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Research article

Recovery of metals from a mixture of various spent batteries by a hydrometallurgical process

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A B S T R A C T

Spent batteries contain hazardous materials, including numerous metals (cadmium, lead, nickel, zinc, etc.) that are present at high concentrations. Therefore, proper treatment of these wastes is necessary to prevent their harmful effects on human health and the environment. Current recycling processes are mainly applied to treat each type of spent battery separately. In this laboratory study, a hydrometallurgical process has been developed to simultaneously and efficiently solubilize metals from spent batteries. Among the various chemical leaching agents tested, sulfuric acid was found to be the most efficient and cheapest reagent.

A Box-Behnken design was used to identify the influence of several parameters (acid concentration, solid/liquid ratio, retention time and number of leaching steps) on the removal of metals from spent batteries. According to the results, the solid/liquid ratio and acid concentration seemed to be the main parameters influencing the solubilization of zinc, manganese, nickel, cadmium and cobalt from spent batteries. According to the results, the highest metal leaching removals were obtained under the optimal leaching conditions (pulp density = 180 g/L (w/v), $[H_2SO_4]$ = 1 M, number of leaching step = 3 and leaching time = 30 min). Under such optimum conditions, the removal yields obtained were estimated to be 65% for Mn, 99.9% for Cd, 100% for Zn, 74% for Co and 68% for Ni. Further studies will be performed to improve the solubilization of Mn and to selectively recover the metals.

1. Introduction

Over the last decades, the development of electronic technologies using a battery as a source of energy has led to an increase in the amount of spent batteries reaching landfill sites or incinerators (Inglezakis and Moustakas, 2015). Alkaline batteries are the most commonly used across the world compared to the other types of batteries (RIS international Ltd, 2007). According to an estimation of the amounts of batteries sold in 2015 in Canada, the alkaline batteries (74%) are the most commonly commercialized followed by zinc carbon batteries (15%), lithium dioxide manganese batteries (5%), zinc air button cell batteries (4%) and silver oxide button cell batteries (2%) (Lachapelle-Charette, 2014). For the secondary one, nickel cadmium batteries are the most consumed (32%), followed by nickel-metal hydride batteries (42%), lithium ion batteries (22%), lithium polymer batteries (2%) and small sealed lead acid battery (2%) (Lachapelle-Charette, 2014). A decrease in Ni–Cd batteries consumption was observed in many countries, especially in Europe, because of their high toxicities (Rudnik and Nikiel, 2007). Alternative batteries, including Ni-MH and Li-ion, have replaced this type of battery for many applications because they contain less toxic metals (Zhang et al., 1998). Alkaline batteries are mainly used in radios, recorders, toys, remote controls, watches, calculators, cameras and in other applications where small quantities of power are required (Sayilgan et al., 2009). For secondary batteries, including Ni-MH, Ni–Cd, and Li-ion, they are considered an important source of energy for many applications across the world. Ni-MH and Li-ion batteries are widely used in several portable electronic applications such as personal computers, video recorders and phones (Zhang et al., 1998).

Spent alkaline batteries are not considered hazardous materials according to the IATA Dangerous Goods Regulations, ICAO Technical Instructions and the U.S. hazardous materials regulations (49 CFR) (Bonhomme et al., 2013; Energizer, 2009) whereas spent secondary

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batteries containing toxic metals such as Cd potentially pose a high risk to human health and living organisms. In Canada, the huge majority of spent batteries are disposed in landfill sites because of the lack of available technologies to collect and recycle spent batteries. Therefore, the Call2Recycle project was adopted by the government of Canada to restrict the amounts of spent batteries entering landfill sites and to encourage the reuse of the metals contained in spent batteries as secondary raw materials. Call2Recycle has promoted the recycling or the reuse of huge amounts of spent batteries (more than 500 000 kg of rechargeable batteries), restricting their landfilling (Call2Recycle, 2012).

Several pyro- and hydrometallurgical processes have been developed to allow the recycling of one or various types of spent batteries. For example, Accurec, a German company, has developed a pyrometallurgical process, which is currently applied at the industrial scale to treat Ni-MH, Ni–Cd, alkaline and lithium batteries (Accurec, 2010). SNAM Company, created in 1981, developed a hydrometallurgical process to recover the metals from saline batteries and sorted batteries according to their chemical and physical properties (SNAM, 2015). Hydrometallurgical processes have several advantages (low energy consumption, ease of operation, low emission of toxic gas, lower costs, etc.) compared to the pyrometallurgical ones (Yazici and Deveci, 2013). Therefore, the use of hydrometallurgical processes to recover the metals from spent batteries has been intensively studied at the laboratory scale and proved to be very promising (Espinosa et al., 2004; Kursunoglu and Kaya, 2014; Smith et al., 2014; Morcali, 2015). Buzatu et al. (2013) developed a hydrometallurgical process to recover the Zn and Mn from spent alkaline cells. The battery powder was dissolved in the presence of H_2SO_4 (2 M) at 60 °C for 60 min. With these conditions, 96.0% of Zn and only 43.0% of Mn could be recovered. Nan et al. (2006) found the optimum conditions for recovering the metals from Li-ion and Ni-MH batteries by using H_2SO_4 (3 M) in the presence of H_2O_2 (3.0%, v/v) with a temperature fixed at 70 °C. The results showed that 99.5% of Co and Ni could be recovered with these optimum conditions after 5 h Zeytuncu (2016) solubilized more than 98% of Zn and Mn from alkaline batteries after 120 min at 100 °C in the presence of H_2SO_4 (2 M) and elemental sulfur. To the best of our knowledge, none of the promising hydrometallurgical processes developed at the laboratory or industrial scales are able to selectively and efficiently recover metals from a mixture of spent batteries comprising alkaline, Zn–C, Ni-MH, Ni–Cd, Li-ion and Li-M batteries, without sorting spent batteries according to their physical and chemical properties.

From the previous reason, the objective of the present study was to design an efficient and economically attractive hydrometallurgical process to recycle spent batteries without any sorting step according to the type of spent batteries. A Box Behnken Design was used in this study to evaluate the influence of several operating conditions (retention time, concentration of leaching agent and solid/liquid ratio) and their potential interaction and to model the leaching of metals from spent batteries. The Box-Behnken methodology was also used to determine the optimal operating conditions for the leaching of metals from spent batteries, considering the processing costs (chemical reagents costs) and the revenues related to the recovery of metals.

2. Materials and methods

2.1. Sample preparation and characterization

Spent battery samples, including alkaline, Zn–C, Ni–Cd, Ni-MH, Li-ion, and lithium primary batteries, were collected at the collection point located at the National Institute of Scientific Research (Quebec, Qc, Canada). Each type of battery was manually separated and dismantled to determine their metals composition. Because of the potential release of hydrogen gas from the spent batteries and the violent reaction of this gas with oxygen, the dismantlement procedure should be performed with care. The lithium primary batteries and Ni-MH spent batteries were frozen in liquid nitrogen and were then immediately dismantled because of their high reactivities. After the dismantlement of each battery, the procedure used for the preparation of the fine powder slightly differs for each type of spent battery. For alkaline, Ni-MH and Ni–Cd batteries, the fine particles were removed from positive and negative electrodes using manual crushing and grinding (with a mortar) steps. Li-ion batteries were manually crushed and the cathode material was uncurled and cut into small pieces and the material was then manually grinded with a mortal. For all the type of spent batteries, the undesirable coarse particles (iron scraps, paper, collector pin, plastic and electrode plaque) present in the samples (Fig. 1a.) were then removed by screening through 1 mm and a 2 mm sieves. The remaining material was then dried at 25 °C for 24 h and manually grinded again using the mortar. After this preparation, all the types of spent batteries were then mixed. To achieve the main objective of the present study, 5 kg of a mixture of the spent batteries was prepared according to their proportion in the Canadian market share. The amounts of each type of spent batteries used to prepare the mixture were selected using the consumption of batteries in the Canadian market (RIS international Ltd, 2007; Lachapelle-Charette, 2014). Finally, the mixture obtained was repeatedly grinded for 5 min using a grinder (Fritsh pulverisette, Serial no. 06 2000/01908, Germany) to obtain the fine powder (Fig. 1b.). The samples were then homogenized and collected to determine the contents of the metals (Al, As, Cd, Co, Cr, Cu, Fe, Li, Mn, Ni, Pb, S, Zn, etc.). The mixture of spent batteries contained 66.5% Zn–MnO_2, 15.4% Zn–C, 15.4% Ni–Cd, 1.7% Ni-MH, 0.3% Li-ion and 0.7% Li-primary batteries.

2.2. Selection of the leaching agent

Several experiments were carried out to evaluate the influence of the nature and the concentration of the leaching agents, the temperature and the retention time on the solubilization of metals from the mixture of spent batteries. In these experiments, different types of leaching agents including inorganic and organic acids, alkaline and chelating agents were tested (Sun and Qiu, 2012; Senanayake et al., 2010; Shin et al., 2009; Oishi et al., 2008; Vatistas et al., 2001; Nan et al., 2006). The leaching experiments were performed using sulfuric acid ($[H_2SO_4]$ = 0.5 and 2.0 M), hydrochloric acid ([HCl] = 0.5 and 2.0 M), oxalic acid ($[H_2C_2O_4]$ = 0.5 M), acetic acid ($[CH_3COOH]$ = 0.5 and 2.0 M), sodium hydroxide ([NaOH] = 0.5 and 2.0 M), ammonium chloride ($[NH_4Cl]$ = 1.0 and 4.0 M) and ethylenediaminetetraacetic acid ([EDTA] = 0.125 and 0.250 M). The leaching solutions were prepared by diluting analytical grade reagents in distilled water. For all the experiments, the solid/liquid ratio was fixed to 10% (w/v). The leaching experiments were carried out onto 20 g of the mixture of spent batteries mixed with the leaching solution (200 mL) in a 500 mL baffled shaker flask. The experiments were conducted at two different temperatures (room temperature and 80 ± 10 °C). The agitation rate was fixed at approximately 200 rpm. The total leaching time was fixed at six hours and different samples were taken at 30, 60, 120, 240 and 360 min. Finally, all samples were filtered with G6 filters (porosity = 1.5 μm) and preserved onto 5% HNO_3.

2.3. Box Behnken methodology

A Box-Behnken design approach was chosen in order to evaluate the influence of several parameters (concentration of leaching