Hydrometallurgical recycling of cobalt, manganese and nickel from lithium-ion batteries black mass through ascorbic acid leaching and chemical precipitation

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Keywords: lithium-ion batteries, recycling, hydrometallurgy, selective precipitation, metals recovery

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Introduction

Recovery of secondary raw materials from end-of-life lithium-ion batteries (LIBs) is crucial to limit environmental impacts of batteries throughout the whole life cycle. LIBs' recycling relies on pyrometallurgical and hydrometallurgical processes. Organic acid leaching has been established as a viable alternative to reduce environmental impacts associated with conventional hydrometallurgical recycling processes, which are usually based on sulfuric acid (Qin et al., 2019). Ascorbic acid has traditionally been utilized as a reducing agent, combined with other acids, or as a leaching agent by itself, with efficiencies ranging from 90% to 100% for Co, 77% to 90% for Mn, and 71% to 100% for Ni. (Lie and Liu, 2021; Mukherjee et al., 2005; Refly et al., 2020).

However, past research on hydrometallurgical recycling with ascorbic acid, overlooked the recovery of Co, Mn and Ni metals from leachate solutions (Li et al., 2014; Refly et al., 2020). This study investigates the leaching of Co, Mn, and Ni with ascorbic acid from and the consequent recovery by chemical precipitation as oxalates. The leaching process involved black mass provided by a LIBs' recycling facility. The novelty of this study relies on the analysis of metal recovery from ascorbic acid leachate. Recovery efficiency and purity of the recovered oxalates have been analysed and a preliminary economic and environmental analysis of the process was performed.

Materials and methods

The black mass was provided by a recycling facility, and thermally treated with microwave roasting and water leaching (Fahimi et al., 2023). Leaching was achieved with 1M ascorbic acid at 75°C for 1 h with a solid-to-liquid ratio of 20 g/L. Co, Mn, and Ni were recovered by adding oxalic acid and stirring at 400 rpm at room temperature for different contact times (30, 60, 90, 120, 150 minutes). Leaching residues and precipitates have been separated by centrifugation, rinsed with deionized water, dried at 70°C and then characterised with a RIGAKU NEX-DE XRF spectrometer. The performances of the overall process have been assessed considering leaching and recovery efficiencies and the purity of the recovered materials. A preliminary economic and environmental analysis was based on chemicals and energy consumption. Energy demand was measured with a PM10 Maxcio power meter and data for economic and environmental analysis were taken from Ecoinvent database (Ecoinvent, 2023).

Results and discussion

The composition of the black mass was: 20.8±2.3% of Ni, 7.3±0.7% of Mn, 6.9±0.2% of Co, 2.2±0.1% of Cu and 1.9±0.2 of Al. This is consistent with a black mass related to NMC(622) cathodes. Ascorbic acid leached 93±11% of Ni, 99±10% of Mn, 97±11% of Co, 89±12% of Al and 73±3% of Cu.

Afterwards, Co, Mn, and Ni were precipitated as oxalates by adding a stoichiometric quantity of oxalic acid. Recovery efficiency values gathered after 30 and 60 min were comparable (around 50-52% for Co, 56-58% for Mn and 42-44% for Ni). Increasing contact time, the recovery efficiency improved (63% for Co, 70% for Mn and 53% for Ni after 120 min), and then decreased after 150 min. Recovery of Al and Cu, instead, were not affected by the duration of the process with efficiencies around 6-7% for Al and 3-4% for Cu.

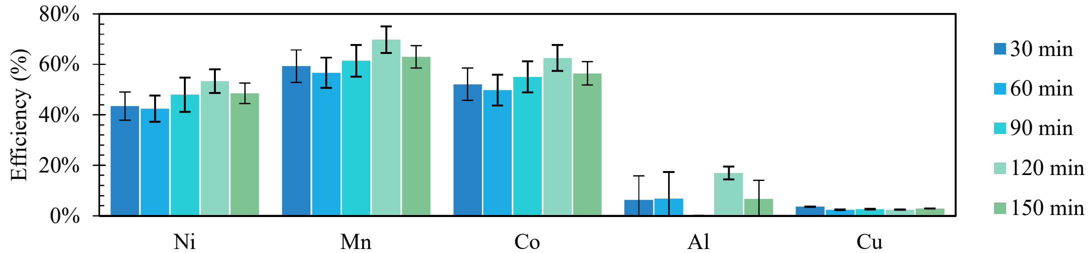

Figure 1. Precipitation efficiency (%) of Ni, Mn, Co, Al and Cu after chemical precipitation with oxalic acid for different precipitation time

According to the material and energy balance, the proposed process is able to recover on average 1.35 g of mixed oxalate (corresponding to a recovery of 63±7% Co, 70±7% Mn, and 53±7% Ni from 1 g of black mass), consuming 8.81 g of ascorbic acid, 1.25 g of oxalic acid, 50.00 mL of water and 0.15 kWh This corresponds to the emissions of 0.11 kg $CO_{2\ eq.}$ and a cost of 0.02 € for 1 g of black mass.

Conclusions

Ascorbic acid can be considered a viable leaching agent for Ni, Mn, and Co from LIBs black mass. Recovery of Ni, Mn, and Co using oxalic acid was effective and performed better with longer precipitation times (up to 120 min). The crystalline structure of the oxalates in the precipitates will be verified using XRD spectroscopy. The results of this study preliminary proved that a process based on ascorbic acid leaching and co-precipitation of Co, Mn and Ni may involve a limited number of precipitation steps and energy demand, since precipitation occurs at room temperature.

Funding

This study was carried out within the MICS (Made in Italy – Circular and Sustainable) Extended Partnership and received funding from Next-GenerationEU (Italian PNRR – M4 C2, Invest 1.3 – D.D. 1551.11-10-2022, PE00000004).

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