Separation of Cd and Ni from Ni–Cd batteries by an environmentally safe methodology employing aqueous two-phase systems

Vânia Gonçalves Lacerda, Aparecida Barbosa Mageste, Igor José Boggione Santos, Luis Henrique Mendes da Silva, Maria do Carmo Hespanhol da Silva *

Grupo de Química Verde Coloidal e Macromolecular, Departamento de Química, Centro de Ciências e Tecnológicas, Universidade Federal de Viçosa, Av. P.H. Rolfs s/n, Campus da UFV, Viçosa, 36570-000, Brazil

A R T I C L E   I N F O

A B S T R A C T

The separation of Cd and Ni from Ni–Cd batteries using an aqueous two-phase system (ATPS) composed of copolymer L35, Li_2SO_4 and water is investigated. The extraction behavior of these metals from the bottom phase (BP) to the upper phase (UP) of the ATPS is affected by the amount of added extractant (potassium iodide), tie-line length (TLL), mass ratio between the phases of the ATPS, leaching and dilution factor of the battery samples. Maximum extraction of Cd $(99.2 \pm 3.1)\%$ and Ni $(10.6 \pm 0.4)\%$ is obtained when the batteries are leached with HCl, under the following conditions: 62.53% (w/w) TLL, concentration of KI equal to $50.00\ mmol\ kg^{-1}$, mass ratio of the phases equal to 0.5 and a dilution factor of battery samples of 35. This novel methodology is efficient to separate the metals in question, with the advantage of being environmentally safe, since water is the main constituent of the ATPS, which is prepared with recyclable and biodegradable compounds.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Nickel–cadmium (Ni–Cd) batteries are rechargeable energy sources widely used in portable electronic devices. This huge demand occurs because these electrochemical systems have several advantages, like low cost, high energy density and high storage capacity [1]. Due to cadmium and nickel concentration levels of about 14% and 24.5% respectively, these batteries are economically attractive candidates for recycling operations, being even considered as secondary sources for those metals. Unfortunately, also due to their high levels of metals, they also constitute hazardous residues, and their inadequate disposal is a potential source of contamination in soil and water bodies [2–5].

Cadmium is a toxic metal with cumulative character, classified as a carcinogenic agent for humans [6], while nickel, besides being a toxic material, induces some harmful health effects from mere allergy to risk of lung and gastrointestinal cancer, being responsible for the increase in the incidence of malign tumors [7].

Several processes to recycle Ni–Cd batteries are currently in course, generally based on pyrometallurgical or hydrometallurgical methods [2,3]. Pyrometallurgical methods involve the selective volatilization of metals at high temperatures with subsequent condensation of cadmium, yielding cadmium oxide or metallic cadmium, both with high purity. Even possessing some disadvantages like high energy consumption and emission of toxic effluents, pyrometallurgical methods are more used in processes chosen by several countries to recycle such batteries, with particular attention to SNAM-SAVAM, adopted by France; SAB-NIFE, by Sweden; INMETCO, by the USA; and ACCUREC, by Germany [8]. However, hydrometallurgical methods have been highlighted in the literature for being considered as selective and efficient in the recovery of high-purity metals from complex residues. Hydrometallurgical methods have some advantages not found in the pyrometallurgical routes, like lower energy cost, possibility of reagents recovery and lower levels of atmospheric pollution. The Dutch process of Ni–Cd battery recycling, for instance, is called TNO and is based on a hydrometallurgical procedure [9–11].

In order to implement a hydrometallurgical recycling methodology, the batteries are initially submitted to acid leaching, and several techniques may be subsequently employed in order to separate the dissolved metal ions, like electrolysis [12–16], chemical precipitation [1] and solvent extraction [17,18].

Several works on the proposal of novel hydrometallurgical routes to recycle Ni–Cd batteries pay particular attention to solvent extraction techniques, which present advantages like high selectivity and facile industrial design and scale-up. In summary, these works focus on different leaching conditions and selectivity

* Corresponding author. Tel.: +55 31 38992175; fax: +55 31 38993065.
E-mail address: mariacarmo@ufv.br (M.C.H. da Silva).

of diverse extracting agents, aiming to provide higher efficiency in metal separation.

Reddy and co-workers [2] and Reddy and Priya [17] were able to separate cadmium from other metals by using the extractant Cyanex 923 (a mixture of trihexyl phosphine oxide, hexyl-dioctyl phosphine oxide, dihexyl-octyl phosphine oxide and trioctyl phosphine oxide) diluted in kerosene. The recovery rates in both processes were over 99.9%. Nogueira and Delmas [9] extracted cadmium initially with the extractant D2EHPA [bis(2-ethyl-hexyl) phosphoric acid], followed by a step whereby Cyanex 272 was used to selectively extract cobalt. The recovery rates of metals during the extraction step were as high as 99.7% for cadmium and 99.5% for cobalt. Reddy and co-workers [3] also used Cyanex 301 [bis(2,4,4-trimetyl-pentyl) dithiophosphinic acid)] in cadmium extraction and Mantuano and coworkers [18] used Cyanex 272 to separate cadmium and nickel, in spite of coextracting cobalt with cadmium.

Nevertheless, the liquid–liquid extraction systems reported above are considered as aggressive to the environment and harmful to human health, because of the organic solvents employed [19]. Therefore, it is important to devise novel extraction methods which are cleaner and environmentally safer. In view of this, aqueous two-phase systems (ATPS) are introduced as very promising liquid–liquid extraction systems for metal separation, since they are mostly composed of water and other constituents which are neither toxic nor flammable [20–22].

ATPS are formed by mixing aqueous solutions of two chemically distinct polymers or solutions of a polymer and an electrolyte, under certain thermodynamic conditions, causing the formation of two phases in equilibrium. One of these phases is rich in polymer and the other is concentrated in the electrolyte or in the other polymer [23].

In this work, a novel methodology is proposed to separate cadmium from other constituents of Ni–Cd batteries, by using an ATPS formed with the L35 copolymer, water and Li_2SO_4 in the presence of KI as extracting agent. The influence of some parameters on the metal extraction yield has been examined, namely the amount of added extracting agent, the length of the tie-lines in the ATPS phase diagram, the mass ratio of the ATPS phases, leaching and dilution factor of samples and batteries. This methodology does not involve the use of organic solvents and allows for recycling; for these reasons, it is strategically compatible with the principles of green chemistry [24].

2. Experimental

2.1. Materials

Copolymer L35, with numerical average molar mass of 1900 g mol^{-1} and molecular structure $(EO)_{11}(PO)_{16}(EO)_{11}$, was purchased from Aldrich (Milwaukee, WI, USA). Monohydrated lithium sulfate, hydrochloric acid, sulfuric acid, hydrogen peroxide, ammonium hydroxide, monohydrated cadmium chloride and potassium iodide were analytical grade. Spent Ni–Cd batteries from Panasonic wireless telephones, model P-P301 (KX-A36A) 3.6 V 300 mAh, were used in this study. Distilled water was used in all experimental assays.

2.2. Leaching of battery samples

Battery leaching was carried out via two different methods: one employing HCl and another using a mixture of H_2SO_4 and H_2O_2. The mass of the accumulators was taken after removal of the plastic wrapping and the connecting wires of the batteries, followed by the leaching step performed in a distillation flask.

The HCl leaching occurred at 40 °C for 10 h, with a ratio of 150.0 g of solid material to 1.00 L of acid. In the leaching with H_2SO_4 and H_2O_2, which was carried out at 70 °C for 2 h, a mixture of 2 mL of H_2SO_4 32% (w/w), 6 mL of distilled water and 1 mL of H_2O_2 30% (w/v) per gram of solid material was used.

In both cases the solutions thus obtained were filtered out and transferred to 500 mL flasks, which were completed with distilled water. Their densities were determined and these samples were called "battery stock solutions". The concentrations of Cd and Ni in these solutions were periodically determined by means of a flame atomic absorption spectrometer (VARIAN SpectrAA-200).

2.3. ATPS preparation and determination of Cd and Ni

Preparation of ATPS was effected by mixing L35 stock aqueous solutions, 59.11% (w/w), and Li_2SO_4 aqueous solutions, 22.40% (w/w), with different amounts of KI and metal, respectively. Potassium iodide solutions were prepared by using the L35 stock solution as solvent, while the diluted battery solutions were prepared with the Li_2SO_4 stock solution as solvent. Blank assays were carried out with L35 stock solutions containing different amounts of KI and Li_2SO_4 stock solutions.

After mixing previously defined amounts of the L35 and Li_2SO_4 solutions, the ATPS were manually stirred for 5 min, centrifuged at 3000 rpm for 15 min and placed in a thermostatic bath at 25 °C for 24 h. The phases were separated and diluted in order to determine the concentrations of Cd and Ni in the upper phase (UP) and in the bottom phase (BP), by atomic absorption spectrometry. The extraction percentage (%E) of the metallic ions was calculated by Eq. (1).

$$\%E = \frac{(n_{M^{2+}})_{UP}}{(n_{M^{2+}})_T} \times 100 \tag{1}$$

where $(n_{M^{n+}})_{UP}$ is the amount of metallic ions in the upper phase (in mol), and $(n_{M^{2+}})_T$ is the total amount of metallic ions in the system.

2.4. Extraction behaviors of Cd and Ni in the ATPS

The extraction percentage of Cd and Ni under different KI concentrations was investigated. The battery sample leached with HCl was used in this study. The ATPS were prepared by adding 2.00 g of the Li_2SO_4 22.40% (w/w) solution containing 1.00 mmol kg^{-1} of Cd (battery stock solution or Cd salt) to 2.00 g of the L35 stock solutions with KI at varying concentrations, ranging between 0 and 700.0 mmol kg^{-1}.

2.5. Dilution of battery samples

The extraction of Cd and Ni was studied with a number of HCl-leached battery stock solutions at different concentrations, expressed by the dilution factor (d_f), i.e, $d_f = m_{final}/m_{bat}$, in which m_{final} is the sample final mass after dilution and m_{bat} is the battery sample mass. A similar procedure to that described in section 2.4 was carried out here, by adding 2.00 g of the Li_2SO_4 22.40% (w/w) solution containing 1.00, 2.00, 7.00, 14.0 and 28.0 mmol kg^{-1} of Cd (corresponding to dilution factors of 70, 35, 10, 5 and 2.5, respectively, with regard to the original battery stock solution) to 2.00 g of the L35 59.11% (w/w) solution containing KI at varying concentrations, ranging between 0 and 700.0 mmol kg^{-1}.

2.6. Effect of pH

The pH of water used to prepare solutions of L35 and Li_2SO_4 affects the extraction percentage of the ions [20]. This was verified by examining samples with pH varying between 1.00 and 6.00. The

initial pH of the distilled water used was 5.30 and was adjusted by adding H_2SO_4 or NH_4OH solutions. In this study, ATPS were prepared by adding 2.00 g of an L35 47.40% (w/w) solution containing 350.0 mmol kg^{-1} of KI to 2.00 g of a Li_2SO_4 16.06% (w/w) solution containing 2.00 mmol kg^{-1} of Cd (stock HCl-leached battery solution).

2.7. Mass ratios of the ATPS phases

The extraction of Cd and Ni from the stock solution of batteries leached with H_2SO_4 and H_2O_2 was examined by using ATPS with mass ratios between the upper and bottom phases equal to 0.5, 1 and 2. The concentration of Cd in the ATPS was constant for all mass ratios and equal to 1.00 mmol kg^{-1}. The amount of KI varied between 0 and 350.0 mmol kg^{-1}. As a result, the concentrations of these species in the L35 and Li_2SO_4 stock solutions varied so as to yield systems with the concentrations cited above.

For example, when a mass ratio of 1 was used, 3.00 g of an L35 59.11% (w/w) stock solution with KI were added to 3.00 g of a Li_2SO_4 22.40% (w/w) stock solution containing Cd. For the mass ratio of 2, on the other hand, 4.00 g of an L35 59.01% (w/w) stock solution with KI were added to 2.00 g of a 22.86% (w/w) Cd-containing Li_2SO_4 stock solution. Finally, for mass ratio 0.5, 2.00 g of an L35 59.30% (w/w) stock solution with KI were added to 4.00 g of a 22.16% (w/w) Li_2SO_4 stock solution containing Cd.

3. Results and discussion

3.1. Extraction of Cd and Ni with ATPS

Liquid–liquid phase equilibrium data for the ATPS $L35 + H_2O + Li_2SO_4$ used in this work were obtained in the literature [25]. In Fig. 1, its phase diagram is depicted. Point G indicates the global composition (L35 = 29.56% (w/w) and Li_2SO_4 = 11.20% (w/w)) of the ATPS used when investigating the extraction of Cd and Ni. Points S (L35 = 58.92% (w/w) and Li_2SO_4 = 0.46% (w/w)) and I (L35 = 0.19% (w/w) and Li_2SO_4 = 21.93% (w/w)) indicate the composition of the copolymer– and salt-rich phases, respectively. Curve SCI is the binodal curve, which establishes the separation between the monophasic and biphasic regions.

As indicated by phase diagram, the phase separation occurs by a segregation process between copolymer molecules and electrolytes. The concentrations of the L35 and Li_2SO_4 aqueous solutions, indicated by point G, were chosen so as to produce phases with well-defined and different intensive thermodynamic properties, thus enhancing the extraction behaviors for ions Cd and Ni [20].
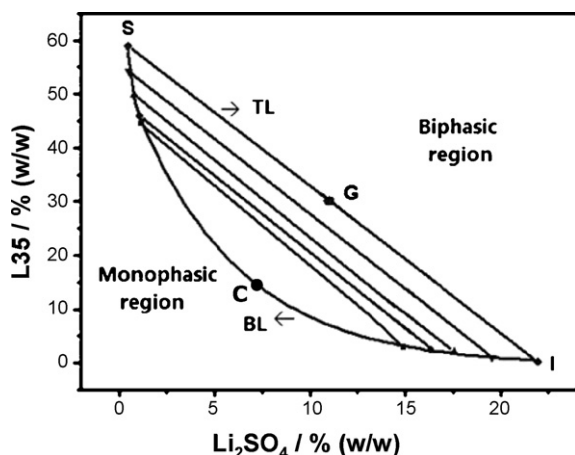

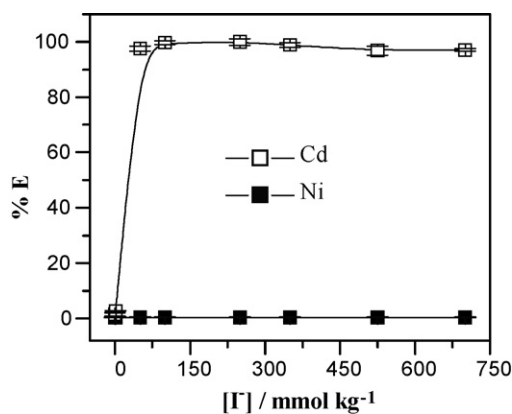**Fig. 1.** Phase diagram for the ATPS $L35 + Li_2SO_4 + H_2O$ at 25 °C.

Fig. 2. Effect of KI concentration on the extraction percentage (%E) of Cd and Ni using the ATPS $L35 + Li_2SO_4 + H_2O$ (Cd 1.00 mmol kg^{-1}; Ni 0.94 mmol kg^{-1}; T = 25 °C).

Fig. 2 is a plot of extraction percentage (%E) of Cd and Ni from a Ni–Cd battery sample leached with HCl as a function of KI concentration in the upper phase. The results show that selective extraction of Cd (100.0 ± 1.2)% is attained from 100.0 mmol kg^{-1} of KI, whereas Ni is extracted with yields as low as 1.00% only, for any KI concentration.

Without I$^-$ addition, the ions Cd and Ni are found in the salt-rich phase, and interact with sulfate ions, according to Eq. (2).

$$M_{(aq)}^{2+} + xSO_{4(aq)}^{2-} \rightleftharpoons M(SO_4)_{x(aq)}^{(2x-n)-} \tag{2}$$
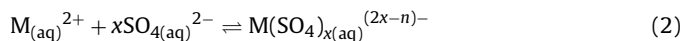
The stability constant (K) of the metal–sulfate complexes may be represented by Eq. (3), from which it is clear that higher $\log K$ values imply higher thermodynamic stability for the complex.

$$\log K_{M(SO_4)_x^{(2x-n)-}} = \log \frac{[M(SO_4)_x^{(2x-n)-}]}{[M^{2+}][SO_4^{2-}]^x} \tag{3}$$

The values of $\log K_{Cd(SO_4)}$ and $\log K_{Ni(SO_4)}$ are 2.3 and 2.4, respectively, which is an indication of small differences in the stability of these complexes [26]. The increment in Cd extraction with increasing KI concentration is caused by the formation of anionic complexes between the metallic ion and the halide, followed by preferential transfer of such complexes from the electrolyte-rich phase to that concentrated in L35.

Upon addition of the iodide extractant (I$^-$), new complexes begin to form due to cadmium and iodide intermolecular interactions. The process of complex formation and the stability constant are represented by Eqs. (4) and (5), respectively.

$$Cd_{(aq)}^{2+} + xI_{(aq)}^- \rightleftharpoons CdI_{x(aq)}^{(x-n)-} \tag{4}$$
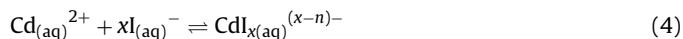
$$\log K_{CdI_x^{(x-n)-}} = \log \frac{[CdI_x^{(x-n)-}]}{[Cd^{2+}][I^-]^x} \tag{5}$$

Cadmium–iodide complexes may have several coordination numbers. There are reports in the literature on the formation of complexes with up to four chelating sites or species $(1 \le x \le 4)$. The values of $\log K_1$, $\log K_2$, $\log K_3$ and $\log K_4$ are reported as 2.4, 1.6, 1.0 and 1.1, respectively [26]. At low KI concentrations, complexes with low coordination numbers are preferentially formed, since they feature higher stability constants. These would be cationic complexes, like CdI$^+$, or neutral species, like CdI$_2$. Increasing iodide concentrations shift the equilibrium shown in Eq. (4) toward the formation of higher amounts of complexes, besides generating chemical species with higher coordination numbers, hence forming complex anions. These anionic species are then partitioned to the copolymer-rich phase due to molecular interactions between the complex ions and copolymer molecules present in that phase. The partitioning behavior of the iodide complex has been attributed to
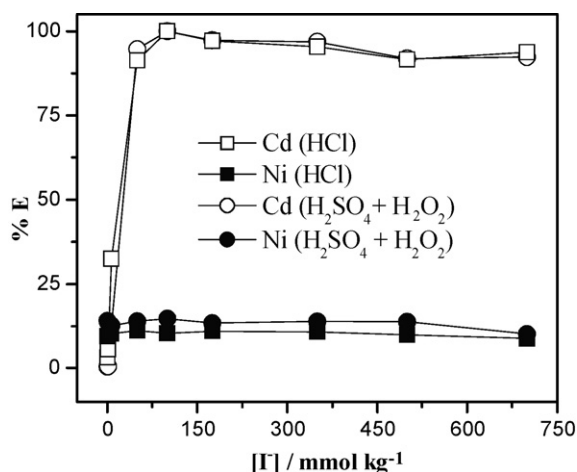
Fig. 3. Effect of leaching conditions on the extraction percentage of Cd and Ni (($\square$, $\bigcirc$) Cd 2.00 mmol kg^{-1}; ($\blacksquare$) Ni 2.00 mmol kg^{-1}; ($\bullet$) Ni, 1.00 mmol kg^{-1}; T = 25 °C).

a specific enthalpic interaction between the anion and EO macromolecular segments present in copolymer molecules. The affinity of CdI$_4$$^{2-}$ with copolymer molecules could be attributed to the acceptor–donor interaction between the anion and EO macromolecules segments (due to the electronic pair found in the oxygen atom). As the electronic densities of the iodide atom when inside of complex structure is very dependent on the nature of the complex central metal [27], the interaction EO-[M(I$_4$)]$^{2-}$ is different depending on the nature of the central metal (EO-[Cd(I$_4$)]$^{2-}$ $\gg$ EO-[Ni(I$_4$)]$^{2-}$. In addition, as has been reported in the previously published papers [28], the great nature salt effect on the metal extraction behavior could be attributed to an interaction between salt cations and the EO macromolecular segments, resulting in a positively charged polymer surface (pseudo-polication), which can interact with the [M(I$_4$)]$^{2-}$ anion. According to this approach, the cation of ATPS salt component plays an important role by simultaneously interacting with complex anions and EO. Cadmium anionic complexes can therefore interact electrostatically with such pseudopolycations [21].

3.2. Leaching of battery samples

Fig. 3 shows how some battery leaching experimental conditions affect the extraction percentage of Cd and Ni ions.

Independent of leaching conditions, the cadmium extraction percentage increases with increasing KI concentration. Up to 25.00 mmol kg^{-1}, Cd extraction was slightly higher when the battery was leached with HCl. However, from 50.00 mmol kg^{-1}, the behavior of Cd extraction is very similar for both leaching methods, and, from 100.0 mmol kg^{-1} of KI, the percentage reached (99.7 ± 1.4)% is maximal and independent of the technique used to open the samples. With regard to Ni extraction, in both systems the extraction percentage was approximately constant at 12%, for all KI concentrations. A slightly higher percentage is reached when the H$_2$SO$_4$ + H$_2$O$_2$ leaching technique is carried out.

Since the complex constant of (NiI$_4$)$^{2-}$ is very small, the low extraction levels of nickel in both cases was an effect of the interaction between the metallic ion and the sulfate ions present in the copolymer-rich phase in low concentrations [26]. Higher extraction percentages are observed when battery samples are leached with H$_2$SO$_4$ and H$_2$O$_2$ because of additional amounts of sulfate anions in the system. These anions originate from the battery sample and are distributed throughout both phases in the system, so as to maintain thermodynamic equilibrium in the ATPS. As a result, the concentration of these species increases in both phases and, hence, higher extraction percentage yields are obtained for nickel ions.

3.3. Tie-line length

The tie-line length (TLL) is a parameter, which expresses the difference in the intensive thermodynamic functions between the top and bottom phases. It is dependent on the difference of salt and macromolecules concentration, % (w/w), present in the top and bottom phases. The TLL is calculated by Eq. (6):

$$\text{TLL} = [(C_P^T - C_P^B) + (C_S^T - C_S^B)]^{1/2} \qquad (6)$$

in which C_P^T and C_P^B are the macromolecule concentration in top and bottom phases, while C_S^T and C_S^B are applied in the same way to the salt.

It is well known that longer tie-lines in ATPS phase diagrams, like the one shown in Fig. 1, correspond to larger differences on the intensive thermodynamic properties of the phases generated for each global composition. In case the partition coefficient of the transferred species varies with the tie-line length, increasing or decreasing, the efficiency of ion extraction will be affected by the differences in phases composition.

The extraction of Cd and Ni was studied by changing the values of TLL in the ATPS diagrams. The ATPS were prepared as indicated in section 2.3, according to a methodology discussed elsewhere [29]. Table 1 shows the TLL values investigated and the concentrations of L35 and Li$_2$SO$_4$ in the bottom and upper phases, respectively, as well as the global composition for each tie-line.

The results obtained in the extraction of Cd and Ni as a function of TLL (Table 1) are depicted in Fig. 4. In Fig. 4a, the values of %E refer to Cd ions obtained from the battery samples, while in Fig. 4b, Cd ions were provided by CdCl$_2$ standard solutions. The behavior of the cadmium extraction process did not depend on the matrix that contained the metal. The maximal Cd extraction was not greatly affected by TLL, and values as high as (98.8 ± 2.3)% were obtained from 100.0 mmol kg^{-1} of KI. These results suggest that the partition behavior of the complexes formed, from the bottom to the upper phase, depends very little on TLL. However, for the shortest TLL investigated, the maximum Cd percentage extraction was reached only with 175.0 mmol kg^{-1} of KI.

As for cadmium, the Ni extraction behavior was not affected much by changing TLL. The lowest %E values were obtained when the system was prepared with the shortest TLL. However, this difference is rather small. These experimental observations were taken into account and led to the decision of selecting the longest TLL in subsequent studies.

Table 1
Concentrations of L35 and Li$_2$SO$_4$ in the upper (UP) and bottom (BP) phases and global composition of the ATPS L35 + Li$_2$SO$_4$ + H$_2$O at 25 °C for each tie-line.

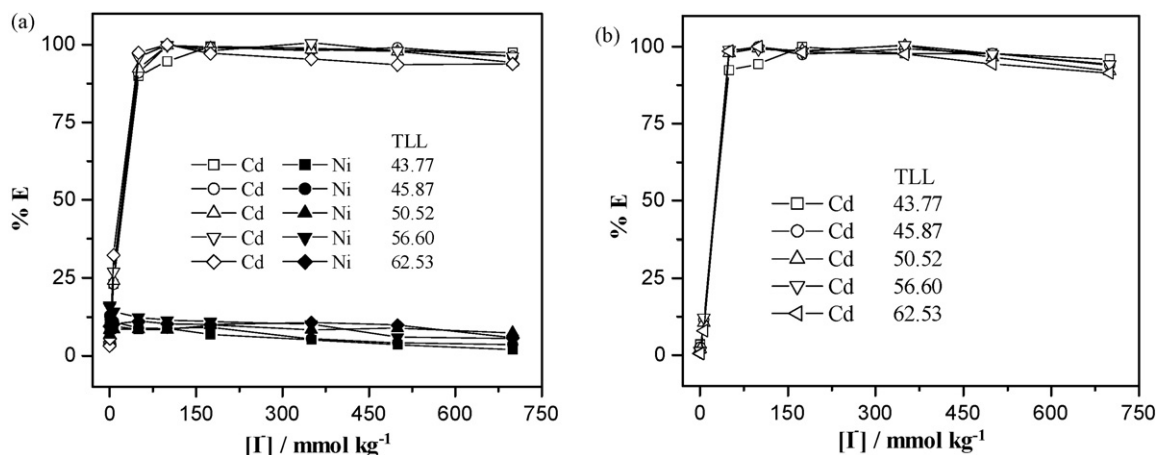| TLL% (w/w)	Global composition% (w/w)		UP composition% (w/w)		BP composition% (w/w)	
	L35	Li$_2$SO$_4$	L35	Li$_2$SO$_4$	L35	Li$_2$SO$_4$
43.77	23.70	8.03	44.48	1.16	2.92	14.90
45.87	24.24	8.73	45.87	1.09	2.62	16.37
50.52	26.01	9.17	49.85	0.80	2.18	17.54
56.60	27.60	10.02	54.25	0.50	0.95	19.55
62.53	29.56	11.20	58.92	0.47	0.19	21.93

Fig. 4. Effect of tie-line length (TLL) on the extraction percentage of Cd and Ni: (a) Extraction of metal from HCl-leached batteries; (b) Extraction of metal from standard solutions (Cd 2.00 mmol kg^{-1}; Ni 2.00 mmol kg^{-1}; $T = 25\,°C$).

3.4. Dilution of battery samples

Fig. 5 shows the effect of battery samples dilution on the extraction of Cd and Ni for different KI concentrations.

The influence of sample dilution on Cd extraction is evident. It can be seen that Cd extraction is impaired when lower dilution levels are promoted with the battery sample in the bottom phase stock solution. To avoid this, higher KI concentrations are required and quantitative extraction is attained. When the sample is diluted by factors of 35 and 70, the extraction behavior of Cd and Ni ions is independent on the battery sample dilution. In particular, for a KI concentration of 175.0 mmol kg^{-1}, the value of %E reaches (99.9 ± 2.3)% in both cases. When a dilution factor of 10 is tested, the maximal level of extraction is reached only for a KI concentration of 350.0 mmol kg^{-1}, and for a dilution factor of 5 this concentration is 700.0 mmol kg^{-1}. The decrease in the %E values caused by the lower dilution level of the battery samples can be explained based on Eq. (4). Once the concentration of metallic ions in the system increases, higher concentrations of chelating agents are necessary in order to effectively form anionic complexes that will be partitioned to the copolymer-rich phase.

Homogeneous systems were obtained when the battery sample was diluted by factors lower than 2.5. This occurred because the ATPS are only formed when specific amounts of salt, polymer and water are mixed under certain thermodynamic conditions (Fig. 1). The existence of both phases is due to a delicate balance

of intermolecular interactions ranging from ion–ion interactions to dipole–dipole interactions. The balance between such numerous interactions and the possible system configurations allow for minimization of the Gibbs free energy. However, by increasing concentrations of the battery components, the new interaction potential pairs modify the Gibbs free energy of the system and render it homogeneous (lower Gibbs free energy) [30,31].

Therefore, in order to attain quantitative Cd ions extraction, with higher amounts of battery samples and lower quantities of chelating agents, the dilution level of the battery sample in the salt stock solution chosen was set at 35, which corresponds to a Cd concentration in the stock solution of 2.00 mmol kg^{-1}.

3.5. Influence of pH

Results showing the influence of pH on the values of %E are shown in Fig. 6. These results were compared to those obtained with distilled water only (pH 5.30). The pH of the medium was lower than or equal to 6.00, since at higher pH values precipitation is induced from the battery samples. It can be observed that for the pH range studied the metal extraction percentage was not greatly affected, but quantitative cadmium extraction was accomplished for any pH value in that range.

This behavior shows that separation of these metals may be carried out by using the L35/Li$_2$SO$_4$ ATPS with L35 and Li$_2$SO$_4$ stock solutions in distilled water, without an intermediate step of pH
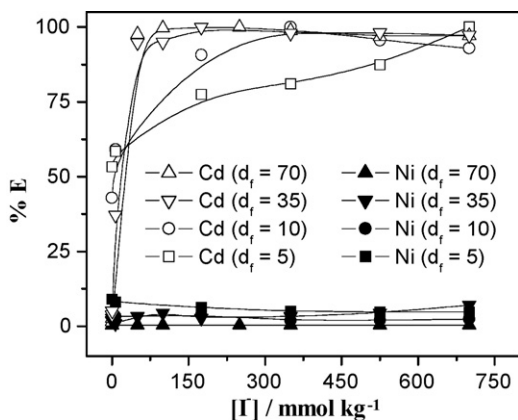

Fig. 5. Effect of battery sample dilution on the extraction of Cd and Ni (($\triangle$) Cd and ($\blacktriangle$) Ni 1.00 mmol kg^{-1} ($d_f = 70$); ($\triangledown$) Cd and ($\blacktriangledown$) Ni 2.00 mmol kg^{-1} ($d_f = 35$); ($\bigcirc$) Cd and ($\bullet$) Ni 7.00 mmol kg^{-1} ($d_f = 10$); ($\square$) Cd and ($\blacksquare$) Ni 14.00 mmol kg^{-1} ($d_f = 5$); $T = 25\,°C$).
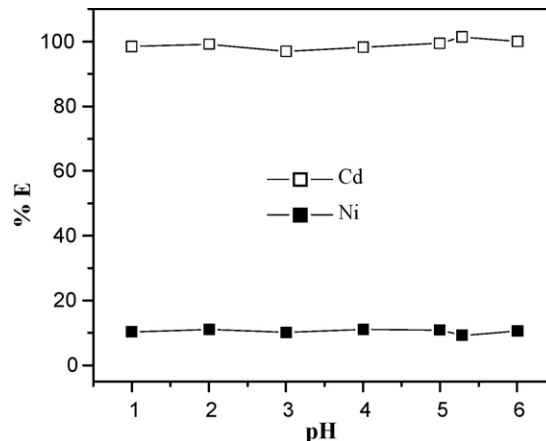

Fig. 6. Effect of pH of the medium on Cd and Ni extraction (Cd 2.00 mmol kg^{-1}; Ni 1.00 mmol kg^{-1}; $T = 25\,°C$).
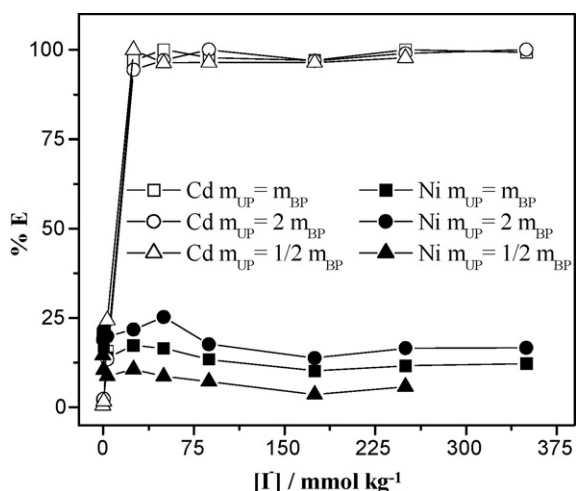
Fig. 7. Effect of the mass ratio between *UP* and *BP* on Cd and Ni extraction (Cd 1.00 mmol kg^{-1}; Ni 0.75 mmol kg^{-1}; $T = 25\,^\circ$C).

adjustment, which implies more practicality and savings on time and chemicals consumption.

The influence of pH on the coordination number of the cadmium-iodide complex, and hence on the metal extraction, using an ATPS formed with polyethylene glycol + (NH$_4$)$_2$SO$_4$ + water was reported by Bulgariu and co-workers [22]. According to this study, for pH values lower than 3.10, CdI$_4{}^{2-}$ is the preferentially formed species and higher extraction yields are reached. The difference in extraction behavior between our work and that of Bulgariu and co-workers may be attributed to hydrophobic difference between the copolymer and PEG macromolecules and the differences in salting-out effects for (NH$_4$)$_2$SO$_4$ and Li$_2$SO$_4$.

3.6. Mass ratio between UP and BP

Fig. 7 shows how the mass ratio between the upper (UP) and bottom (BP) phases of the ATPS affects the Cd and Ni extraction. Three global compositions were fixed in the longest tie-line of Fig. 1 for this study, producing chemical systems with different mass ratios between the upper and bottom phases. The results indicate that the cadmium extraction percentage is little affected by changes in global composition along the same tie-line. In contrary, Ni extraction was greatly affected by the UP/BP mass ratio. When the mass of the upper phase doubles that of the bottom phase, the extraction of nickel is enhanced, reaching a maximal of $(25.2 \pm 0.4)\%$ when the total KI concentration is equal to 50.00 mmol kg^{-1}. On the other hand, the lowest extraction levels were observed when the mass of the bottom phase is twice that of the upper phase, with a maximal of only $(10.6 \pm 0.4)\%$. This behavior is an indication that the distribution coefficient of the cadmium-iodide complex is sufficiently high to produce quantitative extraction even with lower amounts of the upper phase.

4. Conclusions

The methodology proposed in this work proved to be efficient in the separation of Ni and Cd, besides being environmentally safe and complying with the principles of green chemistry. The techniques used are very simple and involve leaching assays with concentrated hydrochloric acid and separation of metals by means of aqueous two-phase systems formed with the L35 copolymer,

Li$_2$SO$_4$ and water. Also, potassium iodide was used as an extraction agent which is selective to cadmium. The best conditions for separation were determined as follows: tie-line length of 62.53% (w/w), concentration of extraction agent added to the ATPS equal to 50.00 mmol kg^{-1}, mass ratio between upper and bottom phases of 0.5 and battery stock solution dilution factor of 35, yielding 99.2% of Cd in the polymer-rich phase and 90.4% of Ni partitioned to the salt-rich phase. The separation of metals using ATPS still opens novel perspectives for the separation of other metals found in batteries, since new ATPS have been constantly developed and other extraction agents may be used.

References

[1] M.B.J.G. Freitas, T.R. Penha, S. Sirtoli, J. Power Sources 163 (2007) 1114–1119.
[2] B.R. Reddy, D.N. Priya, S.V. Rao, P. Radhika, Hydrometallurgy 77 (2005) 253–261.
[3] B.R. Reddy, D.N. Priya, K.H. Park, Sep. Purif. Technol. 50 (2006) 161–166.
[4] C.A. Nogueira, F. Margarido, Waste Manage. 27 (2007) 1570–1579.
[5] M. Sadegh Safarzadeh, M.S. Bafghi, D. Moradkhani, M. Ojaghi Ilkhchi, Miner. Eng. 20 (2007) 211–220.
[6] M.P. Waalkes, J. Inorg. Biochem. 79 (2000) 241–244.
[7] E.L.B. Novelli, R.T. Hernandesa, J.L.V.B. Novelli Filho, L.L. Barbosa, Environ. Pollut. 103 (1998) 295–300.
[8] A.M. Bernardes, D.C.R. Espinosa, J.A.S. Tenório, J. Power Sources 130 (2004) 291–298.
[9] C.A. Nogueira, F. Delmas, Hydrometallurgy 52 (1999) 267–287.
[10] C.A. Nogueira, F. Margarido, Hydrometallurgy 72 (2004) 111–118.
[11] D.C.R. Espinosa, A.M. Bernardes, J.A.S. Tenório, J. Power Sources 135 (2004) 311–319.
[12] M.B.J.G. Freitas, S.F. Rosalém, J. Power Sources 139 (2005) 366–370.
[13] M. Bartolozzi, G. Braccini, S. Bonvini, P.F. Marconi, J. Power Sources 55 (1995) 247–250.
[14] C.-C. Yang, J. Power Sources 115 (2003) 352–359.
[15] A. Rozário, R.K. Silva e Silva, M.B.J.G. Freitas, J. Power Sources 158 (2006) 754–759.
[16] E. Rudnik, M. Nikiel, Hydrometallurgy 89 (2007) 61–71.
[17] B.R. Reddy, D.N. Priya, J. Power Sources 161 (2006) 1428–1434.
[18] D.P. Mantuano, G. Dorella, R.C.A. Elias, M.B. Mansur, J. Power Sources 159 (2006) 1510–1518.
[19] M.C.H. da Silva, L.H.M. da Silva, F.J. Paggioli, A novel micellar medium using triblock copolymer for cobalt determination, Anal. Sci. 21 (2005) 933–937.
[20] M.C.H. da Silva, L.H.M. da Silva, F.J. Paggioli, J.S.R. Coimbra, L.A. Minim, Quim. Nova 29 (2006) 1332–1339.
[21] G.D. Rodrigues, M.C.H. da Silva, L.H.M. da Silva, F.J. Paggioli, L.A. Minim, J.S.R. Coimbra, Sep. Purif. Technol. 62 (2008) 689–695.
[22] L. Bulgariu, D. Bulgariu, I. Sârghie, T. Malutan, Central Euro J Chem. 1 (2007) 291–302.
[23] L.H.M. da Silva, M.D.H. da Silva, A.F. Mesquita, K.S. do Nascimento, J.S.R. Coimbra, L.A. Minim, J. Chem. Eng. Data 50 (2005) 1457–1461.
[24] N. Winterton, Green Chem. 3 (2001) G73–G75.
[25] M.C.H. da Silva, L.H.M. da Silva, J.A. Júnior, R.O. Guimarães, J.P. Martins, J. Chem. Eng. Data 51 (2006) 2260–2264.
[26] L. Meites, Handbook of Analytical Chemistry, first ed., McGraw-Hill, New York, 1963.
[27] L.S. Molochnikov, E.G. Kovalyova, A.A. Zagorodni, M. Muhammed, Y.M. Sultanov, A.A. Efendiev, Polymer 44 (2003) 4805–4815.
[28] L.H.M. da Silva, M.D.H. da Silva, J. Amin Junior, J.P. Martins, J.S.D. Coimbra, L.A. Minim, Sep. Purif. Technol. 60 (2008) 103–112.
[29] J.P. Martins, C.P. Carvalho, L.H.M. da Silva, J.S.R. Coimbra, M.D.H. da Silva, G.D. Rodrigues, L.A. Minim, J. Chem. Eng. Data 53 (2008) 238–241.
[30] L.H.M. da Silva, M.C.H. da Silva, R.A.N. Aquino, K.R. Francisco, M.V.C. Cardoso, L.A. Minim, J.S.R. Coimbra, J. Phys. Chem. B 110 (2006) 23540–23546.
[31] L.H.M. da Silva, M.C.H. da Silva, K.R. Francisco, M.V.C. Cardoso, L.A. Minim, J.S.R. Coimbra, J. Phys. Chem. B 112 (2008) 11669–11678.