LEACHING OF LEAD FROM SPENT MOTORCYCLE BATTERY IN HYDROCHLORIC ACID. PART II: SOLVENT EXTRACTION STUDIES

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Abstract

This work, constituting the second part of acid leaching of total Lead studied the extraction efficiency of Pb (II) by solvent extraction techniques by Dithizone in chloroform. The development of simple hydrometallurgical route for possible recovery of total lead from spent motorcycle battery ash leach liquor in hydrochloric acid solution has been investigated using combination of leaching, cementation, precipitation, solvent extraction and stripping techniques. The influence of extractant concentration on lead extraction and the extraction temperature on the total Lead extraction efficiency were examined. An extraction efficiency of 98% total Pb(II) was obtained by 0.01 mol/L Dithizone in chloroform at pH 8.3 from the initial 10g/L motorcycle ash leach liquor containing mainly 763.1 mg/L Pb, 4.3 mg/L Zn (10.7 mg/L after cementation) and 28.8mg/L Fe. Other constituents such as Cu, Mn, Ca and As whose concentrations in each case are less than 2mg/L after leaching, were first separated by cementation with zinc granules, followed by the total Iron removal by precipitating with 4mol/L ammoniacal solution to a pH 3.5 at 25±2 ^{0}C. Stripping of 98% total Pb(II) from dithizone extract by 0.1 mol/L hydrochloric acid solution was achieved. The values of thermodynamic data obtained on total Pb(II) extraction showed that the extraction by 0.01 mol/L Dithizone in chloroform is thermodynamically favourable. Finally, a simple hydrometallurgical scheme for the operational procedures for the extraction of total Pb(II) from the spent motorcycle ash liquor was presented.

Keywords: Lead (II), Solvent extraction, Spent batteries, Dithizone, Hydrochloric acid

1 Introduction

Over 60% of the world's output of lead is consumed in the manufacture of lead – acid storage batteries, most of which are used in the transportation industry. Growth in electric vehicle demand, coupled with restrictions on lead usage elsewhere, will likely result in a greater fraction of the world's lead output being used lead–acid batteries including motorcycle batteries are readily collected and recycled and, consequently, they are the major feed to the large secondary lead industry. In fact, about half of the world's annual lead output of around 5 million tones originated from secondary sources. In the United States for example, over 70% of the total lead consumed is from secondary materials, mostly from lead acid batteries [1]. In the recent years,

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more than 95% of scrap lead –acid batteries are recycled in Europe, North America and Japan and continue to increase in other parts of the world [1, 2].

Nowadays, recycling rates for metals are growing in many developed countries. In the 1980s, the lead, zinc and tin industries were in a crisis caused by stagnation of the market, and secondary raw materials from lead batteries, zinc plant leach operations and steel plant dusts were accumulated as observed by Engh [3], who proposed an increasing in metal recovery from scrap and wastes. Spent motorcycle batteries could be one of the secondary sources of metals, and thus, the recycling of these wastes could offer economic benefits through the recovery of the valuable materials, as well as the preservation of raw materials in the interest of the sustainable development [4].

It is important to note from the directives published in many countries, that, the adequate destination of spent batteries may involve techniques such as landfill disposition, stabilization, incineration and/or recycling processes [5]. Of these techniques, recycling appears as the most adequate destination of this type of waste, since it may contribute to the benefit of future generations and to the preservation of raw materials [6, 7]. A good number of processing techniques to treat and recycle metals through chloride leaching have been achieved by hydrometallurgical methods [8, 9] due to higher dissolution rate, low price of leaching reagents and non-pollution character. Also, the use of hydrometallurgical techniques is becoming more attractive, since the need of high energy requirements or eventual gas collectors and cleaning systems always necessary in the pyrometallurgical processes are avoided [10-12]. Therefore, the present study which constitutes the second part was focused on the extraction and separation of lead (II) from associated impurities such as iron, zinc and manganese, etc present in spent motorcycle leach liquor by Dithizone in chloroform. The high level of poverty in some developing countries, especially in sub-saharan Africa has steadily increase motorcycle consumption due to its commercial usage, which if not under control can constitute nuisance to the society [13]. Thus, because of increasing battery consumption per capital, metal recovery from spent batteries is convenient for economic reasons, since large amounts of solid waste can be reused as secondary raw material [16]. The first part of this study reported detailed characterization of the spent material including dissolution kinetics data by hydrochloric acid leaching and had earlier been published [13].

2 Experimental Material and Methods

2.1 Experimental Material

The leachate obtained from the leaching of 10g/L spent motorcycle battery ash per litre of 8.42mol/L solution at 353K for 120 minutes was used for the systematic study of extraction and separation of total Pb(II) from other impurities [13]. The leachate has the following major constituents at pH 1: Pb(II) = 763.1mg/L, Zn(II) = 4.3mg/L and Fe = 28.8mg/L. The concentration of other metal ions including Cu, Mn, Ca and As are less than 2mg/L after leaching, before cementation and iron precipitation.

2.2 Chromogenic reagents and analytical method

A stock standard solution of lead (1000 mg/L) was prepared from $Pb(NO_3)_2$, from which solutions of different molarities were prepared for experimental purpose. A calibration curve was plotted by taking different concentration of lead. Predetermined amount of dithizone solutions in chloroform were prepared. Ammoniacal solution of potassium cyanide was prepared by dissolving in 25% NH_4OH solution. Other reagents such as sodium tartrate, ammonia, HNO_3 and Hydroxylamine hydrochloride used in this study were supplied by BDH and Merck. All chemicals used were of analytical grade and were used without further purification [14]. The AQUAMATE Thermo-Electron Corporation UV-Visible spectrophotometer together with EPSON LQ 2070 recorder was used for the analysis.

2.3 Extraction procedure

25ml leach liquor obtained after total iron removal was put in the separating funnel to which 10ml of 10% sodium tartrate and 2ml of 5% ammonia solutions were added. The pH of the solution was 3.1 and was adjusted to 8.3 by addition of a very small amount of dilute NaOH or H_2SO_4 solution under agitation to prevent precipitation of elemental sulphur [17]. From this mixture, total lead was extracted by adding consecutively 5 ml portions of extraction solution until dithizone became green after extraction. The equilibration was achieved within 5 minutes. The chloroform extracts collected in another separating funnel were acidified with HNO_3 and the chloroform layer was removed after shaking for one minute. Then 5ml 20% hydroxylamine hydrochloride, 5ml ammoniacal solution of potassium cyanide were added to the raffinate and it was equilibrated with 10ml extraction solution and shaking at room temperature of 298±2K. {*Hint*: In slightly alkaline medium, dithizone (diphenyl thiocarbazone) forms with lead(II) ions a red-pink lead (II) dithizonate, soluble in chloroform and other non polar solvents over ph range of 7-10. The basic masking agents are cyanides which form stable complexes with Ag, Hg, Cu, Zn, Cd, Ni and Co, thus preventing their reactions with dithizone. Therefore, the precipitation of readily hydrolyzing metals is prevented during addition of tartarate into the solution. Thus, addition of hydroxylamine also provides a reducing medium because dithizone is easily oxidized} [14]. After equilibration and phase separation, the concentration of metal ion in the organic phase was calculated from the difference between its concentration in the aqueous phase before and after extraction [14, 15]. The absorbance at λ_{max}= 523nm was measured by means of AQUAMATE Thermo-Electron Corporation UV-Visible spectrophotometer and the corresponding total Pb(II) concentration was calculated from the established calibration curve, with regression equation: $y = 0.0068x - 0.0013$ (mg/L), $R^2 = 0.9998$ (where x = absorbance reading). The effect of temperature on lead extraction at a fixed dithizone concentration was examined to evaluate the thermodynamic of extraction.

3 Results and Discussion

3.1 Effect of extractant concentration on initial Lead extraction

The effect of the extractant concentration on the extraction efficiency of Pb(II) from synthetic solution is reported in **Fig. 1.** It is evident from Fig. 1 that an increase in the extractant concentration (Dithizone in chloroform) gave rise to increased Pb(II) extraction. This may be due probably to the increasing ratio of extractant to the Pb(II) concentration. However, maximum extraction of Pb(II) by Dithizone was recorded at Dithizone concentration of 0.01mol/L and was kept for use in subsequent investigations. Therefore, it is important to note that increase in the initial Dithizone concentration in the organic phase considerably improves the extraction which reaches 78.24% by 0.010 mol/L Dithizone in chloroform.

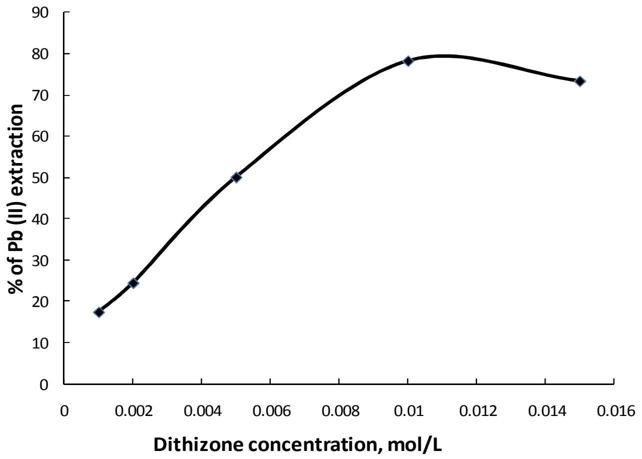

Fig. 1 Plot of % Pb(II) extraction vs. Dithizone concentration, mol/L.

3.2 Total Pb(II) extraction from battery ash liquor

3.2.1 Total iron removal from battery ash leach liquor

The total iron was firstly removed by precipitation using 4 mol/L ammoniacal solution at pH 3.5 [12, 15]. The result of this investigation is presented in **Table 1.**

Table 1 Total iron removal by 4 mol/L ammoniacal solution at pH 3.5

Metal ion	Concentration of total iron before removal (mg/L)	Concentration of total iron after removal (mg/L)	pH before Iron removal	pH after Iron removal
Total Pb(II)	763.11	755.94		
Total iron	28.87	0.033	3.5	2.4
Total zinc	10.7	0.11		

Experimental conditions: pH = 3.5, Temperature = 298±2K. Aeration was done in open container for 25min.

The result from **Table 1** showed that total iron extraction efficiency was 99.9%.

3.2.2 Extraction of total Pb(II) by 0.01mol/L Dithizone in chloroform.

The result of the total Pb (II) extraction by 0.01mol/L Dithizone in chloroform for two- stage extraction is presented in **Table 2.**

Table 2 Result of solvent extraction of total Pb(II) from spent leach liquor after iron separation by 0.01mol/L Dithizone in chloroform

Initial Pb(II) Concentration before extraction (mg/L)	Amount of total Pb(II) extracted into organic phase (mg/L)	Amount of total Pb(II) left un-extracted in aqueous phase	% extracted into organic phase.
755.94	743.72	12.22	98.38%

The result from Table 2 showed that the solvent extraction efficiency by 0.01mol/L Dithizone in chloroform was 98.38%.

3.2.3 Stripping of total Pb(II) from the Dithizone extract by 0.1mol/L HCl

The result obtained for the stripping of total Pb (II) from Dithizone organic phase by 0.1 mol/L in a single stage process is summarized in **Table 3.**

Table 3 Stripping of total Pb(II) from Dithizone organic phase by 0.1mol/L

Concentration of total Pb(II) before stripping mol/L	Concentration of total Pb(II) in aqueous phase after stripping mg/L	% total Pb(II) extracted
743.72	729.84	98.13%

From the result in Table 3, it is evident that the percentage of total Pb(II) stripped from the organic phase was 98.13%.

3.3 Thermodynamic of extraction of Pb(II) by Dithizone

The effect of temperature on total Pb(II) extraction by Dithizone in chloroform was studied. It is evident from Table 4 that increase in temperature leads to a decrease in the total Pb(II) extraction efficiency, thus lowering the equilibrium constant. The relation:

$$\Delta G = -RT\ln K \tag{1.}$$

was used in the determination of the values of the free energy change as a function of the system temperatures **(Table 4)**.

Table 4 Thermodynamic extraction data for total Pb(II) extracted by 0.01mol/L Dithizone in chloroform at different temperatures

Temperature (K)	300	308	313	318	323
Total Pb(II) extraction (%)	98.38	81.33	81.04	73.29	65.21
$K \times 10^4$	0.208	0.166	0.129	0.097	0.071
ΔG^0 (kJ/mol)	-19.06	-18.99	-18.64	-18.18	-17.63

The equilibrium constant, *K* in relation (1) is proportional to temperature coefficient extractability expressed in terms of reacting species consistent with the following relation:

$$Mn^{+}_{aq} + \mathrm{nHL}_{org} \rightleftharpoons \mathrm{MLn}_{org} + \mathrm{nH}^{+}_{aq} \tag{2.}$$

The extractant (dithizone in chloroform) = HL, reacts with a metal ion, M^{n+} in aqueous solution to form a product, MLn [15,17]

The free energy change, ΔG is related to the entropy change, ΔS and enthalpy change, ΔH of the spent motorcycle battery ash extraction process by the following relation:

$$\Delta G = \Delta H - T\Delta S \tag{3.}$$

Thus, the graphical representation of this relation, representing the relationship between ΔG, ΔH, ΔS and the system temperature, T is presented in **Fig. 2**.

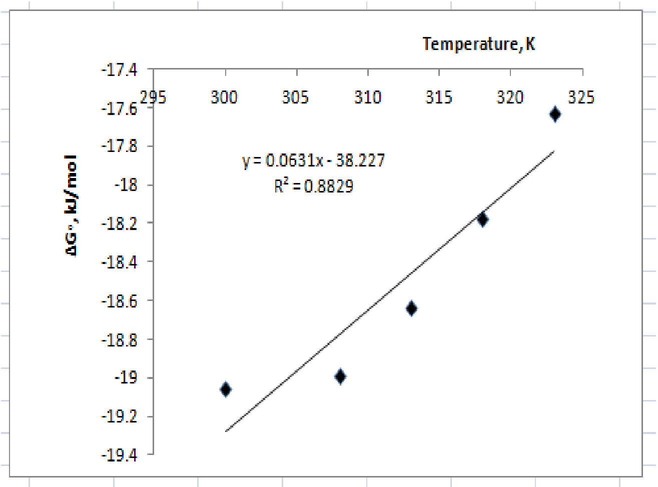

Fig. 2 Thermodynamic relation between change in free energy and the system temperature

From **Fig. 2**, a straight line with correlation coefficient of 0.883 was obtained. The slope of the line is positive (ΔG□0). From this positive slope, ΔG = - ΔS and -63.1JK^{-1} represents the entropy change of the extraction. From equation (3), the enthalpy change for the extraction process at 300K is evaluated as -37.9 kJ/mol. These values suggest that the extraction of total Pb(II) by 0.01mol/L Dithizone occurred by exothermic pathway and this is consistent with some reported literature values [18].

3.4 Hydrometallurgical flow chart for total Pb(II) recovery

A hydrometallurgical flow diagram summarizing the procedures for the quantitative extraction of total Pb(II) from leaching of 10g/L spent motorcycle battery in 8.42 mol/L HCl solution at 353K is presented in **Fig. 3.**

4 Conclusion

Based on the experimental results, the following conclusions can be drawn:

1. The results of solvent extraction of Pb(II) by dithizone in chloroform showed that an increase in the initial dithizone concentration in the organic phase considerably improves the extraction which reaches 78.24% by 0.010mol/L dithizone.
2. Liquid-liquid extraction of total lead(II) using Dithizone in chloroform has the possibility of extracting lead(II) from motorcycle battery ash leachate. For the established optimal conditions, about 98.4% of the total Pb(II) was extracted into the organic phase by 0.01mol/L dithizone in chloroform. Stripping efficiency of 98.1% of total Pb(II) was also achieved by 0.1mol/L HCl solution from the organic phase.
3. Thermodynamic investigations on total Pb(II) extraction by 0.01mol/L dithizone in chloroform showed that the extraction is thermodynamically favourable. At 300K, about 19.06kJ/mol, -37.9kJ/mol and -63.1J/K was recorded for the system free energy, enthalpy and entropy changes, respectively.

4. A practicable, operational hydrometallurgical flow chart for total Pb(II) extraction by dithizone in chloroform for the treatment of spent motorcycle battery ash by acid leaching was presented.

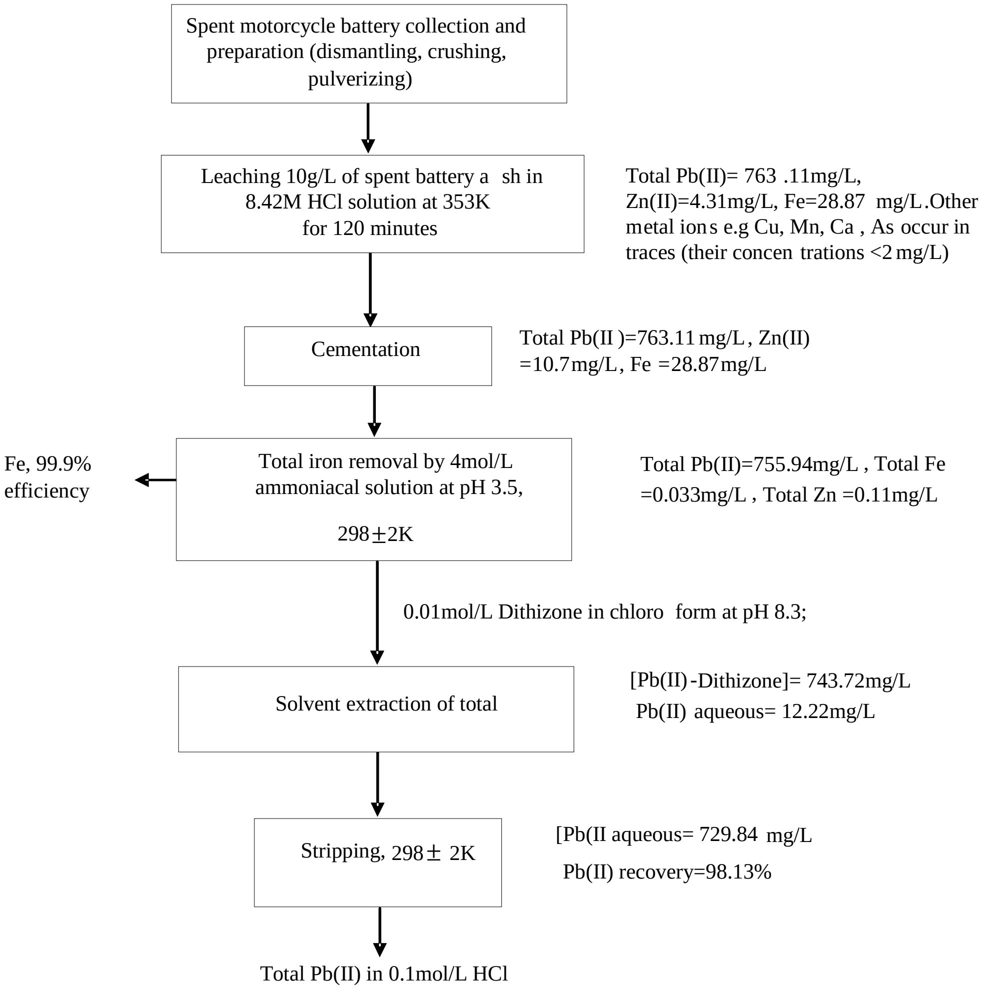

Fig. 3 Operational hydrometallurgical flow chart for total Pb(II) extraction from spent motorcycle battery ash liquor

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