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Short communication

A study of the separation of cobalt from spent Li-ion battery residues

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Abstract

Separation of the main metals contained in spent Li-ion batteries has been investigated using a treatment route consisting of the following steps: manual dismantling, acid leaching, precipitation with NH_4OH and liquid–liquid extraction using Cyanex 272 [bis(2,4,4-trimethylpentyl) phosphinic acid] as the extractant agent. Aluminium, cobalt, lead and lithium were the main metal species identified in the residue. Lead was found solely in the anode of the battery, so this metal can be separated manually from the other metal species, which were found to predominate in the cathode. The following operational variables were investigated in the acid leaching step: temperature, solid/liquid ratio, H_2SO_4 concentration and H_2O_2 concentration which was used as the oxidizing agent. Around 55% of aluminium, 80% of cobalt and 95% of lithium were leached from the cathode when leaching solutions with H_2O_2 were carried out. In the precipitation step, NH_4OH was added to the leach liquor to raise the pH and aluminium was partially separated from cobalt and lithium at pH 5. After filtration, the aqueous solution was submitted to a purification step by liquid–liquid extraction with Cyanex 272 and around 85% of cobalt was separated.
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Keywords: Spent batteries; Li-ion batteries; Leaching; Liquid–liquid extraction

1. Introduction

The mobile phone is one of the most commonly used pieces of electronic equipment today. In the UK, the number of cell phones has surpassed the number of habitants. There will be over 400 million cell phone users in China by 2008. The total number of mobile phone subscribers in the world was estimated at 2.14 billion in 2005. Nowadays, there are around 100 million mobile phones in Brazil according to the National Telecommunication Agency [1]. This represents 50% of the Brazilian population, so the market for mobile phones can still grow in this country. Fig. 1 shows the evolution of the number of mobile phones in Brazil during the last 10 years.

The higher the number of mobile phones in use worldwide, the higher the number of spent batteries that must be recycled. Spent batteries should be recycled not only for environmental reasons. This type of residue represents also an important secondary source of metals that can be normally found at very high concentration levels, sometimes even higher than those found in natural ores. In addition, some metals are quite expensive such as cobalt and nickel, for instance. According to Mantuano et al. [2], NiCd batteries contains $2.0 \pm 0.8\%$ (w/w) of cobalt and $22 \pm 14\%$ (w/w) of nickel, NiMH batteries contains $6.1 \pm 0.7\%$ (w/w) of cobalt and $49 \pm 5\%$ (w/w) of nickel and Li-ion batteries may contain $36 \pm 9\%$ (w/w) of cobalt, excluding the plastic and metallic shells. Therefore, recycling of spent batteries may result in economic benefits [3] but it is still necessary to develop an efficient collection system in order to receive the spent batteries consumed around the world.

An overview of the current processes including pyrometallurgical and hydrometallurgical routes for the recycling of portable batteries is shown elsewhere [2,4–6]. In this paper, the process route proposed by Mantuano et al. [2] to treat spent batteries such as zinc-carbon, alkaline, NiCd, NiMH and Li-ion batteries has been investigated. The original route comprises the following main steps: (1) sorting of batteries by type, (2) dismantling of batteries to remove the plastic and metallic shells, (3) leaching with sulfuric acid solutions, and (4) metal separation by liquid–liquid extraction with Cyanex 272 [bis(2,4,4-trimethylpentyl) phosphinic acid] as extractant agent. In this paper, the route was investigated to treat spent Li-ion batteries only. This type of battery has been chosen for the study

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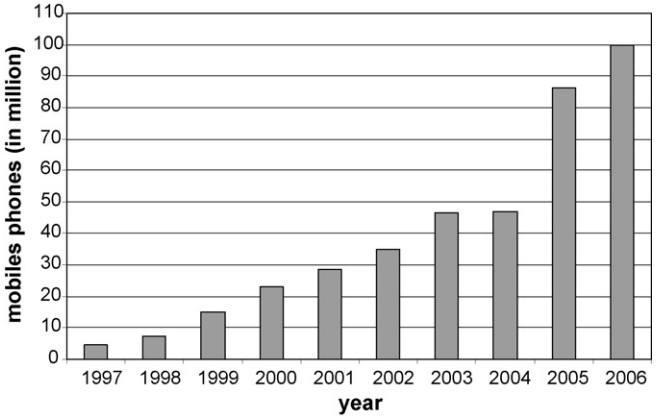

Fig. 1. Evolution of the mobile phone market in Brazil [1].

because NiCd batteries have been progressively replaced by NiMH and Li-ion types in mobile phone applications [7] due to the high toxicity of cadmium. In addition, the price of cobalt is around three times higher than that of nickel and also the concentration of cobalt in Li-ion batteries is higher than found in NiMH.

Li-ion batteries are a type of rechargeable battery commonly used in consumer electronics such as notebook computers, digital cameras and mobile phones. These batteries are made of two thin electrode films; the anode is made of metallic copper and the cathode of metallic aluminium. The cathode film is covered by the active material of the Li-ion battery, thus containing lithium and cobalt as a fine powder of $LiCoO_2$ aggregated with a polymeric binder (polyvinylidene fluoride or PVDF [8]), while the anode is covered by powdered graphite (carbon). These films are rolled up commonly in cylindrical or prismatic shapes. The energy is stored in these batteries through the movement of lithium ions from the cathode to the anode (charge process of the battery) or vice versa (discharge process) according to Eq. (1):

$$LiCoO_2 + C_6 \leftrightarrows Li_{1-x}CoO_2 + Li_xC_6 \quad (1)$$

The leaching of Li-ion batteries has been investigated using H_2SO_4 [2], HCl [9] and HNO_3 [10,11] as leaching agents. Metals were leached according to the following sequence for sulfuric media: aluminium > lithium > cobalt ≫ copper. The leaching of cobalt was found to be very low for economical purposes (around 30%) and it was attributed to the absence of an oxidizing agent like H_2O_2 in the leaching solution. For hydrochloric and nitric media, however, extractions of cobalt and lithium higher than 85% were obtained even at the absence of an oxidizing agent. In the present work, the route proposed by Mantuano et al. [2] has been modified by introducing a selective precipitation step after the leaching step aiming to reduce the concentration of aluminium in the leach liquor to be sent to the liquid–liquid extraction step.

2. Experimental

2.1. Materials

Li-ion batteries from different manufacturers and in different sizes were collected for this study. The leaching solutions used in this work consisted of aqua regia (3:1 HCl:HNO_3 ratio) for characterization studies and sulfuric acid solutions at specified concentrations for battery leaching process studies. Hydrogen peroxide (H_2O_2) was used as oxidizing agent in the sulfuric acid solutions. In the precipitation step, ammonium hydroxide (NH_4OH) was used as precipitating agent. All solutions were prepared in distilled water and all reagents were of analytical grade. For the extraction tests, Cyanex 272 [bis(2,4,4-trimethylpentyl) phosphinic acid, 85 wt.% purity] was used as extractant agent. This reagent was kindly supplied by Cytec Canada and used as received without any further purification. The diluent was kerosene Exxsol D-80 from Exxon (aromatics content 0.1%, w/w). No phase modifier to enhance phase disengagement separation was necessary.

2.2. Dismantling and characterization of the spent Li-ion batteries

Li-ion batteries were dismantled using a manual procedure. The plastic cases of the batteries were firstly removed using a small knife and a screwdriver. Then, in order to remove the metallic shell that covers the battery, it was immersed into liquid nitrogen for 4 min and fixed in a lathe. Such a cryogenic method was adopted for safety precautions. The metallic shell was then cut using a saw; the ends of the metallic shell were removed firstly and a longitudinal cut was done aiming to access the internal material of the battery which was removed using pliers. Anode and cathode were uncurled manually, separated and dried for 24 h at 60 °C. All steps in the experimental procedure were carried out using glasses, gloves and gas masks for safe operation.

In order to characterize the metal content of the Li-ion batteries, dried samples of anode and cathode were submitted to fluorescence for qualitative analysis. The quantitative metal content was assessed by atomic absorption spectrophotometry (GBC 932 plus model) after dissolving samples (anode, cathode and both) in aqua regia.

2.3. Acid leaching tests with H_2SO_4

The leaching of Li-ion batteries was investigated in sulfuric acid media. All tests were carried out using a 1000 ml glass reactor, which was immersed in a bath for temperature control. The reactor was covered to reduce the loss of water by evaporation and the solutions were stirred mechanically at 480 rpm using a glass impeller marine type. Both copper and aluminium dried films were cut into very small pieces using scissors in order to get homogeneous samples of anode and cathode which were leached together and separately. All samples were collected using a Quantachome siewing rifler (model SRR-5 with 8 collecting plates).

In the leaching tests, where the anode and cathode were leached together, the following operational variables were investigated: concentration of H_2SO_4 (2–8%, v/v), solid/liquid ratio (1/10 to 1/50 g ml^{-1}) and temperature (20–80 °C). All tests were carried out using 10 g of battery sample (around 50% of anode and 50% of cathode) and the leaching time was kept constant at

60 min as verified in preliminary experiments to be enough to reach equilibrium. In other sequences of leaching tests, anode and cathode were leached separately using a similar procedure in order to evaluate the effect of H_2O_2 as oxidizing agent (0–4%, v/v). These tests were carried out at fixed conditions of temperature (65 °C), solid/liquid ratio (1/30 g ml^{-1}) and concentration of H_2SO_4 (6%, v/v). At the end of each test, a sample of the aqueous phase was withdrawn and its metal content was assessed by atomic absorption.

2.4. Precipitation tests with NH_4OH

The precipitation tests were carried out using a 1000 ml glass reactor immersed in a bath for temperature control. The leach liquor (250 ml) was placed into the reactor and NH_4OH was added very slowly. NH_4OH was chosen as precipitating agent in order to avoid the addition of other metal into the system. The mixture was stirred mechanically using a glass impeller marine type. The pH of the solution was constantly monitored and tests were done at 50 °C. Samples were withdrawn for a given pH (ranging from 4 to 9), filtered and analyzed by atomic absorption.

2.5. Liquid–liquid extraction tests with Cyanex 272

Extraction and stripping tests were carried out by contacting suitable volumes of aqueous and organic solutions in a cylindrical glass reactor of 400 ml provided with a glass impeller (marine type), a thermometer and a pH electrode (Digimed DM 20). Both phases were stirred at 420 rpm for 20 min (time enough to reach equilibrium as verified in previous studies [2]). The pH was controlled by addition of small quantities of NH_4OH (1, 3, 6 and 12 mol l^{-1}) and H_2SO_4 (12 mol l^{-1}) solutions. After phase separation, the metal concentration in the aqueous phase was analyzed by atomic absorption and the concentrations in the organic phase were determined by mass balance. The extraction tests were carried out at 50 °C and A/O volumetric ratio of unity by contacting the aqueous liquor obtained in the precipitation step with an organic phase consisting of 0.72 mol l^{-1} of Cyanex 272 (monomeric basis) dissolved in diluent Exxsol D-80. For the stripping tests, the metal loaded organic phase was contacted with H_2SO_4 solutions at changing acid concentrations and O/A volumetric ratios as depicted in Table 1, in order to keep constant the ratio between the initial concentration of protons in the aqueous phase and the initial concentration of cobalt in the organic phase.

Table 1
Stripping tests operational conditions (T = 50 °C)

O/A ratio	H_2SO_4 concentration (mol l^{-1})
1	0.5
2	1.0
3	1.5
4	2.0
5	2.5

3. Results and discussion

3.1. Dismantling and characterization of the spent Li-ion batteries

Li-ion batteries from different manufacturers and sizes were dismantled and the following material fractions were found (in wt.%): spent dust to be treated 56.1%, metallic shells 27.7%, plastic cases 9.3%, plastic and others 6.9%. It can be verified that more than 50 wt.% of the spent Li-ion battery residue constitutes the feed to be treated by the hydrometallurgical route investigated in this work.

Table 2 shows the metal content of samples from the spent dust of Li-ion batteries assuming anode and cathode being collected in separate and together. It can be verified that the anode of Li-ion batteries is constituted basically by lead, which is the material from the film as verified elsewhere [8]. Lead was not detected in the cathode. The small fraction of aluminium and cobalt found in the anode might probably be due to some contamination during the manual dismantling operation. According to the fluorescence analysis of the anode, the remaining fraction (around 40–45 wt.%) consists basically of graphite. On the contrary, a significant metal content of aluminium, cobalt and lithium was found in the cathode, these latter possibly in the form of $LiCoO_2$ [11]. The presence of lithium in both electrodes was expected since lithium species move through cathode to anode, and vice versa, during the charge and the discharge processes of this battery, respectively. The metal content determined when anode and cathode were sampled together corroborates previous investigations [2]. Nickel was not found in the Li-ion batteries samples considered in this study.

The results shown in Table 2 points out that lead can be efficiently removed from the residue in the dismantling step if anode and cathode are separated in two distinct fractions. It may require a manual operation process that shows to be advantageous mainly on the regard of cobalt concentration.

3.2. Acid leaching tests with H_2SO_4

Fig. 2 shows the leaching behavior of metals aluminium, cobalt, lead and lithium from Li-ion batteries dust (samples containing anode and cathode) with sulfuric acid at the absence of H_2O_2 as oxidizing agent. The increase on the acid concentration favors the metal leaching due to the increase of reagent in the reactive system. For the operational conditions investigated (T = 65 °C, S/L ratio = 1/30 g ml^{-1}), around 50% of cobalt was

Table 2
Metal composition of the spent dust from Li-ion batteries (in wt.%)

Metal	Anode	Cathode	Anode and cathode
Al	1.93	12.20	8.02
Co	3.22	47.96	29.49
Cu	52.64	n.d.	16.48
Li	0.79	3.14	3.14
Ni	0.03	0.04	0.02

n.d.: not detected.

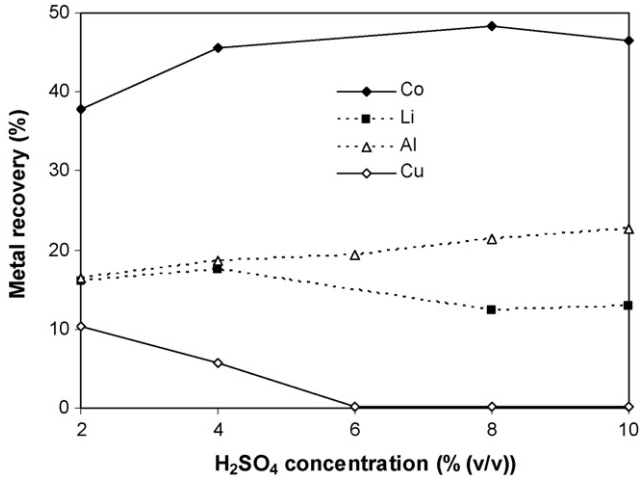

Fig. 2. Effect of H_2SO_4 concentration on the leaching of aluminium, cobalt, lead and lithium from Li-ion battery dust ($T = 65\,^{\circ}C$, S/L ratio = 1/30 g l^{-1}, $t = 60$ min).

leached when leaching solutions containing at least 4% (v/v) of H_2SO_4 was used. The leaching of aluminium, lithium and lead was found to be inferior to 20% and, surprisingly, no lead and a relatively lower leaching of lithium was obtained when the concentration of H_2SO_4 in the leaching solution was 6% (v/v) and higher.

The effect of temperature is shown in Fig. 3 ($H_2SO_4 = 6\%$ (v/v), S/L ratio = 1/30 g ml^{-1}). Again, as verified in Fig. 2, cobalt was leached preferentially from Li-ion batteries dust (samples containing anode and cathode), followed by aluminium, lithium and lead. Excepting for lead, the increase on the temperature favors the metal leaching. For the conditions studied, cobalt leaching has stabilized at temperatures ranging from 65 to 80 °C but leaching of aluminium is considerably higher at 80 °C, so it seems to be advantageous to leach Li-ion batteries at 65 °C (this condition is more selective for cobalt). And again, the leaching of lead has shown an opposite trend, so no lead was leached at temperatures higher than 50 °C.

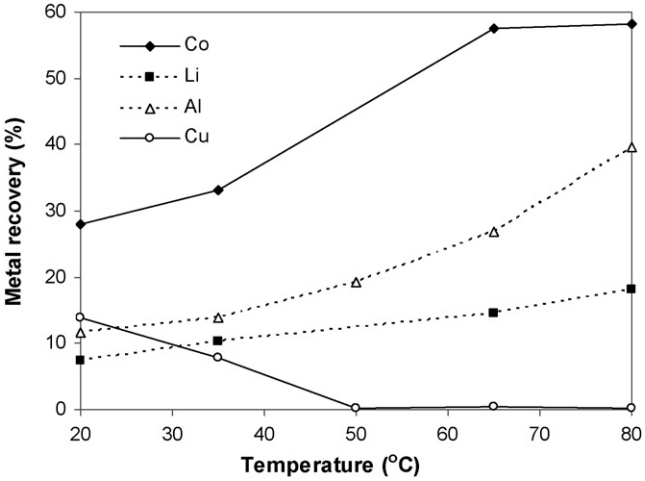

Fig. 3. Effect of temperature on the leaching of aluminium, cobalt, lead and lithium from Li-ion battery dust ($H_2SO_4 = 6\%$ (v/v), S/L ratio = 1/30 g l^{-1}, $t = 60$ min).

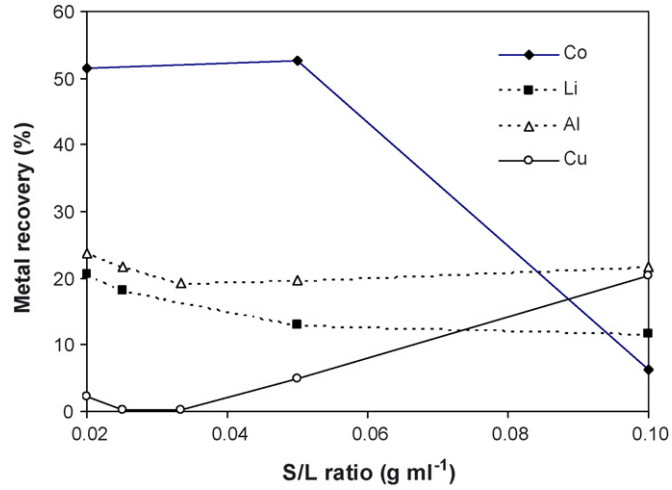

Fig. 4. Effect of S/L ratio on the leaching of aluminium, cobalt, lead and lithium from Li-ion battery dust ($H_2SO_4 = 6\%$ (v/v), $T = 65\,^{\circ}C$, $t = 60$ min).

Fig. 4 shows the effect of the S/L ratio on the leaching of anode and cathode of Li-ion battery dust at 65 °C and H_2SO_4 concentration of 6% (v/v). The increase on the volume of the leaching solution increases the metal leaching due to the higher amount of reagent in the reactive system. Again, a contrary effect was found for the leaching of lead.

From the operational point of view, it seems more interesting to leach the Li-ion battery dust at an S/L ratio of 1/30 g ml^{-1}, temperature of 65 °C and H_2SO_4 concentration of 6% (v/v). So, these conditions were kept constant in order to evaluate the effect of H_2O_2 as oxidizing agent in the leaching of samples of anode and cathode of Li-ion batteries. The results for anode and cathode leaching at changing concentrations of H_2O_2 are summarized in Fig. 5. In general terms, the leaching of lead from the anode, and also of aluminium, cobalt and lithium from the cathode of Li-ion batteries was favored when H_2O_2 was added to the leaching solution; however, no significant effect was verified for the range of H_2O_2 concentration investigated in this study. As verified in Fig. 5, the leaching of lead from the anode sample has

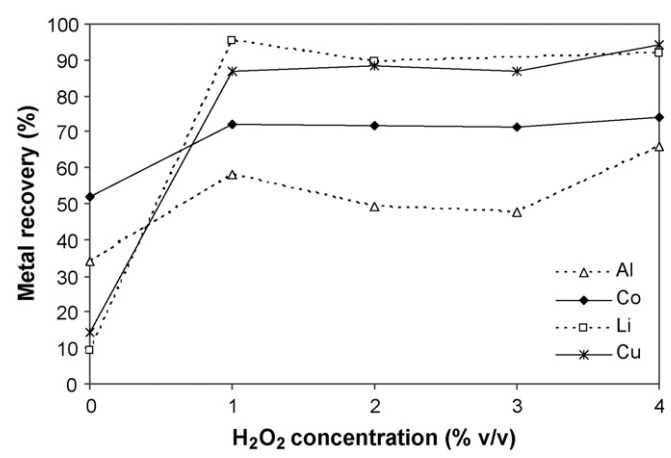

Fig. 5. Effect of H_2O_2 on the leaching of lead from the anode and on the leaching of aluminium, cobalt and lithium from the cathode of Li-ion ($H_2SO_4 = 6\%$ (v/v), S/L = 1/30 g ml^{-1}, $T = 65\,^{\circ}C$, $t = 60$ min).

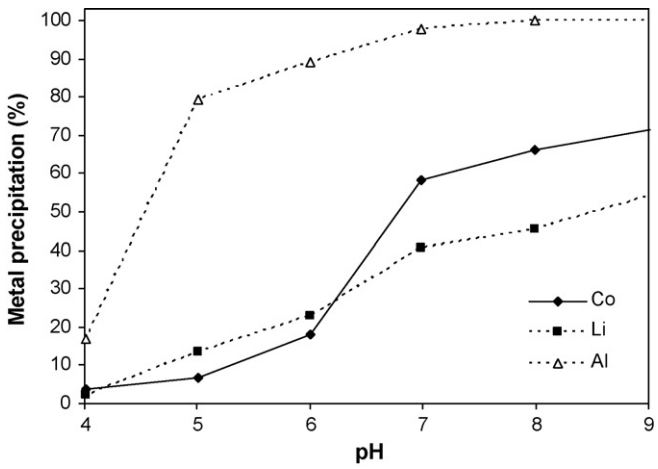

Fig. 6. Precipitation of aluminium, cobalt and lithium with NH_4OH from the leach liquor of Li-ion battery dust ($T = 50\,°C$, initial concentrations: $[Al] = 2.44\,g\,l^{-1}$, $[Co] = 11.48\,g\,l^{-1}$ and $[Li] = 1.01\,g\,l^{-1}$).

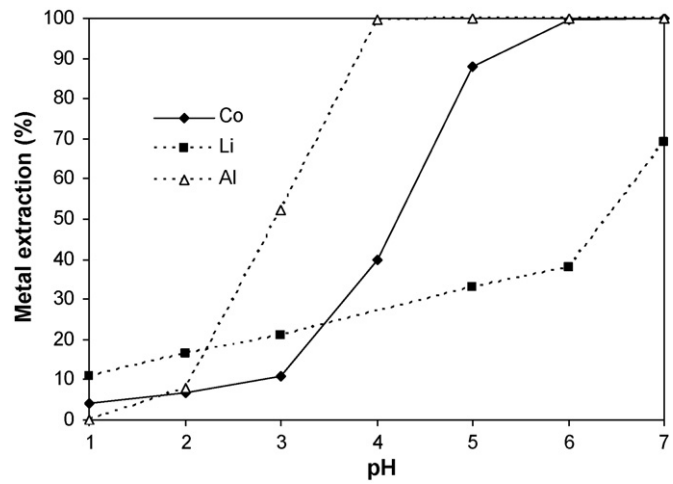

Fig. 7. Extraction of aluminium, cobalt and lithium with Cyanex 272 at changing pH of the aqueous phase (Cyanex 272 concentration = $0.72\,mol\,l^{-1}$, $T = 50\,°C$, A/O ratio = 1).

increased substantially at the presence of H_2O_2 thus reaching around 85–95% independently of the concentration of H_2O_2 range investigated. It probably occurred due to the oxidation of Cu^0 to Cu^{2+} in the presence of peroxide of hydrogen. And, when the cathode samples were leached at oxidizing conditions, around 90–95% of lithium, 70–80% of cobalt and 60–70% of aluminium were dissolved to the aqueous phase independently of the H_2O_2 concentration range investigated in this study.

3.3. Precipitation tests with NH_4OH

The precipitation tests with NH_4OH were carried out using the liquor obtained in the leaching step (S/L ratio of $1/30\,g\,ml^{-1}$, temperature of 65 °C, H_2SO_4 concentration of 6% (v/v) and H_2O_2 concentration of 1.0% (v/v)), which contains $2.44\,g\,l^{-1}$ of aluminium, $11.48\,g\,l^{-1}$ of cobalt and $1.01\,g\,l^{-1}$ of lithium. The presence of aluminium in the leach liquor may hinder the separation of cobalt in the liquid–liquid extraction step with Cyanex 272 because aluminium will be fully extracted with cobalt [2], so it might be advantageous to reduce the concentration of aluminium in the leach solution by precipitation with NH_4OH.

As expected, all metals considered in this study precipitated as hydroxides as long as the pH of the aqueous solution was raised. According to the precipitation curves shown in Fig. 6, at least 80% of the aluminium could be removed from the solution at pH values higher than 5. On the other hand, less than 20% of cobalt would precipitate at pH values lower than 6 but it will increase significantly at $pH \geq 6$ (around 60%). Therefore, the content of aluminium can be significantly reduced in the leach liquor if the pH is raised to pH 5, resulting in an aqueous solution containing around $10.7\,g\,l^{-1}$ of cobalt, $0.5\,g\,l^{-1}$ of aluminium and $0.9\,g\,l^{-1}$ of lithium.

3.4. Liquid–liquid extraction tests with Cyanex 272

Fig. 7 shows the effect of pH on the extraction of aluminium, cobalt and lithium from the leach liquor obtained in the precipitation step. The results indicate that these metals are extracted according to the following sequence using Cyanex 272 as extractant: $Al^{3+} > Co^{2+} > Li^{+}$. The $pH_{1/2}$ values obtained are 3.0 for aluminium, 4.0 for cobalt and 6.5 for lithium. Based on the results shown in Fig. 7, if the liquor is treated at pH 5 (the one that leaves the precipitation step), extraction levels of 100% for aluminium, 88% for cobalt and 33% for lithium can be obtained. The extraction behavior for aluminium and cobalt corroborates previous work [2] but the extraction level of lithium was found too high. In addition, a few number of contact stages will be required to extract cobalt as evidenced by the isotherm of cobalt with Cyanex 272 shown in Fig. 8 with the McCabe-Thiele method.

The stripping of cobalt from the loaded organic phase is shown in Fig. 9. It can be observed that very concentrated aqueous solutions can be achieved, i.e., around $63\,g\,l^{-1}$ of cobalt,

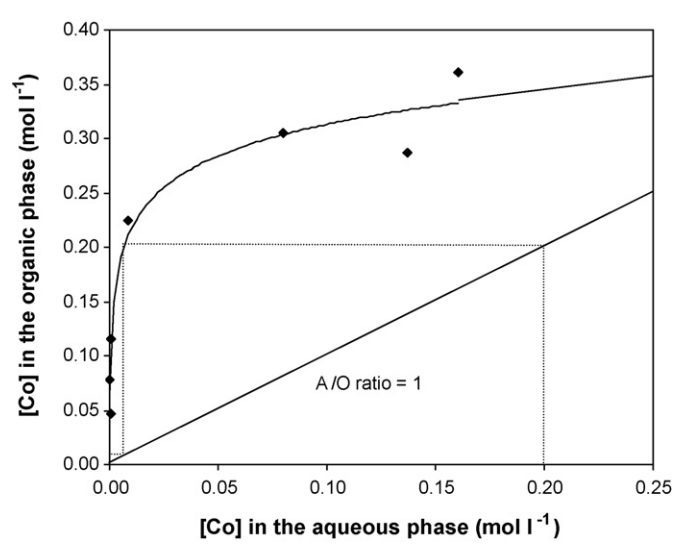

Fig. 8. Equilibrium isotherm for the extraction of cobalt from the leach liquor obtained in the precipitation step ($0.72\,mol\,l^{-1}$ of Cyanex 272, $T = 50\,°C$, pH 5.5, A/O ratio = 1).

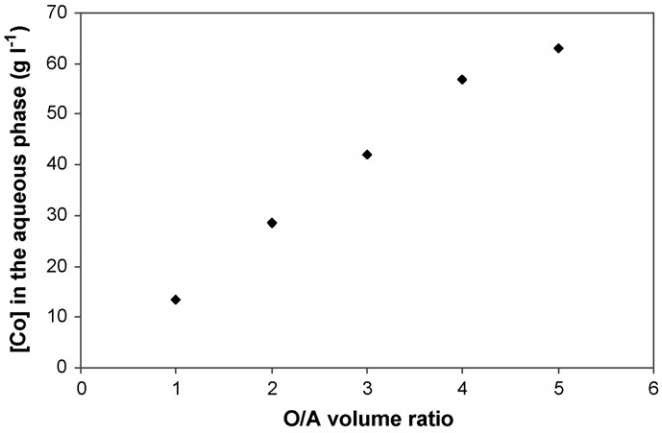

Fig. 9. Stripping of cobalt with H_2SO_4 (0.72 mol l^{-1} of Cyanex 272, $T = 50\,°C$).

0.4 g l^{-1} of aluminium and practically no lithium. Therefore, the process route investigated can separate cobalt efficiently thus resulting in concentrated solutions that might be directly sent to electrowinning.

4. Conclusions

Spent batteries constitute an important secondary raw material for metals such as nickel, cobalt, zinc, cadmium, and many others, with environmental benefits involved. For the case of Li-ion batteries, the recovery of cobalt seems attractive due to the high price of this metal. In the present work, it has been verified that characterization of the metal content of Li-ion batteries has shown that aluminium, cobalt, lead and lithium are the main species to be separated. Cobalt was mainly found in the cathode (around 48 wt.%), which is made of an aluminium film, while lead was found solely in the anode. In this paper, a hydrometallurgical route consisting of the following steps was investigated focusing on the recovery of cobalt from spent Li-ion batteries: (1) manual dismantling, in order to separate iron scraps, plastics and battery dust containing cobalt to be recovered, (2) anode/cathode manual separation, aiming to separate lead from the residue, (3) leaching with sulfuric acid in an oxidizing environment, to transfer metals from the residue to the aqueous solution, (4) precipitation with NH_4OH, to separate aluminium, and (5) liquid–liquid extraction with Cyanex 272, to separate cobalt from lithium resulting in a concentrated metal solution (around 63 g l^{-1} of cobalt) quite adequate for electrowinning. It must be emphasized that these separation steps were investigated using single contacts in batch mode operation, so the process efficiency obtained in this study (around 50% of cobalt was recovered from the battery dust) might increase once optimized.

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References

[1] ANATEL. Agência Nacional de Telecomunicações. http://www.anatel.gov.br (accessed in March 3, 2007).
[2] D.P. Mantuano, G. Dorella, R.C.A. Elias, M.B. Mansur, J. Power Sources 159 (2006) 1510–1518.
[3] B.R. Conard, Hydrometallurgy 30 (1992) 1–28.
[4] A.M. Bernardes, D.C.R. Espinosa, J.A.S. Tenório, J. Power Sources 130 (2004) 291–298.
[5] A.L. Salgado, A.M.O. Veloso, D.D. Pereira, G.S. Gontijo, A. Salum, M.B. Mansur, J. Power Sources 115 (2003) 367–373.
[6] D.C.R. Espinosa, A.M. Bernardes, J.A.S. Tenório, J. Power Sources 135 (2004) 311–319.
[7] C.J. Rydh, B. Svärd, Sci. Total Environ. 302 (2003) 167–184.
[8] M. Contestatible, S. Panero, B. Scrosati, J. Power Sources 92 (2001) 65–69.
[9] P. Zhang, T. Yokoyama, O. Itabashi, T.M. Suzuki, K. Inoue, Hydrometallurgy 47 (1998) 259–271.
[10] S. Castillo, F. Ansart, C. Laberty-Robert, J. Portal, J. Power Sources 112 (2002) 247–254.
[11] C.K. Lee, K.I. Rhee, J. Power Sources 109 (2002) 17–21.