Economic optimization of pre-treatments and operative conditions for leaching of critical raw materials from lithium-ion batteries black mass

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Introduction

The growing demand for critical raw materials like lithium, cobalt, manganese, and nickel, driven by the use of lithium-ion batteries (LIBs), emphasizing the need for more sustainable supply chains. Hydrometallurgical recycling offers a way to reduce reliance on primary resources but faces challenges such as high energy consumption and toxic emissions. Organic acids, like acetic and ascorbic acids, represent more environmentally friendly alternatives but are hindered by slow kinetics and high costs (Gerold et al., 2022). Acetic acid is cost-effective but needs reducing agents like hydrogen peroxide or ethanol, increasing overall costs. While, ascorbic acid, though more expensive, doesn't require these reagents. To address these challenges, microwave-assisted carbothermal reduction has been proposed as a pre-treatment to reduce the valence state of metals in the black mass, improving their leaching efficiency (Fahimi et al., 2023). This study compares acetic and ascorbic acid leaching, with and without microwave carbothermal reduction as a pre-treatment, to identify the most cost-effective and efficient approach for leaching critical raw materials from LIBs black mass.

Materials and methods

Two black mass samples, here on referred to as "BM1" and "BM2" were provided by industrial recycling facilities, and leaching tests were performed through three different routes: direct acid leaching (route A), microwave carbothermal reduction followed by acid leaching (route B), and microwave carbothermal reduction followed by water and acid leaching (route C). Leaching tests were conducted both with 2 M acetic acid, a solid-to-liquid ratio of 30 g/L, for 45 minutes at 70°C; and with 1 M ascorbic acid, a solid-to-liquid ratio of 20 g/L, for 60 minutes at 75°C. The microwave carbothermal reduction process followed the procedure outlined in a previous study (Fahimi et al., 2023). Water leaching was conducted in deionized water at 80°C for 30 minutes, with a $S\cdot L^{-1}$ ratio of 40 $g\cdot L^{-1}$. Black mass samples were characterized with a RIGAKU NEX-DE X-Rat Fluorescence (XRF) spectrometer and a Metrohm 883 Compact IC plus ion chromatographer (IC).

A preliminary economic analysis was conducted, on a functional unit of 5 g of processed black mass, to assess the costs associated with reagents and energy consumption, measured with a PM10 Maxcio power meter. The maximum capacity of the equipment and data from Ecoinvent and Eurostat databases (Ecoinvent, 2024; Eurostat, 2024) were considered. Eventually, the composition of the black mass and the efficiency of each recovery route were taken into account to calculate the recovery cost for 1 g of target metal (Co, Li, Mn and Ni).

Results and Discussion

The samples were characterized as follows: 135000±25456 mg/kg of Co, 44419±2846 mg/kg of Li, 41300±6223 mg/kg of Mn and 53350 mg/kg of Ni for BM1; 28550±4596 mg/kg of Co, 45038±584 mg/kg of Li, 32450±4313 mg/kg of Mn and 84200±14142 mg/kg of Ni for BM2. In route B, BM1 had a 1% mass loss during microwave carbothermal reduction. Whereas, in route C BM2 had a 27% mass loss and 73±6% of Li was recovered during water leaching.

The leaching efficiency achieved by acid leaching in each route varied depending on the black mass sample and the acid used. In route A, BM1 showed a leaching efficiency of 67±14% for Co, 90±7% for Li, 41±7% for Mn, and 33±6% for Ni when using acetic acid, whereas ascorbic acid resulted in higher efficiencies of 87±18% for Co, 98±7% for Li, 87±14% for Mn, and 39±8% for Ni. BM2, under the same route, exhibited significantly lower efficiencies with acetic acid, achieving only 10±2% for Co, 30±2% for Li, 11±2% for Mn, and 10±2% for Ni. However, ascorbic acid drastically improved the recovery rates for BM2, with efficiencies of 99±16% for Co, 88±1% for Li, 99±13% for Mn, and 99±10% for Ni. In route B, leaching tests on BM1 resulted in 85±17% Co, 97±13% Li, 70±11% Mn, and 69±13% Ni recovery with acetic acid, while ascorbic acid yielded 87±17% for Co, 95±7% for Li, 83±14% for Mn, and 35±7% for Ni. For route C, applied to BM2, acetic acid leaching led to efficiencies of 56±10% for Co, 90±6% for Li, 56±8% for Mn, and 52±9% for Ni. The use of ascorbic acid further improved these values, achieving 95±16% for Co, 99±11% for Li, 98±13% for Mn, and 91±15% for Ni.

The preliminary economic analysis considered the energy and reagents (water, acetic acid and ascorbic acid) required to treat 5 g of black mass. The reagents consumption was adjusted to consider the mass loss during microwave carbothermal reduction. The composition of the samples and the recovery efficiency were considered as well to identify the most cost-effective strategy for recovering each metal, see Figure 1.

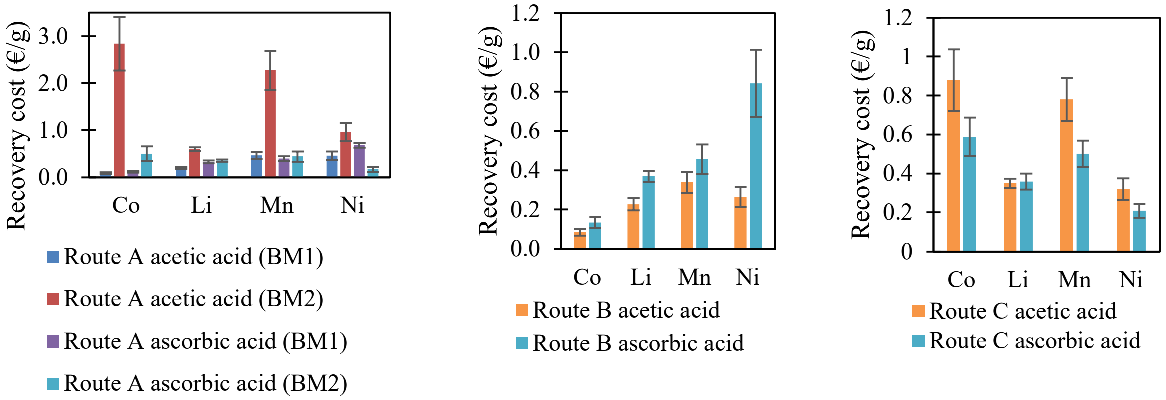

Figure 1. Recovery cost (€/g) for Co, Li, Mn and Ni

The comparison between BM1 and BM2 reveals several key differences that significantly influence the metal recovery efficiency and cost-effectiveness. BM1 contains higher concentrations of Co, Li, Mn and Ni affecting directly the recovery costs. However, economic analysis showed similar trends for both samples when varying operative conditions. In route A, the choice of acid significantly impacts the recovery of metals from black mass. Acetic acid, being less expensive, generally results in lower recovery rates compared to ascorbic acid, which offers lower recovery costs. Metals recovery through acetic acid leaching costed 2.84±0.57 €/g for Co, 0.60±0.04 €/g for Li, 2.27±0.41 €/g for Mn, and 0.96±0.19€/g for Ni. Whereas metals recovery from the same sample with ascorbic acid leaching costed 0.88±0.59 €/g for Co, 0.35±0.20 €/g for Li, 0.78±0.50 €/g for Mn, and 0.32±0.21€/g for Ni.

Microwave carbothermal reduction demonstrates a variable impact on the cost-effectiveness of metals recovery. Ascorbic acid acts both as a leaching and a reducing agent, thereby the additional step of microwave carbothermal reduction. Whereas when acetic acid is use, the recovery costs are reduced to 0.09±0.02 €/g for Co, 0.23±0.02 €/g for Li, 0.34±0.05 €/g for Mn, and 0.26±0.05 €/g for Ni after microwave carbothermal reduction, following route B.

In conclusion, the most cost-effective recovery strategy for each metal has been identified in microwave carbothermal reduction followed by acetic acid leaching for Co (0.09±0.02 €/g) and Mn (0.34±0.05 €/g) and leaching in ascorbic acid without any pre-treatment for Ni (0.17±0.03 €/g). Meanwhile, water leaching significantly improves Li recovery efficiency and purity, further enhancing the overall effectiveness of metal recovery strategies.

Conclusions

Optimizing recovery strategy by balancing technical and economic considerations plays a crucial role in enhancing the sustainability of LIBs recycling. This study highlights the potential of microwave-assisted carbothermal reduction combined with acid leaching to enhance the efficiency and cost-effectiveness of critical metal recovery from LIB black mass. While ascorbic acid generally achieves higher recovery rates, the lower cost makes acetic acid a more viable option when combined with microwave pre-treatment.

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