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Research article

Recovery of valuable materials from spent NIMH batteries using spouted bed elutriation

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ABSTRACT

In recent years, a great increase in the generation of spent batteries occurred. Then, efficient recycling ways and correct disposal of hazardous wastes are necessary. An alternative to recover the valuable materials from spent NiMH batteries is the spouted bed elutriation. The aim of this study was to apply the mechanical processing (grinding and sieving) followed by spouted bed elutriation to separate the valuable materials present in spent NiMH batteries. The results of the manual characterization showed that about 62 wt.% of the batteries are composed by positive and negative electrodes. After the mechanical separation processes (grinding, sieving and spouted bed elutriation), three different fractions were obtained: 24.21 wt.% of metals, 28.20 wt.% of polymers and 42.00 wt.% of powder (the positive and negative electrodes). It was demonstrated that the different materials present in the spent NiMH batteries can be efficiently separated using a simple and inexpensive mechanical processing.

1. Introduction

The increase in the production of portable electronic devices and the continuous technological innovations resulted in a generation of large amounts of spent batteries (Bertuol et al., 2009; Guevara-García and Montiel-Corona, 2012; Fernandes et al., 2013; Yadav and Yadav, 2014; Schneider et al., 2014; Cubas et al., 2015). Nickel metal hydride (NiMH) batteries are commonly used as power source in electronic devices, like, mobile phones, digital camera, computers and hybrid electric vehicles (Rodrigues and Mansur, 2010; Innocenzi and Vegliò, 2012; Fernandes et al., 2013; Gasser and Aly, 2013). These batteries have advantages, such as, high power capability, fast charge–discharge rates and long cycle life (Gabis et al., 2014). However, NiMH batteries have high self–discharge rate (Zhu et al., 2014). The main parts of NiMH batteries are: a cathode composed of nickel hydroxide material (in a discharged state); an anode made of a hydrogen storage alloy, consisting of nickel, manganese, cobalt, aluminum and mischmetal (mainly cerium, lanthanum, praseodymium and neodymium) in an AB_5 type structure (B=Ni, Co, Mn, Al; A = lanthanides) with Y_2O_3 or Yb_2O_3 added for corrosion resistance; a separator between the two electrodes made of fine fibers (usually polyamide, polypropylene fleece or gauze); an electrolyte (typically KOH); a metal case; and a sealing plate provided with a self–releasing safety vent (Pietrelli et al., 2005; Bertuol et al., 2006; Müller and Friedrich, 2006; Larsson et al., 2013). Efficient recycling processes should be developed to recovery these valuable metals from spent NiMH batteries and minimize the wastes generation. The recovery of these elements from spent NiMH batteries were previously examined by leaching, solvent extraction, precipitation, magnetic separation, adsorption and electrochemical deposition (Bernardes et al., 2004; Tzanetakis and Scott, 2004; Yong-Feng et al., 2008; Bertuol et al., 2009; Li et al., 2009).

The recycling of spent NiMH batteries is an important challenge regarding the treatment of hazardous wastes and recovery of valuable metals such as, nickel, cobalt and rare earths (Bertuol et al., 2009). In spent batteries, initially, a pre–treatment process for metals liberation from iron case is necessary. This stage improves the recovery efficiency of target metals. The pre–treatment consists of manual dismantling or mechanical processing including grinding, classification, and separation (by differences of density, weight, size, magnetic properties, etc.) (Ferreira et al., 2009;

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Sayilgan et al., 2009; Huang et al., 2011; Al-Thyabat et al., 2013). Mechanical treatment is characterized by simplicity, efficiency, flexibility and high throughput. Nevertheless, it consumes considerable amount of energy (Huang et al., 2011; Al-Thyabat et al., 2013). Bertuol et al. (2006) used the magnetic separation to recycle spent NiMH batteries, aiming the recovery of Ni, Co and rare earths. The authors verified that this process is viable due to the great amount of metals present in the batteries. It also demonstrates that magnetic separation is a very efficient process to recovery nickel alloys.

An alternative to realize the mechanical treatment for the separation of these materials is the spouted bed elutriation (Bertuol et al., 2015). The elutriation of these materials can be realized based on the differences of particle size and/or density. Recently, Bertuol et al. (2015) separated different materials present in Li–ion batteries using the spouted bed elutriation. The results showed that spouted bed elutriation is a simple and inexpensive way to obtain the separation of the different materials (polymers, metals, active electrode materials) present in spent LIBs.

In this context, the aim of this study was to separate different materials (polymer, metals and powder which is constituted by the active materials of the anode and cathode) present in the spent NiMH batteries using mechanical processing such as grinding, sieving and spouted bed elutriation. In the first step, spent NiMH batteries were separated in manual dismantling and characterized regarding to the quantity of each components. In the second step, mechanical processing (grinding, sieving and spouted bed elutriation) were applied to separate the different materials of NiMH batteries.

2. Materials and methods

2.1. Characterization of spent NiMH batteries

The spent NiMH batteries were obtained from discarded mobile phones in a collection point located in Santa Maria–RS–Brazil. For characterization purposes, six spent NiMH batteries of the same model were used. All batteries were composed by prismatic accumulators (external case containing the positive and negative electrodes as well as the separators), polymers and metals (electronic circuits and contacts). The negative electrode of the prismatic accumulator consists of a plate symmetrically perforated and covered by a dark paste. The positive electrode of the prismatic accumulator is a very fine metallic screen impregnated also by a dark paste. The components were manually separated and classified according its mass percentage (wt.%).

The metals present in the spent NiMH batteries were identified by Scanning Electron Microscopy (SEM) coupled with X–ray Dispersive Spectroscopy (EDS) (Philips, XL–30 FEG).

2.2. Mechanical processing

The different materials present in the spent NiMH batteries were separated using the following sequential steps: grinding, sieving and spouted bed elutriation (Fig. 1).

2.2.1. Grinding and sieving

The batteries were ground in a hammer mill (Tiger A4) with a 10 mm sieve in the output. All grounded materials (powder, polymers and metals) were sieved (1st size separation in Fig. 1). From this sample, due to easy detachment, part of the powder (which is composed of the active material of both electrodes) was removed using a 65 Tyler sieve (see Fig. 1).

2.2.2. Spouted bed elutriation

The spouted bed elutriation was performed in pilot scale equipment, as presented in Fig. 2. The equipment consists in an acrylic cylindrical column with stainless steel cones in the base and top. A Lapple cyclone was coupled in the output of the equipment. More details of the equipment can be seen in Bertuol et al. (2015).

The spouted bed elutriation experiments were made as follows: In the 1st elutriation step (Fig. 1), all comminuted materials (metals, powder and polymers) were put into the bed and the air flow was supplied to the system. The metallic fraction, which presented larger particle size and higher density, was retained in the bed. The powder and polymers were dragged and collected by a cyclone. In the 2nd elutriation step (Fig. 1), powder and polymers were put into the bed and the air was supplied to the system. Since the powders are strongly attached in the polymers, a wire mesh was adapted in the bed outlet. This way the polymeric fraction was retained in the bed due to the wire mesh and the powder was dragged and collected by a cyclone.

2.3. Characterization of the separated fractions

The obtained fractions (powder, metals and polymers) were characterized. The volumetric mean diameter of the powder fraction was obtained in Malvern equipment (Mastersizer Microplus, MAF 5001). The mean diameter of the metals and polymers were obtained by sieve test using the Sauter definition (Filippa et al., 2012). The densities of the different fractions were obtained by Helium picnometer (Micromeritics, Accupyc 1330). Particle sphericity (ϕ) was determined by shape factor (S_f). The particle is more spherical when the value of S_f is closer to 0 (Yen et al., 1998). Calculation of particle shape factor and sphericity follows the steps below (Carter and Yan, 2005; Liao et al., 2010 and Chen et al., 2014):

$$r_{mean} = \frac{\sum_{i=1}^{n} r_i}{n} \tag{1}$$

$$r_{rms.d} = \sqrt{\frac{(r_{\max} - r_{mean})^2 + (r_{\min} - r_{mean})^2}{2}} \tag{2}$$

$$S_f = \frac{r_{rms.d}}{r_{mean}} \tag{3}$$

$$\phi = 1 - S_f \tag{4}$$

where $r_{rms.d}$ (μm) is the radius deviation of root mean square (RMS), r_{mean} (μm) is the mean diameter, r_{min} (μm) is the minimum diameter, r_{max} (μm) is the maximum diameter. The values of r_{mean}, r_{min}, r_{max} were determined by analyzing the images obtained in an optical microscope with program Image Pro Plus 7.0.

The terminal velocity u_t of particles was determinate using two dimensionless quantities: a dimensionless terminal velocity u_* and a dimensionless particle diameter d_* as follows (Haider and Levenspiel, 1989):

$$u_* = u_t \left[\frac{\rho_f^2}{g\mu\left(\rho_s - \rho_f\right)} \right]^{\frac{1}{3}} \tag{5}$$

$$d_* = d_{sph} \left[\frac{g\rho_f\left(\rho_s - \rho_f\right)}{\mu^2} \right]^{\frac{1}{3}} \tag{6}$$

where u_t is terminal velocity of particle in fluid (m s^{-1}), d_{sph} is