COIN BATTERY LEACHING WITH *Acidithiobacillus ferrooxidans* FERMENTED BROTH

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ABSTRACT

Residues of batteries are regarded as hazardous substances for both the ecosystem and human well-being because of their toxic components and extended decay periods. The current research delved into the process of bioleaching lithium and manganese from spent coin cells, employing *Acidithiobacillus ferrooxidans* fermented broth under heat and no heat application. About 3% and 45% of Mn and Li were leached under a retention time of 120 min and ambient temperature, while under 80 °C it was observed a selectivity of Li leaching with 50% recovery without a significant recovery of Mn. It was discovered that the addition of temperature improved the kinetics without much influencing the final recovery valor. The experimental results obtained can support a sustainable and desirable process for the comprehensive recovery of metal from spent batteries.

Keywords: Acidophilic Bacteria. Bioleaching. Button Cell. CR2032. Kinetics.

INTRODUCTION

Batteries are in basically everything that is used in the day by people such as smartphones, cars, alarms, and toys, but when it comes to the end of their cycle life most of these components are not correctly discarded. It is known that the improper disposal of batteries is a major environmental problem that affects the environment, public health, and natural resources worldwide. Although they are small, batteries contain a variety of toxic substances, as well as corrosive chemicals and heavy metals, which can pollute soil, water, and air when improperly discarded. This practice can result in irreparable damage to the environment and human health. Therefore, it is of utmost importance to raise awareness about the importance of proper battery disposal, as well as to promote safe and appropriate recycling and disposal practices.[1]

Some of the forms that batteries are disposed of in the current days are by incinerating, which can concentrate heavy metals in the air, or by disposing of in landfills that can contaminate the soil and water. Among the alternatives is the recycling process, which can occur in different ways as the hydrometallurgical process which shreds the battery to separate the parts after that uses electrolysis to separate metals in solution, or the processing of lithium batteries through pyrolysis.[2] However, the use of pyrolysis has several disadvantages, such as high equipment and maintenance costs, requiring constant cleaning services, another point is the high energy demand as it operates at high temperatures, which causes another source of expense.[3]

With the increasing application of microbial processes in the mining industry, the bacterium *Acidithiobacillus ferrooxidans* is highly relevant in the bioleaching process.[4,5] Bioleaching is a process that utilizes microorganisms to extract metals from minerals and solid wastes, it consists of a method that is considered environmentally friendly, low-cost, and accessible. The most used bacterium for bioleaching is *A. ferrooxidans*, it is a chemolithotrophic bacteria, and its energy comes from the oxidation of inorganic compounds, such as metallic sulfides, sulfur, and ferrous iron, meaning it can convert toxic and hazardous compounds into less aggressive compounds.[6]

MATERIAL & METHODS

The *A. ferrooxidans* strains were isolated from a uranium mine in the state of Parana, Brazil, and courteously donated by Professor Denise Bevilaqua from the biohydrometallurgy laboratory of the Institute of Chemistry at the State University of Sao Paulo (UNESP), Araraquara, Sao Paulo. The culture was maintained once a week using a synthetic culture medium. The *A. ferrooxidans* were cultured in a T&K medium formed by the mixture of solutions A (0.5 g L^{-1} $(NH_4)_2SO_4$, $MgSO_4{\cdot}7H_2O$, and KH_2PO_4) and B (33.3 g L^{-1} $FeSO_4{\cdot}7H_2O$).

The bioleaching test with *A. ferrooxidans* was carried out in 250 mL Erlenmeyer flasks, prepared with 80 mL of basal medium with the pH adjusted to 1.80, closed adequately with cotton and gauze stoppers. The flasks were sterilized in an autoclave for 20 min at 1 atm and 121 °C. After that, 10 mL of inoculum with an initial concentration of 107 cells/mL measured by a Neubauer chamber and 20 mL of iron (II) sulfate heptahydrate ($FeSO_4{\cdot}7H_2O$) were added to the medium. The *A. ferrooxidans* strain was incubated for 7 days on a shaker table at 100 rpm and 30 °C until the color changed from greenish-white to brick red.[7] After fermentation, the *A. ferooxidans* broth was used as a source of acid solution, it was centrifugated at 5000 rpm for 12 min and the supernatant was reserved to use.

This work used coin batteries as the raw material and its methodology was based on Chen et al. (2016)[4], from it was selected the following conditions: 2 h of reaction time and 20 g L^{-1} of pulp density (0.6 g of battery powder in 30 mL). The batteries were opened in a bench vise to separate the metal casing parts, then they were taken to a fume hood to complete the disassembly and powder storage for the experiments.

Penicillin bottles of 50 mL were used in the reaction, the powder mass was inserted in the as well as supernatant reserved, and sacrifice flasks were collected during different times: 5 min; 15 min; 30 min; 1 h; 1 h 30 min; 2 h. After this, the hot solution was filtered in a 2 µm paper filter, diluted in deionized water, and read in a flame atomic absorption spectrum (Shimadzu AA-7000). The percentage of soluble metal recover in the middle was calculated using Equation 1, where r is the value from AA analysis, d is the dilution factor, Vf and Vi are the final and initial volume, respectively, mi is the initial powder mass and mp is the metal mass percentage in the sample.

$$R\,(\%) = \left(\frac{0.001 \cdot r \cdot d \cdot \left(\frac{V_f}{V_i}\right) \cdot V_f}{m_i \cdot m_p}\right) \cdot 100\% \qquad (1)$$

With the aim of investigating the leaching properties of the water and middle, experiments were carried out in the optimum point of the reaction to verify its efficiencies in the recoveries.

RESULTS & DISCUSSION

During the experiment, it was possible to observe that the pH did not vary, it stayed around 2. In Figures 1a and 1b, it was noted that higher extractions of lithium were achieved than manganese, which could be caused due to the lack of cells in the medium.

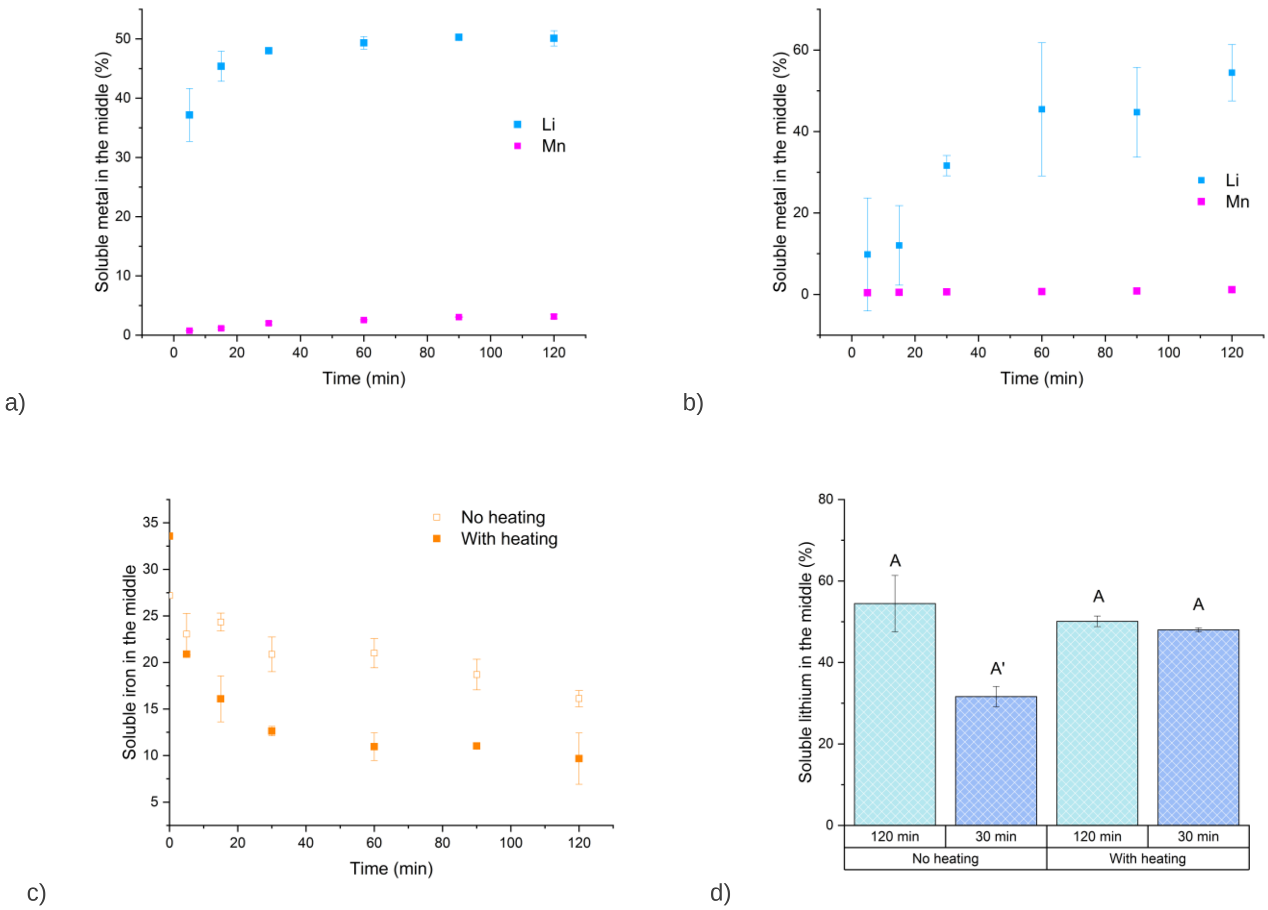

Figure 1 Metal extrations. a): Kinetics with heating; b) Kinetics without heating; c) Iron's kinetic; d) comparison between treatments. Letters with different markers are statistically different by Tuckey test with a 0.05 significance level.

According to the state of the art, Mn oxidation occurs at the cell surface, where there are oxidants and enzymes responsible for it.[8,9] Another possibility of non-reduction is due to the iron precipitation, which removes Fe^{3+} from the medium and makes the oxidation of Mn impossible.[10] During the fermentation process, the iron present in the medium decants, is removed with the cells in the centrifugation, this decrease is shown in Figure 1c at 0 min (before powder battery addition). The remaining iron in the medium promoted Mn oxidation subtly (Figures 1a and 1b), where the manganese leaching increases when the soluble iron decreases, indicating that there was oxidation of manganese (it passed to the aqueous phase) and reduction of iron, which was precipitated subsequently (solid phase), not being detected by AA analysis.

It was done a Tuckey test with the results of lithium extractions to verify its similarities (between 50%), which is presented in Figure 1d. It was possible to verify that only the leaching of 30 min with no heating was considered significantly different. Unfortunately, isn't possible to determine if the treatment with heating for 30 min or the one without heating for 120 min is more economically viable, because for that it would be necessary an economic analysis of the process, but it allows both options to be open for application where they fit best.

The growth and activities of microorganisms can be inhibited by the presence of toxic metals, organic compounds, high temperatures, or harsh pH. Therefore, this study showed that the *A. ferrooxidans* broth after the fermentation was a candidate for bioleaching or bioremediation applications due to the potential oxidation of lithium.

1 CONCLUSION

In conclusion, it was proposed an innovative way to recover metal from spent batteries by a separated bioleaching process, i.e., the production of fermented broth and sequential leaching. So, after the application of *A. ferroxidans* fermented broth, it was observed a selectivity of Li towards Mn. Leaching efficiencies of 45% and 50% for Li were attained at an ambient temperature and 80 °C, respectively. The results showed that bioleaching as an eco-friendly process is a potential route for Li recovery.

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