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STATISTICAL OPTIMIZATION OF ETTRINGITE PRECIPITATION IN LANDFILL LEACHATE

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Abstract - In the present study, experiments were conducted to optimize sulfate removal efficiency with ettringite precipitation from landfill leachate using Response Surface Methodology (RSM) and Central Composite Design (CCD). The statistical analysis of the results showed that the operating parameters such as molar rates of Ca/SO_4 and Al/SO_4, and pH had a significant effect on sulfate removal efficiency. Aluminum hydroxide and calcium hydroxide were used for external sources of aluminum and calcium. The goodness of the model was checked by different criteria including the coefficient of determination (R^2 = 0.94), p value (<0.0001), adequate precision (14.78), and coefficient of variance (7.30). The RSM results indicated that the fitted model could be appropriate to predict sulfate removal efficiency. A 55.7% maximum sulfate removal efficiency was obtained at pH 11.95 for 2.29 Ca/SO_4 and 0.74 Al/SO_4 molar ratios. Sulfate inhibition effects on treatment methods such as the anaerobic process decreased with increasing COD/SO_4 ratio from 14:1 to 25:1 by ettringite precipitation.

Keywords: Ettringite Precipitation, Landfill, Leachate, Response Surface Methodology (RSM), Sulphate Removal

INTRODUCTION

Municipal solid waste management is one of the major environmental problems for the cities in the world. Landfills are commonly a cost-efficient way to dispose of municipal solid waste. One of the important environmental problems in landfills is production of leachate having high organic and inorganic contents such as sulfate (SO_4^{2-}) and sulfide (S^{2-}), ammonium (NH_4^+), phosphate (PO_4^{3-}), heavy metals, and chloride (Talalaj, 2015).

There are no common methods offered for treatment of leachate produced from landfills. However, one of the biological, physical (air stripping and adsorption), and chemical treatment methods (coagulation, flocculation and chemical oxidation) or their combination can be used (Agdag and Sponza, 2005; Aygun et al., 2012; Campagna et al., 2013; Derco et al., 2010; Ilhan et al., 2008; Trebouet et al., 2001; Yilmaz et al., 2010).

Leachate composition mainly depends on the age of the landfill, as well as the waste type and hydrogeological factors (de Morais and Zamora, 2005). Leachates classified as young, middle-aged, and mature need to be treated in a proper way (Sari et al., 2013).

Biological treatment methods such as aerobic, anaerobic, and anoxic processes are usually applied for young landfill leachate due to its high organic content, which are highly desirable for biodegradation. But, inhibitory compounds such as sulphate affect both anaerobic biodegradation of high organic content in leachate and treatment performance (Percheron et al., 1997). Excess amount of sulphate will promote

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enhanced growth of sulfate-reducing bacteria, which compete with methane bacteria, resulting in a decrease of methane production (Fang et al., 1997). Yilmaz et al. (2012) investigated the effects of COD/SO_4 ratio up to 20:1 on anaerobic process performance. Their study showed that the performance sharply increased when the COD/SO_4 ratio ranged from 4:1 to 10:1.

Ettringite precipitation based on formation of sulphate salts with low solubility can be used as a pretreatment method to overcome sulfate inhibition in anaerobic process. Calcium alumina-sulfate is commonly used to identify ettringite mineral. The following equation shows the basic chemical reaction to form ettringite Eq (1):

$$6Ca^{2+} + 3SO_4^{2-} + 2Al(OH)_{4^-} + 4OH^- + 26H_2O \rightarrow 3CaO.Al_2O_3.3CaSO_4.32H_2O_{(s)} \quad (1)$$

Ettringite precipitation can be applied for removal of sulfate from textile wastewater (Tunay et al., 2014), acidic mine drainage (Madzivire et al., 2010), tap water (Woroszynska et al., 1996) and as well as heavy metals removal from aqueous phases (Zhang and Reardon, 2003).

Response Surface Methodology (RSM) is widely accepted as a statistic-based method for designing experiments, evaluating the individual and interaction effects of independent variables, and optimizing the process parameters with a limited number of experimental runs (Sudamalla et al., 2012).

RSM provides predicted experimental data which might have an effect on the response using predetermined ranges of the independent variables. Thereafter, experimental data are used as input for the model optimization. Some major outcomes of RSM optimization are used to estimate the coefficients, predict the responses and examine an adequacy of the mathematical model.

The purpose of the current study is to investigate optimum conditions for high sulfate (SO_4^{2-}) removal from landfill leachate by using an ettringite precipitation process. As a result of a literature review, no scientific work has been published dealing with the application of RSM to ettringite precipitation in landfill leachate. The most widely used form of RSM, Central Composite Design (CCD), was applied by using Design Expert software to determine the interactions of important process variables such as Ca/SO_4 and Al/SO_4 molar rates, and pH on the sulfate (SO_4^{2-}) removal efficiency.

MATERIALS AND METHODS

Leachate sampling and analytical methods

Konya with a population of 2 million is located in the central part of Turkey. Leachate samples were collected from the active detention pond in a municipal landfill site of Konya. The leachate samples taken from the active detention pond, which is less than 5 years old (classified as young landfill leachate), were stored in plastic bottles and kept in 4 ºC until the required analysis. Characterization of leachate is given in Table 1.

Table 1. Characterization of raw leachate.

Parameter	Unit	Value
pH	-	7.77
COD	mg/L	27545
BOD	mg/L	17500
SO_4^{-2}	mg/L	1965
PO_4-P	mg/L	23.3
NH_4-N	mg/L	3890

Batch experiments were conducted in a jar test apparatus for the following minutes and rpms; 5 min at 120 rpm, 20 min at 45 rpm and finally 30 min for settling. pH was adjusted with either 6M HCl or NaOH.

All chemicals used in this research were analytical grade supplied by Merck. COD, BOD_5, Sulfate, Phosphate-phosphorus, Ammonium-nitrogen, and pH were analyzed based upon Standard Methods (APHA et al. 2012).

Experimental design and data analysis

The Design Expert Software (version 8.0.7.1) was used for the statistical design of experiments and data analysis. In this study, CCD and RSM were applied to optimize the three most important operating variables, which are pH and molar ratios of Ca/SO_4 and Al/SO_4.

In the present work, CCD with three replicates at the center point was used to find the relationship between the response function and variables (Table 2). A total of 17 experiments were conducted. Ca/SO_4 molar ratios (A), Al/SO_4 molar ratios (B), and pH (C) were set at five coded value levels: −1.68 (minimum), −1, 0 (central), +1, and +1.68 (maximum).

Ettringite precipitation was performed to optimize sulfate removal for predetermined Ca:SO_4:Al molar ratios that ranged from (0.32:1.00:0.11) to (3.68:1.00:1.21), and pH values from 9.32 to 12.68,

Table 2. Experimental range and levels of the independent variables used in RSM

Independent process variables code	Real values of coded levels				
	-1.68	-1	0	1	1.68
A: Ca/SO_4 molar ratios	0.32	1	2	3	3.68
B: Al/SO_4 molar ratios	0.11	0.33	0.66	0.99	1.21
C: pH	9.32	10	11	12	12.68

respectively. Aluminum hydroxide and calcium hydroxide were used to form ettringite minerals.

RSM postulates the functional relationship between the controllable input parameters and the obtained response surfaces. The lowest-order polynomial was chosen to adequately describe the sulfate removal. For evaluation of experimental data, the response variable was fitted by a second-order quadratic polynomial model as follows Eq (2):

$$y=\beta_0+\sum_{i=1}^{k}\beta_i X_i+\sum_{i=1}^{k}\beta_{ii}X_i^2+\sum_{i=1}^{k-1}\sum_{j=2}^{k}\beta_{ij}X_iX_j+\varepsilon \tag{2}$$

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 ε is the random error. The analysis focused on verifying the influence of individual parameters on the percentage of sulfate removal. The actual design parameters of experiments and their responses as sulfate removal efficiency for ettringite precipitation are given in Table 3.

The method of least squares was used to best fit a model equation by minimizing the residual error. The calculated coefficients for the model equation were tested for statistical significance. Stepwise elimination method and the p-values criterion were used to improve the reliability of the RSM model and also to automatically reduce the terms that are not significant.

Analysis of variance (ANOVA), known as a model independent probabilistic sensitivity analysis method, was used to obtain the interaction between the process variables and the response. Based on the ANOVA data, the fitted polynomial model was checked for coefficient of determination R^2, predicted R^2, adjusted R^2 and Fisher's F-test value and by the p-value (probability) of model terms with 95% confidence level. Three-dimensional plots and their respective contour plots were obtained for sulfate removal based on the three factors at five levels of Ca/SO_4 and Al/SO_4 molar ratios and pH.

Table 3. The actual design parameters of ettringite precipitation and sulfate removal efficiencies.

Exp No	Ca/SO_4 (x_1)	Al/SO_4 (x_2)	pH (x_3)	Sulfate removal (%)
1	3.00	0.99	10.00	45.0
2	2.00	0.66	12.68	55.6
3	3.00	0.33	10.00	30.3
4	2.00	0.66	11.00	52.2
5	2.00	0.66	11.00	52.2
6	2.00	1.21	11.00	39.4
7	2.00	0.66	9.32	32.0
8	1.00	0.33	12.00	44.0
9	1.00	0.99	10.00	34.9
10	2.00	0.11	11.00	20.6
11	3.00	0.33	12.00	37.7
12	3.00	0.99	12.00	50.2
13	1.00	0.99	12.00	45.5
14	0.32	0.66	11.00	35.9
15	2.00	0.66	11.00	52.2
16	3.68	0.66	11.00	45.0
17	1.00	0.33	10.00	35.4

RESULTS AND DISCUSSION

Statistical Analysis

Traditional optimization methods are not sufficient to express the combined effects of all operating parameters (Ozer et al., 2009). Therefore, RSM was used to optimize each parameter in order to determine the combined effects of all inputs. RSM and CCD experimental design were employed to determine the single and combined effects of Ca/SO_4 and Al/SO_4 molar ratios and pH on sulfate removal efficiency. The optimization process involved three steps; (1) performing the statistically designed experiments, (2) estimating coefficients of the proposed model and predicting the response of the process, and (3) checking the validity of the model (Rao and Satyanarayana, 2003).

Experimental data was analyzed by using the RSM procedure. Significant model terms are sought to obtain a good fit of the model. For evaluation of experimental data, the response variable was fitted by a second-order quadratic polynomial model. The final mathematical model equation was obtained by using Design Expert software as follows in terms of actual factors Eq (3):

$$\%(Sulfate\ Removal) = -336.71 + 9.94(Ca/SO_4) + 57.24(pH) + 8.79(Ca/SO_4)(Al/SO_4) - 3.54(Ca/SO_4)^2 - 66.42(Al/SO_4) - 2.35(pH)^2 \quad (3)$$

Table 4 shows that the model to predict sulfate removal was significant at the 5% confidence level since the *p* value was less than 0.05. Fisher's F-test is used to compute both *p* and the lack of fit (LOF) values that describe the variation of the data around the fitted model. If the model does not fit the data well, this LOF is significant when the LOF value is smaller than 0.05. Both insignificant LOF and significant *p* values indicate good correlation between the process variables and the response. A high R^2 coefficient is desirable and it ensures a good fit of the second-order quadratic model to the experimental data (Ghafari et al., 2009). The adjusted R^2 value is particularly useful when comparing models with different numbers of model terms. This comparison is, however, done in the background when model reduction is taking place. The differences between the predicted R^2 and the adjusted R^2 was 0.16. The model fitted the data and can reliably be used to interpolate because the difference was less than 0.2 (Nair et al., 2014).

A low value (7.30%) of the coefficient of variance (CV), which is similar to previously published data, indicates a high degree of precision of the experimental values (Yusuf et al., 2013). Adequate Precision (AP), calculated as 14.78 for the signal-to-noise ratio for the fitted model, was higher than 4, indicating an adequate model discrimination (Rahbar and Haji, 2013).

The Predicted Residual Sums of Squares (PRESS) statistic gives a good indication of the predictive power of the fitted model and minimizing of PRESS is desirable. In our study, the PRESS value of the obtained second-order quadratic model is smaller than those of the linear, two-factor interactions (2FI), and cubic equations.

Actual values were obtained from experimental runs, and the predicted values were evaluated from the model and generated by using the approximating functions. The actual and the predicted sulfate removal efficiency is shown in Figure 1. The plot indicates an adequate agreement between actual and predicted data. As a result, the predicted model is reliable and can be used to navigate the design space defined by the CCD.

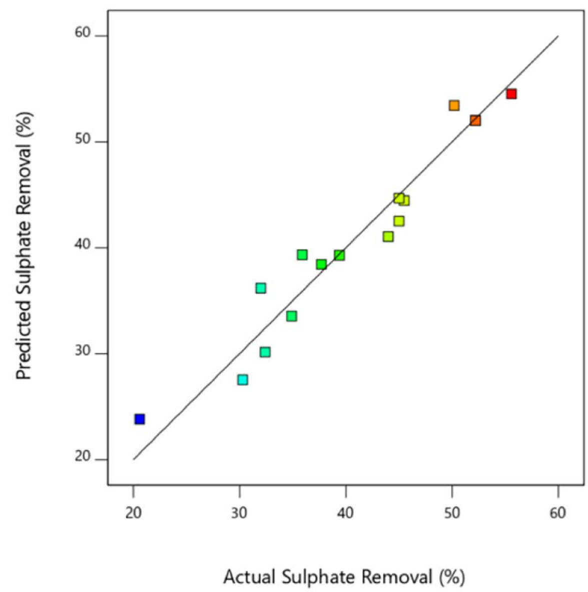

Figure 1. The actual versus the predicted sulfate removal efficiency.

Figures 2, 3 and 4 show the response surface contour plots of the second-order quadratic model with one variable kept at the central level and the other two variables within the experimental ranges. Different surfaces can be obtained by adjusting the constant variable.

Figure 2 shows the response surface obtained at constant pH of 11.00. It is clearly seen in Figure 2 that the effects of Ca/SO_4 and Al/SO_4 molar ratios were significant on sulfate removal efficiency. Maximum sulfate removal efficiency was observed at the central point of the plot. However, sulfate removal efficiency by ettringite precipitation sharply decreased at either the highest or lowest molar ratios of Ca/SO_4 and Al/SO_4 values.

When pH value and Ca/SO_4 molar ratio are compared to each other for sulfate removal efficiency

Table 4. ANOVA results for response parameters.

Response	*p*	LOF	R^2	AdjR^2	PrdR^2	AP	S.D.	CV	PRESS
Sulfate Removal	<0.001	0.345	0.94	0.90	0.74	14.78	3.03	7.30	389.6

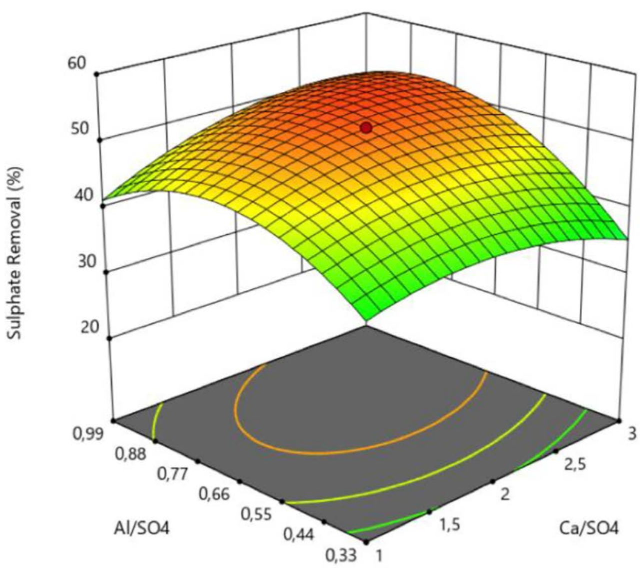

Figure 2. The effect of Ca/SO_4 and Al/SO_4 molar ratios on sulfate removal (pH: 11.00).

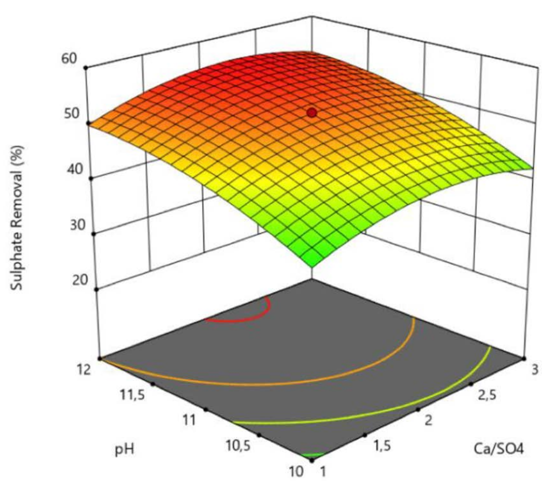

Figure 3. The effect of Ca/SO_4 molar ratio and pH on sulfate removal (Al/SO_4:0.66).

at constant molar ratio of 0.66 Al/SO_4, the effects of pH changes on sulfate removal efficiency are greater than that of the Ca/SO_4 ratio. For pH 10.00 and Ca/SO_4 molar ratio of 1.00, sulfate removal efficiency reached 35%, which is the minimum value given in Figure 3.

In Figure 4, sulfate removal efficiency ranged from 30% to 55% for different pH and Al/SO_4 molar ratios. Minimum removal efficiency was observed at pH 10.00 and 0.33 Al/SO_4 molar ratio. Higher pH values and Al/SO_4 ratios increased the sulfate removal efficiency. Al/SO_4 molar ratio was a more influential parameter compared with pH.

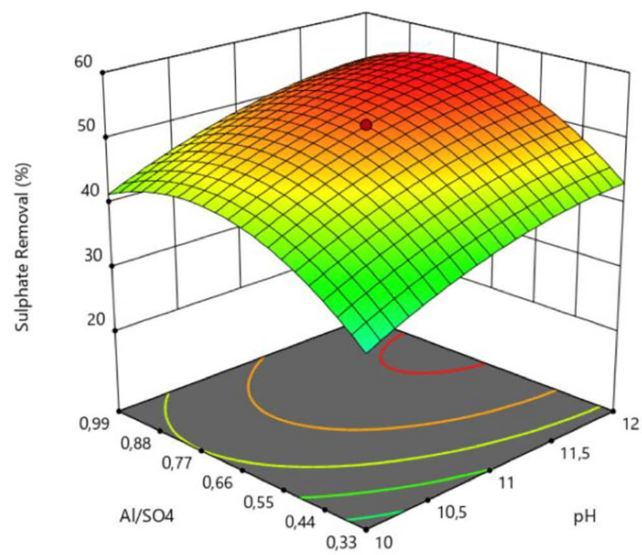

Figure 4. The effect of Al/SO_4 molar ratio and pH on sulfate removal (Ca/SO_4:2.00).

Optimization of the process parameters and verification

Numerical optimization tools of RSM can be used to find the best solution for maximum removal efficiency by using independent variables such as pH, molar ratio of Ca/SO_4 and Al/SO_4 selected to be within the study range. Selection constraints for each parameter are given in Table 5.

Based on optimization results, maximum sulfate removal efficiency was estimated as 55.7% at pH 11.95, 2.29 Ca/SO_4 and 0.74 Al/SO_4 molar ratios. The desirability function value was found to be 1.00, showing that our model could be successfully applied to experimental data.

A pH of 12 previously published for sulfate removal using an ettringite precipitation process in textile wastewater is similar to the optimum pH value estimated in this study. The ratios of each reagent were found a little bit higher than the stoichiometric ratio (Kabdasli et al., 2016).

Verification experiment was performed with the predicted conditions for maximum sulfate removal efficiency. The experimental value (55.8%) was very close to the predicted value (55.7%), confirming the validity of the fitted models. These results confirm that the model can be used for sulfate removal efficiency.

Evaluation of COD/SO_4 ratio

Methane production in anaerobic processes can be dramatically affected by the ratio of COD/SO_4. During the ettringite precipitation process, sulfate

Table 5. Selection constraints for each parameter in the optimization.

Parameter	Goal	Lower Limit	Upper limit	Importance
Ca/SO_4 molar ratio	In range	1	3	3
Al/SO_4 molar ratio	In range	0.33	0.99	3
pH	In range	10	12	3
Response (% sulfate removal)	Maximize	20.6	55.6	3

concentration decreased from 1965 mg/L to 870 mg/L, but COD removal efficiency was only around 20%. Raw leachate had a COD/SO_4 ratio of 14:1 which was slightly above 10:1, the termination level of methane production (Parkin et al., 1990; Percheron et al., 1997; Vavilin et al., 1994). A high ratio of COD/SO_4 such as 20:1 was found to minimize the inhibition effect on anaerobic methane production (Yilmaz et al., 2012).

Ettringite precipitation increased the ratio of COD/SO_4 from 14:1 to 25:1, which was above the required ratio. This result supports that ettringite precipitation may be used as pretreatment of landfill leachate to improve methane production and to decrease corrosion in cogeneration units.

CONCLUSIONS

The present study corroborates the benefit of RSM over traditional methods to optimize process conditions for sulfate removal efficiency from landfill leachate. A 55.7% maximum sulfate removal efficiency was obtained at pH 11.95 for 2.29 Ca/SO_4 and 0.74 Al/SO_4 molar ratios. The CCD and RSM were used to develop a reasonable mathematical model for prediction of the optimum process conditions for ettringite precipitation. Increasing the COD/SO_4 ratio from 14:1 to 25:1 resulted in less sulfate inhibition on anaerobic methane production. The cost-effective approaches for sulfate removal can be derived from optimized Ca/SO_4 and Al/SO_4 molar ratios in RSM. The ratios of each reagent were found to be a little bit higher than the stoichiometric ratio.

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