Journal of Power Sources 320 (2016) 257–266

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Bioleaching of valuable metals from spent lithium-ion mobile phone batteries using *Aspergillus niger*

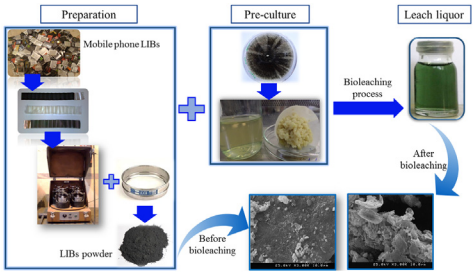
N. Bahaloo Horeh, S.M. Mousavi*, S.A. Shojaosadati

Biotechnology Group, Chemical Engineering Department, Tarbiat Modares University, Tehran, Iran

HIGHLIGHTS

- Bioleaching of spent lithium-ion mobile phone batteries using *Aspergillus niger* was studied.
- The highest metal recovery yields were obtained in spent medium bioleaching.
- Leaching using biogenic acids had higher metals recovery than chemical leaching.
- HPLC results indicated citric acid plays an important role in bioleaching of LIBs.
- 100% Cu, 95% Li, 70% Mn, 65% Al, 45% Co and 38% Ni were leached in spent medium.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 8 March 2016
Received in revised form
7 April 2016
Accepted 21 April 2016
Available online 29 April 2016

Keywords:
Bioleaching
Spent Li-ion batteries
Metals recovery
Organic acids
Aspergillus niger

ABSTRACT

In this paper, a bio-hydrometallurgical route based on fungal activity of *Aspergillus niger* was evaluated for the detoxification and recovery of Cu, Li, Mn, Al, Co and Ni metals from spent lithium-ion phone mobile batteries under various conditions (one-step, two-step and spent medium bioleaching). The maximum recovery efficiency of 100% for Cu, 95% for Li, 70% for Mn, 65% for Al, 45% for Co, and 38% for Ni was obtained at a pulp density of 1% in spent medium bioleaching. The HPLC results indicated that citric acid in comparison with other detected organic acids (gluconic, oxalic and malic acid) had an important role in the effectiveness of bioleaching using *A. niger*. The results of FTIR, XRD and FE-SEM analysis of battery powder before and after bioleaching process confirmed that the fungal activities were quite effective. In addition, bioleaching achieved higher removal efficiency for heavy metals than the chemical leaching. This research demonstrated the great potential of bio-hydrometallurgical route to recover heavy metals from spent lithium-ion mobile phone batteries.

1. Introduction

Nowadays, by reason of the development of industry, communication, and new technologies, the usage of such portable electronic devices as mobile phones, laptops, notebooks, and cameras, to name a few, has substantially risen. Therefore, the demand for rechargeable batteries as electrochemical power sources has rapidly increased. The increase in the production and consumption of rechargeable batteries has augmented the amount of spent batteries [1]. Among rechargeable batteries, lithium-ion batteries (LIBs) have extensively been employed. For example, the

* Corresponding author.
E-mail address: mousavi_m@modares.ac.ir (S.M. Mousavi).

http://dx.doi.org/10.1016/j.jpowsour.2016.04.104
0378-7753/

consumption of LIBs reached 4.49×10^9 units in 2011 [2] and in China, the quantity and weight of spent LIBs in 2020 can exceed 25 billion units and 500 thousand tons, respectively [3]. Indeed, LIBs have played a leading role in the global rechargeable battery market today [4], by virtue of their high energy density, long life cycle, low self-discharge rate, safety, high cell voltage, wide temperature domain of use, light weight, absence of memory effect, and the fact that, unlike older generation of batteries like nickel–cadmium (Ni–Cd) batteries, they do not contain hazardous heavy metals such as cadmium [5,6].

LIBs consist of an anode, a cathode, a separator, collectors, electrolyte, and a metal protective shell. The electrolyte, consisting of a lithium salt such as $LiPF_6$, $LiBF_4$ or $LiCF_3SO_3$, is dissolved in organic solvents like dimethyl carbonate (DMC), ethylene carbonate (EC) and diethyl carbonate (DEC). Polyethylene (PE) or polypropylene (PP) is used as a separator between the two electrodes. The anode contains graphitic carbon, and the anode collector is Cu foil. The cathode is made of lithium mixed metal oxide, and the cathode collector is Al foil. $LiCoO_2$ is used as the cathode material in 37.2% (w w^{-1}) of the LIBs, $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ is employed in 29.0% (w w^{-1}), $LiMn_2O_4$ in 21.4% (w w^{-1}), $LiNiO_2$ in 7.2% (w w^{-1}) and $LiFePO_4$ is made use of in 5.2% (w w^{-1}) of the LIBs. Furthermore, polyvinylidene fluoride (PVDF) is used in the electrodes so as to hold the material particles together [7,8]. Cathode and anode are folded into a prismatic or cylindrical form and the assembled battery is fitted into a metal shell [4].

Nonetheless, owing to the vast amount of spent LIBs and its concomitant environmental and economic ramifications, recycling has become a significant issue. Safe disposal of hazardous wastes has led to strict global regulations. For instance, according to the EU Battery Directive 2006/66/EC, by 2011, at least, 50% by mean weight of waste batteries should be recycled into substances for their primary application or for other applications, except energy recovery [9]. Although spent LIBs are not deemed as dangerous waste, due to their toxic and flammable ingredients, their disposal in the environment entails a potential hazard to the environment and human health [10]. Unfortunately, most spent batteries are disposed of in landfills as domestic waste. In landfills, organic electrolytes and heavy metals present in spent batteries gradually leach into the soil, groundwater, or surface water. Additionally, the capacity of landfill spaces is limited. Therefore, landfilling is undesirable. On the other hand, LIBs contain valuable metals like aluminum, copper, nickel, lithium, cobalt, and manganese. LIBs can, as a matter of fact, act as a secondary and a cheaper mineral source of valuable metals and be even richer than mineral ores [11]. Previous studies have indicated that if only the cobalt and nickel of LIBs are recycled and reused instead of withdrawing from virgin mineral sources, 51% of natural resources will be saved [9].

It is anticipated that the usage of LIBs will expand more in the future, therefore, finding new methods and technologies for recycling spent batteries is as crucial as optimizing the current strategies [4]. Pyrometallurgical and hydrometallurgical processes or combination both of them are traditional metal recovery methods [4,11]. In all pyrometallurgical LIBs recycling processes, lithium cannot be recovered and it is the major disadvantage of this method [12]. It is indispensable, however, to find an economic and eco-friendly process that can discard certain disadvantages of traditional methods, including low efficiency, high energy consumption, being expensive and involving risk, not to mention the secondary pollution caused by chemical reagents and by-products [13]. Biohydrometallurgy, environmentally friendly and suitable for low-grade sources, is an effective method of metal recovery that consumes less energy, and needs a mild reaction condition along with a few industrial requirements [14]. In this method, interactions between microorganisms (including both bacteria and fungi) and surfaces of ore or waste cause the metals solubilization [15]. Most previous studies conducted on bio-recovery of spent LIBs were done using bacteria [2,13,16–19]. To the best of our knowledge, no studies have been reported as to the fungal leaching of LIBs. Compared to bacteria, fungi have more ability to tolerate toxic materials, have a shorter lag phase and a faster leaching rate; what is more, they grow in alkaline and acid-consuming materials. Moreover, the metabolites excreted by fungi, like organic acids, help leach the metals [20] by way of replacing metal ions from the waste with hydrogen ions, or by forming soluble metal complexes and chelates [21]. Accordingly, heavy metal toxicity is reduced for biomass thanks to the formation of metal complexes or precipitation by excreted metabolites. In fact, such excreted metabolites act as lixiviants for bioleaching of solid wastes [20,22].

Several fungi like *Penicillium simplicissimum*, *Penicillium chrysogenum*, *Aspergillus niger* and so forth, are used for the recovery of heavy metals from different solid wastes such as municipal solid waste incinerator fly ash [20,23–25], spent catalyst [20,25,26], electronic scraps [29] and red mud [26,30].

The main objective of this study was to examine the ability of *A. niger* to leach heavy metals from spent LIBs and to find out the most suitable method among one-step, two-step and spent medium bioleaching methods. In addition, the characteristics of spent LIBs including their composition, component phases, and acid neutralization capacity were examined. Prior to bioleaching experiments, the properties of fungal growth, including pH, biomass and organic acid concentration were determined. In order to investigate the progress of bioleaching, the XRD, FTIR, and micromorphology analysis of spent LIB particles were done and the metal recovery from spent LIBs was ultimately examined. Chemical leaching was performed to compare the bioleaching efficiency of spent LIBs.

2. Experimental

2.1. Spent LIBs

Spent mobile phone batteries were collected from mobile phone markets. All batteries were Li-ion made from different manufacturers with different sizes and types of cathode. At first, all spent batteries were discharged to avoid self-ignition and short-circuiting. Spent batteries were then dismantled and separated manually into cathodes, anodes, plastic separators and metal cases. Afterwards, the classified portions were weighed. Next, cathodes and anodes were dried at 60 °C for 24 h to remove moisture. After drying, the classified cathodes and anodes were once again weighed so as to calculate the percentage of battery components. The average percentage of different parts of batteries is shown in Fig. 1.

Cathodes and anodes were manually crushed into small particles with a pair of scissors and then ground by a ball mill (Fritsch, Germany) until transmuted to fine powder. The powder was sieved by vibrator shifter with mesh# 200 to get homogeneous mixture. All battery powders used in this research were of a particle size less than 75 μm. The final mixture was used for all subsequent experiments, yet prior to use, it was autoclaved at 121 °C for 15 min.

2.2. Characterization of spent LIBs

2.2.1. LIBs composition

The metal composition of LIB powder was determined by both chemical digestion and submitting to X-ray fluorescence (XRF) and subsequent analysis with XRF analyzer (PW2404, Philips, Netherland). In chemical digestion, the metal contents were determined using four acids, namely HCl, HNO_3, $HClO_4$ and HF. At first, 0.5 g of