ADVANCING CRITICAL MATERIALS RECOVERY VIA BIOBASED RECOVERY PROCESSES

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Abstract

The demand for critical minerals and materials (CMMs) is rising with the increased needs of industry and transportation sectors. With dwindling natural reserves and significant supply risks, it is critical to harvest CMMs not only from primary resources (e.g., ore deposits), but particularly the secondary resources from the domestic waste streams (e.g., e-scrap, black mass from recycled batteries, mining waste, processed water, and manufacturing scrap). Biohydrometallurgy processes present promising avenues toward establishing sustainable and economically viable methods for separating, recovering, and concentrating critical materials from the recycled batteries and e-scraps. Bioleaching is the first step in biohydrometallurgy, where microbial activity facilitates the solubilization of CMMs. Argonne's patented arrested methanogenesis technology (Urgun-Demirtas, 2024) produced high-titer organic acids and microbial exudates as biolixiviant. Several factors including pH, operating temperature, solid/liquid ratio (pulp density), and reactor residence time were evaluated to determine the optimal conditions for CMMs leaching from black mass, aiming to surpass the extraction efficiencies previously reported in the literature. An in-depth analysis of experimental data was performed to characterize the key performance indicators across a range of CMMs concentrations and profiles to scale up the new bioleaching process. Our results demonstrate the development of a new eco-friendly bioleaching process, achieving over 90% recovery of critical metals like cobalt and lithium from spent batteries.

Introduction and Motivation

The demand for critical minerals and materials (CMMs) is rising. For example, global electric vehicle (EV) sales have increased from around 1 million vehicles in 2017 to more than 10 million vehicles in 2022 (IEA, 2023) and the global electric mobility market is expected to reach $4,720 billion by 2034, growing 22.96 % annually from 2024 to 2034 (Electric Mobility Market, 2024). This rapid expansion has caused a surge in demand for essential components like lithium-ion batteries, rare earth magnets, electrical steel for motors and charging infrastructure, and power electronics. The global cobalt reserve is predicted to be depleted by 70% by 2040, and the demand for lithium-ion batteries is expected to exceed the supply of raw materials by 2030 (Alinapah et al., 2023; Roskill, 2020). In July 2023, U.S. Department of Energy (DOE) published a Critical Materials Assessment (CMA) report identifying seven materials (dysprosium, neodymium, gallium, graphite, cobalt, terbium, and iridium) as critical in the short term (2020 to 2025) based on their importance to the energy and supply risk, while materials like lithium and nickel were considered near-critical in the short term and are expected to become critical in the medium term (2025-2035) (Bauer et al., 2023). The current supply chain of these CMMs relies heavily on foreign sources (US Geological Survey, 2023). As global demand for batteries in various electronic devices and EVs escalates, the surge of used battery disposal poses significant environmental pollution problems. Black mass, a byproduct of EV battery recycling, is rich in valuable metals like cobalt, nickel, and lithium, presenting both an environmental concern and an untapped resource. The global Black Mass Recycling market was estimated to reach over $50 billion by 2030, exhibiting a CAGR of 19-21% during the forecast period (Black mass recycling market size report, 2023). According to S&P Global research (2023), recycled materials in new battery synthesis could account for 30% of nickel, 27% of lithium, and 40% of cobalt demand between 2020 and 2050.

To de-risk the CMM supply chain in the U.S., it is essential to establish a robust domestic manufacturing sector with a diverse set of producers that leverages the latest research and development (R&D) in material extraction, substitution, recycling, reuse, and remanufacturing (Bauer et al., 2023). There is a need for the development of environmentally sustainable and economically viable technologies that enable the recovery and reuse of these critical materials in new battery production to reduce the carbon footprint required for new mining activities and enable a circular economy for critical materials.

Review of Related Work

The increasing demand for critical metals and materials cannot be fulfilled by classical mining alone. Waste management of used batteries is an environmental, social, and economic liability and requires compliance with reporting requirements. Through effective recycling and recovery processes, valuable CMMs can be extracted from domestic waste streams (e.g., e-scrap, black mass from recycled batteries, mining waste, processed water, and manufacturing scrap). A comprehensive review of battery recycling technologies, their potential challenges in the development of cost effective and sustainable technologies environmental considerations, and the feasibility of recovered critical materials in remanufactured batteries has been discussed significantly in review articles published in the past decade (Srinavasan et al., 2025). Currently, pyrometallurgical and hydrometallurgical processes are the primary and well-established methods, while direct regeneration has been an emerging approach to recover CMMs and other components from the battery components. However, most of these techniques remain energy-intensive and require large quantities of hazardous chemicals, particularly potent mineral acids like hydrochloric, sulfuric, and nitric acids. The residual strong mineral acids in the resulting waste product are of severe environmental concern and treatment incurs high capital costs. The limitations of current recycling methods show that they are not sustainable techniques in the long run (Chen et al., 2019). There is a need to replace energy and chemical intensive leaching processes with cost-effective and environmentally friendly technologies to leach the bounded CMMs from waste streams.

Technology Approach

Microbially-produced lixiviants (predominantly gluconic acid) are reportedly more effective at solubilizing CMMs than abiotically prepared solutions with high gluconic and phosphoric acid concentrations, likely due to the biological production of additional organic acids that lower the pH of the medium (Castro et al, 2021; Alipanah et al, 2023). Experimental data from bioleaching of rare elements also showed that the gluconic acid concentration in the reaction environment was not necessarily the prime determinant of leaching efficiency, and other components of the microbial exudates also contributed to acidity of the reaction medium (Reed et al., 2016). Most bioleaching studies are still at the lab-scale due to complexity of processes and the challenge of achieving high recovery efficiencies. At full scale, low pulp densities (solid to liquid ratio in the reactor) reduce recovery efficiencies. Biolixiviants production also depends on enzymatically treated feedstocks such as corn stover or potato hydrolysate, which require pretreatment (e.g., hot water treatment) and the use of costly enzymes (Jin et al., 2019). Additionally, the process utilizes Pikovskaya phosphate-modified (Pkm) medium containing yeast extract and dextrose, which may not be cost-effective for scaling up the bioleaching process (Alipanah et al., 2023). The potential cost of aeration is also a concern, with biolixiviants production using *Gluconobacter oxydans* requiring 0.55 to 2.2 vessel volumes per minute (Thompson et al., 2018).

Resource recovery from waste streams is crucial to achieving environmental sustainability via the circular economy. This requires the development of next-generation treatment and recovery technologies to produce new feedstocks and products from waste streams. From our work to date in a BETO-EERE-DOE project, we developed an innovative organic acid (aka short chain carboxylic acids) production process (Urgun-Demirtas, 2024) for converting low-value or negative-value organic waste streams into high-value organic acids, such as butyric acid (Wu et al., 2021, Wu et al., 2023). We have successfully scaled up Argonne's novel, low-cost treatment process from bench-scale digesters (0.5 liters) to pilot-scale digesters (375 liters) (TRL 5). The reported values are the highest acid titers yet to be reported in published literature (Wu et al., 2021, Wu et al., 2023).

The objective of this study was to replace fossil based organic acid-based leaching process with cost-effective and environmentally friendly biobased organic acid and microbial exudates (aka biolixiviants) production technology from organic waste streams to dissolve black mass, hence leaching of the bounded CMMs from spent batteries.

Discussion

The black mass samples from spent EV batteries were analyzed using inductively coupled plasma (ICP) to determine their elemental composition. Table 1 shows the key composition of spent battery black mass which was composed of 4.07% lithium, 13.58% cobalt, 12.23% nickel, and 8.94% manganese by mass. The test results showed high cobalt concentration, the most valuable metal in spent lithium-ion batteries. Moreover, the black mass included significant amounts of lithium, nickel, and manganese.

Table 1. Key Composition of Spent Battery Black Mass (BM)

Element	Al	Co	Fe	Li	Mn	Ni
Concentration in BM (wt.%)	0.32	13.58	0.14	4.07	8.94	12.23

Five organic acids including lactic acid, succinic acid, citric acid, acetic acid, and gluconic acid at 0.2 mol/L were used for testing leaching capability of critical materials and minerals from spent batteries. These acids were chosen because they can potentially be produced from biodegradation of organic waste streams, which could significantly decrease the leaching cost and environmental impact. Organic acids were mixed with black mass at 2.5% pulp density in abiotic conditions to explore their abilities as biolixiviants on extracting critical minerals from spent battery. Leaching experiments were conducted for up to 140 h at 40 °C and samples were collected periodically to understand the bioleaching kinetics. Early results showed that organic acids exhibited highest leaching levels at low pH levels ($pH<4.0$) (data not shown). Longer retention time (140 h) significantly promote leaching capability of acids (Figure 1). Citric acid was the most efficient leaching solvent with highest recovery percentage at 90%, 88%, 89% and 92% for Co, Li, Mn and Ni, respectively. Lactic acid and gluconic acids were also effective for Co, Li, Mn, and Ni recovery from the black mass samples.
The same experiments were conducted by replicating with a reducing agent, specifically ferrous sulfate. The role of a reducing agent is to donate electrons, facilitating the leaching process. Leaching capabilities of all acids were enhanced with the stoichiometric addition of ferrous sulfate (Figure 2). Citric acid, lactic acid, and gluconic acid are the three most efficient leaching agents for critical minerals (i.e., Co, Li, Mn, Ni) recovery (% 100 recovery in most cases). Succinic acid and acetic acid leaching capabilities were enhanced greatly for Co, Li, Mn and Ni recovery.

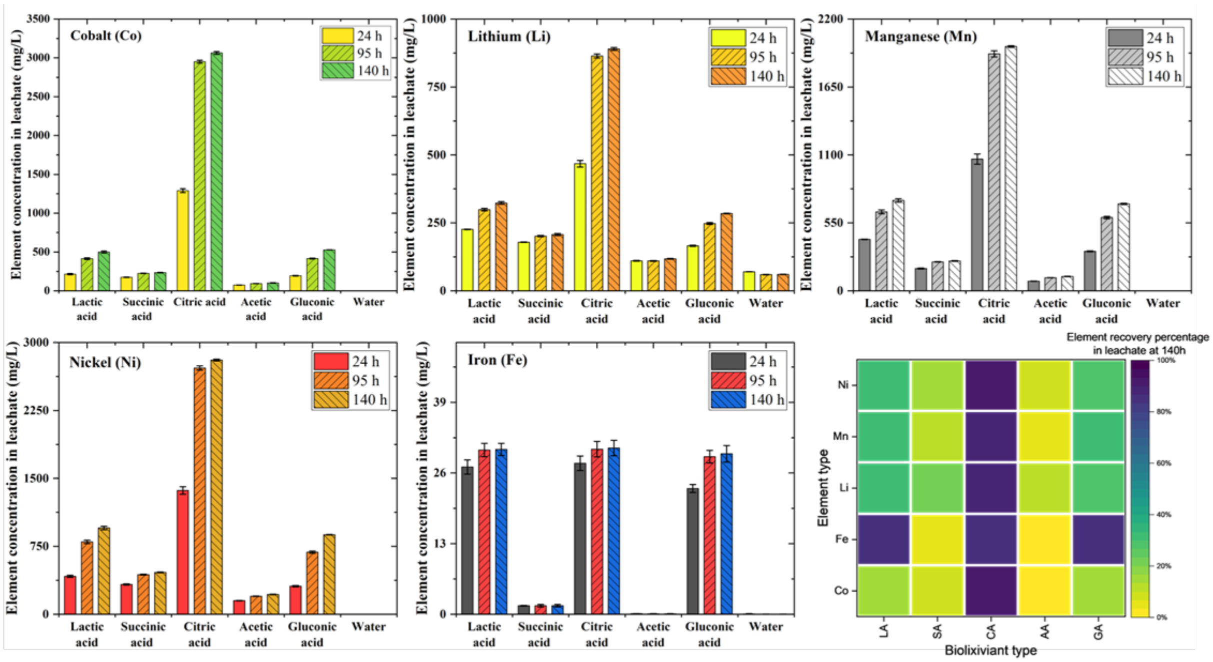

Figure 1. CMM concentration in leachate.

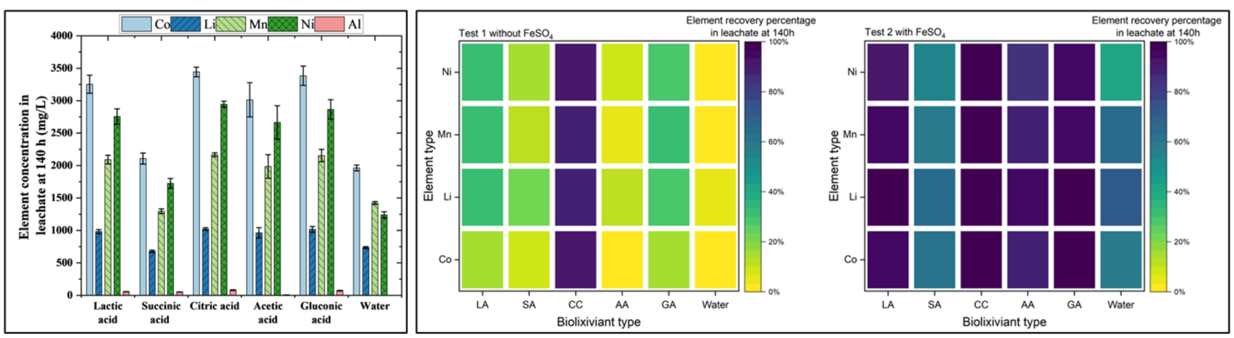

Figure 2. CMM concentration in leachate with reductant agent ($FeSO_4$).

The next-generation biometallurgy process was developed based on Argonne's novel arrested methanogenesis (AM) technology to reduce the biolixiviant production costs as well as explore alternative reducing agents. AM enables direct conversion of organic waste streams into high-titer organic acids with no need for additional carbon sources and sterilization. This process is strictly anaerobic, eliminating the production costs associated with aeration. High-titer organic acids (e.g., acetic acid, lactic acid) and microbial exudates produced from renewable carbon (e.g., wastewater) via AM were used as biolixiviant to solubilize the black mass. Pulp density, organic acid concentration, leaching temperature, pH, and time were investigated to determine optimum conditions for process scale up. Figure 3 shows solubilized cobalt, lithium, nickel, and manganese concentrations from black mass. With the addition of a reducing agent (FeSO4) addition, the leaching capabilities of the fermentation broth with acidic pH were further enhanced for Co, Li, Mn, Ni and Al.

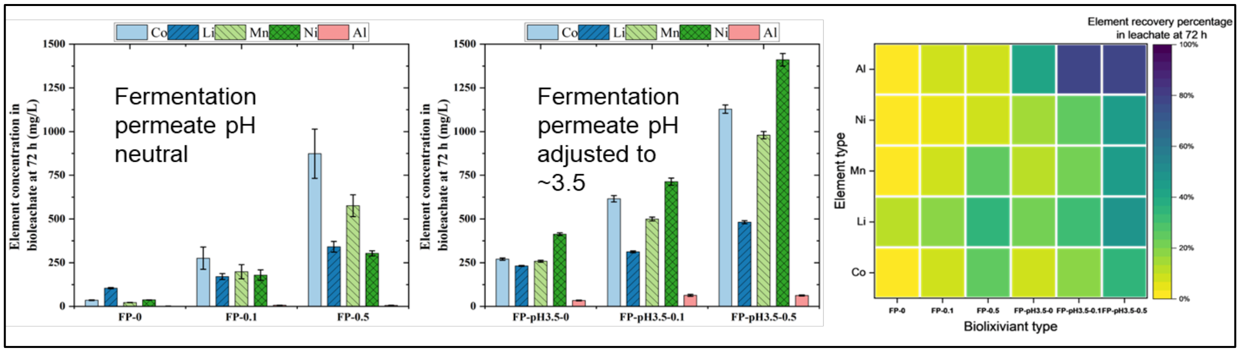

Figure 3. Bioleaching with fermentation permeate from waste streams. FP-0, FP-0.1 and FP-0.5 indicate filtered fermentation broth with near neutral pH supplemented with 0, 0.1, and 0.5 g of $FeSO_4$; FP-pH3.5-0, FP-pH3.5-0.1 and FP-pH3.5-0.5 indicate filtered acidic fermentation broth supplemented with 0, 0.1, and 0.5 g of $FeSO_4$.

Conclusion & Recommendations

A variety of organic acids produced from fossil fuels with a cost-effective ferrous sulfate reductant demonstrated over 90% recovery of cobalt, nickel, and lithium from black mass. A comparison of overall process yields requires literature data that is based on the same critical materials content of spent batteries and pulp density ratio. However, there is limited data availability to facilitate this comparison. Our results were aligned with those presented in Alipanah et al (2023) and Xin et al. (2016). Alipanah reported that 100% of lithium, 71-86% of cobalt, and 57-84% of nickel recovery, while Xin et al reported 97% of lithium, 96% of cobalt, and 97% of nickel recovery from spent lithium-ion batteries. The next generation biometallurgy process was developed based on Argonne's novel arrested methanogenesis (AM) technology to solubilize the black mass. With combined reaction of biolixiviants and ferrous sulfate addition, CMMs in black mass were effectively dissolved and recovered after bioleaching. Our test results showed that medium chain organic acids are the most efficient leaching agent. Optimum operating conditions were determined as pH= 3.0, 2.5% w/v pulp ratio, 40 °C, with iron sulfate addition. Microbially-produced biolixiviants showed about 50% leaching of critical materials within 72 h. The results demonstrate the viability of biohydrometallurgy as a promising solution to critical mineral shortages, offering a more efficient, environmentally friendly, and cost-effective recovery method. Future experiments will focus on increasing pulp density and reducing leaching time to scale up new bioleaching process from lab-scale to pilot-scale.

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