



# Green selective recovery of lanthanum from Ni-MH battery leachate using aqueous two-phase systems

Wbiratan Cesar Macedo de Oliveira<sup>a</sup>, Guilherme Dias Rodrigues<sup>b</sup>, Aparecida Barbosa Mageste<sup>c</sup>, Leandro Rodrigues de Lemos<sup>a,\*</sup>

<sup>a</sup> Departamento de Química, FACET, Universidade Federal dos Vales do Jequitinhonha e Mucuri, Diamantina, Minas Gerais, Brazil

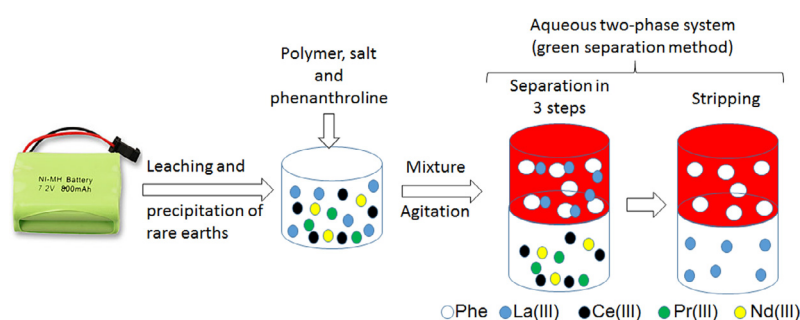
<sup>b</sup> Laboratório de Soluções Analíticas Verdes (LaSAV), Departamento de Química, Instituto de Ciências Exatas (ICEx), Universidade Federal de Minas Gerais (UFMG), Belo Horizonte, Minas Gerais, Brazil

<sup>c</sup> Departamento de Química, ICEB, Universidade Federal de Ouro Preto, Campus Morro do Cruzeiro, CEP 35400-000 Ouro Preto, Minas Gerais, Brazil

## HIGHLIGHTS

- Environmentally safe method for the recovery of rare metals from electronic waste.
- Optimized lanthanum extraction using aqueous two-phase systems.
- Mechanistic elucidation of phase transfer of metal ion in aqueous two-phase system.
- Selective extraction of La(III) from Ni-MH battery waste.
- High values of separation factors between the analyte and other rare earths.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 8 February 2017

Received in revised form 7 April 2017

Accepted 8 April 2017

Available online 9 April 2017

### Keywords:

Aqueous two-phase systems

Lanthanum

Ni-MH batteries

Hydrometallurgy

Green chemistry

Rare earths

## ABSTRACT

In view of the importance of resource recycling and the use of environmentally safe systems to extract the metals contained in wastes, the present study concerns the extraction/separation of lanthanum from spent Ni-MH batteries. Investigation was made of the extraction behavior of lanthanum using aqueous two-phase systems (ATPSs), and a new environmentally safe hydrometallurgical method was developed for the selective extraction of La from Ni-MH battery leachate. The extraction behavior of La was evaluated considering the influence of the following parameters: concentration of different extractant; pH; ATPS-forming electrolyte ( $\text{Li}_2\text{SO}_4$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{MgSO}_4$ ,  $\text{Na}_2\text{C}_4\text{H}_4\text{O}_6$ , or  $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ ); ATPS-forming polymer (L64 or PEO1500). The recovery efficiency was evaluated by analyzing the extraction percentage (%E), and the best conditions for analyte extraction were achieved using the ATPS formed by PEO1500 +  $\text{Li}_2\text{SO}_4$ , at pH 6.00, with 1,10-phenanthroline as the extractant agent (%E = 74.1%). The method was applied to a real Ni-MH battery leachate. After three successive extraction steps, high separation factor (S) values were obtained for the separation of lanthanum from concomitant metals ( $S_{\text{La,Ce}} = 180$ ;  $S_{\text{La,Pr}} = 184$ ;  $S_{\text{La,Nd}} = 185$ ). A stripping assay was carried out, and after a single step, 88.5% of the lanthanum was available for a possible electrowinning step.

© 2017 Elsevier B.V. All rights reserved.

## 1. Introduction

Waste electronic equipment is electrical and electronic equipment, including all its components, that has become obsolete,

\* Corresponding author.

E-mail address: [leandrolemos.ufvjm@gmail.com](mailto:leandrolemos.ufvjm@gmail.com) (L.R. de Lemos).

stopped working, or presented defects during its production [1]. Conservative estimates suggest that the electronic waste stream increases by 2.7% every year, while other assessments suggest a greater increase of about 4% per year and a total incidental waste of 20–50 million tons [2]. Some of these materials have toxic effects on human health and in the environment, while the metals

contained in the waste have economic value, as in the case of the rare earth metals [3]. Batteries are one of the types of electronic waste most likely to become dispersed in the environment, including nickel–metal hydride (Ni–MH) batteries that contain not only the base metals, but also valuable metals such as lanthanum and other rare earth elements (REEs) [4,5].

Recycling of spent nickel–metal hydride batteries is therefore of great interest from the point of view of resource recovery, especially concerning the rare earth metals [6]. In recent years, several hydrometallurgical processes have been developed for the recovery of rare earths from spent Ni–MH batteries [7]. Most of these methods extract the rare earths together, due to the difficulty of individually separating them [8]. Their recovery involves physical and chemical aspects of selective extractive systems, since the separation of REE mixtures into individual elements is usually a complex and expensive process [9].

One of the most widely used techniques for the separation of rare earth metals contained in waste is solvent extraction (SE), involving leaching with an acid solution, followed by the extraction and recovery of target metal ions from the leachate. However, such feed solutions contain a variety and/or large amounts of non-target metal impurities, requiring multi-stage operations for the separation of rare earth metals [10]. Problems that have considerable impact on extraction efficiency and selectivity include crud formation, organic and aqueous phase entrainments, and variable and unpredictable times for phase separation in the settlers [11]. Furthermore, the organic solvents used can be harmful to the environment and human health [12]. To address these limitations, novel extraction methods are needed that are economically viable, fast, clean, and environmentally safe.

Aqueous two-phase systems (ATPSs) offer an excellent alternative for the selective extraction of metals in hydrometallurgical procedures. The technique requires only a short time for phase splitting, without stable emulsion formation, and the system is composed mainly of water together with other components that are low cost, nontoxic, non-flammable, and in some cases biodegradable and recyclable [12,13]. The ATPS can be formed by the mixing of aqueous solutions of certain electrolytes and a polymer, followed by phase separation to obtain a top phase (TP) enriched in polymer and a bottom phase (BT) enriched in electrolyte [14]. The ATPS method has been used for metallic ion partitioning since 1984 and offers high potential for metal extraction [15]. It has been employed for the extraction of copper from ores [11], the separation of Co, Ni, and Cd [12], speciation of chromium [16], and other applications [17–21].

The goal of this work was to develop a novel, green, and efficient method for the separation of lanthanum from other rare earths present in the leachate of spent nickel–metal hydride batteries. The study contributes to understanding the mechanisms of metal ion extraction in ATPSs. The method was optimized in terms of parameters including the nature of the ATPS electrolyte (considering cations and anions) and macromolecule, pH, and the presence and concentration of different extractant agents.

## 2. Materials and methods

### 2.1. Materials

The polyethylene oxide polymer with an average molar mass (MM) of  $1500 \text{ g mol}^{-1}$ , denoted PEO1500, was purchased from Synth (Diadema, Brazil). The triblock copolymer poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) with average molar mass ( $M_m$ ) of  $2900 \text{ g mol}^{-1}$  and 40% ethylene oxide ((EO)<sub>13</sub>(PO)<sub>30</sub>(EO)<sub>13</sub>), denoted L64, was purchased from Sigma Aldrich (Milwaukee, USA). Sodium tartrate ( $\text{Na}_2\text{C}_4\text{H}_4\text{O}_6$ ), trisodium citrate

( $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ ), potassium chloride (KCl), sodium sulfate ( $\text{Na}_2\text{SO}_4$ ), lithium sulfate ( $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ ), magnesium sulfate ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ), sodium hydroxide (NaOH), lanthanum nitrate ( $\text{La}_2(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ), and cerium nitrate ( $\text{Ce}_2(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ) were obtained from VETEC (Rio de Janeiro, Brazil). Iron chloride ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ), cobalt chloride ( $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ), nickel chloride ( $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ), cadmium chloride ( $\text{CdCl}_2 \cdot \text{H}_2\text{O}$ ), copper chloride ( $\text{CuCl}_2$ ), and zinc chloride ( $\text{ZnCl}_2$ ) were purchased from ISOFAR (Duque de Caxias, Brazil). Sulfuric acid ( $\text{H}_2\text{SO}_4$ ), hydrochloric acid (HCl, 37%), and nitric acid ( $\text{HNO}_3$ , 65%) were obtained from Merck (Darmstadt, Germany). The extractants 1-(2-pyridylazo)-2-naphthol (PAN), 8-hydroxyquinoline (Hyd), 1,10-phenanthroline (Phe), xylenol orange (Xyl), and dithizone (Dit) were purchased from VETEC (Rio de Janeiro, Brazil). Praseodymium nitrate ( $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ) and neodymium nitrate ( $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ) were obtained from Sigma Aldrich (Milwaukee, USA). All reagents were of analytical grade quality and were used as received, without further purification.

### 2.2. Compositions of the aqueous two-phase systems

The aqueous two-phase system formed by the macromolecule (L64 or PEO1500) and the salt ( $\text{Na}_2\text{C}_4\text{H}_4\text{O}_6$ ,  $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{Li}_2\text{SO}_4$ , or  $\text{MgSO}_4$ ) was prepared by mixing 3.00 g of a polymer stock solution and 3.00 g of a salt stock solution, which are shown in Table 1. The phase composition of the polymer and salt in the ATPS was defined according to the equilibrium phases (Table 1) [22–24]. All concentrations are expressed in weight percent (w) and similar tie-line length (TLL) values were used for all the systems [14].

### 2.3. Influence of pH, ATPS type, and quantity of extractant

Previous adjustment was made of the pH (3.0, 6.0, or 9.0) of the water used to prepare the salt and polymer solutions. The effect of the cation used was evaluated using sulfate salts (lithium, sodium, and magnesium), while sodium salts (sulfate, citrate, and tartrate) were used to evaluate the effect of the anion used. The PEO1500 polymer and the L64 copolymer were used to evaluate the effect of the type of macromolecule. The salt solution was used to prepare the La(III) ion solution ( $3000 \text{ mg kg}^{-1}$ ). The extractant solutions were prepared using the polymer solution as solvent. The maximum concentrations of the extractants were limited by their solubilities in the polymer solution (Xyl:  $0.0247 \text{ mol kg}^{-1}$ ; PAN:  $0.00625 \text{ mol kg}^{-1}$ ; Dit:  $0.0122 \text{ mol kg}^{-1}$ ; Hyd:  $0.155 \text{ mol kg}^{-1}$ ; Phe:  $0.121 \text{ mol kg}^{-1}$ ). Aliquots (3.00 g each) of the metal solution and the extractant solution (at appropriate concentrations) were weighed out into a centrifuge tube. The tube was stirred for 1 min and allowed to settle for 30 min at  $25.0 \pm 0.1 \text{ }^\circ\text{C}$  in a temperature-controlled bath. The top phase was then removed, suitably diluted, and the metal concentration was determined using flame atomic absorption spectrometry (FAAS) (Varian AA50) or energy-dispersive X-ray fluorescence spectrometry (EDX) (Shimadzu 7000). The extraction percentage (%E) of the metal ions was calculated using Eq. (1):

$$\%E = \frac{nM^{TP}}{nM_T} \times 100, \quad (1)$$

where  $nM^{TP}$  is the quantity of metal ions in the upper phase and  $nM_T$  is the total quantity of metal ions in the system (both in mol). The scheme of the methodology is shown in Fig. 1.

### 2.4. Influence of the presence of concomitant metal ions

Cerium, praseodymium, and neodymium ions were added to the system at different concentrations (0, 1000, 2000, 3000, 4000,

Download English Version:

<https://daneshyari.com/en/article/6465640>

Download Persian Version:

<https://daneshyari.com/article/6465640>

[Daneshyari.com](https://daneshyari.com)