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Selective extraction and separation of metal values from leach liquor of mixed spent Li-ion batteries

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ABSTRACT

This work describes the extraction and separation of Mn(II), Co(II), Ni(II) and Li(I) from the leach liquor of mixed lithium ion batteries using 0.04 M Na-CYANEX272. Before the extraction step, elimination of some impurities such as Fe(III), Cu(II) and Al (III) was carried out by 20% Acorga M5640 in kerosene with agitation for 5 min at 30 °C at equal phase ratio of unity. The effects of the different parameters affecting the extraction rate, such as mixing time, pH, extractant concentration and temperature, were separately investigated. The obtained results indicate that the extraction behavior of the investigated metal ions depends on the pH value, where 91.2% Mn(II), 89.3% Co(II) and 95.6% Ni(II) were extracted at pH 3.5, 5.0 and 8.0, respectively, while the extraction of Li(I) was almost constant regardless of the pH value. Mn(II), Co(II) and Ni(II) were extracted in the organic phase as $(MA_2{\bullet}3HA)_{(org)}$ while Li(I) was extracted as $(MA{\bullet}2HA)_{(org)}$. The thermodynamic parameters were calculated by applying Van't Hoff equations. A complete stripping and precipitation from the organic and aqueous phases could be achieved with different stripping and precipitating agents. Precipitates of Mn(II), Co(II), Ni(II) and Li(I) with purity $>$ 99% could be obtained under the investigated conditions.

1. Introduction

In the last few years, production of lithium-ion batteries (LIBs), which is regarded as a type of rechargeable battery, is increasing due to its demand for use in different types of portable electronic devices such as cellular phones, laptop computer [1,2]. The consumption of LIBs and the amount of spent batteries waste has grown rapidly worldwide owing to the wide applications of these batteries [3]. Spent LIBs contain hazardous materials and some metal values of strategic and industrial importance such as manganese, lithium, cobalt, nickel, copper, *etc*. which can used in different strategic fields such as nuclear field. Therefore, recycling processes have received a great deal of attention and have become highly desirable from the viewpoints of environmental preservation and economic benefits [4,5].

Recently, many investigations have been reported for treatment and recycling of the spent LIBs waste following pyrometallurgy, hydrometallurgy or bio-hydrometallurgy processes [6]. Generally, cathodic active materials of LIBs contain $LiCoO_2$, $LiMn_xO_y$ and $LiMPO_4$ (M = Fe, Mn) [7]; the spent LIBs contain 5–15 wt.% cobalt and 2–7 wt.% lithium and other important metals [8]. Therefore, the recovery of such constituents is one of the primary objectives in the recycling processes of these spent batteries [8].

Several studies have been reported to develop hydrometallurgical processes to leach and recover the metals from spent LIBs materials by H_2SO_4 and H_2O_2 [4,9,10]. The leach liquor usually contains different metal ions such as Al(III), Ni(II), Fe(III), Co(II), Mn(II), Cu(II), Li(I), *etc*. [4,9–11]. Compared with raw and natural sources of metals, such leach liquor wastes have high content of various metal ions. Many purification methods for the recovery and separation of these metal ions from leach solution, such as solvent extraction (SX), ion exchange, and precipitation has been studied and tested [12]. Solvent extraction and precipitation methods were found as effective separation techniques proposed to treat leach liquor solutions by commercial extractants such as CYANEX 272(*bis* (2,4,4-trimethylpentyl) phosphinic acid), D2EHPA (*bis* (2-etylhexyl) phosphoric acid), Acorga M5640 and PC-88A or precipitating agents such as NH_4OH, citric acid and ammonium oxalate [13].

Literature review reveals that the solvent extraction technique has received more attention and seems to be the most effective one used for the extraction and separation of various metals from their aqueous media and from different types of wastes (*i.e.* electronic devices, spent catalysts, spent batteries and other wastes) [13–15]. Separation of metals from waste LIBs by leaching followed by precipitation and solvent extraction has been reported using different cationic extractants such as PC-88A, HDEHP, CYANEX 272, or CYANEX 302 [8,16–18].

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The extraction behavior of some metals such as Fe(II,III), Mn(II), Co(II), Ni(II), Cu(II), Cd(II), and Zn(II) from sulfate solution was carried out using CYANEX 272, CYANEX 302 and CYANEX 301 [19–22]. Provazi, et al. [19] reported that, the liquid–liquid extraction using CYANEX 272 seemed to be more efficient in the selective separation of different metals from leach liquor solution than selective precipitation. CYANEX 272 has good separation ability for many metal ions from acidic media compared with other acidic extractants.

Recently, due to the high selectivity of CYANEX 272, various studies on the extraction and separation of different metals ions from both synthetic solutions and leach liquor of cathodic waste material using this extractant have been reported [7,8,10,19,23].

As reported in the literature, Acorga M5640 is a combination of 5-nonylsalicylaldoxime (active substance) and a fatty ester, 2,4,4-trimethyl-1,3-pentanediol diisobutyrate (modifier). The key advantage of Acorga M5640 is that it is a very selective extractant for some cations and contaminants such as Cu(II), Fe(II, III) and Al(III) from acidic sulfate solutions which contain (Co(II) Ni(II), Zn(II), Mn(II), Cd(II), Mg(II)) at specific low pH values [24].

In the present work, the main objective is directed to extract and separate Mn(II), Co(II), Ni(II) and Li(I) from the leach liquor of spent LIBs. In this context, liquid–liquid extraction using Acorga M5640 (to remove some impurities) and CYANEX 272 in kerosene is carried out. The effects of the different parameters affecting the extraction efficiency of these metals such as mixing time, pH, extractant concentration, and temperature are separately investigated. Thermodynamic parameters depending on the behavior of the investigated metal ions are calculated. Scrubbing and stripping processes are studied to separate the metal ions in a pure form. Precipitation of Mn(II), Co(II), Ni(II) and Li(I) from both stripping and leach liquor was also carried out to obtain these metal ions in a pure form.

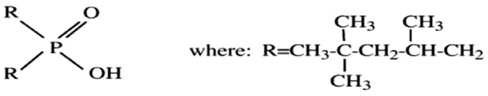
2. Experimental

2.1. Chemicals and reagents

All chemicals and reagents used in this work were of analytical reagents (AR) grade. Double distilled water was used throughout the experiments. H_2SO_4, HCl, Na_2CO_3 and NaOH were obtained from BDH while odorless kerosene (non-aromatic) was supplied by Misr Petroleum Ltd Company, Egypt.

Acorga M5640 (5-nonylsalicylaldoxime modified with TXIB /2,2,4-trimethyl-1,3 pentanediol di-isobutyrate) was manufactured by Cytec Canada Inc., and CYANEX 272 (*bis*(2,4,4-trimethylpentyl) phosphinic acid) was kindly supplied by Cyanamid Canada, Inc. They were used as received without any further purification, unless otherwise stated.

The commercial extractant (CYANEX 272) has the following structure [25]:



The sodium salt of CYANEX 272 was prepared by adding a stoichiometric amount (at organic/aqueous ratio equals unity) of concentrated and standard NaOH solution to change CYANEX 272 into its sodium salt (Na-CYANEX 272). The phases were stirred to form a single phase, followed by careful washing several times by distilled water and ethyl alcohol. The neutralization degree of the extractant was calculated from the mass balance of OH^- determined before and after the neutralization process and was equal to about 65%. The extent of neutralization was limited due to polymerization of the organic phase.

As reported by Sarangi et al. [26], the partial neutralization reaction can be shown as:

$$Na^+_{(aq)} + 1/2\,(HA)_{2(org)} \rightarrow NaA_{(org)} + H^+_{(aq)} \tag{1}$$

where, the acidic form of the extractant CYANEX 272 exists as dimer while its saponified form exists as monomer [26,27].

Then, these organic solutions were diluted with kerosene as required.

2.2. Extraction mechanism

The mechanism by which a divalent metal ion is extracted from an aqueous phase by using the sodium salt of CYANEX 272 (which is regarded as cation exchange extractant) is as follows [8]:

$$M^{2+}{}_{(aq)} + A^-{}_{(org)} + 2(HA)_{2(org)} \Leftrightarrow (MA_2 \cdot 3HA)_{(org)} + H^+{}_{(aq)} \tag{2}$$

The equilibrium constant, K_{ex} of the extraction reaction can be written as

$$K_{ex} = \frac{[(MA_2.3HA]_{(org)}[H^+]_{(aq)}}{[M^{2+}]_{(aq)}[A^-]_{(org)}[(HA)_2]^2_{(org)}} \tag{3}$$

$$K_{ex} = \frac{D_{ex}[H^+]_{(aq)}}{[A^-]_{(org)}[(HA)_2]^2_{(org)}} \tag{4}$$

where the distribution ratio, D_{ex}, was calculated from the relation:

$$D_{ex} = \frac{[(MA_2.3HA]_{(org)}}{[M^{2+}]_{(aq)}} \tag{5}$$

Then, by taking logarithms on both sides and re-arranging Eq. (4) the following equation can be derived:

$$\log D_{ex} = \log K_{ex} + \mathrm{pH} + \log\,[A^-]_{(org)} + 2\log\,[(HA)_2]_{(org)} \tag{6}$$

where $\mathrm{pH} = -\log\,[H^+]$

While in case of monovalent metal ions, the mechanism of the extraction process from an aqueous phase by using Na-CYANEX 272 can be proposed as;

$$M^+{}_{(aq)} + A^-{}_{(org)} + (HA)_{2(org)} \Leftrightarrow (MA \cdot 2HA)_{(org)} \tag{7}$$

The equilibrium constant, K_{ex} of the extraction reaction can be rewritten as:

$$K_{ex} = \frac{D_{ex}}{[A^-]_{(org)}[(HA)_2]_{(org)}} \tag{8}$$

Then, by taking logarithms on both sides and re-arranging Eq. (8) the following equation can be derived:

$$\log D_{ex} = \log K_{ex} + \log\,[A^-]_{(org)} + \log\,[(HA)_2]_{(org)} \tag{9}$$

2.3. Samples and leaching procedure

As reported by Nayl et al. [9], nine types of spent LIBs were used in this study. The resulted active components of all samples were mixed and dismantled. Once dismantled, the anodes and cathodes were crushed carefully and sieved [9]. The black powder was then collected and washed with water to remove entrained electrolyte. The resulted powder (carbon corresponds to 16–18 wt.% of the overall sample) was dried for 24 h at 60 °C. The resulted powder was analyzed by X-ray fluorescence (XRF spectrometer, Asios, Sequential WD–XRF spectrometer, PANalytical 2005) at National Research Centre, Egypt and the results are given in Table 1. Lithium concentration was analyzed by ICP-OES (Perkin Elmer Optima 2000 DV) at the Central Metallurgy R&D Institute, Helwan, Egypt [9]. The particles finer than 0.5 mm (gives better recovery efficiency) was treated with NH_4OH and the resulted residue (alkali paste) was washed by double distilled water and dried at 80 °C for 24 h. In the decomposition process, 97.8% Al and 64.7% Cu have been leached by using 4.0 M NH_4OH with an L/S mass ratio of 15/1 at 60 °C for 60 min. About 97.8% Mn, 99.4% Ni, 99.6% Co and 98.8% Li have then been leached from the alkali residue of spent LIBs using 2.0 M H_2SO_4 with 4.0% H_2O_2 for 120 min