Bio-extraction of critical raw materials (CRMs) from spent lithium-ion batteries

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Keywords: bioleaching, critical raw materials, NMC, black mass, acidophilic bacteria
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Nowadays, the majority of spent lithium-ion batteries ends up in landfills, where the present metals (as well as other components) pose a severe environmental threat. On the other hand, metals like Co, Ni, Mn, and Li have been identified as critical raw materials by the European Commission due to their limited availability and economic importance in Europe (European Commission, 2023). As a result, a new EU Battery Regulation was published stating that 65 and 70% of Li-based batteries should be recycled in 2025 and 2030, respectively. In addition, recycling rates of Li should be increased to 50 and 80%, and 90 to 95% of Co, Ni and Cu should be recycled in 2027 and 2031, respectively (European Union, 2023).

Current recycling processes are mainly based on pyrometallurgical, mechanical, and hydrometallurgical methods, having disadvantages including the production of large amounts of hazardous wastes (Boyden et al., 2016). To recover metals from spent LIB cathode materials, mainly strong inorganic acids, such as HCl, H_2SO_4, and HNO_3 are used. This approach provides high metal recovery rates, but harsh chemicals have a negative environmental impact and produce hazardous wastes (Mossali et al., 2020).On the other hand, biotechnology can provide a viable option for low-cost and more environmentally friendly treatment technologies. Herein, the use of extreme acid tolerant (acidophilic), chemolithotrophic microorganisms for metal solubilization (bioleaching) from different waste materials brings advantages such as a lower production of hazardous waste and lower energy consumption (Hansford and Vargas, 1999).

Normally, bioleaching applications are time-consuming and show lower metal extraction efficiencies with increasing material loading rates. To improve the leaching performance and efficiency for higher loading rates of NMC black mass, the two sulfur oxidizing bacteria *Acidithiobacillus thiooxidans* and *A. caldus* were used to produce biogenic sulfuric acid out of waste elemental sulfur. A combined culture of both bacteria was used in a previous study to generate a 0.61 M biogenic acid, with a very low pH-value of around 0.3 (Kremser et al., 2022). This acid was used in indirect bioleaching of different concentrations of black mass (i.e. 6 and 10% (w/v)) for up to 48 h. Additionally, the effect of catalysts like H_2O_2 and Fe^{2+} was assets by testing them separately or in combination.

Complete metal extraction of Li and Mn was reached from 6% black mass already after 1 hour of indirect bioleaching (Fig. 1a) which was faster and more effective compared to previous studies on direct and indirect bioleaching (Biswal and Balasubramanian, 2023; Do et al., 2022; Li et al., 2023). Other investigated metals such as Al, Co, and Ni were leached up to 90, 86, and 57% within 48 h, respectively, showing comparable or better bioleaching behavior. The lower efficiencies compared to Li and Mn, as well as the absence of copper leaching, result from the absence of ferric iron (Fe^{3+}) enabling metal dissolution from oxidic minerals by a combination of acidolysis and redoxolysis via Fe^{2+}/Fe^{3+} cycling, normally present when using iron-oxidizing bacteria (Xin et al., 2009).

Another experiment with 10% (w/v) was conducted with a reduced contact time of only two hours (Fig. 1b). It revealed that complete Li and Mn bioleaching was already obtained after only 40 minutes, while other metals remained mostly in the solid fraction. These results indicate, that a selective extraction of certain metals is possible, which is normally a limiting factor in bioleaching applications. To test the effect of catalysts in optimization of the leaching behavior of metals like Al, Co, and Ni, three different concentrations of H_2O_2 and Fe^{2+} were tested separately and in combination. While Fe^{2+} addition alone did not show any significant increase in metal extraction compared to only biogenic acid leaching, the combination of low amounts of H_2O_2 and Fe^{2+} had a positive effect. Bioleaching efficiencies of Li and Mn reached higher values and almost complete extraction already after 20 min. Furthermore, extraction efficiencies of Co and Ni increased to 90 and 60% within 100 minutes, respectively, showing similar values compared to the 6% bioleaching experiment after 2 days.

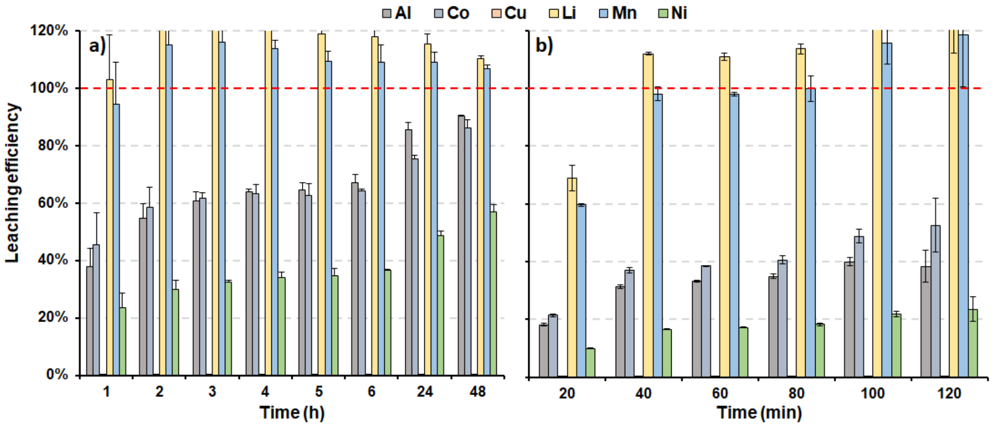

Figure 1: Bioleaching efficiencies of non-contact bioleaching using 6% (a) and 10% (b) NMC type black mass. Error bars indicate the standard deviation (n=3).

The conducted study shows that bioleaching can be applied with economically and industrially relevant concentrations of NMC black mass under more environmentally friendly and cost-efficient conditions. Furthermore, a certain selectivity in metal extraction, as well as potential application of low concentrations of catalysts further highlights the potential of the proposed indirect, non-contact bioleaching method.

Acknowledgements

This research received funding from the module FuLIBatteR which is supported by COMET (Competence Center for Excellent Technologies), the Austrian programme for competence centres. COMET is funded by the Federal Ministry for Climate Action, Environment, Energy, Mobility, Innovation and Technology, the Federal Ministry for Labour and Economy, the Federal States of Upper Austria, and Styria as well as the Styrian Business Promotion Agency (SFG). Furthermore, Upper Austrian Research GmbH continuously supports K1-MET. Besides the public funding from COMET, this research project FuLIBatteR is partially financed by the scientific partners acib GmbH, Coventry University, Montanuniversitaet Leoben, University of Natural Resources and Life Sciences, UVR-FIA GmbH, and the industrial partners AUDI AG, BRAIN Biotech AG, Ebner Industrieofenbau GmbH, RHI Magnesita GmbH, Saubermacher Dienstleistungs AG, TÜV SÜD Landesgesellschaft Österreich GmbH, VTU Engineering GmbH and voestalpine High Performance Metals GmbH.

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