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Influence of H_2SO_4 and ferric iron on Cd bioleaching from spent Ni–Cd batteries

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ABSTRACT

The paper is concerned with biohydrometallurgical methods of cadmium recovery from spent Ni–Cd batteries. Cd leaching efficiency from electrode material in different media (H_2SO_4 and $Fe_2(SO_4)_3$ solutions), at different Fe(III) concentrations and using the bacteria *Acidithiobacillus ferrooxidans* were investigated. The main aim of this study was to understand which from the bioleaching products (sulphuric acid or ferric sulphate) play a main role in the bioleaching process of Cd recovery. The influence of Fe ions on Cd leachability was confirmed. The best leaching efficiency of Cd (100%) was reached by bioleaching and also by leaching in $Fe_2(SO_4)_3$ solution. The results of X-ray diffraction confirmed that no cadmium was present in solid residuum obtained after the Cd bioleaching as well as Cd leaching using solely ferric iron. The use of H_2SO_4 solution resulted in the lowest efficiency of Cd leachability, the presence of hydroxides in electrode materials caused neutralization of the leaching solution and inhibition of Cd leaching.

1. Introduction

Spent Ni–Cd batteries contain a high amount of heavy metals (51–67%) therefore the interest associated with valuable metal recovery has become more increasing. Electrode material contains up 22–46% of Cd (Vassura et al., 2009) depending on the type of Ni–Cd batteries while in the Earth's crust cadmium makes up about 0.1–0.5 ppm. In nature cadmium occurs as a part of other minerals (e.g. Cd content in sfalerite is 0.6%, in galena 0.02%, in chalcopyrite 0.12%). Cadmium has many common industrial uses as cadmium pigments (11%), stabilizers and alloys (3%), coatings (7%) and it plays a key role in battery production (79%) (ICdA, 2012). In the past a little amount of Cd (~10%) was obtained by recycling process, especially, by recycling of ash from steel processes.

EU Member States have committed themselves to adhere to the EU Battery Directive which ordered 25% collection target by September 2012. EBRA (European Battery Recycling Association) ensures the recycling of more than 85% of the spent batteries of the EU market. Based on EBRÁs statistics for the year 2010 was find 18% increase in recycling Ni–Cd spent batteries compared to 2009 (EBRA, 2010). However, the actual number of recycled batteries is higher because it is necessary to take into account the processors who are non members of EBRA (CITRON, 2012).

In comparison with Cd mining, recovery of cadmium by the recycling process is environmental friendly and economically more convenient. Several processes of spent Ni–Cd batteries treatment based on pyrometallurgical (Sumitomo, Snam-Savam, Sab Nife, Waelz, Accure processes, vacuum metallurgy separation), hydrometallurgical (TNO, BATENUS processes) and combined processes (Recytec proces) have been developed so far (Espinosa et al., 2004; Nogueira and Margarido, 2004; Rudnik and Nikiel, 2007; Karnchanawong and Limpiteeprakan, 2009; Huang et al., 2010). Due to the great energy consumption, high cost, low efficiency and serious secondary pollution the conventional techniques generally used for metal recovery from low grade ores and waste has been gradually replacing by the alternative and more efficient technology, which is biohydrometalurgy. Biohydrometallurgical processing of solid waste is similar to natural biogeochemical metal cycles and reduces the demand of natural resources, energy and landfill space (Brierley and Brierley, 2001; Zhu et al., 2003; Bernardes et al., 2004; Nogueira and Margarido, 2007; Ndlovu, 2008; Brierley, 2008). This technology can be also successfully applied for recycling of such waste as batteries or electronic scrap consisted of heterogeneous material like ceramics, polymers and also higher amount of different metals compared with natural sources.

A key microorganism in metal bioleaching from sulfide ores is the iron and sulphur oxidizing bacterium *Acidithiobacillus ferrooxidans*, which has been studied extensively. Different from metals sulfides the spent Ni–Cd batteries are characterized by elemental metals, metal oxides and hydroxides therefore different bioleaching mechanisms of this non-sulphidic waste may be expected

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(Vassura et al., 2009; Huang et al., 2011). It is of value to find the main factors responsible for metal recovery by bioleaching since each material obtained is to a certain extent specific and requires distinctive treatment.

The main aim of our work was to examine the influence of leaching agents (sulphuric acid and ferric sulphate) on the bioleaching of particular metal in detail. Therefore chemical leaching using two different media was carried out in order to simulate the effect of particular metabolites microbially produced during bioleaching process on cadmium recovery from spent Ni–Cd batteries. The first one was based on the leaching ability of sulphuric acid and the second one on the leaching ability of ferric iron at the same and different concentration (18 g/l, 9 g/l, 4.5 g/l and 0.9 g/l Fe) as that of present in 9 K medium (9 g/l Fe).

2. Experimental materials and methods

2.1. Characteristics of used Ni–Cd batteries

In this research spent rechargeable Ni–Cd battery pack, model No OF31NC 5H for cordless drill was used as an experimental material. Batteries were weighted and manually cut up into different portions. The mean weight of batteries was 40 g. Electrode material forms about 55% of the battery weight (cathode 11 g and anode 12 g). All remaining components of battery were metal parts (16 g) and separator with plastic parts (3 g).

For experiments cathode and anode electrode materials were used separately. To obtain the electrodes, the steel case was manually opened and rolled electrodes were separated. The active electrode material, cathode and anode powders were physically removed from the metal grid, ground and sieved to obtain a mesh size of less than 40 μm.

AAS analysis results of the cathode and anode input samples showed that the content of cadmium in the battery was 6.5% and 38% for the cathode and anode respectively. X-ray diffraction showed that the anode was covered by cadmium and cadmium hydroxide in combination with metallic Ni while the cathode was covered by nickel hydroxide and nickel oxy-hydroxide. Cathode also contains additives and conducting agents (graphite or Ni powder) and a small amount of cadmium. A small amount of cobalt was also present in both samples (Figs. 1 and 2).

2.2. Experimental set-up

2.2.1. Bacteria

A pure culture of *A. ferrooxidans* was obtained from the Institute of Geotechnics of Slovak Academy of Science, Košice. The organism was cultured in Erlenmeyer flasks containing 200 ml of 9 K medium (Silverman and Lundgren, 1959) at initial pH 1.5 at 30 °C. The basic 9 K medium was composed of $(NH_4)_2SO_4$ – 2.0 g, KH_2PO_4 – 0.25 g, $MgSO_4{\cdot}7H_2O$ – 0.25 g, KCl – 0.1 g, $FeSO_4{\cdot}7H_2O$ – 44.2 g and distilled water, 1000 ml. The same medium was also used for the bioleaching experiments.

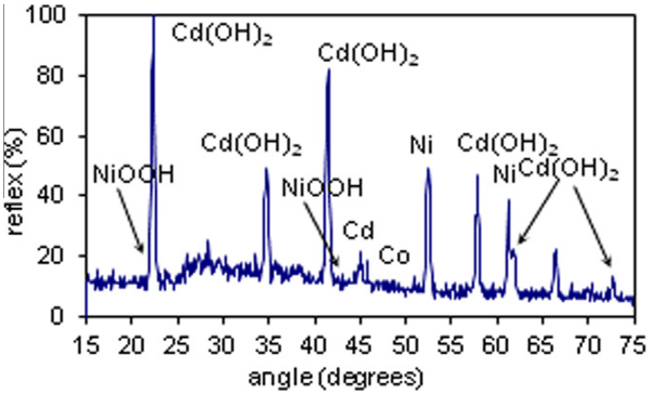

Fig. 1. X-ray diffraction pattern of the initial anode material of spent Ni–Cd battery.

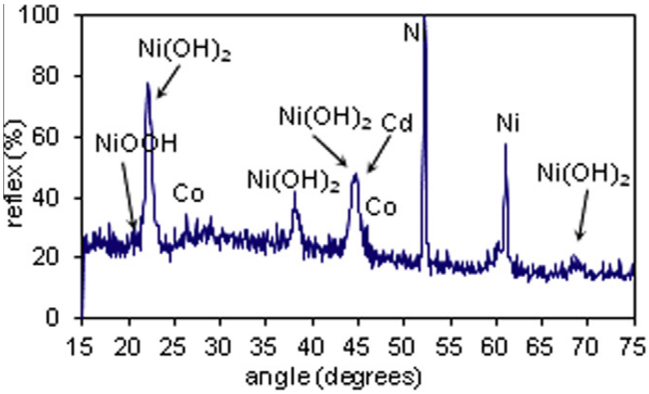

Fig. 2. X-ray diffraction pattern of the initial cathode material of spent Ni–Cd battery.

2.2.2. Leaching experiments

Experiments were carried out separately with the cathodic and anodic material obtained from nickel–cadmium batteries in three different media:

1. Bioleaching media (9 K medium).
2. H_2SO_4 solution.
3. $Fe_2(SO_4)_3$ solution.

In order to follow the importance of sulphuric acid and ferric iron the chemical leaching was conducted in media with H_2SO_4 and $Fe_2(SO_4)_3$ without bacteria. The H_2SO_4 solution was prepared by dilution of 96% H_2SO_4 in distilled water to obtain the final pH value of 1.5 (0.15% H_2SO_4 solution). The leaching medium with $Fe_2(SO_4)_3$ was prepared using the different concentration of ferric irons, 18 g/l, 9 g/l, 4.5 g/l and 0.9 g/l. The final pH values were adjusted to 1.5 with 5 M NaOH. To the prepared media 2 g of the cathodic and anodic powder material, respectively, was added. Simultaneously 2 g of electrode powder was added to the 200 ml of 9 K medium with cultured bacteria and incubated at 30 °C. After 3 weeks, when the medium colour turned into redbrown due to the Fe(III) formation, 5 ml of adapted bacteria were poured into the Erlenmeyer flask containing 295 ml of pure 9 K medium. After 4 days of precultivation 3 g of electrode material was added.

The experiments were carried out in the incubator at 30 °C, the solid/liquid (w/v) ratio was 1/100 in all flasks. The initial pH values of all three media were adjusted to 1.5. The samples for analysis were withdrawn at these days: 1, 3, 7, 10, 13, 21, and 28. All experiments were conducted in triplicates.

2.2.3. Analytical determinations

The pH of each experiment was measured throughout the experimental period by pH meter GRYF 208 L using a combine electrode.

The leachant (5 ml) was periodically taken and filtrated. Cd concentration in each filtrate was determined by Atomic Absorption Spectrometry (AAS) (SpectrAA 20 PLUS VARIAN at 326 nm).

Chemical composition of the initial cathodic and anodic material and the final leaching residues was determined by AAS and X-ray diffraction (URD-6 (Rich. Seifert-FPM, German), radiation source Co).