, structure of landfill and finally the age of landfill (9,10). The COD of young leachate (leachate from landfill of less than 1- 2 years age) is 30- 40 times greater than municipal wastewater with the high BOD_5/COC ratio (>0.6) and high concentrations of low molecular weight organics. Therefore biological treatment methods (anaerobic and aerobic) are commonly applied for treatment of young leachate (11). However, biological methods do not have enough efficiencies for treatment of mature leachates (leachate from landfills of more than 5–10 years of age), due to their low BOD_5/COD ratios (<0.3) and high fraction of high molecular weight, refractory organics (9. For this reason, there has been increased interest in physicochemical alternative treatment methods for pretreatment and full treatment of mature leachate (12, 13).

Coagulation and flocculation are simple physical-chemical methods for water and wastewater treatment. Coagulation is the destabilization of colloids by addition of chemicals that neutralize the negative charges and flocculation is the agglomeration of destabilized particles into a large size particles known as floc which can be effectively removed by sedimentation or flotation. This method has been successfully used for mature leachate treatment (14,15).

In recent years polymeric forms of aluminum such as poly aluminum chloride (PACl) have been suggested to be the most economical and available for water and wastewater treatment. Many researchers reported that PACl has many advantages to other common coagulants some of them such as: more efficiency of organic matter removal, less usage of alkalinity and the less sludge production (16,17).

Amokrane et al reported that common coagulant efficiency for COD removal from leachate and mature leachate are 10- 25 % and 50- 65% respectively (15).

There are no reports about polymeric coagulant effects on mature landfill leachate. Coagulant dosage and pH are two important effective parameters on coagulation efficiency. Generally, the trial and error procedure is used to optimize coagulation-flocculation. In this usual method reciprocal effects of variables can not be evaluated, therefore accuracy and reliability of optimization will be low (18).

In this research application of response surface methodology (RSM) and central composite design (CCD) to optimization of coagulation–flocculation for landfill leachate treatment using poly-aluminum chloride (PACl) and alum have been investigated. Central composite design is one of the common methods of RSM model that is useful and applicable for design of experiments. In this method every parameter defined in five levels and in comparison to other experiments design methods have more ability to predict responses.

In this study independent variables were pH and coagulant dosages in different levels and dependent variables were COD, Turbidity, Color, and TSS.

MATERIALS AND METHODS

Landfill leachate was collected from the Lia County Landfill in the city of Qazvin in northern Iran which has been a landfill for 30 years. Leachate was reserved in a stabilization pond for natural treatment. Sampling was done for 6 months and every two other weeks. The collected leachate was stored in a plastic bottle at 4 ◦C until use.

Table -1 Qualitative characteristics of leachate

Parameter	Range	Mean
Temperature(O^C)	23-30	25
pH	7.5-8.5	8
COD(mg/L)	6500-8000	7550
BOD_5(mg/L)	800-950	870
TSS	1200-2500	2100
NH_4(mg/L)	1500-1700	1620
Color(Pt-CO)	5100-7100	6100
Alkalinity (mg/L as $CaCO_3$)	5500-6500	6100
Turbitity(NTU)	3000-4500	3500
BOD_5/COD ratio	0.11-0.12	0.115

Table-1 shows the characteristics of collected leachate.

All coagulation-flocculation reactions were performed in jar test equipment with 6 compartments. Rapid and slow mixing, settling time, adjusted automatically to 1, 20 and 30 min respectively. Mixing was done with plastic paddles jointed to an epoxy coated shaft. The shaft was connected to a variable speed electromotor. Agitation rate of 90-30 rpm was used in all testes for rapid and slow mixing respectively. For the study on coagulation-flocculation of leachate many parameters such as coagulant dosage, COD, pH, color, turbidity and retention time were evaluated. All analytical methods were according to the standard methods for water and wastewater examination (19)

Research Design

Design Expert7 soft wear was used for statistical analysis of experiments. To optimize two main variables (pH and coagulant dosage), response surface methodology (RSM) and central composite design (CCD) were used. Preliminary tests were done before design research. A limited range of coagulant dosage and pH were obtained using pretests. Therefore, initial dosage of coagulant was 0.1gr/L and pH 2-12 was selected. Results from pretests indicated that the optimum dosage of coagulants for starting the experiments were 1-3 mg/L and 9-10 mg/L for PACl and alum respectively, also optimum pH of 6.5-8.5 for PACl and 6-8 for alum obtained from pretests.

Table-2 central composite design (CCD) for study on pH and coagulant dosage (PACl)

Run No	Experimental design				Results (removal (%)			
	A: PACl Dose(gr/L)	code	B: pH	Code	COD	Color	Turbidity	TSS
1	1	-1	6.5	-1	24	44	43.3	41.1
2	3	1	6.5	-1	25.2	46.5	39.1	45.5
3	1	-1	8.5	1	16	50	46.5	62.9
4	3	1	8.5	1	17.4	60.1	28.3	53
5	1.5	-0.5	7.5	0	31.3	78.4	77.8	75
6	2.5	0.5	7.5	0	30.5	81.6	85	79.4
7	2	0	7	-0.5	34.5	78.5	78	74
8	2	0	8	0.5	29.9	86.1	75.4	85
9	2	0	7.5	0	41	94	89.4	84
10	2	0	7.5	0	40.5	88	84.6	94.6
11	2	0	7.5	0	44.3	94.4	91.7	93.4
12	2	0	7.5	0	46	94.1	93	86.3
13	2	0	7.5	0	49.5	92	91	91.5

Table-2 shows the removal of COD, turbidity, color, TSS and the levels of independent variables. In this table coagulant dosage as (A) and pH as (B) have adjusted in 5 levels (-1, -0.5, 0, 0.5 and 1).Removal of COD, turbidity, color and TSS, has been studied as response.

Second order statistical model as equation 1 has been used for prediction of optimum condition.

$$Y=\beta_0+\sum_{i=1}^{k}\beta i.xi+\sum_{i=1}^{k}\beta ii.xi^2+\sum_{ii\leq j}^{k}\sum_{j}^{k}\beta ij.xi.xj+\cdots+e \quad (1)$$

As:

i= linear constant, j= second order constant, $\beta_=$ regression constant, k= number of studied factors and e= random error

For graphical analysis of data and obtaining the reciprocal effects of independent variables analysis of variances has been used. Quality of model fitness determined by R^2 coefficient and for control of signification of data F-test was used. With overlaying the three dimensional graph for two coagulants the optimum zone was determined.

In this research relationship between two variables (pH and coagulant dosage) and four important responses (removal efficiencies of COD, turbidity, color and TSS) in coagulation –flocculation process have been studied using surface response methodology.

RESULTS

Table-2 and 3 show the results of CCD about removal efficiencies of turbidity, color, TSS and COD in coagulation-flocculation process using PACl and alum.

Table-3 central composite design (CCD) for study on pH and coagulant dosage (alum)

Run No	Experimental design				Results (removal (%)			
	A: Alum Dose(gr/L)	code	B: pH	Code	COD	Color	Turbidity	TSS
1	9	-1	6	-1	44.2	74	44	45
2	10	1	6	-1	47.8	50	42	44
3	9	-1	8	1	32.4	51	47.3	63.4
4	10	1	8	1	36	55	45.8	52.4
5	9.25	-0.5	7	0	58.5	80	78.5	73.3
6	9.75	0.5	7	0	56.3	82	83.9	79.7
7	9.5	0	7	-0.5	34.5	78.5	78	74
8	9.5	0	6.5	0.5	62.5	80	77.8	77.4
9	9.5	0	7.5	0	54.4	85	75.5	85.2
10	9.5	0	7	0	73.3	84	88.4	87.4
11	9.5	0	7	0	71	83	83.4	92.1
12	9.5	0	7	0	81.6	87	91.2	83
13	9.5	0	7	0	85.1	83	89.6	91

Table-4 analysis of variances of response parameters.

Response	Final equation in terms of code factors	P	POL F	R^2	Adj. R^2	A.P	S.D.	C.V	PRESS
PACl									
COD	$40.06+0.49A-4.02B+0.05AB-12.26A^2-7.48B^2$	0.0251	0.0634	0.79	0.64	5.69	6.44	19.5	12.97
Turbidity	$89.09+31.13A+5.22B+1.92AB-24.72A^2-15.52B^2$	<0.0001	0.0964	0.97	0.95	16.4	4.2	5.5	607
Color	$87.98-4.18A-1.98B-3.5AB-15.11A^2-33.91B^2$	<0.0001	0.1107	0.97	0.955	17.7	6.88	4.88	2911.7
TSS	$87.08-0.73A+7.73B-3.57AB-23.09A^2-13.89B^2$	0.0003	0.248	0.946	0.907	12.7	5.55	4.74	1408.7
Alum									
COD	$71.53-1.36A-6.42B-2.5AB-17.65A^2-14.21B^2$	0.238	0.0614	0.794	0.647	5.75	10.27	17.05	3505
Turbidity	$85.21-4.22A-3.44B+7AB-16.85A^2-10.85B^2$	<0.0001	0.1677	0.961	0.934	14.5	3.6	4.76	2238.8
Color	$86.71-0.18A+1.32B+0.13AB-12.01A^2-30.22B^2$	<0.0001	0.205	0.978	0.962	16.95	3.81	5.29	1138.5
TSS	$86.88-1.96A+6.82B-2.5AB-27.65A^2-8.45B^2$	0.0002	0.217	0.95	0.915	12.8	5.15	6.92	1900

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

To be significant of model components is necessary to develop a proper model. CCD showed in table 2 and 3 have been used for mathematical equations for prediction of results (Y) as function of coagulant dosage (A), pH (B), constant value, two first order effects (A and B components), one reciprocal effect (AB) and two second order effects(B^2 and A^2)

Analysis of variances, have been used for determination of good fitness of data .The equations from the first analysis of variances, enhanced by elimination of insignificant components.

Table 4 shows data of modified second order model with independent variables and other statistical parameter. In this study all data were significant with 95% confidence level.

Distribution of data from experimental tests versus predicted value from model are shown in figure 1 and 2 Level response plots for removal of COD, turbidity, color and TSS using PACl and alum are given in figure 3 and 4 respectively

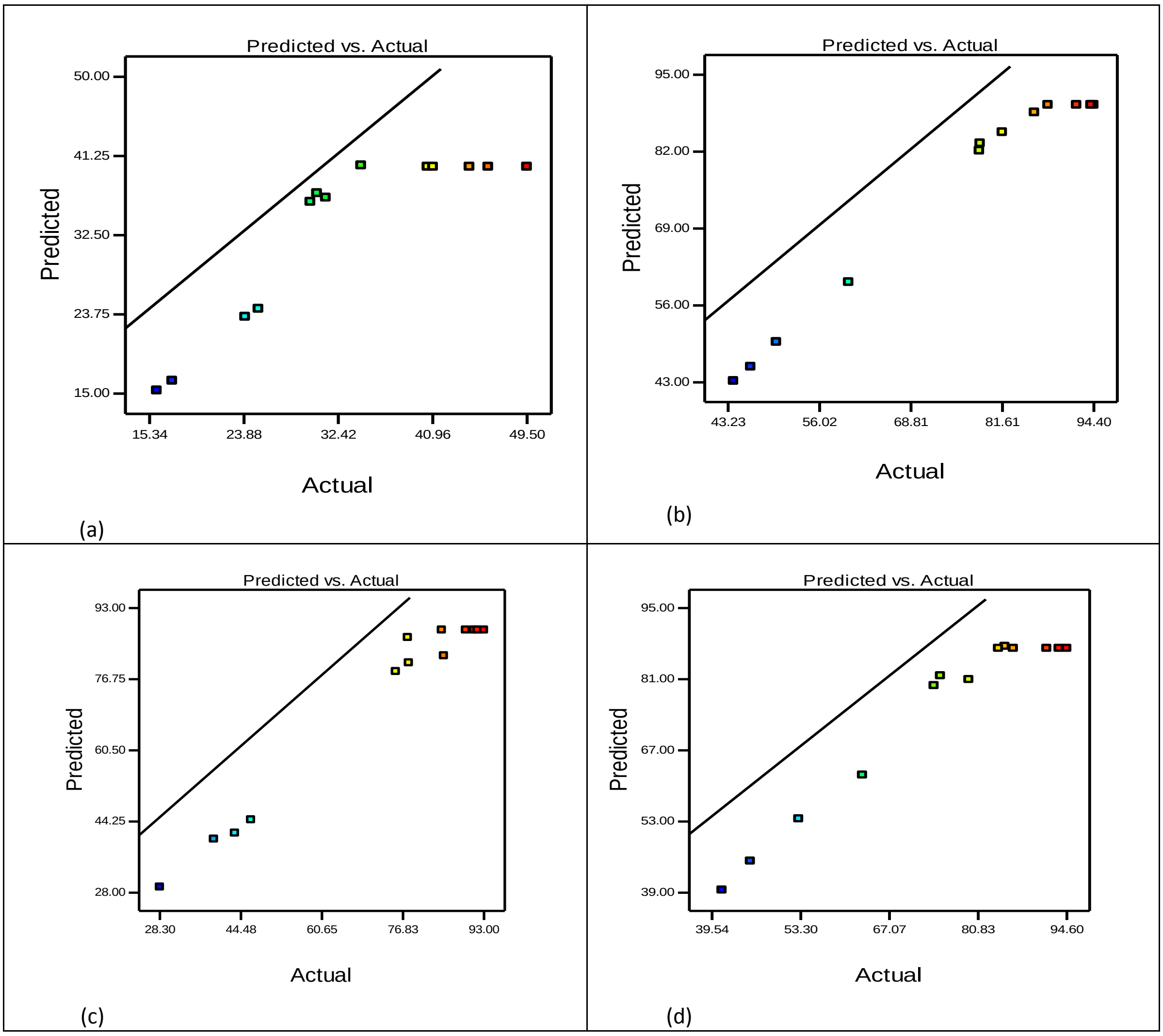


Figure-1 Distribution of data from actual tests using PACl versus predicted value from model (COD-a, turbidity-b, color-c and TSS-d)

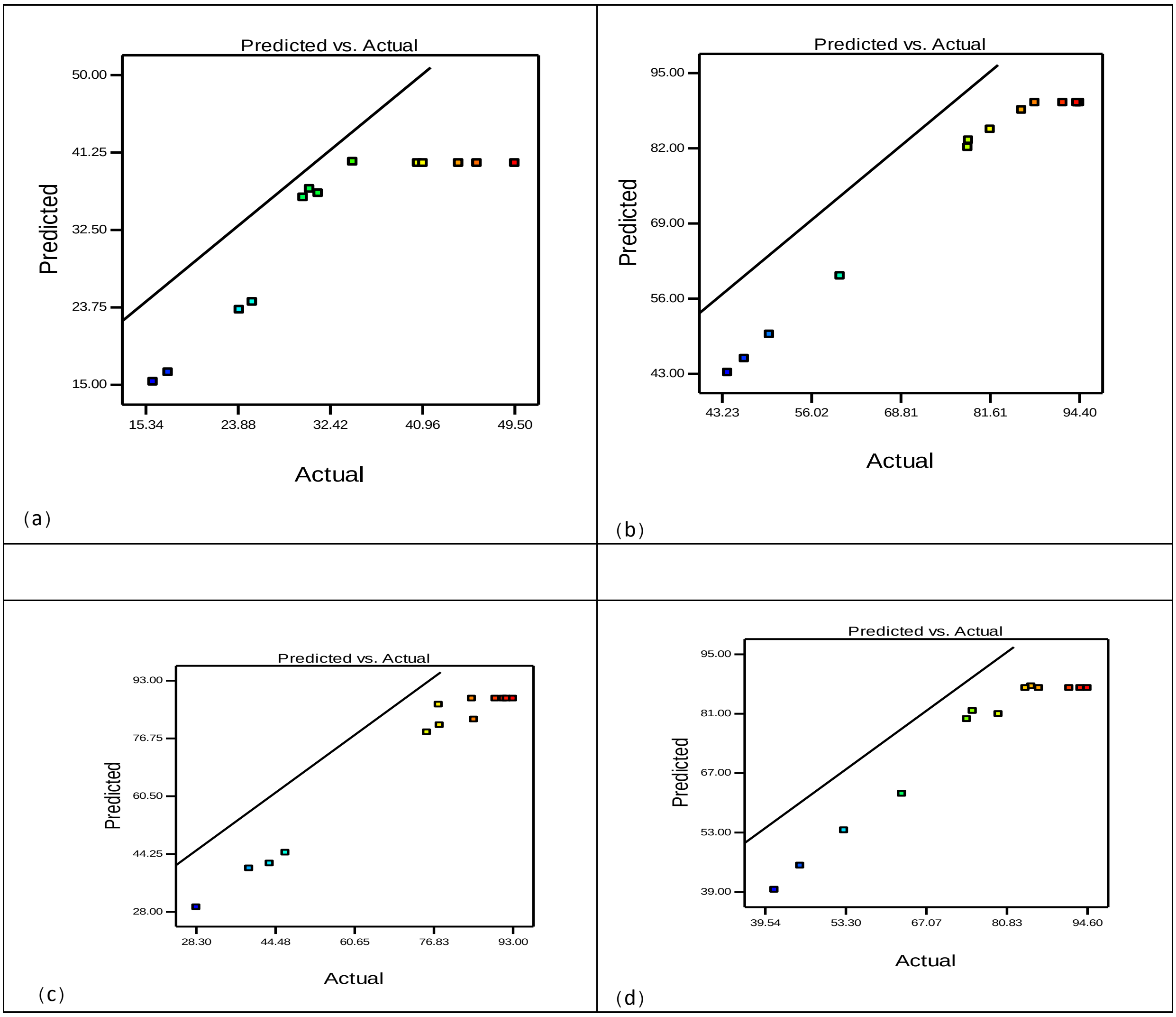


Figure-2 Distribution of data from actual tests using alum versus predicted value from model (COD-a, turbidity-b, color-c and TSS-d)

DISCUSSION

Figures 3 and 4 show the response level plots. Plots are almost concurrent and have circle balance. All response level plots have clear peak point, that indicate optimum condition, for maximum response to pH and coagulant dosage is very dependent to design circumstance.

Responses levels diagrams in figure 3 show the optimum point for PACl. It can be seen that coagulant dosage is equal to 2 gr/L and pH= 7. Optimum point for alum can be seen in figure 4 (pH=7 and alum dosage= 9. gr/L). To go farther away from these points, removal efficiency drop and its meaning is increasing or decreasing every variable will cause decreasing responses level.

Response levels of COD using alum indicated in figure 4-a. it can be seen that removal efficiency is 62% that is according to Amokran et al (15). In comparison to results of figure 3 it is observed that removal efficiency of COD using PACl is less than alum (39.95%). Response levels in figure 3 for PACl indicates removal efficiencies of 90%, 87.9% and 87.3% for turbidity, color and TSS respectively in optimum point. Removal efficiencies of turbidity, color and TSS using alum were 78.8%, 82.4% and 85.1% respectively. In other word, COD removal efficiency of alum is greater than PACl but removal efficiencies of turbidity, color and TSS of PACl are greater than alum. This result is according to the Tatsi et al reports (14)

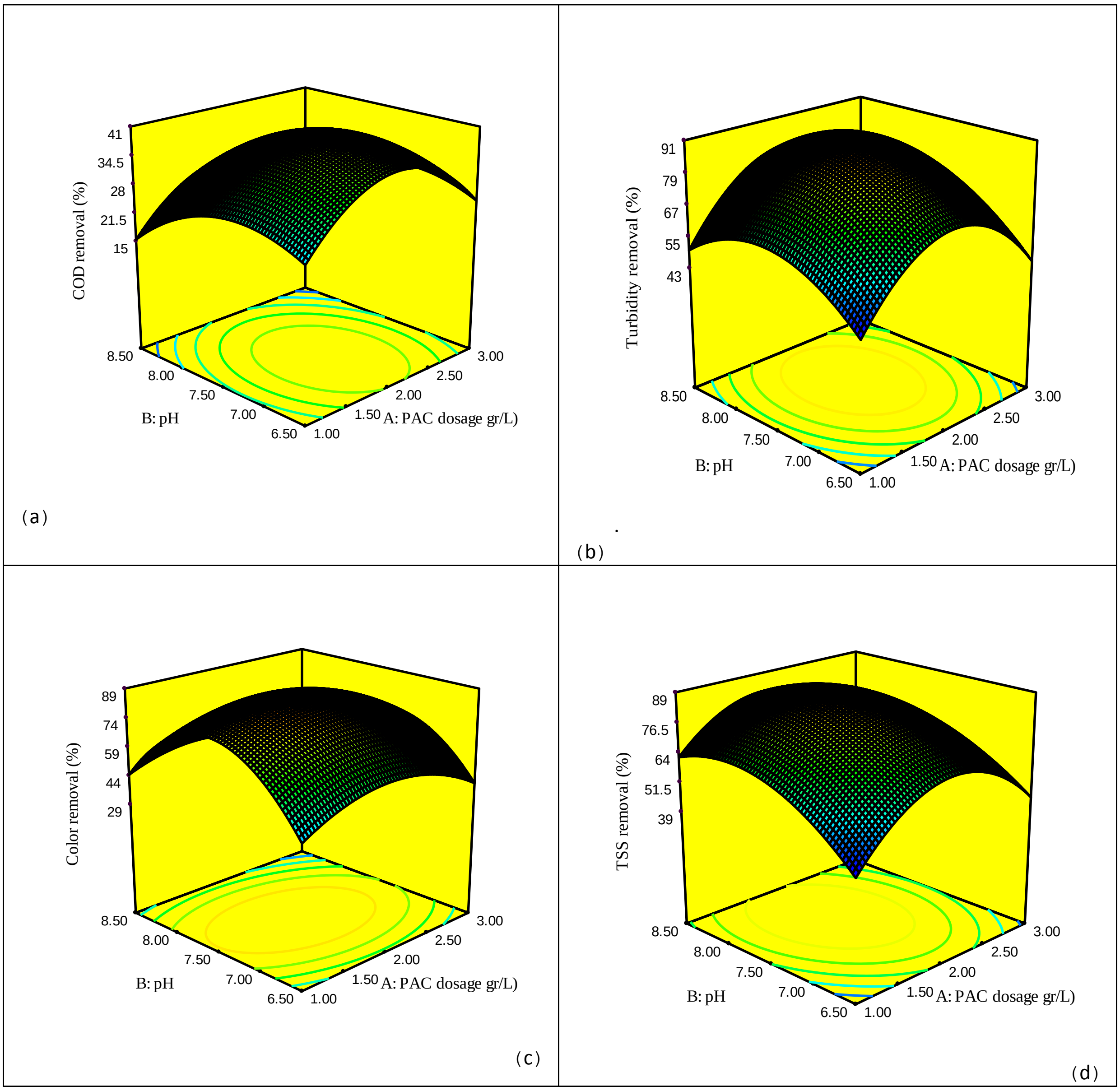


Figure-3 level response plot for removal of (COD-a, turbidity-b, color-c and TSS-d) using PACl

Optimization of process

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 (20).

Optimum condition for all parameters can be found with overlaying all response levels balance in a diagram. Graphical optimization shows the possible values of response level in operative region as zone of fitness with optimization criteria indicated as darker (20).

Table-5 minimum response values for determination of optimum condition of tests

Coagulant	Minimum removal%			
	COD	Turbidity	Color	TSS
PACl	40	85	89	89
Alum	65	82	82	86

Selective response for each parameter was showed in table-5. It indicates the minimum removable values. These zones are near to points that have maximum removal efficiencies therefore a small zone can be selected as optimum zone.

Darker zones of figure 5 show the optimum condition for PACl and alum respectively. Optimum condition for PACl was pH=7.5 and coagulant dosage= 2 gr/L and for alum was pH= 7 and coagulant dosage=0.5 gr/L. For confirming the obtained data from model with experimental data from these coagulants, two extra tests were conducted. Table-6 shows results of coagulation test in comparison to model prediction. From table-6 it can be observed that results of tests are very proximate to model prediction.

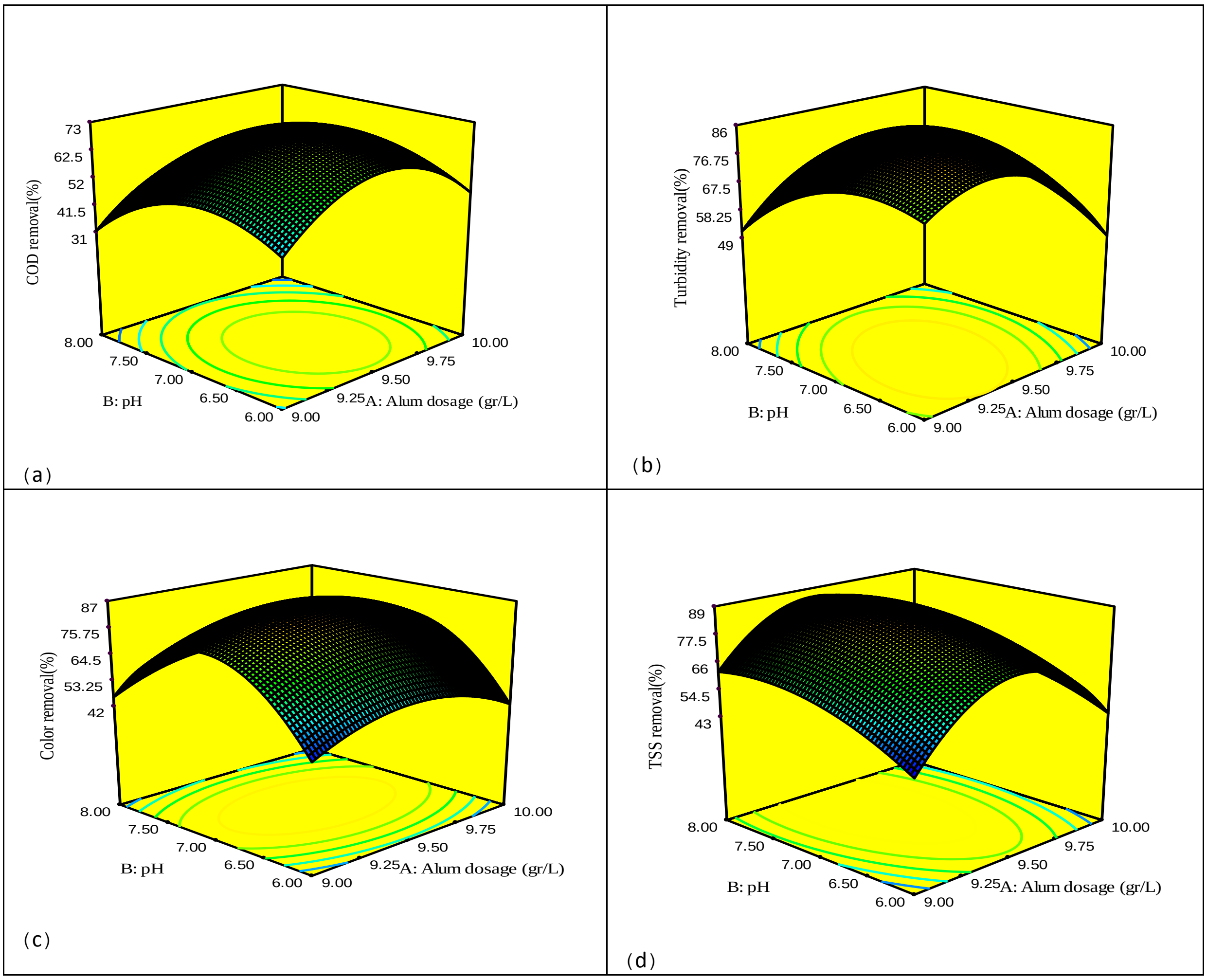
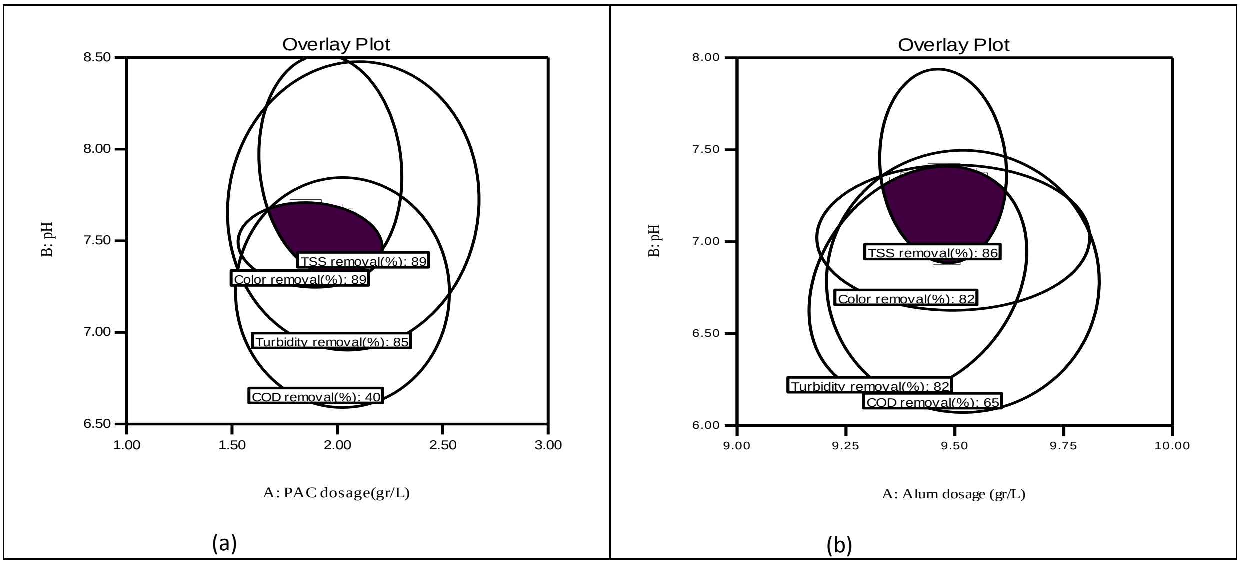


Figure-4 level response plot for removal of (COD-a, turbidity-b, color-c and TSS-d) using alum

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, LOF will be undesirably significant. lack of fitness test describes variables changes around the model. If the model does not have proper fitness, this test will be significant. P value greater than 0.05 of poor of fitness that given in table 4 confirms that test of lack of fitness is insignificant and it is indicated that there is correlation between independent variables and responses.
R^2 coefficient shows the ratio of total variation of unpredictable responses (SSR /SST). The greater R^2, near to 1 the more acceptability of model and agreement of number 1 to adjusted R^2 is necessary (Beg et al 2003). A grater R^2 shows adaptation to the second order model. Adequate precision (AP) compares predicted value in design point with average of prediction error. AP greater than 4 indicates differentiation of second order equation from other equations (22,23).

Table-6 Verification of experiments at optimum condition

Condition	Responses (Removal%)			
	COD	Turbidity	Color	TSS
PACl(2gr/L at pH7.5)				
Experimental Values	43	91	90	88.8
Model response	40	89.9	88	87.1
Error	3	1.1	2	1.7
Standard deviation	±1.5	±0.8	±0.65	±0.66
Alum(9.5gr/L at pH7)				
Experimental Values	69	89.8	87.8	89.5
Model response	65.4	87.7	85.9	85.5
Error	3.6	2.1	1.9	4
Standard deviation	±2.4	±2.3	±1.4	±2.8



(a) (b)

Figure-5 overlay plot for determination of optimum zone (a-PACl, b-alum)

Distinguish plots such as fig-1 and fig-2 help us to make decision about satisfaction of model. This figures show that there is adaptation between results of experiments and data from model. Adequate precision (AP) compares the range of the predicted values at the design points to the average prediction error. Ratio greater than 4 indicates adequate model discrimination. (24,25,26).

So that, AP greater than 4 in all results confirms that all model of CCD can be used in design range. Coefficient of variation (CV) defines the repetition of model. Only if CV is more than 0.1, the model will be repetitious. According to table 4 only model for COD removal by PACl and alum are not repetitious (19.5 and 17.5 respectively).

CONCLUSION

Coagulation- Flocculation process using poly aluminium chloride (PACl) compared with conventional coagulants such as alum. It was very effective on Turbidity, Color and TSS of aged landfill leachate, but on COD removal, the efficiency was less than Alum.

Results from this study showed that alum and PACl can be used as pretreatment of leachate for COD removal. Removal efficiency of PACl for turbidity, color and TSS is more than alum and alum usage is 5 times greater than PACl, therefore it is concluded that PACl is better coagulant for enhancement of leachate characteristics than alum.

Results from model indicated that predicted values by model are according to the experimental values.

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