LEAD RELEASE FROM LEAD-ACID BATTERIES SLAG USING WASTE MATERIALS: FULL FACTORIAL DESIGN ANALYSIS

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ABSTRACT

The present research includes the safe disposal of lead-acid batteries slag using waste materials such as red mud and fly ash. The aim of this study is to investigate the adsorption of lead removal from lead acid-batteries slag on red mud and fly ash using 2^4 full factorial design. The combined effects of adsorbent amount, temperature, adsorbent type and leachate solution on the lead removal adsorption were studied. Factorial design of experiments is employed to study the effect of four factors adsorbent amount (10% and 30%), temperature (20 and 60 ^oC), adsorbent type (red mud and fly ash) and leachate solution (TCLP DIN), at two levels low and high. The results were statistically analyzed by using the student's t-test, analysis of variance (ANOVA) and an F-test to define important experimental factors and their levels. A regression model that considers the significant main and interaction effects was suggested. The results showed that leachate solution is the most significant factor that affects the lead removal.

Keywords: Lead-acid batteries slag, immobilisation, red mud, fly ash

1. Introduction

Lead is a material very easy to recycle and, provide that adequate procedures are implemented, the final product is indistinguishable from the primary lead produced from ores. Currently, the main application for lead is the manufacturing of car batteries. These batteries consist of 60% lead, 12% plastic and 28% electrolyte. Electrolyte is made up 55% - 60% water and 40% - 45% sulfiricacid. Lead-acid batteries represent about 60% of batteries sold in the entire world. Lead-acid batteries are among the most frequently recycled products in the US, with a reported collection and recovery rate of 99%. In Turkey, lead is produced from secondary process, mainly from the recycling of lead-acid batteries. The slag generated in the rotary furnaces is classified hazardous waste. For each ton of metallic lead produced, 100-400 kg of slag is generated (Kreusch *et al*., 2007; Gomes *et al*., 2011, Kurt 2012). The poor quality of the char coal used in the process strongly in fluence the quantity of lead produced if it is not used proportionally to the other raw materials, thus generating larger quantities of slag (Chang *et al*., 2001).

In this regard, landfill disposal of lead-acid batteries slag is not feasible since a few hundred tons are produced per year; leaching of heavy metals into ground water is of concern. The disposal of slag is becoming more expensive each year due to large land areas needed for its disposal. The best way to solve the disposal problem of waste materials is to decrease the quantity for disposal with utilization of waste materials in the industry.

Fly ash, a waste material originating in large quantities from modern power stations, is composed of metallic oxides, silicates and other particulate matter. The worldwide production of coal ash for instance is estimated to exceed 550.10^6 ton per year. The disposal of fly ash is becoming more expensive each year due to large land needed for its disposal (Reijnders, 2005; Lin *et al*., 2008). The best way to solve the disposal problem fly ash is to decrease the quantity for disposal with utilization of fly ash in the industry. Fly ash has been increasingly utilized in construction application, such as fills, concrete, pavements, wastewater treatment, landfill barrier material, grouts and others. The utilization of fly ash as adsorbent for heavy metals removal from industrial wastewater could be rewarding to both environment and economy (Shen *et al*., 2007; Lin *et al*., 2008; Min *et al*., 2008). Red mud is a bauxite processing residue discarded in alumina production.

Approximately 1-2 tons of red mud residues are produced for a ton of alumina. Red mud, due to its high aluminum, iron and calcium content has been suggested as a cheap adsorbent for the removal of heavy metals, dyes, phosphate, nitrate, fluoride and arsenic (Santona *et al*., 2006; Çoruh, 2008; Zhao et.al, 2009; Wang et al.,2005).

The aim of this study focus on the safe disposal and leaching behavior of the lead smelting slag using red mud and fly ash.

2. Materials and methods

2.1. Materials

2.1.1. Lead smelting slag

The chemical composition of lead smelting slag is given in Table 1.The chemical composition of the lead smelting slag shows iron oxides (40.77 %) and silica (15.41 %), together with some other oxides as Al_2O_3, Na_2O and CaO.

Table 1: Chemical composition (wt. %) of lead smelting slag, sepiolite and clay

	Lead smelting slag	Red mud	Fly ash
SiO_2	15.41	15.64	55.17
Fe_2O_3	40.77	36.24	6.80
Al_2O_3	3.01	20.10	24.56
TiO_2	0.24	4.76	1.12
CaO	2.08	2.68	2.65
SO_3	0.61	0.06	0.89
CO_2	-	2.93	-
K_2O	0.46	23.55	0.84
MgO	0.42	-	2.75
Na_2O	5.35	9.99	0.28
MnO	0.46	-	0.42
P_2O_5	-	0.023	-
Others	6.32	8.39	4.52

2.1.2. Natural Materials

The red mud used in this study was obtained from SeydişehirAluminium Plant, Konya, Turkey. The specific surface area (BET) of red mud is around 14.2 m^2/gThe chemical composition of red mud is presented in Table 1 and it shows that red mud is primarily a mixture of Fe, Al, Si, and Ti oxides. In this study, scanning electron microscopy (SEM, Zeiss Supra 50VP) was used for micro-structural investigations.

The fly ash sample used for this study was obtained from Soma thermal power plant in Turkey. The specific surface area of the fly ash is 0.207 m^2/g. The chemical composition of the fly ash is presented in Table 1. The total amount of SiO_2, Al_2O_3, Fe_2O_3 and CaO content is about 90%.

2.2. Experimental procedure

TCLP test, widely used by state and national agencies, was designed to simulate leaching of heavy metals and organics from industrial wastes to be codisposed in municipal solid landfills. The TCLP test was performed as specified in the EPA method. For this purpose, 5 g of wastewater sludge was placed separately in a plastic bottle together with 100 ml of leach solution, sodium acetate/acetic acid buffer solution. The mixture was then agitated at 30 rpm and 23 °C for 18 h. The lead metal concentration in the leachate was determined using AAS (Atomic Absorption Spectrophotometry, UNICAM 929 Model). Each leachate was analysed in triplicate and the average values were reported to ensure the reproducibility of data.

Batch leaching studies were used to evaluate the leaching of pollutants in lead-acid batteries slag samples. Effects of the adsorbent amount, temperature, adsorbent type and leachate solution on the lead removal adsorption were investigated. These experiments were carried out in the batch reactors containing adsorbent amount (10% and 30%), temperature (20 and 60 ^{o}C), adsorbent type (red mud and fly ash) and leachate solution (TCLP and DIN).The Table 2 provides a summary of selected experimental factors and their values. The samples were mixed at predetermined periods at a temperature of 20^{o}C in a shaker at 175 rpm until equilibrium was reached. After equilibrium, the mixtures were then filtered with 0.45 μm filter and acidified with HNO_3 to decrease the pH to below 2 before measurement. The batch adsorption experiments were conducted in duplicate; results differed by ≤5%. The lead metal concentration in the filtrate was determined using AAS (Atomic Absorption Spectrophotometry, UNICAM 929 Model).

3. Result and discussion

Experiments are essential to the development and improvement of engineering and scientific methods. If we call p the number of variables to be tested, in order to measure the effect of all the variables combinations when each variable is tested at high and low level, 2^p experiments will be needed. Factorial experiments investigate the effects of two or more factors or input parameters on the output response of a process. A 2^p factorial experiment, where *p* is the number of factors, is a special type of factorial design and allows the experimenter to simultaneously study several factors with two levels (Zhao et al., 2009)

In this study, three continuous (i.e., adsorbent dosage, temperature and leachate solution) and one categorical (i,e., adsorbent type) experimental factors were examined at two levels, high (+) and low (-), resulting in a 2^4 full factorial design.The experimental ranges and the levels of the independent variables are given in Table2. The resulting outcome measures the percentage of silver removed, or removal efficiency. Two measurements were made for each combination of factors.

Data from 16 factorial experiments (2^4=2.2.2.2=16) with two replications are presented. The results of the experimental data were studied and interpreted by Minitab 16 statistical software.

Table 2: The Levels of experimental factors

Factor	Low Level (-1)	High Level (+1)
Adsorbent amount (%)**(A)**	10	30
Temperature (^{o}C) **(B)**	20	60
Adsorbent type **(C)**	Red mud	Fly ash
Leachate solution**(D)**	TCLP	DIN

The effect of a factor is the change in response that is produced by a change in the level of the factor. When the effect of a factor depends on the level of another factor, the two factors are said to interact. Signs for the interactions are found by multiplying the signs which correspond to the factors in the interaction. For a 2^p factorial experiment, the estimate for any effect or interaction can be found by using the following formula (Zhao et al., 2009; Montgomery et.al., 2001) :

$$\text{Effect Estimate} = \frac{Contrast}{2^{p-1}} \quad (1)$$

The estimated effects of the experimental factors are listed in the second column of Table 3. The coefficient in the third column is equal to one-half the corresponding effect. Every coefficient has the same standard deviation, which is shown in the next column. For each effect and interaction, the null hypothesis, which states that the effects are equal to zero, is tested by using the student's *t* statistic. The column labeled "*T*" presents the value of the *t* statistic and the column labeled "*P*" presents the P-values. The *t*-tests reveal that the main effects of *A*, *B*, *C*, and *D* and the interactions *AB*, *CD*, *ABC* and *ABCD* are significant at the 5% level.

In Table 4, the column labeled "F" presents the *F* statistic for testing the null hypothesis that states that the main effects and the (2-way, 3-way and 4-way interactions are equal to zero, respectively. The column labeled "*P*" presents the *P*-value for the *F* test. The small *P*-values (<0.05) mean that not all the main effects and interactions are zero at the 5% significance level. In other words, there is reasonably strong evidence that at least some of the main effects and interactions are not equal to zero.

These results indicated good agreements between the experimental and predicted values of lead release. It was found that the predicted values matched the experimetal values reasonably well with ^{R2}= 0.9675. Adjusted R^2 (Adj) is also a measure of goodness of a fit, but it is more suitable for comparing models with different numbers of independent variables. In tihs study, Adj-R^2value (0.9371) was very close to the corresponding R^2 value.

Table 3: Estimated Effects and Coefficients for Lead Release

Term	Effect	Coef	SE Coef	T	P
Constant		142.43	7.883	18.07	0.000
Adsorbent Dosage	76.59	38.30	7.883	4.86	0.000
Temperature	4.17	2.09	7.883	0.26	0.795
Adsorbent Type	32.46	16.23	7.883	2.06	0.056
Leachant Solution	-55.71	-27.86	7.883	-3.53	0.003
Adsorbent Dosage*Temperature	17.88	8.94	7.883	1.13	0.273
Adsorbent Dosage*Adsorbent Type	227.18	113.59	7.883	14.41	0.000
Adsorbent Dosage*Leachant Solution	130.72	65.36	7.883	8.29	0.000
Temperature*Adsorbent Type	58.57	29.28	7.883	3.71	0.002
Temperature*Leachant Solution	32.39	16.19	7.883	2.05	0.057
Adsorbent Type*Leachant Solution	178.02	89.01	7.883	11.29	0.000
Adsorbent Dosage*Temperature* Adsorbent Type	42.97	21.48	7.883	2.73	0.015
Adsorbent Dosage*Temperature* Leachant Solution	8.94	4.47	7.883	0.57	0.579
Adsorbent Dosage*Adsorbent Type* Leachant Solution	-10.34	-5.17	7.883	-0.66	0.521
Temperature*Adsorbent Type* Leachant Solution	-33.08	-16.54	7.883	-2.10	0.052
Adsorbent Dosage*Temperature* Adsorbent Type*Leachant Solution	-11.24	-5.62	7.883	-0.71	0.486

S = 44.5946 PRESS = 127275
R-Sq = 96.75% R-Sq(pred) = 87.01% R-Sq(adj) = 93.71%

Table 4: Analysis of variance for removal efficiency

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	4	80331	80331	20083	10.10	0.000
2-Way Interactions	6	841547	841547	140258	70.53	0.000
3-Way Interactions	4	25019	25019	6255	3.15	0.044
4-Way Interactions	1	1010	1010	1010	0.51	0.486
Residual Error	16	31819	31819	1989		
Pure Error	16	31819	31819	1989		
Total	31	979727				

The adequacy of the models was also evaluated by the residuals. Residuals are thought as elements of variation unexplained by the fitted model and then it is expected that they occur according to a normal distribution.The observed residuals are plotted againts the expected values, given by a normal distribution in figure 1. Trends seen in figure1., reveal reasonably well behaved residuals.

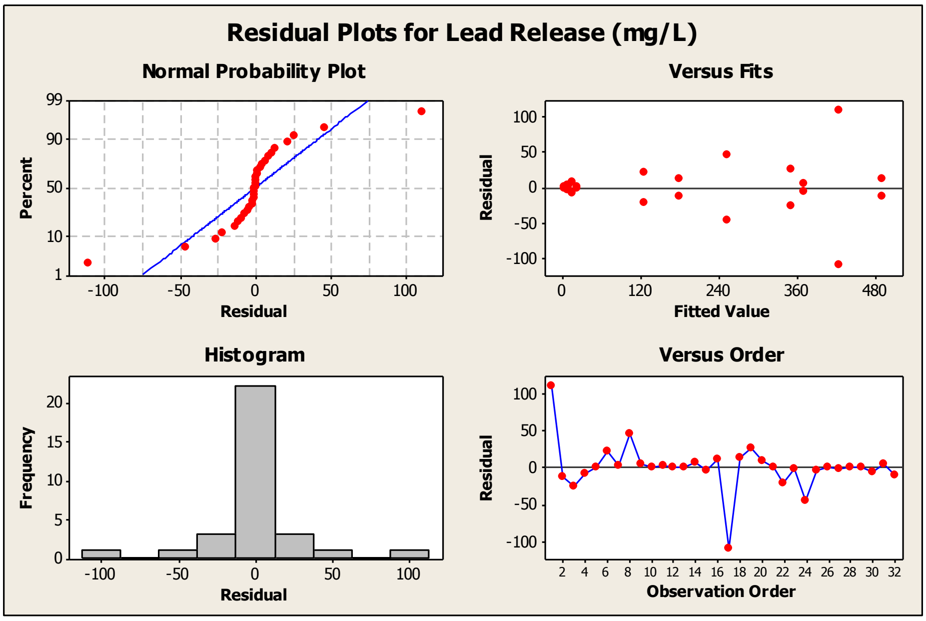

Figure 1: Residual plots for lead release from lead-acid batteries slag using red mud and fly ash

A normal probability plot of the standardized effects, the aim of which is to determine the statistical significance of both main and interaction effect, is given in figure 2. The insignificant effects will fall along a line; on the other hand, the significant effects will stray farther from the line. According to figure 2, the main effects *A*, and *D* and the interactions *AC*, *CD*, *AD,BC and ABC* are statistically significant. Since D lie on the left- hand side of the line, their contributions haves a negative effect on the model. The reverse is true for the rest of the significant effects, which lie on the right- hand side. The adsorbent dosage and adsorbent type factors (*AC*) appear to have a largest effect because it lies furthest from the line.

In any designed experiment, it is important to examine a model for predicting responses (Ismail et.al., 2008). Equation 2 presents the regression model to obtain predictions from a 2^4 factorial design (Ponnusami et.al.,2007)

$$\begin{aligned} Y = {} & \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_4 X_4 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{14} X_1 X_4 + \\ & \beta_{23} X_2 X_3 + \beta_{24} X_2 X_4 + \beta_{34} X_3 X_4 + \beta_{123} X_1 X_2 X_3 + \beta_{124} X_1 X_2 X_4 + \beta_{123} X_1 X_2 X_3 + \\ & \beta_{124} X_1 X_2 X_4 + \beta_{134} X_1 X_3 X_4 + \beta_{234} X_2 X_3 X_4 + \beta_{1234} X_1 X_2 X_3 X_4 \end{aligned} \tag{2}$$

whereβ_0 is the constant term which represents the overall level of process, β is the coefficient of the respective effect and X is the experimental factor.

Third column of Table 4 gives the coefficient estimates of the regression model. Some terms which seem insignificant according to the student's t-test were neglected. The reduced model which includes the effects determined as "significant" in Table 4, figures 2 and 3, is as follows:

$$\begin{aligned} Y = {} & \beta_0 + \beta_1 X_1 + \beta_3 X_3 + \beta_4 X_4 + \beta_{13} X_1 X_3 + \beta_{14} X_1 X_4 + \beta_{23} X_2 X_3 + \beta_{24} X_2 X_4 + \\ & \beta_{34} X_3 X_4 + \beta_{123} X_1 X_2 X_3 + \beta_{234} X_2 X_3 X_4 \end{aligned} \tag{3}$$

with the coefficients calculated in Table 4. Y=f(X) equation for the release of lead is given in Equation (4):

$$\begin{aligned} Y = {} & 142.43 + 38.30 X_1 + 16.23 X_3 - 27.86 X_4 + 113.59 X_1 X_3 + 65.36 X_1 X_4 + \\ & 29.28 X_2 X_3 + 16.19 X_2 X_4 + 89.01 X_3 X_4 + 21.48 X_1 X_2 X_3 - 33.08 X_2 X_3 X_4 \end{aligned} \tag{4}$$

The positive coefficient means that the lead release increases as the factor is changed from low to high levels. On the other hand, if the coefficient is negative, a reduction in the lead release occurs as the factor is changed from the low to high level. The magnitude and sign of X_1X_3 indicates that the contribution of this factor to efficiency is 113.59% for the high (+1) level. The effect of other factors on the regression model is relatively small in comparison to X_1X_3. For example, the contribution of adsorbent dosage variation from 10% to 30% was found to be 38.30%. That is, adsorbent dosage variation from low to high level has little influence on the lead release capacity.

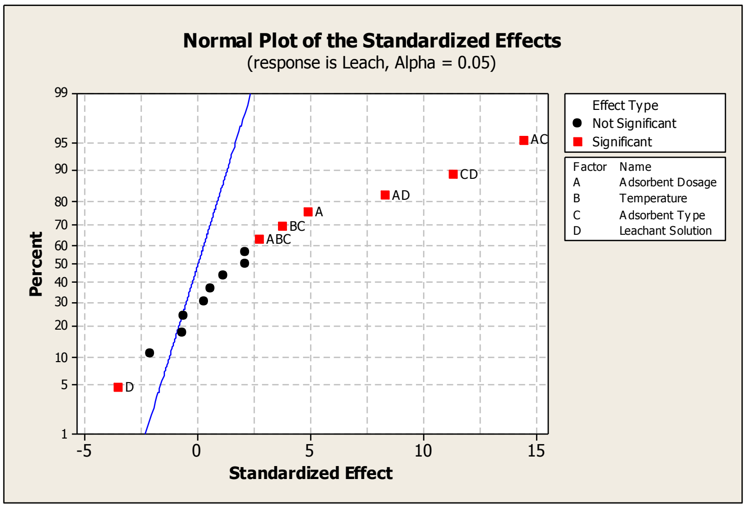

Figure 2: Normal probability plot of the standardized effects

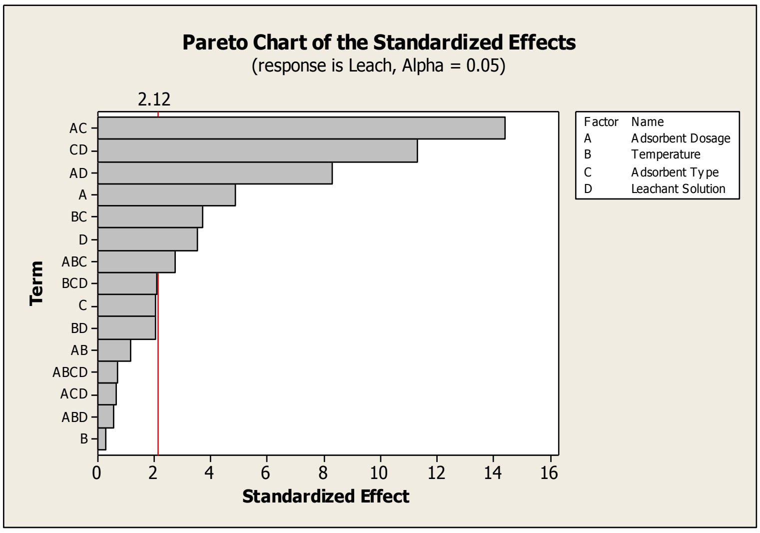

Figure 3: Pareto chart of the standardized effects

The pareto chart of the standardized effects illustrating both the magnitude and the importance of the effects is given in figure3. On the pareto chart there is a reference line and any effect that extends past this line is potentially important. According to figure 3, the main effects *A*, D and*C*, and the interactions *AC, CD, AD, B*cand *ABC,* that extend beyond the reference line are significant at the level of 0.05. This result confirms previous graphical analysis of the normal probability plot.

The main effect plots in figure 4 are helpful in visualizing which factors most affect the response. Each level of the factors affects the response differently. If the slope is close to zero, then the magnitude of the main effect would be small. *D* factor at their low level result in higher mean responses which compare to that at the high level. For *A* and *C* factors, the reverse is true. Additionally, the factor *A* appears to have a greater effect on the response, as indicated by a steeply slope.

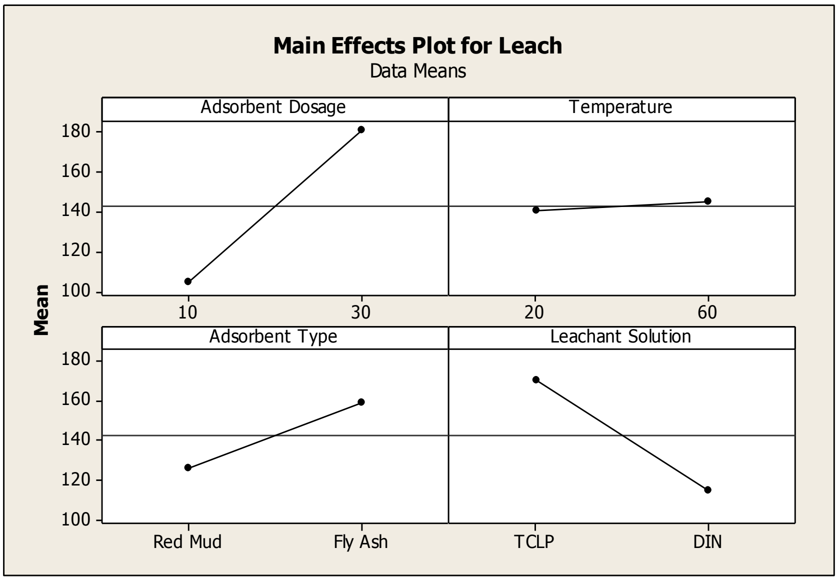

Figure 4: Main effects plot

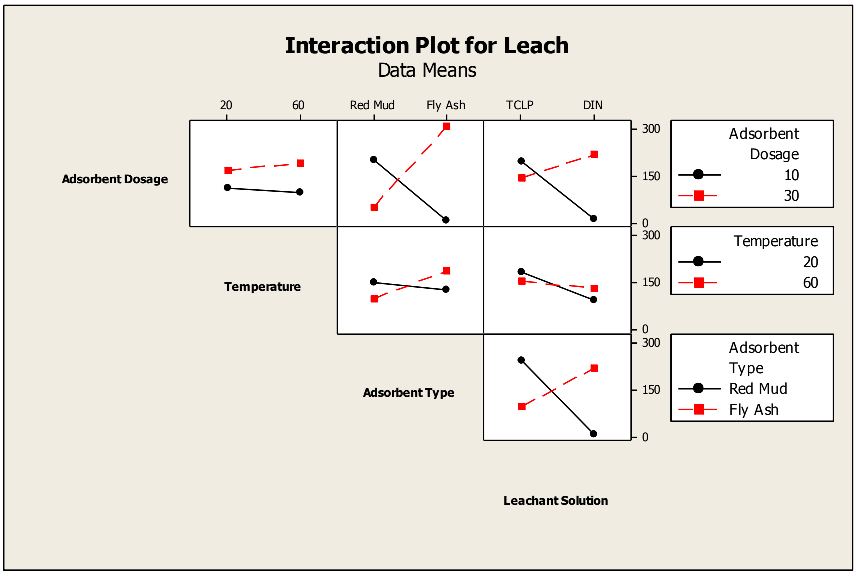

Figure 5: Interaction effects plot for lead release

If there were no significant interactions between the factors, a main effects plot would adequately describe where it is possible to obtain the biggest payoff for changes to the process. An interaction plot details the impact that the act of changing the settings of one factor has on another factor. Therefore, if the lines of two factors are parallel, there is no interaction. On the contrary, when the lines are far from being parallel, the two factors interact. The interaction plot in figure 5 confirms the significance of *AC* and *CD* as stated earlier.

The surface plot is used to provide a graphical representation of how two factors can simultaneously affect the output, or lead release, at on time. When there are more than two experimental factors, those that are not displayed in the graphs are held constant. The surface plots in figure 6 were specially used to investigate the effect of material type on adsorption efficiency. From the figures, the strong effect of adsorbent dosage - adsorbent type (*A*C*) on the percentage of lead release is clearly observed. However, it has been determined that the effect of adsorbent type - leachate solution (C**D*), as well adsorbent dosage – leachate solution (A**D*) and adsorbent dosage (*A*), is relatively small in comparison to adsorbent dosage –adsorbent type.

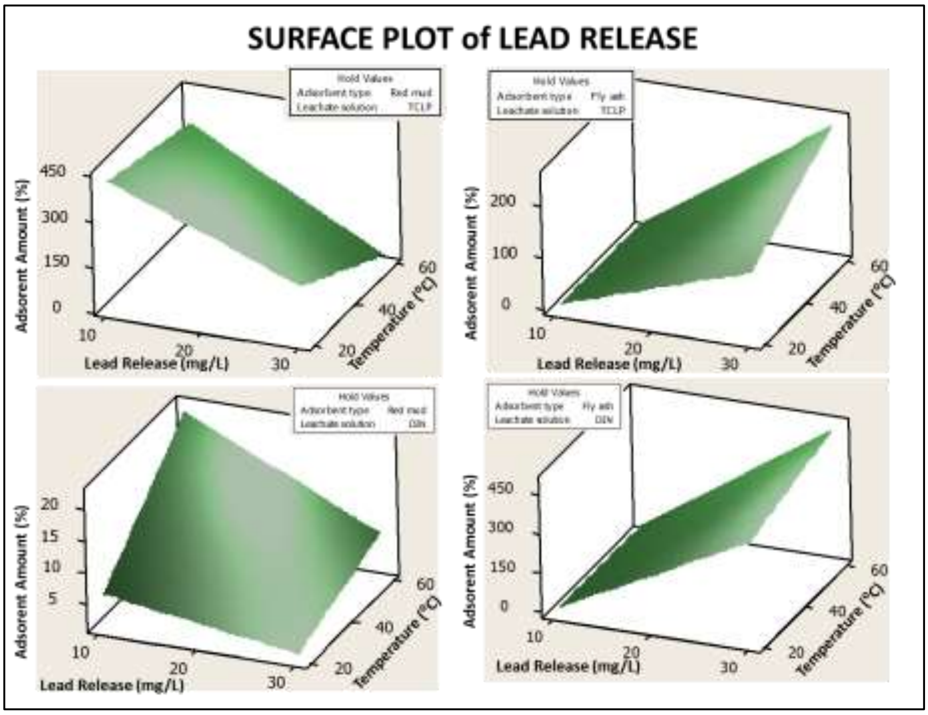

Figure 6: Surface plots

4. Conclusion

The main factors which affect the lead release were studied by using statistically design experiments. The minimum lead releases were obtained by DIN solution. The lead releases in the DIN solution for 10% and 30% red mud and 10% and 30% fly ash were found to be 6.11mg/L and 1.49 mg/L, and 5.99 mg/L and 371 mg/L, respectively. Based on these results, it can be concluded that red mud is a relatively more effective adsorbent than fly ash. The fly ash has negative effect ro lead release. The experimental design results also indicated that the leachate solution and adsorbent typeare important significant factor in lead release. Additionally, it is clearly shown that the effect of temperature is relatively small in comparison to other factors. The results of the present study indicate that red mud is effective adsorbents for the lead release from slag.

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