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Technical Note

Process controls for improving bioleaching performance of both Li and Co from spent lithium ion batteries at high pulp density and its thermodynamics and kinetics exploration

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HIGHLIGHTS

- Bioleaching behavior of spent LIBs at pulp density (PD) of 1–4% was explored.
- Great decline in leaching efficiency was observed for Co/Li with increase in PD.
- Maximum leach yield of 89% for Li and 72% for Co was reach by process control.
- Bioleaching has greater potential than chemical leaching based on thermodynamics.
- Product layer diffusion model described best bioleaching behavior of Co and Li.

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ABSTRACT

Release of Co and Li from spent lithium ion batteries (LIBs) by bioleaching has attracted growing attentions. However, the pulp density was only 1% or lower, meaning that a huge quantity of media was required for bioleaching. In this work, bioleaching behavior of the spent LIBs at pulp densities ranging from 1% to 4% was investigated and process controls to improve bioleaching performance at pulp density of 2% were explored. The results showed that the pulp density exerted a considerable influence on leaching performance of Co and Li. The bioleaching efficiency decreased respectively from 52% to 10% for Co and from 80% to 37% for Li when pulp density rose from 1% to 4%. However, the maximum extraction efficiency of 89% for Li and 72% for Co was obtained at pulp density of 2% by process controls. Bioleaching of the spent LIBs has much greater potential to occur than traditional chemical leaching based on thermodynamics analysis. The product layer diffusion model described best bioleaching behavior of Co and Li.

1. Introduction

Lithium ion batteries (LIBs) were widely used as small power supplier owing to high energy density, no memory effect and longer life cycles (Broussely and Archdale, 2004). Not only that, LIBs will be the first category of dynamic batteries to provide power for electronic automobile in the future (Castillo et al., 2002; Xu et al., 2008). While global consumption of LIBs reached 4.49×10^9 units in 2011, and the compound annual growth rate of the global consumption was as high as 14.5% from 2006 to 2011. As a consequence, massive amount of spent LIBs as solid wastes have been generated, even more in the future (Castillo et al., 2002; Xu et al., 2008).

Although spent LIBs are not classified as dangerous waste, their discharge into environment still causes potential ecosystem hazard and human health due to the toxic elements or compounds (Hal and Angelica, 2008). On the other hand, the spent LIBs contain dense valuable metals such as Co and Li in the proportion of 5–20% cobalt and 5–7% lithium (Lee and Rhee, 2003). Under the circumstance, the huge contrast between the dense valuable metals in the LIBs and the increasing shortage of nature resource has prompted scientists to recover Co and Li in recycling spent LIBs from the viewpoints of both environment protection and resource conservation (Castillo et al., 2002; Xu et al., 2008).

Hydrometallurgical processes have been commercially adopted for recovery of Co and Li from spent LIBs (Swain et al., 2007; Li

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et al., 2009; Wang et al., 2009; Ferreira et al., 2009; Wang et al., 2012; Zhu et al., 2012). However, their inherent drawbacks including stringent requirements of equipments, hard operation conditions and great energy consumption make it urgent to look for alternative strategies (Castillo et al., 2002; Xu et al., 2008). In mining, bio-hydrometallurgy (bioleaching) has been gradually replacing hydrometallurgical ones due to higher efficiency, lower costs, green process and few industrial requirements (Rohwerder et al., 2003; Cui and Zhang, 2008). Lately, extraction of Co and Li from spent LIBs by bioleaching has obtained increasing attentions (Mishra et al., 2008a; Xin et al., 2009; Zeng et al., 2012).

Pulp density is a very important factor which determines commercial application of bioleaching to some degree. An increase in pulp density from 1% to 2% (w/v) means a sharp reduction of 50% in both quantity of leaching media and size of bioreactor, resulting in a great drop in bioleaching cost. In bio-hydrometallurgy of low-grades ores, the pulp density is generally 10% or higher (Rohwerder et al., 2003). In contrast, the optimizing pulp density was only 1% or lower with spent LIBs possibly thanks to the toxic electrolyte (Mishra et al., 2008a; Xin et al., 2009; Zeng et al., 2012), keeping the promising biotechnology away from its practical application.

In this work, bioleaching of spent LIBs at higher pulp density of 2% or above was explored. The goals of this study were (i) to analyze the bioleaching performance of Co and Li from spent LIBs when pulp density varied from 1% to 4%; (ii) to assess the feasibility to improve bioleaching efficiency of Co and Li at pulp density of 2% based on process controls; (iii) to probe the bioleaching thermodynamics and dynamics of Co and Li at pulp density of 2%; and (iv) to expound the bioleaching microprocess of Co and Li at pulp density of 2% using XRD and SEM.

2. Materials and methods

2.1. Preparing spent LIBs powder and determining content of Li and Co

The spent LIBs were manually dismantled into different portions including plastic shell, cathode, anode, aluminum foil and so on. Then the separated active cathode and anode containing dense Co and Li were mixed, ground by milling and sieved to obtain a mesh size of less than 200 μm (Mishra et al., 2008a). The resulting powder, used for bioleaching experiments, was digested by HF–HNO_3–HCl method (USEPA, 1996) to determine the content of Co at 358 mg g^{-1} and Li at 45 mg g^{-1} using AAS.

2.2. Acclimation of LIBs-tolerant bacteria and media

The *Alicyclobacillus* sp. as sulfur-oxidizing bacteria (SOB) and the *Sulfobacillus* sp. as iron-oxidizing bacteria (IOB) were utilized for bioleaching the spent LIBs in the form of mixed culture after acclimation of 30 d by contact with the spent LIB powder at dose ranging from 0.25% to 1.0% (w/v) (higher dose of over 1.0% evidently inhibited the growth of both cells). The detailed procedures and methods about screen, culture, maintain, inoculum and identification of the SOB and IOB were described in the previous paper (Xin et al., 2011).

2.3. Bioleaching experiments

Bioleaching experiments were conducted according to the previous paper (Xin et al., 2009). Unless specifically stated, bioleaching media containing 4.0 g L^{-1} of mixed energy matters (sulfur and pyrite) was inoculated respectively with SOB and IOB as the mixed culture, followed by incubation at 30 °C until the pH value dropped to ca 1.0 and the ORP value rose to ca 450 mV. At that time, the spent LIB powder was added into the media to a final concentration of 2% to initiate the bioleaching after its pH value was adjusted precisely to pH 1.0. Three pulp densities (1%, 2% and 4%) were set to examine bioleaching behavior of Co and Li when pulp density increased from 1% to 4%. Three doses of mixed energy substrates (2.0, 4.0 and 8.0 g L^{-1}) were set to assess the feasibility of improving extraction of Co and Li by lifting energy matters dose. The pH value of the media was controlled at pH 2.0 during bioleaching by adding H_2SO_4 to assess the possibility of suitable pH for cells growth to promote extraction of Co and Li (bioleaching dose was obtained by measured dose subtracted released one in blank flasks with addition of the same amount of exogenous H_2SO_4). Three bioleaching temperatures (30, 35, and 40 °C) were set to inspect the feasibility of rising temperature to improve performance. The suitable controls including cells-free media, pure H_2SO_4 solution at pH 1.0, H_2SO_4 at pH 1.0 + $FeSO_4$ at 2.0 g L^{-1}, H_2SO_4 at pH 1.0 + $Fe_2(SO_4)_3$ at 2.0 g L^{-1} were run. During bioleaching, release dose of Co and Li, Fe^{2+} and Fe^{3+} dosage, pH, ORP and cell number were periodically monitored. All experiments were carried out in triplicates.

2.4. Bioleaching thermodynamics of Co and Li under different temperatures

The thermodynamics ΔG, ΔH, ΔS between bioleaching and chemical leaching were calculated and compared based on the following formula (Dean, 1999):

In the case of standard state (298 K, 101 kPa)

$$\Delta_r G_m^\theta\ (298\ \mathrm{K}) = \sum V_i \Delta_r G_m^\theta\ (298\ \mathrm{K}) - \sum V_j \Delta_r G_m'\ (298\ \mathrm{K}) \quad (1)$$

$$\Delta_r H_m^\theta\ (298\ \mathrm{K}) = \sum V_i \Delta_r H_m^\theta\ (298\ \mathrm{K}) - \sum V_j \Delta_r H_m^\theta\ (298\ \mathrm{K}) \quad (2)$$

(*i*, products; *j*, reactants; *V*, stoichiometric number of *i* or *j*).

$$\Delta_r S_m^\theta\ (298\ \mathrm{K}) = \left(\Delta_r G_m^\theta\ (298\ K) - \Delta_r H_m^\theta\ (298\ \mathrm{K})\right)/298\ \mathrm{K} \quad (3)$$

In the case of non-standard state

$$\Delta_r G_m^\theta = \Delta_r H_m^\theta - T \Delta_r S_m^\theta \quad (4)$$

(*T*, reaction temperature, K)

Assuming that both $\Delta_r H_m^\theta$ and $\Delta_r S_m^\theta$ was independent of *T*.

2.5. Bioleaching dynamics of Co and Li at different temperatures

The bioleaching kinetics of Co/Li from spent LIBs under different temperatures were compared by establishing the mathematical relationship between the fraction of Co and Li dissolved and the leaching time using various kinetic models according to Mishra et al. (2008b).

2.6. Apparatuses and conditions

The pH value of bioleaching media was determined using a pH meter, the ORP value was determined by portable ORP meter; the Co and Li was determined by AAS after the samples were centrifuged at 10000*g* for 10 min to remove the cells and solid matters. Fe^{2+} and Fe^{3+} dosage were measured by spectrophotometry (Harvey et al., 1955). The cell number of the mixed culture was counted using a microscope after the samples were treated by ultrasonic to release the adherent bacteria. Structure change analysis was performed by XRD. Morphology variation of the spent LIB powder after bioleaching was analyzed by SEM.