Kinetic analysis of total Lead from spent Car battery by hydrochloric acid leaching

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Abstract

A study of the kinetic analysis of total lead from spent Car battery ash by hydrochloric acid leaching has been examined. The physico-chemical analysis of the ash powder was carried out by the Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) and X–ray diffraction (XRD). The effects of the acid concentration, temperature and particle size on the rate of battery ash dissolution have been investigated. The dissolution rate increased with hydrochloric acid concentration and temperature with decreasing particle size. The kinetic study indicated that the dissolution of total lead could be represented by a shrinking core model with product layer diffusion control mechanism at lower temperatures and a surface chemical reaction controlled mechanism at higher temperatures. The activation energy, E_a and reaction order of 44.13 kJ/mol and 1.14 were obtained, respectively for the dissolution process under the following established conditions: solid/liquid ratio = 10 g/L, HCl concentration = 4M, temperature= 80 °C, Stirring speed = 300 rpm, Particle size = 0.050–0.063 mm for 120 minutes.

1. Introduction

Lead is one of man's most valuable commodities occurring naturally in the environment. The metal is mined and processed in some 60 countries. The usage continues to increase and has risen from 4 million tons per year worldwide in the 1960s to 6 million tons per year in the 1990s and even till date. Of this, nearly 2 million tons per year are produced in Europe. Secondary production or recycling is now widely practiced and currently accounts for some 70 % of usage worldwide, especially in producing batteries used extensively as a Car battery and vehicles; as a coloring element in ceramic glazes; for polyvinyl chloride (PVC) plastics which coats electrical cords; as an anti-knock additive for aviation fuel in piston driven aircraft; as electrodes in the process of electrolysis, etc. [1, 2].

The tremendous increase in the use of heavy metals including lead over the past few decades has inevitably resulted in an increased flux of metallic substances in the environment. The metals

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are of special concern because they are non-degradable and persistent. Therefore, it is essential to remove these elements from industrial effluents and radioactive wastes before discharging into natural water bodies or into land [3].

It has prompted the society to look for technical alternatives in order to treat these types of residues since the consumption of batteries including Car batteries is considerable around the world. In the USA and Europe, for instance, it is estimated to be 8 billion units per year. In Japan, around 6 billion batteries were produced in 2004 while almost 1 billion units are consumed ever year in Brazil [4,5].

In Africa, production of primary refined lead declined by 45 % compared with that of 2000. The decrease maybe attributed to lower lead mine production in Morocco and Algeria. Morocco, the leading African producer of primary refined lead accounted for 88% of condimental output from 2000 to 2005. South Africa accounted for 86% of African secondary lead output; Kenya, Morocco and Nigeria accounted for the remainder [6]. In Nigeria, the consumption of Car batteries has grown substantially in the last few years accompanying the increasing automobile market.

Consequently, the increasing public concern about the environment in the last decade has resulted in stricter regulations worldwide, particularly those related to the disposal of hazardous residues containing heavy metals such as lead, cadmium and mercury [4]. Therefore, disposal of spent batteries is a major concern to the environment in terms of heavy metals contained therein [7]. All types of materials present in Car battery will contribute to some extent to the increase in environmental pollution. When discarded, some of them such as carbon are not so aggressive to the environment and can quickly merge into the ecosystem without noticeable impact. Thus, lead, cadmium and mercury are the heavy metals most likely to be the target of environmental concern [8,9].

In order to promote a general recycling route, the metal composition for the batteries must be known. Therefore, the recycling of spent Car batteries would seem to benefit not only the environment, but also the economy. Hence, there has been an increasing interest in developing processes for the recovery of these metals from secondary sources. Usually, pyrometallurgical and hydrometallurgical processes are employed for treating such secondary materials. Although, pyrometallurgical processes are the most used [7, 10], it may not be popular in a developing economy due to its high energy requirement. The hydrometallurgical processes are more environmentally suitable and economical to treat low metal containing materials on small scale [11-14].

In this paper, an aspect hydrometallurgical route (leaching) has been considered for studying the physico-chemical characterization and dissolution kinetics of the spent material in HCl media. The preliminary treatment by this route consists of battery sorting and dismantling. The collected batteries are first sorted by type (i.e. by chemical composition) in order to make leaching and liquid –liquid extraction operations more efficient. In the dismantling step, the spent battery dust is separated from plastic, iron scraps, paper and other residues which cannot be recycled. The dust is leached by HCl acid solution in order to transfer the metals of interest from the dust to the aqueous liquor [4,9].

2. Experimental

2.1 Materials

The spent dry cell Car battery: DELPHI standard s6 5AL (5) 12 V 65 Ah, 450 A, manufactured by Delphi automotive system © 1999, was kindly supplied by Farouq Battery Charger, Ipata- Oloje, Ilorin – West Local Government Area of Kwara State, Nigeria. This was dismantled using a hammer mill and ashed in a muffle furnace at a temperature of about 550 °C for 60 minutes. This is an optimum period for the completion of the ashing [9,13]. The ashing was done for the removal of organic matters present in the sample.

2.2 Characterization of the powder

The ash was sieved into three particle sizes and the fraction with particle diameter: 0.050 – 0.063 mm originating from the first dismantling step was submitted to Inductively Coupled Plasma - Mass Spectrometer (ICP-MS, Yokogowa model HP-4500, equipped with an auto sampler, peristaltic pump and Babington nebulizer under the following conditions: plasma, auxiliary and carrier gas flow rates of 1.5L/min, 1.2L/min and 1.04L/min, respectively); and X-ray diffraction (XRD, Philips PW 1800 with $CuK_{\alpha1}$: 1.54 Å radiation generated at 40 kV and 55mA. The cabinet houses a high speed, high precision Goniometer; high efficiency generator X-ray and an automatic sample loading facility). The two instruments were used in quantitative and qualitative analysis, respectively.

2.3 Leaching investigation

The leaching experiments were carried out in a 250 ml glass reactor equipped with a glass stirrer. The reactor was filled with 100 ml of 0.1 M HCl solution which was then heated to the desired temperature 55 °C. When the desire temperature was attained, a charge of 10g/L ashed sample was added to the HCl solution, stirring was started and the temperature of the reaction mixture was maintained constant [13,15,16]. Typically, 1ml of solution was withdrawn from the reactor with a pipette at various time intervals and diluted to 50 ml in a volumetric flask. The reaction kinetics was determined by measuring the total lead dissolved in the leach liquor as a function of time. Total lead dissolved in the leach liquor was analyzed using APLHA 4 Atomic Absorption Spectrophotometer.

For calculation of the fraction of total lead dissolved, an equation developed by Demopolous and Papengelakis [17] was used which includes correction factors to account for volume losses during sampling.

The same procedure was repeated for other HCl concentrations (0.1 M - 8.06 M) at intervals up to 120 minutes. The concentration which resulted in maximum dissolution (4M) was subsequently used for optimization of other leaching parameters such as system temperature and particle size. The energy of activation, E_a and the rate constants were calculated from the Arrhenius plots. The post leaching residual product at 80 °C after dissolution in 4M HCl solution was also subjected to X- ray diffraction examination and its level of purity tested [13,18].

3. Results and discussions

3.1. Physico-chemical characterization studies

The result of the elemental analysis of the spent Car batteries ash by ICP-MS is summarized in Table 1.

It is evident from Table 1 that the results of chemical analysis by ICP-MS showed expressive.

Table 1
Elemental composition of the spent Car battery ash by ICP-MS

Constituent	PbO	CaO	MnO	Fe_2O_3	K_2O	Na_2O	ZnO	TiO_2
Composition %	84.63	4.07	2.18	0.93	0.29	0.0061	1.67	0.15

* Other composition including α- SiO_2 = 6.08% obtained by difference

Amount of lead, which represent about 85% of the total mass of the sample. The list of the compounds identified according to XRD examination is shown in Table 2.

Table 2
The X-ray diffraction data of the spent Car battery ash

2θ°	Lattice planes			Compounds	JCPDS File No.
	h	k	l		
20.8534	0	1	1	SiO_2	82-1570
23.4664	1	1	6	$FeTiO_3$	50-0505
27.9649	-1	3	2	$Pb_3O_2(NO_3)_2$	40-0614
28.4013	3	0	0	$Pb_3O_2(NO_3)_2$	40-0614
30.8295	-2	0	-2	$Pb_3O_2(NO_3)_2$	40-0614
33.6315	2	-3	0	K_4ZnO_3	40-1164
46.3264	5	0	1	$Pb_3O_2(NO_3)_2$	40-0614

* JCPDS File No. = Joint Committee on Powder Diffraction Standard File Number responsible for the attributions of the various intense peaks for the compounds identified.

The X-ray data in Table 2 did compliment the results of chemical analysis. It confirmed the presence of $Pb_3O_2(NO_3)_2$ as the main compound found. In addition, the following compounds: SiO_2, $FeTiO_3$, and K_4ZnO_3 occur as minor to trace levels (≤5%).

3.2. Results of leaching tests

3.2.1. Influence of HCl concentration

In order to determine the influence of HCl concentration on the rate of spent Car battery ash, experiments were performed by varying the initial HCl concentration in the range of 0.1 M - 8.06 M at 55 °C with optimal stirring of 300 rpm [9] (Fig. 1).

From Fig. 1, it is observed that the total lead extracted at lower HCl concentrations was insignificant. However, as the HCl concentration is increased (>0.5M), dissolution proportionately increases. It is also observed that above 4M HCl concentration no further increase was noticed. The possible reason for this observation could be due to possible precipitation of metal chloride [19].
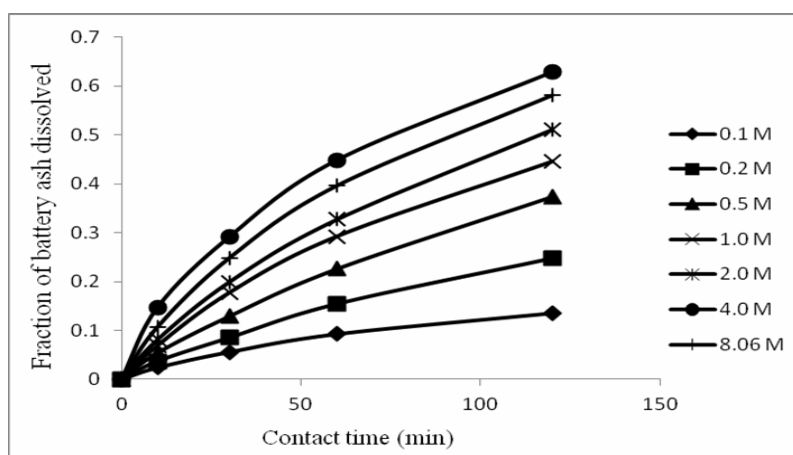

Fig. 1. Effect of HCl concentration on battery ash dissolution. Experimental conditions: HCl Concentration = 0.1 M - 8.06 M, Temperature = 55 °C, Solid/Liquid ratio = 10 g/L, Particle size = 0.050-0.063 mm, Stirring speed = 300 rpm.

3.2.2. Influence of system temperature

The effect of system temperature on the battery ash dissolution was studied under the conditions: 4 M HCl, 300 rpm, 0.05-0.063 mm size. Not surprisingly, fraction dissolved of total lead (Fig. 2) increased with the temperature. It is important to note that the system temperatures over 343K have a moderate effect on the rate [16]. Hence, the investigation was limited to 80 °C, purposely to avoid significant loss of HCl vapor at higher temperatures [23].
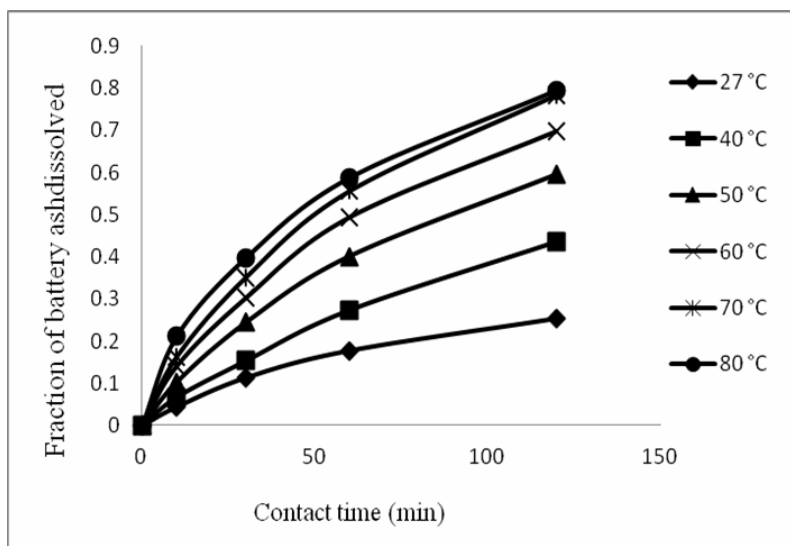

Fig. 2. Effect of temperature on battery ash dissolution. Experimental conditions: HCl Concentration = 4 M, Solid/Liquid ratio = 10 g/L, Particle size = 0.050-0.063 mm, Stirring speed = 300 rpm.

3.2.3 Influence of particle diameter

The effect of particle diameter on the rate of battery ash dissolution was studied by treating three size fractions (0.050 0 0.63, 0.063- 0.080, 0.080- 0100 mm) at 353 K in 4 M HCl solution within 120 minutes. The results (Table 3) showed that the smaller the battery ash, the faster the ash powder dissolution.

Table 3
Effect of particle diameter on battery ash dissolution.

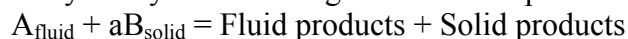| Particle size (mm)	Fraction of battery ash dissolved
0.050-0.063	0.838
0.063-0.080	0.628
0.080-0.100	0.312

Experimental conditions: HCl concentration = 4 M, System temperature = 80 °C, Solid/Liquid ratio = 10g/L, Stirring speed = 300 rpm.

3.3. Discussions

3.3.1. Dissolution kinetic analysis

Basic understanding of the mechanism of dissolution of the spent Car battery ash is the main consideration. Leaching of a material of this nature may be described by a number of reaction models already proposed in the literature [7, 9, 13-16]. Reactions involved in this process are

heterogeneous in nature involving mass transport of reactant and product ions which are analyzed by the shrinking core model represented by the following relations [16]:

$A_{fluid} + aB_{solid}$ = Fluid products + Solid products

The typical model has a reaction zone that originates from the outside layer of unreacted core [16, 20, 21]. The shrinking core model considers that the leaching process is controlled either by diffusion of the reactant through the product layer or by rate of the surface chemical reaction [9, 22, 24, 25]. Therefore, the shrinking core model when either the diffusion or surface chemical reactions are the slowest step can be respectively expressed by the following equations:

$$1 - \frac{2}{3}\alpha - (1-\alpha)^{\frac{2}{3}} = \frac{2M_s D C_A t}{\rho_s a r_o^2} = k_1 t \qquad (2)$$

$$1 - (1-\alpha)^{\frac{1}{3}} = \frac{K_o M_s C_A t}{\rho_s a r_o} = k_2 t \qquad (3)$$

Where α is the fraction of spent battery ash dissolved, K_o is the reaction constant, M_s is the molecular weight of the solid, C_A is the concentration of the HCl solution in the bulk solution, D is the diffusion coefficient, a is the stoichiometric coefficient of the reagent in the leaching reaction, r_o is the initial radius of the solid particle, t is the contact time (min), ρ_s is the molar density of the solid and k_1, k_2 are the reaction rate constants, evaluated from the equations (2) and (3), respectively.

Consequently, all dissolution data earlier presented in Figs. 1, and 2 were fitted to the model equations (2) and (3). Of the two tested kinetic models, only equation (2) fitted perfectly the aforementioned data with good average correlation of ≈ 0.965 and was used in the construction of the kinetic plots. The linearized graph of Fig. 2 is shown in Fig. 3.

The results of the rate constants for the tested models Eq. (2) and (3) at different temperatures with their corresponding correlation coefficients are summarized in Table 4.

Table 4
Rate constants, k_1, k_2 with their correlation coefficient values at various temperatures

Temperature °C	Apparent rate constant (10^{-4} min^{-1})		Correlation coefficient (R^2)	
	k_1	k_2	k_1	k_2
27	0.5080	3.923	0.9957	0.7017
40	0.1363	7.568	0.9583	0.8518
50	2.403	16.60	0.9561	0.9768
60	5.738	26.63	0.9516	0.9872
70	10.29	37.13	0.9210	0.9979
80	10.88	38.70	0.9430	0.9900

It is important to note from Table 4, that, the highest correlation coefficient was obtained for k_2 for temperatures 50°C to 80°C, calculated from the slopes of straight lines in Fig. 3B. For temperatures 27°C and 40°C, the correlation coefficient was higher for k_1, calculated from the slopes of straight lines from Fig. 3A. Thus, the apparent rate constants, k_2, obtained from the slopes of model fitting lines in Fig. 3B (excluding 27°C and 40°C) were then used in plotting the Arrhenius graph shown in Fig. 4, from which the activation energy, E_a of 44.13 kJ/mol was derived. This trend shows that the reaction is diffusion controlled at lower temperatures due to the low diffusivity value of the product ions. With rise in temperature, the diffusivity increases, and hence increasing the rate of diffusion and shifting the reaction to chemical reaction controlled mechanism [20].
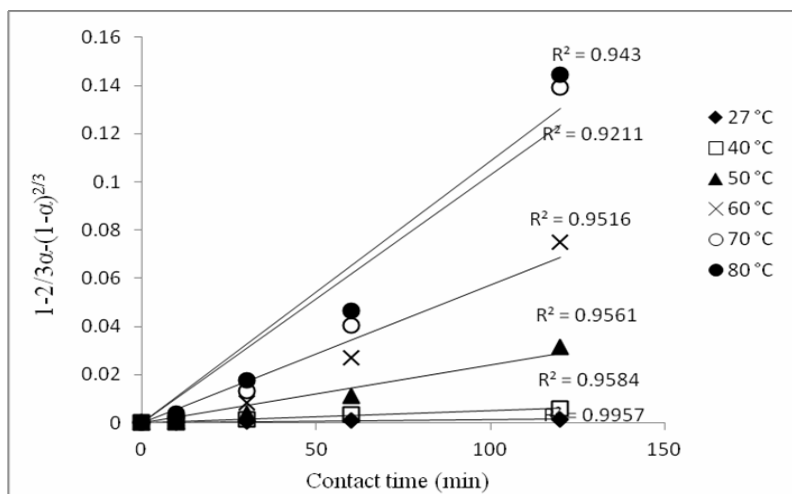
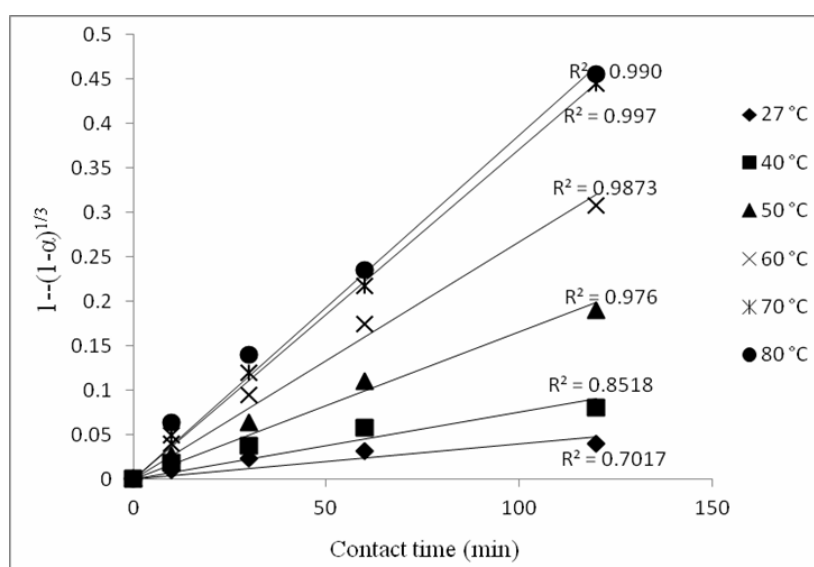**Fig. 3A.** The variation of $1-2/3\alpha-(1-\alpha)^{2/3}$ with contact time at various temperatures.

Fig. 3B. The variation of $1-(1-\alpha)^{1/3}$ with contact time at various temperatures. *Experimental conditions*: - Same as in Fig. 2.

It is seen from Fig. 5 that the plots for effect of concentration followed diffusion controlled since it was carried out at a low temperature. The experimental rate constants, k_1, for the leaching system were calculated from the slopes of the graph (Fig. 5) which is a linearized form of Fig. 1. The plot of $\ln k_1$ vs. $\ln[\text{HCl}]$ was made in Fig. 6. The slope of the resulting plot is 1.14 ~ 1. Thus, the reaction order for the dissolution with respect to HCl concentration ≤ 4 M is assumed to be first order kinetics.
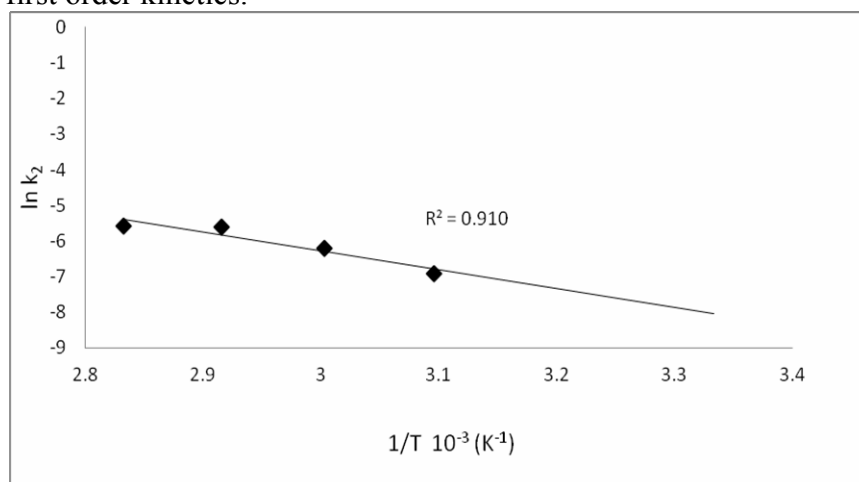
Fig. 4. Arrhenius plot of data extracted from Fig. 3. Experimental conditions: - Same as in Fig. 3.
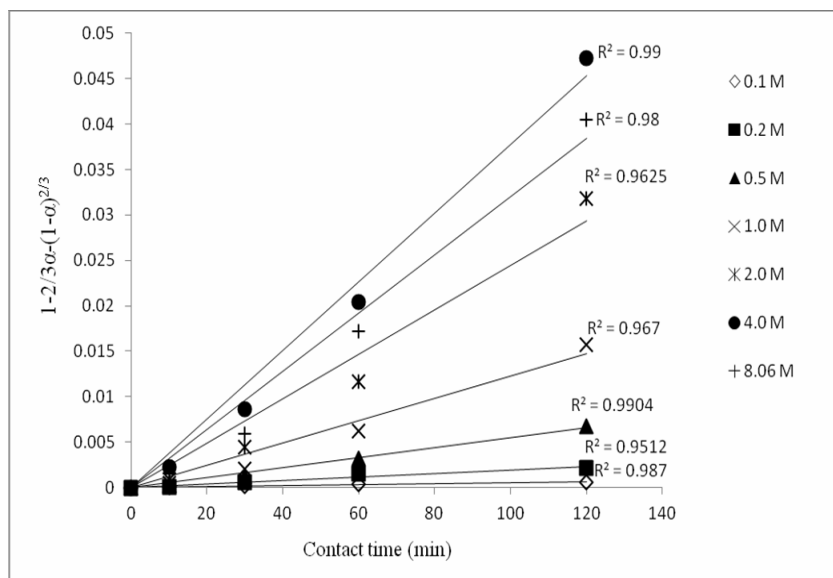

Fig. 5. Variation of $1-2/3\alpha-(1-\alpha)^{2/3}$ with contact time at various HCl concentrations. Experimental conditions: - Same as in Fig. 1.
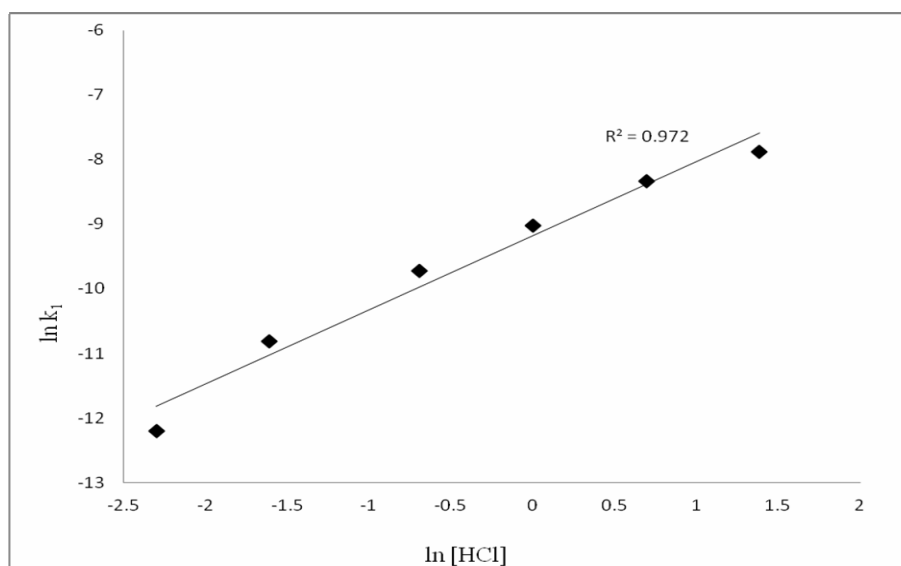

Fig. 6. Plot of ln k1 vs. ln [HCl], from the data extracted in Fig. 5.

3.3.2 Analysis of residual product

The analysis of the residual product after optimal leaching of 10g/L of spent battery ash in 4M HCl solution at 80 °C by XRD is summarized in Table 5.

Table 5
X-ray diffraction analysis of the residual product

2θ	Lattice planes			Compounds	JCPDS File No.
	h	k	l		
20.8614	-1	1	1	SiO_2 (cristobalite)	02-0471
26.6423	1	0	1	α-SiO_2 (α-quartz)	46-1045
38.4113	-2	0	2	SiO_2 (cristobalite)	02-0471

It is evident from Table 5 that the analysis of the residual product by XRD revealed the presence of silica (α – quartz and cristobalite). There is, however, no trace of lead in the residual products.

4. Conclusions

The result of this study showed that dissolution kinetics of Car battery ash increases with acid concentration, system temperature and with decreasing particle size. The optimum leaching conditions with 10g/L solid/liquid ratio battery ash were evaluated as: 4 M HCl, 80 °C, stirring speed 300 rpm with a particle size of 0.050-0.063 mm. Under these conditions, about 83.8% dissolution efficiency was extracted within 120 minutes of leaching. Activation energy of 44.13 kJ/mol, supporting the proposed reaction controlled mechanism was obtained. Also, the reaction order with respect to H^+ ion concentration was 1.14, suggesting first order reaction kinetics for the dissolution process.

Acknowledgements

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