Recovery of Metals from Lithium-ion Batteries using Biologically Available Benign Organic Acids

Bhavisha Nandkishor Kini

The production of lithium ion batteries (LIBs) is increasing due to their extensive usage in a variety of energy-related applications. Spent LIBs include a number of important metals, including cobalt (Co), Nickel (Ni), and lithium (Li), whose supplies cannot be sustained over the long run due to rising demand. Recycling spent LIBs is a popular practice that uses a variety of techniques to recover valuable metals and prevent environmental damage. The environmentally friendly technique of bioleaching, also known as biohydrometallurgy, has drawn more attention recently due to its cost-effectiveness and ability to selectively extract Co, Ni, and Li from spent LIBs using appropriate microbes. To design a good bioleaching strategy, it is important to understand the ability of different organic acids produced by microbes in extracting metals from LIB waste. Therefore, the objective of this project is to compare the metal extraction efficiency and selectivity of a group of biologically relevant organic acids. Black mass, provided by commercial recyclers and consisting of cathode and anode materials ground into powder form, was leached in organic acids including citric acid, succinic acid, malonic acid, gluconic acid, and glycine for up to 48 hours at room temperature or 60 oC. Leaching was also carried out using the conventional method (i.e., Piranha solution of concentrated H2SO4 and H2O2) to allow for comparison. Samples were taken periodically and analyzed for metal concentrations. The amounts of metals extracted and their leaching rates vary significantly with organic acid used. At equal concentrations, succinic, malonic, and succinic acids extract Co and Ni most effectively, while oxalic acid is able to leach out Li selectively. The data point out the feasibility of using biologically derived acids to extract and separate minerals in LIBs.

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Learning with Purpose

Introduction

- The rising demand for lithium-ion batteries (LIBs) calls for effective recycling methods to recover valuable elements such as cobalt (Co), nickel (Ni), and lithium (Li) from spent batteries.
- Most of the valuable minerals in LIBs is contained in cathode materials, which is ground into fine powder during recycling and is known as ***black mass***.
- Current LIB recycling uses pyrometallurgy or hydrometallurgy, the latter uses sulfuric acid and hydrogen peroxide.
- Organic acids may offer a more sustainable recycling method because of their biodegradability, low toxicity, and low costs.

Objectives

- This project aims to compare common biologically available organic acids in terms of their mineral extraction efficiency and selectivity.
- The data will enable assessment of mineral recovery via bioleaching as a potentially cost-effective and environmentally friendly technology for recycling of LIBs.

Methods

Black mass was provided by Cirba Solutions, a leading LIB recycler.

Black Mass Extraction Conditions

Solid to solution ratio: 10 g/L.

Leaching time: up to 48 h.

Other conditions are summarized in the table below.

Extractant	Concentration	Temperature	Sonication	3% Hydrogen peroxide
Citric Acid	0.2 M	60 °C	None	None
Citric Acid	0.8 M	Room Temperature	None	None
Gluconic Acid	0.8 M	60 °C	None	None
Succinic Acid	0.8 M	60 °C	Yes	3%
Malonic Acid	0.8 M	60 °C	None	None
Acetic Acid	0.8 M	Room Temperature	None	3%
Glycine	0.8 M	Room Temperature	None	None
Oxalic Acid	0.8 M	Room Temperature	None	None
Sulphuric Acid	0.8 M	60 °C	None	3 %

Analysis of Metal Concentrations

- The amount of lithium, cobalt, and nickel extracted into different solutions was measured using inductively coupled plasma-optical emission spectrometer (ICP-OES).
- All samples were diluted with 2% nitric acid.

Overview of Black Mass Extraction Procedure

Black Mass

→ Extraction of black mass with sulphuric acid and 3 % hydrogen peroxide

→ Extraction of black mass with organic acid

Extraction Procedure

- Add black mass of 10 g/L ratio to each extractants
- De-gas the extractant sample which contain 3% peroxide.
- Stir the extractant sample well ,place the extractants sample at room temperature or 60 °C

↓

Collect the sample in HDPE bottle at the interval of 2-hour, 5-hour ,24-hour and 48-hour

↓

Filter the sample with 0.2 mm nylon filter

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Dilute extracted samples with 2 % nitric acid (400 times dilution)

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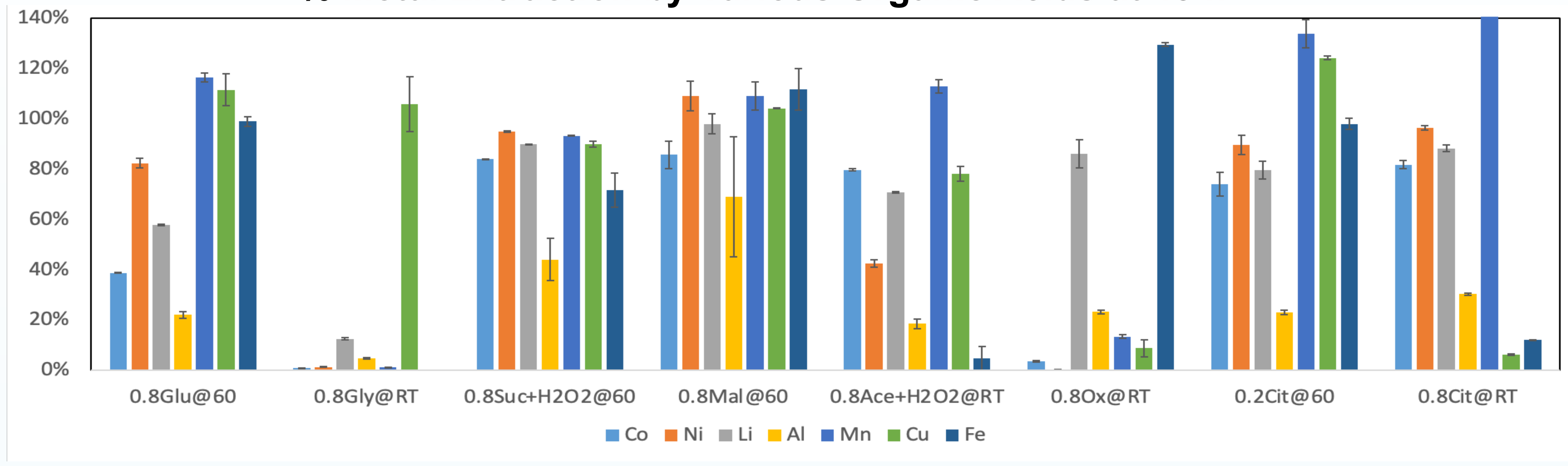
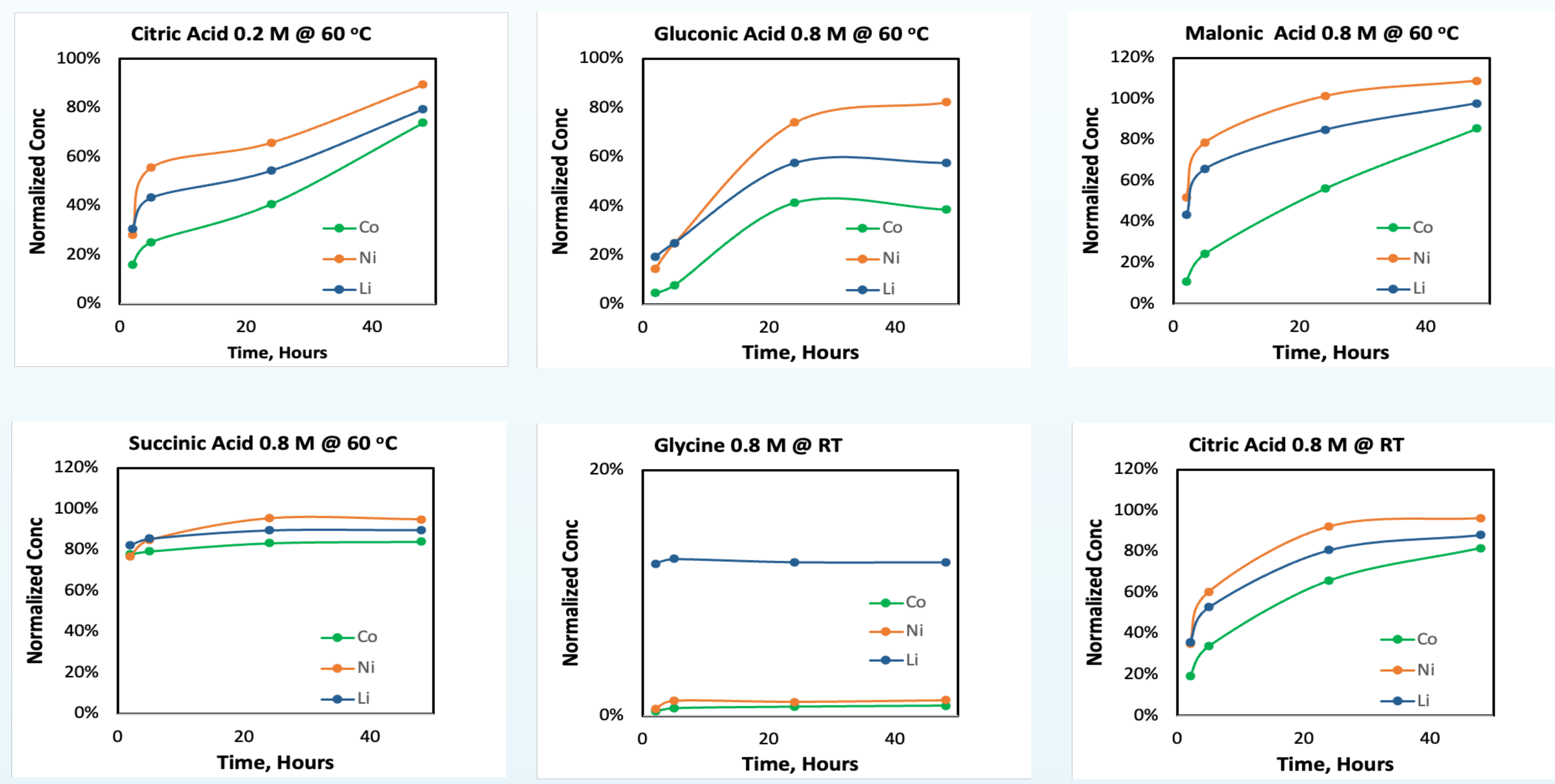
Analyze the extracted sample in ICP-OES instrument

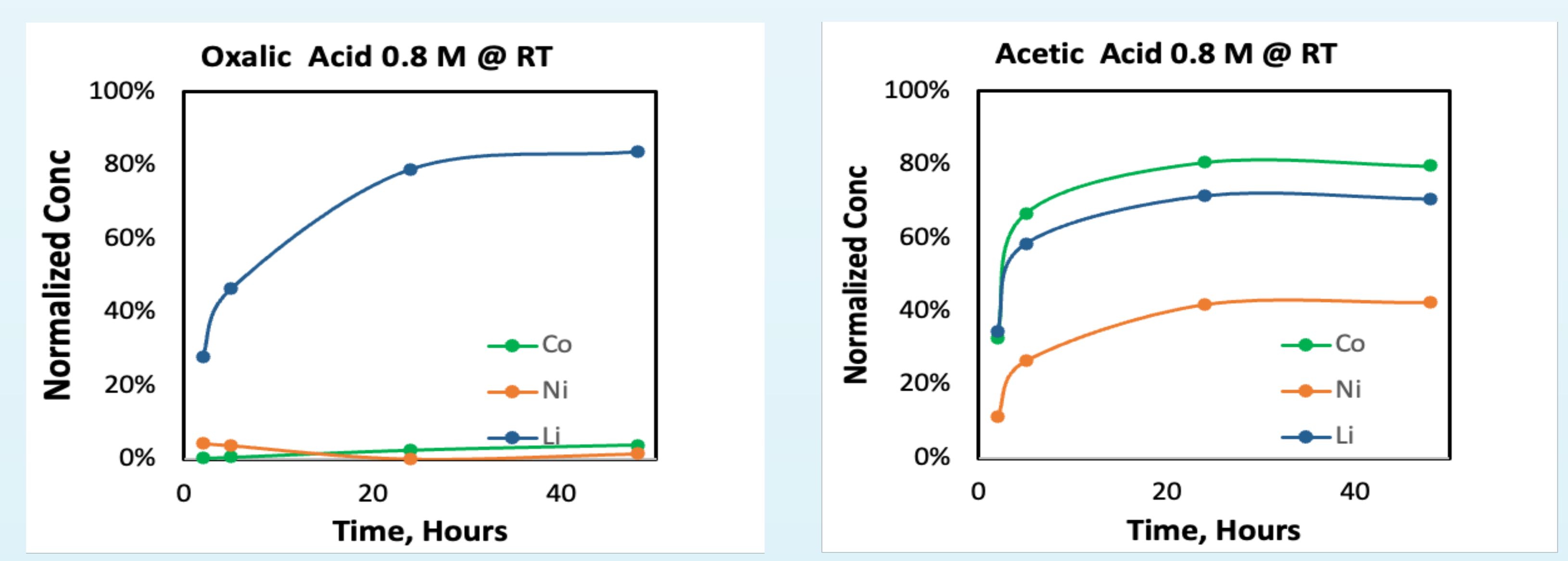
Results

% Metal Extraction by Various Organic Acids at 48 h



Metal Release Rates during Organic Acid Extraction





Conclusions

- Succinic acid at 60 °C shows the *highest extraction rates* and a high % extraction efficiency for all three metals (Li, Co, and Ni).
- Li, Ni and Co were gradually extracted in citric, gluconic, and malonic acids at 60 °C.
- Glycine and oxalic acids extracted Li *selectively* with minimal leaching of Ni and Co.
- Acetic acid at 60°C exhibits a moderate selectivity for Co over Ni.
- Increasing temperature seems to increase metal release rates (based on citric acid data).

Acknowledgement

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