

# Immobilisation and leaching performance of lead-acid batteries smelting slag using natural and waste materials

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## Abstract

The slag generated in the rotary furnaces is classified hazardous waste. In this regard, landfill disposal of lead smelting slag is not feasible since a few hundred tons are produced per year; leaching of heavy metals into ground water is of concern. The release of heavy metals into the environment has resulted in a number of environmental problems. 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. The toxicity of the waste is determined by leaching tests and depending on the characteristics of the waste the spent abrasive must be disposed of as solid or hazardous waste. The aim of this study is to investigate leaching characteristics of lead smelting slag according to leaching tests such as TCLP, and TS EN 12457-4 tests methods. In this study, mixed-level factorial design was applied to optimize process parameters for lead removal from lead smelting slag using natural (sepiolite, montmorillonite, illite and seashell) and waste material (red mud). The established model was then used as a predictor to achieve better understanding of the adsorption process and to obtain optimal settings of the experimental factors. The present study includes the safe disposal of lead smelting slag using natural and waste materials. Experimental results indicated that red mud and seashell can be used as environmentally friendly adsorbents that are capable of lead release from lead smelting slag.

**Keywords:** Lead smelting slag, lead leachability, immobilisation, natural and waste materials, factorial design

## 1. Introduction

Lead mining and metallurgy are significant branch of industry worldwide. Lead produced is fifth common metal production after steel, aluminium, copper and zinc by 1970s (Mining Specialization Commissions Report, 2001). The world production of lead from both primary and secondary resources was 3.9 Mt in 2009 (Ogundiran *et al.*, 2013). The main application of lead is acceptable for batteries (Smaniotto *et al.*, 2009). There are two types of

batteries: 'primary batteries' and 'secondary batteries'. Lead-acid batteries are called secondary batteries or accumulators since they are rechargeable. The recovery of metals from metal scrap has the advantage that it is easier and far less energy dependent than the production of primary lead from ores. In Europe lead used for car batteries originated from secondary sources has now increased to more than 70% and in the USA to more than 90% (Vest and Jantsch, 1999; Ogundiran *et al.*, 2013; Kaksonen *et al.*, 2016). Currently, lead is produced from pyrometallurgical recycling technologies in Turkey. Although no primary lead production occurs in Turkey, the country has a significant secondary lead market. In 2007 between 80,000 and 90,000 tonnes of scrap lead acid batteries were collected and recycled, representing 45,000 to 50,000 tonnes of secondary lead production. According to Kurt (Kurt, 2012), all of the lead - acid batteries are recycled and about 80% - 85% of lead acid batteries comes from secondary smelting in Mutlu Corporation in Turkey. Lead acid batteries are recycled using a high-temperature, pyrometallurgical process. At the smelting step (900 – 1200 °C), the lead compounds from the break are reduced to provide metallic lead, by smelting the battery paste with coke or other reducing agent rich in carbon and sodium hydroxide and sodium nitrate for the removal of other metals in the oxide form. Initially the lead presents in the sulphate form and after of the first stage of the reaction that occurs in the presence of the reducing agent (charcoal) in a temperature of about 650 °C. The lead is present in the form of sulphide where it is reduced in one second stage of the reaction in a temperature of about 1000 °C. The properties established in the melting of the lead would also be improved, and less lead would be lost in the slag, with the use of Na<sub>2</sub>CO<sub>3</sub> to work at a lower temperature and a better viscosity (Kreusch *et al.*, 2007).

Approximately, 100 - 400 kg of slag for each ton of metallic lead produced is generated. It contains approximately 5% - 10% of lead compounds (Kreusch *et al.*, 2007; Special waste statistics (2003-2009), 2011; Smaniotto *et al.*, 2009). These slags are composed mainly of iron (approximately 60%) and lead (approximately 6%), and also trace elements such as Cr<sub>2</sub>O<sub>3</sub>, CuS, ZnO, TiO<sub>2</sub>. These residues cannot be disposed in conventional landfill due to the high lead content. All kinds of slags from secondary lead smelters are classified as

hazardous waste in the European Waste Catalogue (*European Waste Catalogue (EWC), 2000*). The re-recycling technologies to treat hazardous waste are value recovery from the waste. If this is not technically and economically feasible, immobilisation is the next option. Waste immobilization techniques are the recent technologies proposed to prevent the free movement of contaminants in hazardous waste and surrounding media. Some natural and waste materials produced by the alkali activation of solid aluminosilicate precursors. These materials have been proposed as matrices for immobilization of various hazardous wastes. Toxic elements that are present in hazardous waste materials can be captured in such 3-dimensional network structures. Although there are many researches on immobilisation technology, very few have considered in depth the leaching performance of lead smelting slags treated by different binders from different studies (Coz *et al.*, 2009; Ogundiran *et al.* 2013; Kogbara, 2014;). This study presents a detailed leaching behavior of slag with and without natural and waste materials as immobilisation agents. These agents have high adsorption properties. Adsorption is a process where the atoms, ions or molecules of dissolved solids from liquid grips on the surface of solid; i.e. it is a process of mass transfer in which the dissolved solid from liquid gets deposited on the surface of solid because of physical or chemical interaction. The removal of heavy metals by using low cost adsorbent is found to be more encouraging in extended terms as there are several materials existing locally and profusely such as natural materials, agricultural wastes or industrial

by-products which can be utilized as low-cost adsorbents. These adsorbents should have high selectivity to facilitate quick separations, favorable transport and kinetic characteristics, thermal and chemical stability, mechanical strength, resistance to fouling, regeneration capacity and low solubility in the liquid in contact (Çoruh and Geyikçi, 2012; Tripathi and Ranjan, 2015).

The present study focuses on the safe disposal and leaching behavior of the lead smelting slag using natural and waste materials. Also, this study aims to optimize process parameters for lead removal from lead smelting slag using natural and waste materials.

## 2. Materials and Methods

### 2.1. Materials

#### 2.1.1. Lead smelting slag

The chemical composition of lead smelting slag in experimental studies is summarized in Table 1. The chemical composition of the major constituents listed in the lead smelting slag illustrates Fe<sub>2</sub>O<sub>3</sub> (40.77%), SiO<sub>2</sub> (15.41%), PbO + PbS (11.50%) and some other oxides as Al<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O and CaO. The chemical composition of lead smelting slag refers to a multicomponent silicates system. The very high content of iron oxides indicates the potential of this slag to develop magnetic phases upon appropriate processing. The crystalline phase composition of the lead smelting slag in this study was characterized by SEM (SEM, Zeiss Supra 50VP) in Fig. 1 (a).

**Table 1.** Chemical composition (wt. %) of lead smelting slag, sepiolite, seashell, red mud, montmorillonite and illite

	Lead smelting slag	Sepiolite	Seashell	Red mud	Montmorillonite	Illite
pH	9.91	8.83	9.77	10.16	8.62	9.03
SiO <sub>2</sub>	15.41	53.47	0.3	15.64	50.3	76.9
Fe <sub>2</sub> O <sub>3</sub>	40.77	0.16	0.1	36.24	6.0	1.5
Al <sub>2</sub> O <sub>3</sub>	3.01	0.19	0.2	20.10	13.7	12.0
TiO <sub>2</sub>	0.24	-	<0.1	4.76	0.6	0.2
CaO	2.08	0.71	38.5	2.68	7.1	0.8
SO <sub>3</sub>	0.61	-	-	0.06	-	-
CO <sub>2</sub>	-	-	-	2.93	-	-
K <sub>2</sub> O	0.46	-	<0.1	-	2.8	4.0
MgO	0.42	23.55	0.1	-	2.3	<0.1
Na <sub>2</sub> O	5.35	-	0.4	9.99	0.6	1.2
Mn <sub>2</sub> O <sub>3</sub>	0.46	-	-	-	-	-
P <sub>2</sub> O <sub>5</sub>	-	-	0.1	0.02	0.2	<0.1
LOI	6.32	-	-	7.58	-	-
PbO + PbS	11.50	-	-	-	-	-
Others	13.37	21.92	60.2	-	16.4	3.3

#### 2.1.2. Sepiolite

The sepiolite is used as natural material additives for leaching experiments. The sepiolite samples used for this study were obtained from Eskişehir in Turkey. The chemical composition of sepiolite is presented in Table 1 and it shows that sepiolite is primarily a mixture of Si and Mg oxides. The specific surface area (BET) of sepiolite is 82.35 m<sup>2</sup>/g. The crystalline phase composition of the sepiolite in this study was characterized by SEM (SEM, Zeiss Supra 50VP) in Fig. 1 (b).

#### 2.1.3. Sea shell waste

The sea shell is used as natural material additives for leaching experiments. The seashell samples used for this study were obtained from Samsun in Turkey. The chemical composition of seashell is presented in Table 1 and it shows that sea shell is primarily a mixture of C and Ca oxides. The specific surface area of sea shell is around 1.21 m<sup>2</sup>/g. The crystalline phase composition of the sepiolite in this study was characterized by SEM (SEM, Zeiss Supra 50VP) in Fig. 1. The crystalline phase composition of the sea shell in this

study was characterized by SEM (SEM, Zeiss Supra 50VP) in Fig. 1 (c).

#### 2.1.4. Red mud

The red mud sample was obtained from Seydişehir Aluminium Plant, Konya, Turkey. The 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 Na oxides. The specific surface area of red mud is 14.20 m<sup>2</sup>/g. The crystalline phase composition of the red mud in this study was characterized by SEM (SEM, Zeiss Supra 50VP) in Fig. 1 (d).

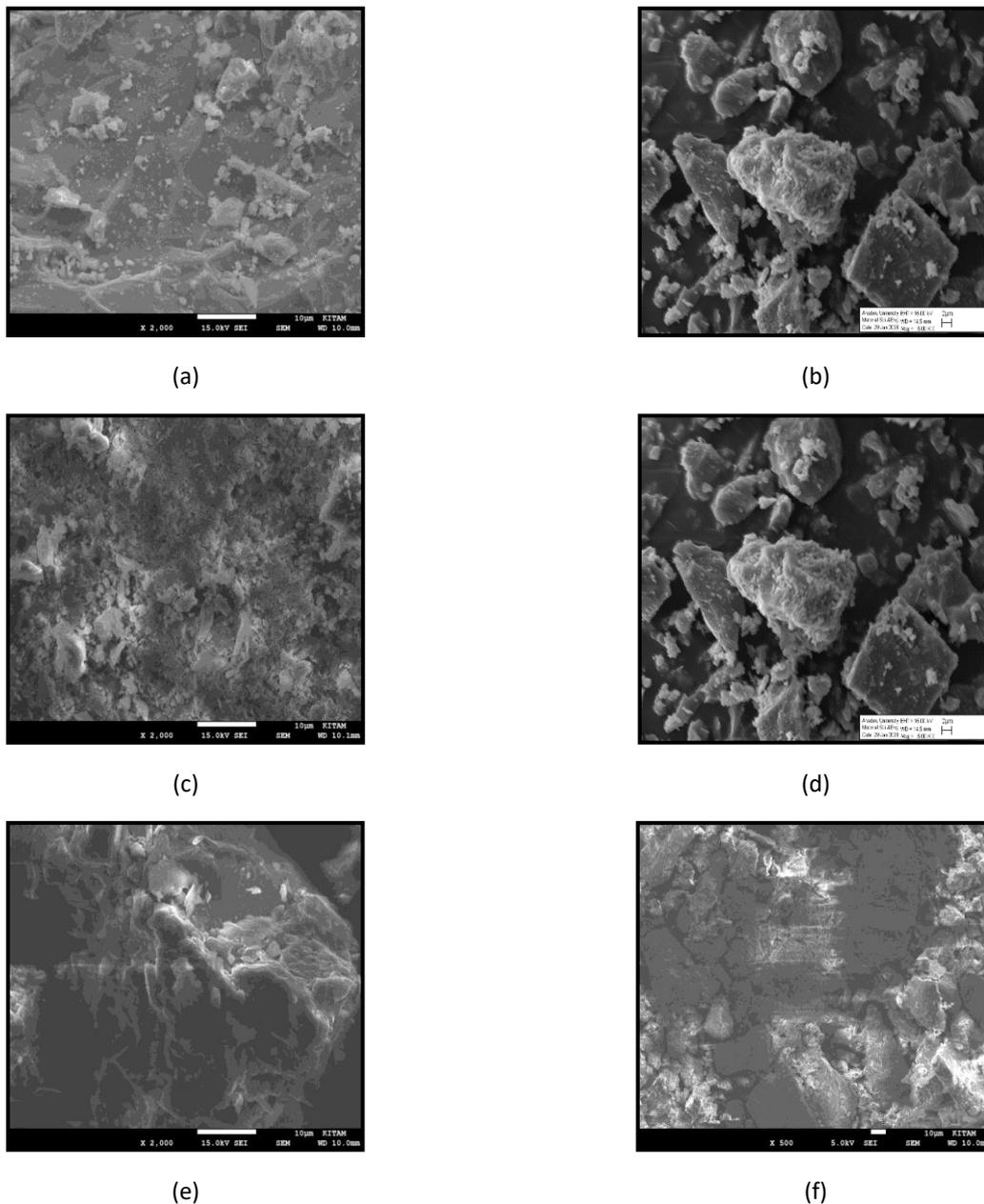
#### 2.1.5. Montmorillonite

The montmorillonite is used as natural material additives for leaching experiments. The montmorillonite samples used for this study were obtained from Artvin in Turkey.

The chemical composition of montmorillonite is presented in Table 1 and it shows that montmorillonite is primarily a mixture of Si, and Al oxides. The specific surface area of montmorillonite is around 46.90 m<sup>2</sup>/g. The crystalline phase composition of the montmorillonite in this study was characterized by SEM (SEM, Zeiss Supra 50VP) in Fig. 1 (e).

#### 2.1.6. Illite

The illite is used as natural material additives for leaching experiments. The illite samples used for this study were obtained from Samsun in Turkey. The specific surface area is 6.31 m<sup>2</sup>/g. The chemical composition of illite is presented in Table 1. The total amount of Si and Al content is about 89%. The crystalline phase composition of the illite in this study was characterized by SEM (SEM, Zeiss Supra 50VP) in Fig. 1 (f).



**Figure 1.** Scanning electron microscope (SEM) micrograph of the lead smelting slag, sepiolite, sea shell, red mud, montmorillonite and illite: (a) lead smelting slag; (b) sepiolite; (c) seashell; (d) red mud; (e) montmorillonite; (f) illite

## 2.2. Experimental procedure

The leach tests are intended to measure the release of components from a solid waste sample in aqueous solution, e.g., acidic rainwater or landfill leachate, and can be used to simulate contaminant migration in groundwater. The TCLP is designed to determine the mobility of both organic and inorganic analyses present in liquid, solid as well as multiphase samples. One of the requirements of this batch test is that it should be quick, simple to carry out and that the results should be reproducible. The TCLP analysis simulates landfill conditions. The TCLP test was performed as specified in the United States Environmental Protection Agency EPA method (USEPA, 1992). Toxicity Characteristic Leaching Procedure (TCLP) leaching test is often used to evaluate the immobilization efficiency. Acetic acid solution is used as extraction fluid in the TCLP test. The TCLP analysis determines which of the contaminants identified by the EPA are present in the leachate and their concentrations. For this purpose, the solid material is then extracted for at least 18 hours with sodium acetate/acetic acid buffer solution equal to 20 times its weight. The materials are placed in a tumbler to simulate the leaching action of water seeping through waste in the landfill. TCLP test is used for characterizing a waste as hazardous or non-hazardous, it is recognized to have little predictive value for long-term behavior (Cohen and Petrie, 2005; Demotica et al 2012).

TS EN 12457-4 test was performed in Turkish standards. Before doing this test, the solid matrices were crushed. The particle size of the crushed sample was kept less than 4 mm according to requirement of the TS EN 12457-4 procedure. A 10:1 liquid/solid (L/S, L/kg) ratio was employed, and the mixture was rotated for 24 h at 30 rpm using a rotary agitation apparatus (Regulation of landfill of wastes, 2010). Batch leaching tests were conducted to evaluate the leaching of pollutants in lead-acid batteries slag samples. The present study was undertaken to investigate the effect of the adsorbent amount, temperature, adsorbent type and leachate solution on the lead adsorption. These

experiments were run in the batch reactors at different conditions such as adsorbent amount (10%, 30% and 50%), temperature (20 and 60 °C), adsorbent type (sepiolite, sea shell, red mud, montmorillonite and illite) and leachate solution (TCLP and TS EN 12457-4). The samples were mixed at predetermined periods at a temperature of 20 °C in a shaker at 150 rpm. The pH of the leaching solutions for all tests were measured and thereafter acidified with HNO<sub>3</sub> to decrease the pH to below 2 prior to instrumental analysis. In selected experiments, the solution was filtered by using a membrane filter and analyzed for residual metal content AAS (Atomic Absorption Spectrophotometry, UNICAM 929 Model).

## 2.3. Factorial designs

Factorial design is the system which is based on all trial combinations formed by levels of factors. Factorial design is not a designation but an experiment which tests whether there is a significant difference between trials. The method is used for simultaneously studying main effects and interactions of two or more factors. 2 level or 3 level experimental designs are special designs and named according to level number. Since factor number is represented as  $k$ , these systems are identified as  $2^k$  or  $3^k$  factorial orders.

Experimental combination number is equal to the multiplication of factor level numbers. In experiments for lead removal, 4 factors have been used: adsorbent type, leachate solution applied, adsorbent amount and temperature. Adsorbent type is composed of 5 levels, leachate solution is composed of 2 levels, adsorbent amount is composed of 3 levels and temperature is composed of 2 levels. The trial number of factors shown in Table 2 is  $5 \times 2 \times 3 \times 2 = 60$ ; and each experiment has been conducted iteratively. Outcomes of the experiment have been evaluated by full factorial design method using Minitab (Version 17) statistical software (Montgomery *et al.*, 2001; Ai *et al.*, 2006; Erbaş and Semra, 2006; Zhao and Chen, 2012a, 2012b; Şenoğlu and Acıtaş, 2014; Yin and Zhou, 2015).

**Table 2.** The Levels of experimental factors

FACTORS				
	Adsorbent Type (A)	Leachate Solution (B)	Adsorbent amount (%) (C)	Temperature (°C) (D)
LEVELS	Sepiolite	TS EN 12457-4	10	20
	Seashell	TCLP	30	60
	Red Mud		50	
	Montmorillonite			
	Illite			

## 3. Result and Discussion

### 3.1. Effect of leachate solution on lead release from lead smelting slag

Lead release from lead smelting slag as a function of leachate solution is presented in Fig. 2. As can be seen from the Fig.2, lead releases for TS EN 12457-4 test solution at different temperatures (20 and 60 °C) were obtained as

17.74 and 18.05 mg/L, respectively. The highest lead release by TCLP methods was observed. TCLP lead releases for 20 and 60 °C were found to be 525.60 and 431.20 mg/L, respectively. It was also reported that the metal concentrations in the TCLP leachate were significantly higher than the TS EN 12457-4 leachate. This is due to the pH difference between the applied leachate fluids and also between the final leachate pHs. The pH of the TCLP leachate

fluid was around 4.93-5.91, but that of TS EN 12457-4 was around 9.50-10.60. Therefore, the TCLP conditions for the lead smelting slag samples than TS EN 12457-4. Also, the TCLP leach test results in slag in solid breakdown both due to attack by the acetic acid and, to a lesser degree, attrition. The result of breakdown increases exposed surface area and also reduces the intra-particle diffusion path.

This result can be explained by the chemical nature of the leaching solution, the affinity of metal(s) with the leaching ion, and the competing redox conditions in the solution (Singh and Pant, 2006; Demotica *et al.*, 2012; Kumar *et al.*,

2014; Yadav and Yadav, 2014; Yu *et al.*, 2015,). The leaching tests showed the lead release from lead smelting slag exceed the limits of Turkish and EPA standards. Leaching concentration for lead in Turkish and EPA standards are 1mg/L and 5 mg/L, respectively.

The lead smelting slag samples were subjected TCLP and TS-EN 12457-4 tests to determine the leachability characteristics and adsorption ability for heavy metals in the slag using natural (sepiolite, montmorillonite, illite and sea shell) and waste material (red mud). These results are summarized in Table 3.

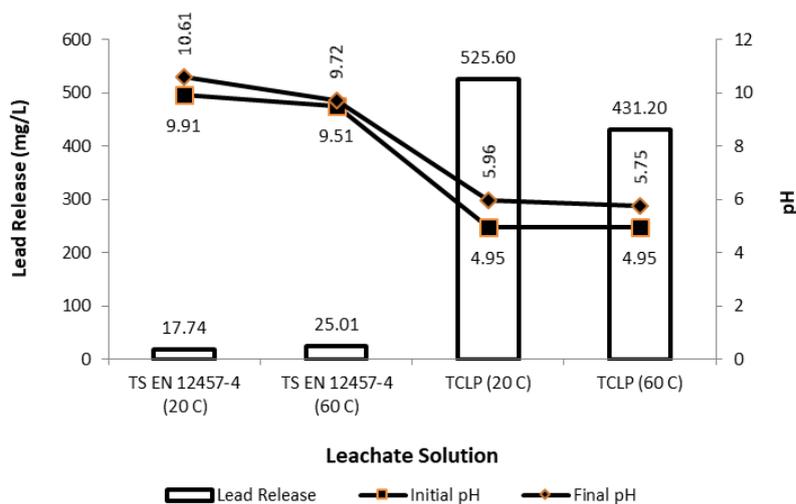


Figure 2. Effects of leachate solution for lead release from lead smelting slag

Table 3. Lead removal efficiency (%)

Adsorbent Amount		10%		30%		50%	
Adsorbent Type	Temperature	TS EN 12457-4	TCLP	TS EN 12457-4	TCLP	TS EN 12457-4	TCLP
Sepiolite	20 °C	41.68	9.02	95.55	18.70	99.28	25.39
	60 °C	96.76	98.81	98.04	99.49	97.28	99.16
Seashell	20 °C	27.40	99.63	58.74	99.70	91.04	99.78
	60 °C	96.84	99.75	97.16	99.46	97.84	99.32
Red Mud	20 °C	35.68	12.58	86.98	72.85	97.13	96.12
	60 °C	17.03	12.24	72.49	94.61	53.46	97.43
Montmorillonite	20 °C	24.46	69.58	66.23	97.67	94.02	99.11
	60 °C	97.08	0.26	98.43	4.85	99.80	41.19
Illite	20 °C	0.17	8.43	9.90	20.11	9.53	32.91
	60 °C	96.24	0.26	97.28	0.39	96.56	17.86

3.2. Effect of particle size on lead release from lead smelting slag

Lead leaching as a function of particle size is presented in Fig. 3. The particle size during all study was chosen as 0.35+0.50 mm. An increase in lead ions in the TS-EN 12457-4 leachate as particle size decreases was observed. Lead leachate concentrations for +1.19- 2.0 mm and 0.35+0.50 mm particle sizes were found to be 7.24 and 17.74 mg/L.

Fig.4 presents the effects of particle size on lead release by TCLP leachate solution from lead smelting slag as a function of particle size. As can be seen from the Fig.4 as the particle

size decreased, metal release increased. The highest lead release by TCLP methods was observed as 525.6 mg/L for 0.35+0.50 mm particle size. The result of TCLP test was higher than TS-EN 12457-4 test methods. Apparently the metal concentrations obtained by the TCLP method were rather high, which is consistent with the general principles that TCLP always presents the maximum leachate concentration for environmental samples (Al-Abed *et al.* 2006). These results demonstrate that the pH value of the extraction medium, liquid:solid ratio and extraction time are predominant parameters affecting leachability.

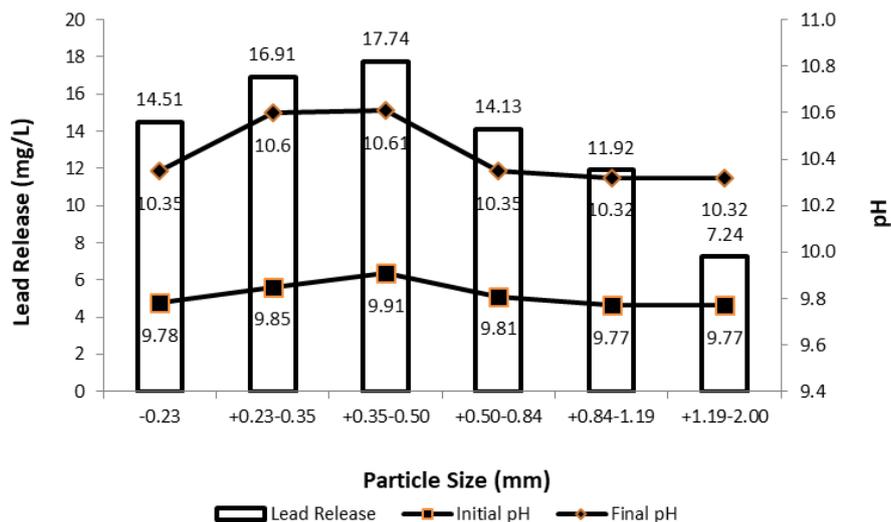


Figure 3. Effects of particle size on lead release by TS-EN 12457-4 leachate solution from lead smelting slag

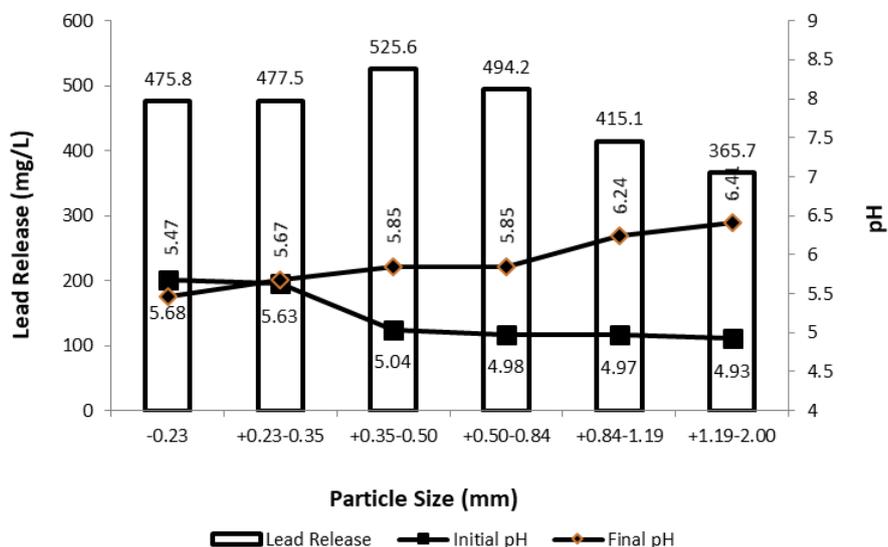


Figure 4. Effects of particle size on lead release by TCLP leachate solution from lead smelting slag

3.3. Factorial design evaluation

The analysis of variance show that the main effects of Adsorbent Type (A), Leachate Solution (B), Adsorbent Amount (C), and Temperature (D) and the interactions AB, AC, AD, BC, BD, CD, ABC, ABD, ACD and ABCD are significant at the 5% level. In Table 3, the column labeled “P” presents the P 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 slight P-values (<0.05) mean that all of the main effects and interactions are effective at the 5% significance level.

These results argued good agreements between the predicted and experimental values of lead removal efficiency. The fit models submitted square correlation coefficient (R<sup>2</sup>) of 0.9994 was in good agreement.

In F-Value of Table 4, it can be observed that the adsorbent type (23.08%) has most significant effect on lead removal

of lead smelting slag compared to the other parameters. The influence values of the parameters follows as interaction of adsorbent type\*leachate solution\*temperature, interaction of adsorbent type\*temperature and adsorbent amount with the ratios of 20.88%, 11.6% and 10.95, respectively. The representation of the main effect and the interaction factors most affecting the response is shown in Table 5.

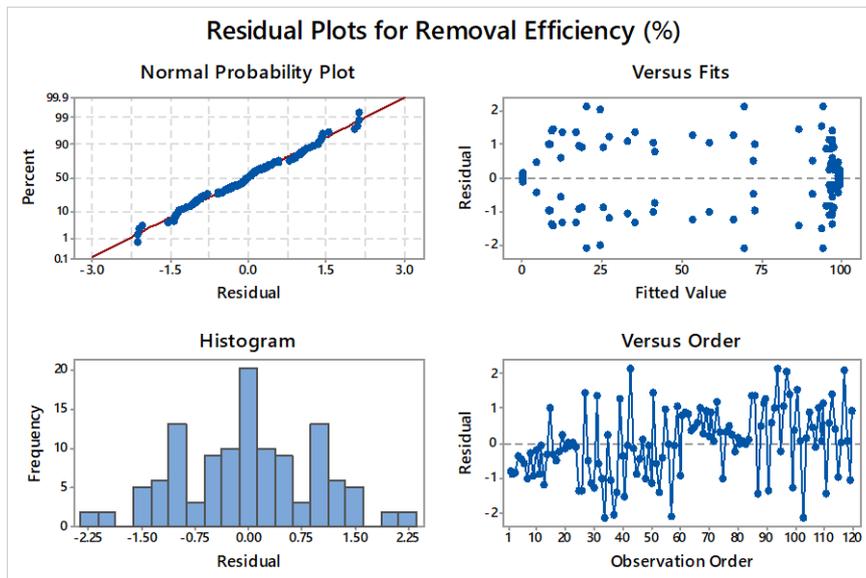
The sufficiency of the models was also appraised by the residuals. Residual is the difference between the observed and the predicted response value. Residuals are thought as elements of variation unexplained by the fitted model and then it is expected that they occur according to a normal distribution. The observed residuals are plotted against the expected values, given by a normal distribution in Fig.5. Trends seen in Fig.5 reveal reasonably well behaved residuals. In this graphics, the residuals seem to be randomly scattered.

**Table 4.** Analysis of variance for removal efficiency

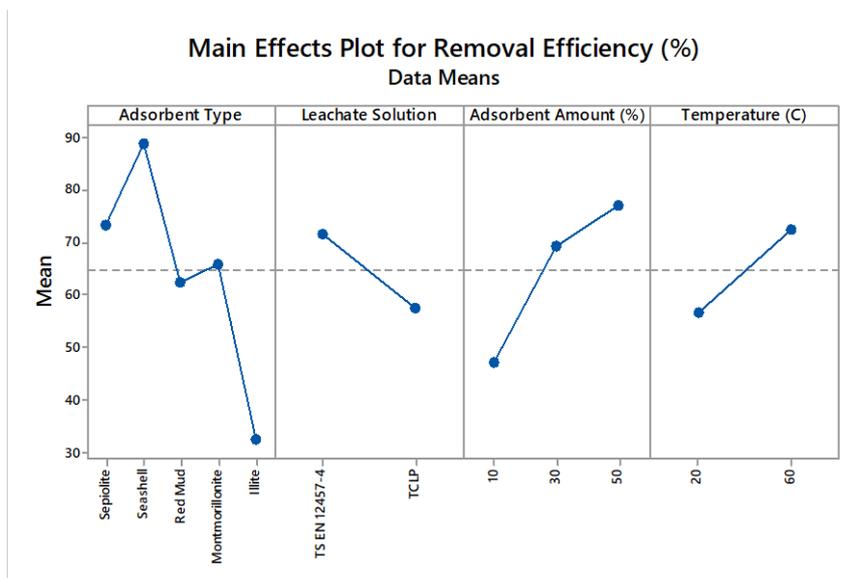
Source	D.F.	Seq SS	Adj MS	F-Value	P
Model	59	177132	3002.2	1597.16	0.000
Linear	8	73909	9238.6	4914.81	0.000
Adsorbent Type	4	40904	10226.1	5440.15	0.000
Leachate Solution	1	5976	5976.1	3179.24	0.000
Adsorbent Amount (%)	2	19412	9706.0	5163.49	0.000
Temperature (C)	1	7616	7616.1	4051.69	0.000
<i>2-Way Interactions</i>	21	57897	2757.0	1466.69	0.000
Adsorbent Type * Leachate Solution	4	15615	3903.7	2076.74	0.000
Adsorbent Type * Adsorbent Amount	8	11323	1415.4	752.99	0.000
Adsorbent Type * Temperature	4	20658	5164.6	2747.49	0.000
Leachate Solution * Adsorbent Amount	2	153	76.6	40.74	0.000
Leachate Solution * Temperature	1	7395	7394.7	3933.89	0.000
Adsorbent Amount * Temperature	2	2752	1376.2	732.15	0.000
<i>3-Way Interactions</i>	22	44088	2004.0	1066.11	0.000
Adsorbent Type * Leachate Solution * Adsorbent Amount	8	3148	393.5	209.32	0.000
Adsorbent Type * Leachate Solution * Temperature	4	37004	9251.1	4921.47	0.000
Adsorbent Type * Adsorbent Amount * Temperature	2	1727	215.9	114.84	0.000
Leachate Solution * Adsorbent Amount * Temperature	2	2209	1104.5	587.60	0.000
<i>4-Way Interactions</i>	8	1238	154.8	82.35	0.000
Adsorbent Type * Leachate Solution * Adsorbent Amount * Temperature	8	1238	154.8	82.35	0.000
Error	60	113	1.9		
Total	119	177245			
S=1.37104    R <sup>2</sup> = 99.94%    R <sup>2</sup> (adj) = 99.87%    R <sup>2</sup> (pred) = 99.75%					

**Table 5.** Effect of factors

Source	Contribution (%)
<b>Model</b>	<b>99.94</b>
<b>Linear</b>	<b>41.70</b>
Adsorbent Type	23.08
Leachate Solution	3.37
Adsorbent Amount	10.95
Temperature	4.30
<b>2-Way Interactions</b>	<b>32.66</b>
Adsorbent Type*Leachate Solution	8.81
Adsorbent Type*Adsorbent Amount	6.39
Adsorbent Type*Temperature	11.66
Leachate Solution*Adsorbent Amount	0.09
Leachate Solution*Temperature	4.17
Adsorbent Amount *Temperature	1.55
<b>3-Way Interactions</b>	<b>24.87</b>
Adsorbent Type*Leachate Solution*Adsorbent Amount	1.78
Adsorbent Type*Leachate Solution*Temperature	20.88
Adsorbent Type*Adsorbent Amount *Temperature	0.97
Leachate Solution*Adsorbent Amount *Temperature	1.25
<b>4-Way Interactions</b>	<b>0.70</b>
Adsorbent Type*Leachate Solution*Adsorbent Amount *Temperature	0.70
Error	0.06
Total	100.00



**Figure 5.** Residual plots for lead removal efficiency from lead smelting slag



**Figure 6.** Main effects plot for lead removal efficiency from lead smelting slag

Fig 6 shows a main effects plot, offering the effect of each variable on the response factor. This type of figuration shows the contribution to the response factor of changing one of the influential variables. When the effect of a factor is negative, removal efficiency decreases as the factor changes from low to high levels. In contrast if effect is positive, an increase in removal efficiency occurs for high level of the same factor. If the magnitude of the main effect is small, the slope would be close to zero.

Adsorbent type is the most influential variables for lead removal. According to the TCLP method, the lead removal efficiencies from lead smelting slag with 10%, 30% and 50% seashell material for 20 °C temperature were obtained as 99.63%, 99.70% and 99.78%, respectively. However, in the same temperature, according to the TS-EN 12457 testing procedure, the lead removal efficiencies from lead smelting slag including those percentages of seashell material were established as 27.40%, 58.74% and 91.04%,

respectively. Furthermore, the lead removal efficiencies from lead smelting slag with 10%, 30% and 50% seashell material for 60 °C temperature were found as 99.75%, 99.46% and 99.32%, respectively, when performing TCLP method, while those values were 96.84%, 97.16% and 97.84%, respectively, by utilizing TS-EN 12457 testing procedure. Increasing the adsorbent amount results in an increase in the lead removal efficiency. The seashells are composed of a mixture of calcium carbonate, protein and chitin, with relatively small amounts of lipid, phosphate and pigment. Several authors have found that comminuted, ground or powdered shell material has very high heavy metal adsorption capacities. An alternative mechanism to adsorption is that metal uptake occurs through ion exchange and conversion of calcium and magnesium carbonates to mixed-metal carbonates in the inorganic fraction of the shell structure. Kim and Park (Kim and Park, 2001) confirmed that  $K^+$ ,  $Na^+$ ,  $Mg^{2+}$  and  $Ca^{2+}$  were released from crab shell in association with  $Pb^{2+}$

uptake to the crab shell suggesting that the mechanism of uptake was through ion exchange and the formation of mixed-metal carbonates (Craggs *et al.*, 2006). Sepiolite, montmorillonite and red mud materials indicate similar results for lead removal from lead smelting slag. Silanol groups (SiOH) to especially sepiolite are present at the border of each block in the external of surface of silicate and act as neutral sites for lead adsorption (Vaclavikova *et al.*, 2005; Güneren, 2010; Eren and Gumus, 2011; Ozdes *et al.*, 2011; Djukić *et al.*, 2013; Sahu *et al.*, 2013; Araç, 2014; Kumar *et al.*, 2014).

The interaction plot shows the possible interaction between the mean responses of the factors under assessment. An interaction plot circumstances the impact that the act of changing the settings of one factor has on another factor. Graphically, two parallel lines of factors indicate no interaction between them; however non-parallel lines suggest that the two factors interact together. The interaction plot in Fig.7 confirms all of the interactions are significant. Fig. 8 (a) indicates the removal efficiency dependence on adsorbent type and adsorbent amount. For lead removal efficiency, a significant increase in the

amount adsorbent at equilibrium with the increase of adsorbent amount from 10% to 50% can be observed. This expected observation is a result of the increase in the specific surface on the adsorbent. These results demonstrated that the presence of aragonite and calcite phases in seashell is effectively able to remove lead metal ions. The increase in the removal of lead metal ion caused by the seashell amendment could be due to the higher pH value in the equilibrium solution promoted by the seashell. The higher pH value would cause an increase in the hydroxylation of the metals, and even its precipitation at high doses, as well as an increase in the negative charge of the variable charge components of the slag, thus favoring the adsorption of metals present in cationic form. Du *et al.* (Du *et al.*, 2011) and Sipos *et al.* (Sipos *et al.*, 2008), investigating the adsorption of Cd, Pb and Zn on soil mineral phases found that alkaline conditions due to the carbonate content of soils resulted both in increased adsorption on the mineral particles for Cu, and in enhanced role of precipitation for all the studied metals, and they indicate that in this case not the adsorption but the precipitation is the most important immobilization process (Filiz, 2007; Ghasemi *et al.*, 2013; Wu *et al.*, 2014).

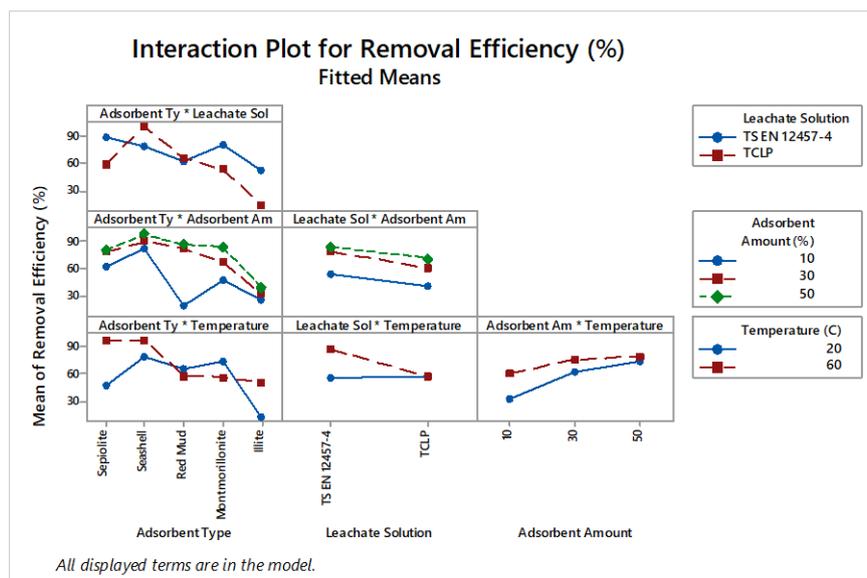


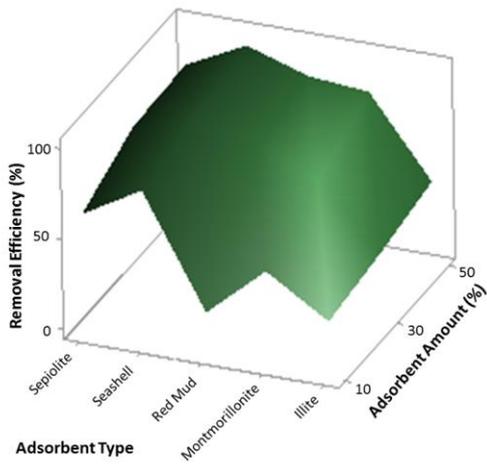
Figure 7. Interaction effects plot for lead removal efficiency

Fig. 8 (b) and (d) shows that an increase in temperature between 20 and 60 °C causes a linear slight increase in the lead removal efficiency for adsorbent amount and leachate solution. Fig 8. (c) illustrates the effect on lead removal of temperature. The efficiency of lead removal changes according to adsorbent type in temperature between 20 and 60 °C. While the seashell shows high removal efficiency, illite material shows lower removal efficiency.

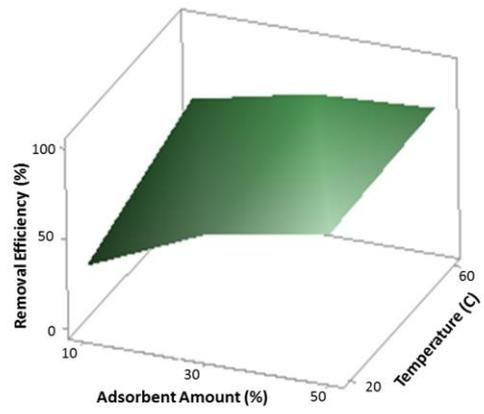
#### 4. Conclusions

In this study, the leaching characteristics of the lead smelting slag originating from lead recovery of exhausted batteries were investigated. Adsorptions modelling for lead removal in experiments, 4 factors have been used:

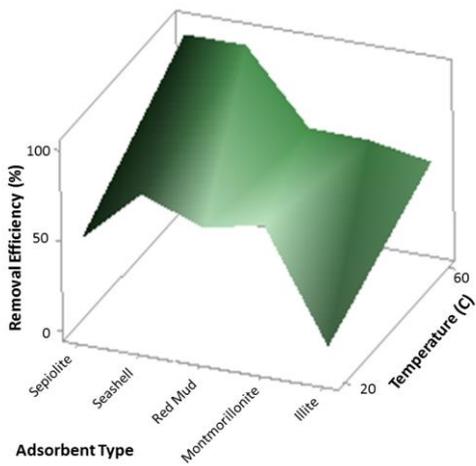
adsorbent type, leachate solution applied, adsorbent amount and temperature. Adsorbent type is composed of 5 levels, leachate solution (toxicity test) is composed of 2 levels, adsorbent amount is composed of 3 levels and temperature is composed of 2 levels. Toxicity tests, including TCLP and TS EN 12457-4 tests methods, were applied to lead smelting slag. The TCLP and TS EN 12457-4 test results show that decrease in particle size leads to an increase in lead ion releases. The results of laboratory leaching tests demonstrate that adding of sepiolite, montmorillonite, illite, sea shell and red mud to the lead smelting slag drastically reduces the lead metal content in the leachate and the seashell and red mud performs better than the other materials.



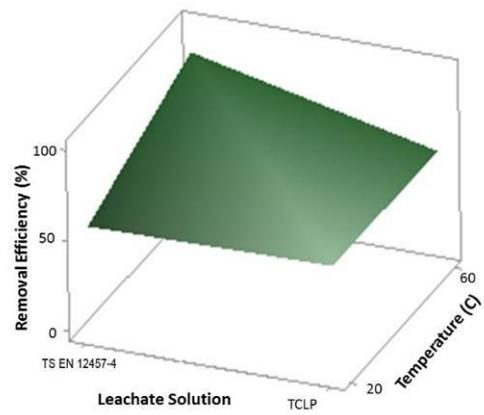
(a)



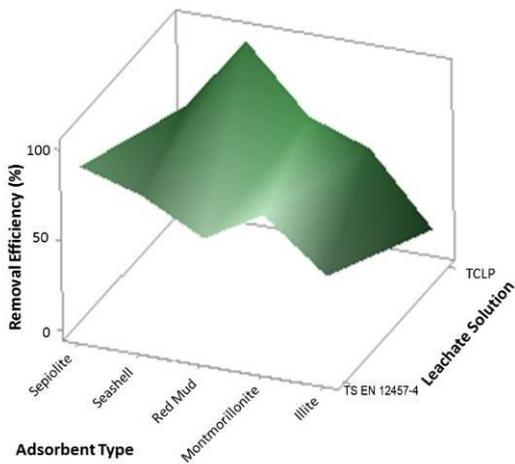
(b)



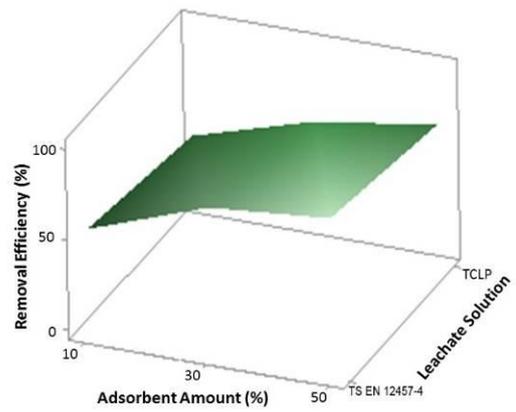
(c)



(d)



(e)



(f)

Figure 8. Surface plots for lead removal from lead smelting slag

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