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Application of a mixed culture of adapted acidophilic bacteria in two-step bioleaching of spent lithium-ion laptop batteries

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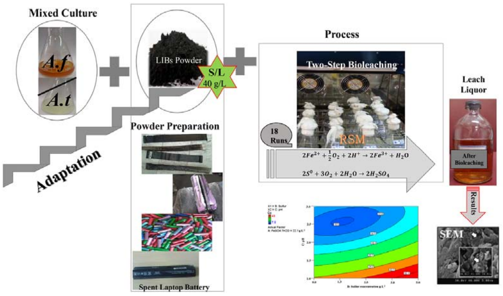
HIGHLIGHTS

- Two-step approach and biogenic acid were used in bacterial mixed culture adaptation.
- Energy sources concentration and pH were optimized in spent LIBs detoxification.
- Oxidation reduction and acid dissolution mechanisms caused Li, Ni and Co recovery.
- 99.2% of Li, 89.4% of Ni and 50.4% of Co was recovered under optimum conditions.
- Toxicity assessment tests confirmed safe disposal of the bioleached spent LIBs.

GRAPHICAL ABSTRACT



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ABSTRACT

The rapid increase in the production of electrical and electronic equipment, along with higher consumption of these products, has caused defective and obsolete equipment to accumulate in the environment. In this research, bioleaching of spent lithium-ion batteries (LIBs) used in laptops is carried out under two-step condition based on the bacterial activities of a mixture of *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans*. First, the best inoculum ratio of two acidophilic bacteria for the mixed culture is obtained. Next, adaptation is carried out successfully and the solid-to-liquid ratio reaches 40 g L^{-1}. Response surface methodology is utilized to optimize the effective variables of initial pH, iron sulfate and sulfur concentrations. The maximum recovery of metal is about 99.2% for Li, 50.4% for Co and 89.4% for Ni under optimum conditions of 36.7 g L^{-1} iron sulfate concentration, 5.0 g L^{-1} sulfur concentration and initial pH of 1.5 for the best inoculum ratio of 3/2. Results of FE-SEM, XRD and FTIR analysis before and after bioleaching confirm that bacterial activity is a promising and effective route for metal recovery from spent LIBs. Toxicity assessment tests demonstrate the suitability of the bioleached residual as a nonhazardous material that meets environmental limitations for safe disposal.

1. Introduction

The consumption of portable electronic devices such as mobile phones, laptops and cameras has increased sharply with technological development [1]. Electrochemical power sources such as rechargeable batteries are important electronic components of these devices and are in high demand [2]. Lithium-ion batteries (LIBs) having desirable characteristics such as high energy density, low self-discharge rate, high cell voltage and no memory effect have been employed more extensively in the global market than the other types of rechargeable

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batteries [3]. The very short lifespan of LIBs (less than 3 years for consumer products and roughly 10 years for electronic vehicles (EVs)) and the high rate of their consumption has increased the accumulation of spent LIBs in the environment [4].

Recycling of spent LIBs is a crucial strategy for protecting the environment and produce economic revenue from the valuable metals such as Co (5%–20%) and Li (5%–7%) recovered from cathodes, which can also reduce consumption of natural resources [5]. Studies have shown that from 2021 to 2023, a shortage of Li will occur [6]. If 20 million LIBs are produced annually, in 60 years, the Co deposits on earth will be exhausted and the required amount of Ni would be 170 times greater than the current capacity of mines [7]. The use of recovered metals for the production of LIBs can significantly save energy [8] and reduce the percentage of natural resource usage 51.3%, decreasing rock mining and fossil fuel and nuclear energy consumption [9].

The material used in anodes of LIBs is usually a Cu foil that is covered by a layer of carbon [10,11]. The material used in a cathode is Al covered by toxic materials like $LiXMA_2$ ($LiCoO_2$, $LiNiO_2$, $LiNiMnCo_2$) that must be recovered and treated before disposal in the environment [11–13]. Heavy metals are conventionally removed from waste electrical and electronic equipment (WEEE) by pyrometalurgical and hydrometallurgical methods; however these methods are not desirable because of the difficulty of the control of secondary waste produced, the high cost and the risks associated with the process [14]. In recent years, most of the researches are focused on developing environmentally sustainable processes for metals recovery from e-waste which can simultaneously reduce the operational cost and energy requirements. For this purpose, the most promising technology is bioleaching by the application of naturally occurring microorganisms [15]. Biohydrometallurgical routes by overcoming the operational and technical challenges can be considered as a suitable alternative to the chemical leaching methods. No requirement of hazardous and toxic chemicals usage and harsh operational conditions (operation at ambient temperature and pressure) makes bioleaching process more feasible than the conventional processes [16,17]. In general, bioleaching process is more simple, and economical and less energy intensive in comparison to the hyrometallurgical and pyrometallurgical methods [18]. It was reported that the capital cost required by biological method is one-third to one-half of the conventional methods [19]. On the other hand, bioleaching is more efficient and environmentally sound process which does not need skilled workers and large amount of industrial requirements [5]. It must be considered that lithium recovery from LIBs can not be achieved with pyrometallurgical methods [1]. The best comparison of the bioleaching, pyrmetallurgical and hydrometallurgical methods can be done by performing a comprehensive life cycle assessment (LCA) technique, in which all the above mentioned and environmental aspects are considered [17].

In the bioleaching method, a microorganism can convert insoluble solids to soluble and extractable forms. Among chemolithoautotrophic mesophilic bacteria, *Acidithiobacillus ferrooxidans* can act as a powerful oxidizing agent to oxidize ferrous iron to ferric iron [15] and *Acidithiobacillus thiooxidans* oxidizes sulfur by reducing S^0 to SO_4^{2-} as an energy source [20]. These bacteria also consume CO_2 as a carbon source [21]. One limitation of bioleaching is the sensitivity of the microorganism to the high pulp density of the waste, which requires the use of a high quantity of media [3]. The use of a mixed culture of *A. thiooxidans* and *A. ferrooxidans* increases metal recovery in comparison with their individual use [22,23]. Bioleaching can be performed in one or two-step condition through biomass exposure to waste and spent-medium using a cell-free medium. In the one-step method, the LIBs powder is added immediately to the microorganism in the culture medium. In two-step bioleaching, LIBs powder is added after the microorganism attains maximum growth (logarithmic growth phase) [24–26]. The two-step method is a more efficient metal mobilization process in which the growth of bacteria to its logarithmic phase occurs in pure culture (in the absence of LIBs) [27].

Mishra et al. [5] first studied bioleaching of spent LIBs. Several researchers have studied the bioleaching of WEEE for metal recovery [1,3,12,18,19,28,29] using bacteria [3,5,12,18,28,29] and fungal strains [1,19], primarily with the one-step method of bioleaching. Bahaloo et al. [1] studied two-step and spent-medium bioleaching of LIBs and in the other study, they optimized the process with the aim of maximizing organic acid production by fungi using response surface methodology (RSM) [19]. The catalytic effects of metals (Cu and Ag) on the bioleaching of LIBs has been studied [12,28].

Researchers have studied the different factors and variables that can affect the bioleaching of E-waste. The only study that has used RSM for the optimization of metal recovery from LIBs was one using fungal microorganisms [19,30].

RSM has been used several times for metal recovery from other WEEE. Ijadi et al. [15] studied bioleaching of household batteries and evaluated the effects of initial pH, particle size and initial Fe^{3+} ion concentration. Copper and gold bioleaching from computer printed circuit boards was optimized using the central composite design (CCD) of RSM. The four factors used for optimization were initial pH, pulp density, particle size and glycine concentration with the goal of obtaining maximum metal recovery [31]. RSM is a suitable method that has been used by several researchers to optimize the bioleaching of E-waste [15,19,32,33].

In this work, a mixture of *Acidithiobacillus* bacteria has been used for the recovery of Co, Li and Ni from spent LIBs. Selection of the best inoculum ratio and adaptation of mixed bacteria to waste was the first step. The acids produced by *A. thiooxidans* were used for pH adjustment. In comparison with other works, higher pulp densities were achieved with a novel method which used one-step for adaptation up to pulp density of 10 $g\ L^{-1}$ and then two-step to a pulp density of 40 $g\ L^{-1}$. For bioleaching, a two-step method was used to recover Li, Co, Ni from LIBs. The process was optimized considering three variables influencing the process; initial pH, initial iron sulfate ($FeSO_4{\cdot}7H_2O$) concentration and initial sulfur concentration. The influence of each variable on metal recovery was studied by statistical methods and the results confirmed the bioleaching mechanisms reported in previous studies for different metals. The results of FE-SEM, XRD and FTIR were used to evaluate the bioleaching. Toxicity assessment of the powder was performed to confirm the suitability of the bioleached LIBs for landfill.

2. Experimental

2.1. Spent LIBs preparation

In this work, 20 spent laptop batteries composed of 100 LIBs were purchased from the market. First, metal case of the battery was longitudinally incised and the cathode, anode and the plastic layer were manually disassembled. The disjoint segments were then weighed and the cathodes and anodes were dried in an oven at 75 °C for 90 h to remove the electrolyte liquid. The samples were weighed again after drying. The electrolyte weight was calculated as the difference between the weights before and after drying. This allowed the percentage of battery components to be calculated (30% case, 15% anode, 35% cathode, 5% plastic, 12% electrolyte and 3% loss). The copper layer of the anodes and the aluminum layer of the cathodes were scratched from the electrode surface. The cathodic and anodic layers were then mixed and ground using a ball mill for 6 h. The LIBs powder was sieved through #200 mesh to obtain a particle size of < 75 µm.

2.2. Strains and mixed culture medium

A mixture of the chemolithoautotrophic mesophilic bacteria *A. thiooxidans* and *A. ferrooxidans* was used in this study. Mäkinen et al. [23] found that the regular growth of these acidophilus bacteria in a