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Kinetics study of the dissolution of black mass material using oxalic acid as a leaching agent

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ABSTRACT

This study investigates the dissolution mechanisms of black mass by employing oxalic acid as a leaching agent at different temperatures. The concentration of oxalic acid and the solid-to-liquid ratio of the leaching are maintained at a fixed molar ratio of 1:2.5. This work aims to study the impact of the leaching temperature on the kinetics and the leaching residue composition or morphology. The findings confirm that increasing the temperature significantly enhances the rate of lithium dissolution from the black mass; 6 h is needed to reach a dissolution equilibrium at 30 °C against less than 30 min at 80 °C. The dissolution rate is shown to be chemically controlled, with a pseudo-homogeneous model of 2^{nd} and 3^{rd} order, and the Avrami model best fitting the experimental data. The energy of activation was determined via the Avrami model to be at 76 kJ/mol. Additionally, this study identifies the anionic oxalate complexes formed in the aqueous solution during the leaching process, which is essential to developing an adequate purification method for the leachate. Finally, residues are characterized using various techniques, including XRD, SEM-EDS, and particle size analysis, which revealed that oxalate precipitate is formed majorly in the bulk of the solution as a disordered (Co,Ni,Mn)C₂O₄ · 2 H₂O phase.

1. Introduction

Lithium-ion batteries (LiB) are essential in our society's electrification transition. They have witnessed extensive proliferation across multiple domains, including portable electronics, electric vehicles (EV), and stationary energy storage, over the last three decades (Neumann et al., 2022). This trajectory is expected to persist, supported by governments or worldwide organizations that have enacted policies to promote EV adoption, i.e. the European Union's (EU) plan to only sell zero-emission vehicles by 2035 (European Commission Zero). As a consequence, EVs alone may yield between 0.33 to 4 MMT of LiB waste from 2015 to 2040 (Winslow et al., 2018).

LiBs comprise a series of layers of cathodes and anodes wrapped multiple times within a casing, forming a battery cell. Depending on the application, the produced battery cells are interconnected in series to form a module, and these modules are further connected to create a battery pack. An EV battery pack can weigh around 300–900 kg, with a capacity ranging from 30 to 100 kWh (Hayagan et al., 2024). The different components of a battery cell are the following (diagram provided in Supplementary material Fig. S1):

- The anode electrode is composed of an active material, commonly graphite (about 10-20 wt % of the battery cell) (Heelan et al., 2016; Jung et al., 2023). Its specific capacity can be improved by adding silicon particles up to 5–10 %wt of the active electrode material, which can be problematic for recycling. The active material is bound to a Cu current collector foil using a binder; polyvinylidene difluoride (PVDF) is commonly employed. Although greener alternatives such as carboxymethyl cellulose and styrene butadiene rubber are increasing in popularity (Heelan et al., 2016; Jung et al., 2023; Latini et al., 2022). The Cu foil constitutes approximately 7 to 17 wt % of the cell.
- 2. A separator prevents electrode contact and allows lithium ions to flow through. It is commonly a porous polyolefin membrane representing 3 to 12 wt % of the cell. The composition of the separator includes polyethylene, polypropylene, and their blend (Heelan et al., 2016; Latini et al., 2022).

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- 3. The electrolyte (4–20 wt % of the battery cell) is composed of lithium salt, with LiFP₆ being the most widely used, and a solvent comprising a mixture of alkyl carbonates, among which ethylene carbonate, propylene carbonate, dimethyl carbonate, diethyl carbonate can be identified (Heelan et al., 2016; Jung et al., 2023).
- 4. The cathode (15–41 wt %) is composed of a mixture of active material bound to an Al current collector foil (4–7 wt % of the cell) with a binder, typically PVDF and carbon black, which serves as an electronic conductor. The cathode active material (CAM) is lithium-transition metal oxide, giving the battery its name, i.e. lithium cobalt oxide (LiCoO₂, LCO), lithium manganese oxide (LiMn₂O₄), lithium iron phosphate (LiFePO₄, LFP), lithium nickel cobalt Manganese oxide (LiNi_xCo_yMn_{1-x-y}O₂, NCM), and lithium nickel cobalt aluminum oxide (LiNi_xCo_yAl_{1-x-y}O₂). Nowadays, Ni-rich chemistries and LFP dominate the EV market (Ding et al., 2024; International Energy Agency 2024).

Concerns are arising around the supply of raw materials. For instance, LiBs currently consume 74 % of the total Li production, which has increased from 41.5 kt in 2017 to 93 kt in 2021 (U.S. Geological Survey (USGS), 2018). The International Energy Agency forecasts a significant rise in Li demand by 2030 under various policy scenarios (International Energy Agency, 2022). In 2020, the EU recognized the critical role of Li and included it in its list of critical raw materials, along with graphite, Co, Ni, Mn, or Cu (the last three added in 2023 (European Commission, 2023)). Critical raw materials are identified and listed based on their significant economic importance and elevated supply risk for the EU (European Commission, 2020). To ensure comprehensive oversight from raw material extraction to end-of-life management, the EU introduced a new regulation, adopted in July 2023 (European Parliament and the Council of the European Union Regulation (EU) 2023/1542 - Batteries and Waste Batteries, 2023). This regulation is designed to promote a circular economy by endowing stringent end-of-life requirements and restricting the presence of harmful substances within batteries across the EU. It provides a legal framework for the entire battery life cycle, particularly emphasizing recycling practices. Notably, the regulation mandates that all spent LiB collected by the end of 2030 must undergo recycling processes, achieving a minimum recycling efficiency of 70 % by weight. Furthermore, it imposes minimum recovery rates of 80 %, 95 %, and 95 % for Li, Ni, Cu, and Co, respectively, by the end of 2031 (European Parliament and the Council of the European Union Regulation (EU) 2023/1542 - Batteries and Waste Batteries, 2023). The regulation mandates that recyclers employ the best available techniques to meet established recovery rate targets. Consequently, research groups and recycling companies have been working on developing robust recycling processes over the last decade.

2. Background

2.1. Battery Recycling Background

Three major recycling routes exist: pyrometallurgy, hydrometallurgy, and a combination of both. Pyrometallurgical techniques exploit high temperatures to recover metals in a mixed alloy (Makuza et al., 2021). The losses of Li and Al in the slag, the toxic emissions, and the high energy consumption make this route less favorable regarding environmental impact (Harper et al., 2022; Chen et al., 2022). On the other hand, hydrometallurgical techniques offer higher recovery rates and lower energy consumption despite their complexity and intensive use of chemicals (Neumann et al., 2022; Lv et al., 2018). Hydrometallurgy techniques refine the black mass (a blended mixture of graphite and CAM with some impurities such as Al, Cu, separator, or binder) to recover its valuable metal content. This black powder is obtained after the battery pack's discharge, dismantling, and mechanical treatment (Amalia et al., 2024; Mousa et al., 2023). Industrial processes already exist, but research is still being performed to optimize the active

material's liberation and enhance electrolyte recovery (Amalia et al., 2024; Zachmann et al., 2024). The black mass then undergoes dissolution in inorganic acids, predominantly H₂SO₄. Typically, a reducing agent, such as H₂O₂, is introduced to facilitate the leaching of Co and Mn. Leaching parameters encompass acid concentration (1-5 M), H₂O₂ dosage (3-10 vol %), temperature (50 to 90 °C), duration (1-6 h), and solid-liquid ratio (20 to 200 g/L) (Neumann et al., 2022; Heelan et al., 2016; Latini et al., 2022; Lv et al., 2018; Partinen et al., 2024). Impurities such as Al, Cu, and Fe can be eliminated through precipitation with NaOH (Ekberg and Petranikova, 2015; Chernyaev et al., 2023). Still, the possibility of Co or Li co-precipitation necessitates exploring ion exchange or solvent extraction to mitigate losses. Later, the separation of Ni, Co, and Mn is typically executed through solvent extraction, ion exchange, or precipitation methods. Although precipitation with LiOH, NaOH, or Na₂CO₃ is efficient and viable, pH control complexities may lead to co-precipitation of other elements and subsequent Li losses (Neumann et al., 2022; Siqi Zhao and GL, 2019; Zhang, 2022; Swain, 2017). Processes generally end with the Li recovery accomplished through precipitation with Na₂CO₃. Li is recovered as carbonate, and Na₂SO₄ is produced as secondary waste, which will be an additional burden to handle (Swain, 2017; Stallmeister et al., 2017).

Inorganic acids have been proven effective for the dissolution of CAM; good dissolution of Li, Co, Ni, and Mn (\approx 90 % for Li and 70 °C for the transition elements) can be achieved by leaching at 70 °C with 2M and without a reducing agent (Shi et al., 2023; He et al., 2017). Sulfuric acid is usually selected for its cost-effectiveness, but a reducing agent is needed to achieve completion. H₂O₂ is mainly used, but it is associated with some environmental issues (Che et al., 2022). Despite high metal recovery, inorganic acid can lead to emissions such as NO_x or SO_x, and their strong acidity implies the generation of various aqueous waste streams (Ding et al., 2024; Zhang, 2022; Verma et al., 2021), raising the need to explore environmentally friendly alternatives, such as organic acids (Zhang, 2022). Oxalic acid emerges as a favorable selective leaching agent, acting as a reducing and complexing agent, forming strong complexes with metals. The associated environmental impact is generally lower, and its low acidity makes it easier to handle (less corrosion, easier pH neutralization) (Lv et al., 2018; Partinen et al., 2024; Meshram et al., 2020).

Several studies have explored this technique, outlining key parameters influencing the optimal lithium leaching yield. For instance, Renjie Chen et al. (Zhang et al., 2018) observed differences in leaching behavior between NMC and LCO cathode materials, noting residual NMC presence and limited lithium leaching yield due to morphology changes and size increases in NMC oxalate aggregates hindering the reaction. Additionally, they identified a higher concentration of manganese oxalate in the leachate solution than Ni and Co. Ka Ming et al. (Li et al., 2019) also investigated NMC leaching with oxalic acid, demonstrating high lithium and manganese dissolution rates under optimal leaching conditions, without studying the contact time effect on leaching behavior. Lastly, Verma et al. (Verma et al., 2022) developed a recycling route for LCO using oxalic acid as a leaching agent. They identified a minimum molar ratio of LCO to oxalic acid of 1 to 3 to ensure the dissolution of the LCO and reduction of Co (III), sustaining its precipitation as simple cobalt oxalate. They also highlighted that acid regeneration is necessary to develop an economically feasible process. For this, an ionic exchange resin is used after the recovery of Li and Co. Despite their claim that the process can be applied for NMC, no experiments have been performed to our knowledge. Acid regeneration is indeed essential, as oxalic acid is more expensive than inorganic acids (Zhang, 2022; Meshram et al., 2020), a high regeneration rate would already make the process more cost attractive.

In our previous work (Rouquette et al., 2023), regression models and contour plots were employed to depict the leaching efficiency of Li, Al, Cu, Co, Mn, and Ni from industrial black mass. The design of experiments is an effective tool for screening the major impacting factors of a process with a minimal number of experiments and a low volume of material spent. The key finding of this investigation is that a minimal molar ratio of cathode material to oxalic acid (NMC:OA) of 1:2 (0.45 M of oxalic acid with 50 g/L) is required for optimal Li dissolution. Moreover, the Li dissolution is positively affected by all parameters chosen for the design (oxalic acid concentration, temperature, and time). Al demonstrated complete dissolution under most tested conditions, and the oxalic acid concentration did not influence its dissolution. This constitutes a very important fact as Al is one of the major impurities of the process (Chernyaev et al., 2023). Oxalic acid concentration influences the recovery of other valuable elements, such as Ni, Co, Mn, or Cu. The identified optimal operating parameters include a temperature of 60 °C, a residence time of 60 min, and an oxalic acid concentration of 0.6 M (NMC:OA of 1:2.5) at an initial fixed S/L ratio of 50 g/L. Under these conditions, we ensure the presence of enough reagent to achieve a complete reaction, and the low S/L ratio decreases the mass transfer limitations. The ensued leaching yields were 98 % for Li, 100 % for Al, 1.5~% for Mn, and less than 0.5~% for Co and Ni. These results show that oxalic acid is very selective towards Li and competitive with other inorganic acids regarding the recovery yield.

2.2. Theory

2.2.1. Leaching operation

The leaching operation consists of a solid-liquid reaction, hence a heterogeneous reaction occurring within the two phases. Such reactions result from multiple phenomena that operate in series; the solid particle morphology will have a strong influence on the mechanism (Faraji et al., 2022). If one dense spherical particle is considered, its dissolution in the leaching reactant will likely follow these steps: 1) feed the reactant from the bulk to the solid particle (transport phenomena), 2) diffusion of the reactant at the solid-liquid interface (diffusion phenomena), 3) interface reaction, 4) diffusion of the product from the interface (diffusion phenomena), and 5) removal of the product to the bulk (transport phenomena). To study intrinsic reaction (interface reaction) and not bother with the transport of the reactant, it is necessary to work with a stirring factor that makes the liquid composition on the surface equal to the bulk (Faraji et al., 2022). At a fixed stirring speed, it is possible to identify which of the diffusion or intrinsic reactions is rate-controlling. Chemically speaking, the oxide dissolution mechanism usually comprises different reaction steps, starting with protonation, followed by complexation and/or reduction. These last two can be combined, one promoting the other. In general, the protonation mechanism is the slowest step (Rosenqvist, 1974).

2.2.2. Kinetics

Kinetic studies have different benefits; through the investigation of chemical reaction rates, it can be possible to understand the chemical mechanism behind an operation, thereby helping in the engineering design (Faraji et al., 2022, Rosenqvist, 1974). While thermodynamics provide insights into how a system can evolve by considering only the initial and final states, kinetics offer information about the timing of various phenomena. Different models have been developed focusing mainly on the physical properties of the particle; the progressive conversion model (PCM) and shrinking core model (SCM) are the two most applied models (Faraji et al., 2022). SCM considers that the reaction starts from the particle surface and continues until the particle center is reached. Different scenarios can be considered, i.e., the particle size remains constant or decreases during the reaction.

An empirical rate expression can be derived for one target leaching agent through experimentation. Generally, the reaction rate depends on two major factors: the temperature and the concentration of different species (solid-liquid ratios and concentration of the reagent). The observed rate can then be juxtaposed with a rate expression derived from a theoretical sequence of intermediate reactions (Faraji et al., 2022; Rosenqvist, 1974; Kim et al., 2022). This comparative analysis allows for the elimination of mechanisms that do not align with the

observed expression. However, it's essential to note that multiple mechanisms can yield the same expression rate. Consequently, solely relying on experimentation may not always definitively determine which mechanism is truly at play (Rosenqvist, 1974).

If all steps have a rate constant of similar magnitude, the precise calculation of the reaction rate will be difficult. Usually, the rate constant for one of the above steps is significantly smaller, and this step is rate controlling, whereas other steps are close to equilibrium (Rosenqvist, 1974). Several models can describe the dissolution rate; the most relevant ones were selected based on literature (Faraji et al., 2022; Rosenqvist, 1974; Kim et al., 2022; Schorr and Yahalom, 2008; Meshram et al., 2015). They are presented in Table 1. The leaching conversion or yield is noted Y, k is the reaction rate constant (min-1), and m is a constant proper to the used model. The significance of each model evaluated will be discussed in the result section. Eqs. (1)-(4) describe the diffusion limiting, and Eqs. (5) to (7) describe the chemical order of the reaction, manifesting a chemically controlled process. Eqs. (8) and (9) are derived from the shrinking core model, describing a disk shrinking or a contracting sphere. Lastly, the Avrami model is considered. Developed from crystallization models, the applied assumptions can accurately describe a phase transformation (from liquid to solid or solid to liquid) and have been widely used for dissolution operations (Choi et al., 2022; Khawam and Flanagan, 2006; Golmohammadzadeh et al., 2018). Unlike other models, it will not identify which phenomenon is rate controlling but can efficiently give an accurate rate constant. Hence, it was considered in the study (Shirzad and Viney, 2023).

The effect of temperature on reaction rate is described by the Arrhenius law as described in Eq. (12). Temperature can also affect the solubilities of a reactant or formed product (Daintith, 2008).

$$k = k_0 e^{\frac{-L_a}{RT}} \tag{12}$$

With E_a , the energy of activation is expressed in kJ, R is the gas constant, and T is the temperature. E_a can be determined by plotting log (k) as a function of 1/T. The energy of activation represents the energy barrier the reaction needs to overcome to occur (Schorr and Yahalom, 2008). Knowing its value will have different benefits for industrialization, such as determining the process's sensitivity to temperature control or giving guidance on the optimization tools that could be implemented.

Verma et al. (Verma et al., 2022) applied the shrinking core model to the leaching of LCO material with oxalic acid, and they found that the rate-limiting step for Li extraction from LCO was the diffusion of oxalic acid through the cobalt oxalate product layer. Moreover, the apparent activation energy for the Li extraction with only oxalic acid was estimated to be 61.0 ± 2.5 kJ/mol. Knowing the controlling rate mechanism and overall energy of activation of the leaching provides essential information to select the appropriate reactor equipment and the procedure applied. For instance, they defined that using H₂O₂ in the

Table 1	L			
Models	describing	the	dissolution	rate.

Model	Equation
1D Diffusion	$Y^2=k \ . \ t(1)$
2D Diffusion	$(1 - Y)\ln(1 - Y) + Y = k \cdot t(2)$
3D Diffusion	$\left[1 - \left(1 - Y^{\frac{2}{3}}\right)\right]^2 = k \cdot t(3)$
3D Diffusion	$\left(1-\frac{2}{3}Y\right) - (1-Y)^{\frac{2}{3}} = k.t(4)$
First order	$-\ln(1-Y) = k \cdot t(5)$
Second order	$\frac{1}{(1-X)} - 1 = k \cdot t(6)$
Third order	$\frac{1}{2} \left[(1-Y)^{-2} - 1 \right] = k.t(7)$
Shrinking disk	$1 - (1 - Y)^{\frac{1}{2}} = k \cdot t(8)$
Contracting sphere	$1 - (1 - Y)^{\frac{1}{3}} = k \cdot t(9)$
Avrami, order m	$-\ln(1 - Y) = k \cdot t^m(10)$ $\ln(-\ln(1 - Y)) = m\ln(k) + m\ln(t)(11)$

leaching would decrease the energy of activation but increase the process's chemical usage (Verma et al., 2022). Besides, Zheng et al. (Verma et al., 2022) demonstrated that the leaching operation of LCO black mass with oxalic acid is chemically controlled, with a kinetic constant rate of 0.034 min⁻¹ under the leaching condition of 15 g/L, 150 min, 95 °C, and 1 M oxalic acid concentration. They advocate that the operation is chemically controlled, with the product form in the bulk.

2.3. Research scope

Oxalic acid leaching is the first step in a recycling process, which aims to be shorter than traditional methods and based on more ecofriendly chemicals. It would promote circular material use by refining the NMC solution into new cathode material, thereby avoiding many recycling steps and enabling a more direct LiB production process. Metal oxalates are already known to have substantial potential as precursors for CAM or as energy material in some storage devices (Choi et al., 2022; Wang et al., 2019; Ang et al., 2015; Ghosh et al., 2021). The proposed process is visible in Fig. 1. Only the first leaching is dealt with in this work. Leaching batch experiments are performed under optimal conditions, detailed above, at different temperatures. The general purpose of this article is to dive deeper into the oxalic acid leaching mechanism, focusing on the kinetics of the dissolution of the NMC and impurities in this media to identify the rate-controlling mechanism under optimal leaching conditions. As seen above, previous authors have focused mainly on LCO dissolution and simpler matrices (absence of graphite and left electrolyte or binder in their feed material). Moreover, there was an evident lack of characterization of the residue after leaching, which can provide essential information regarding the precipitation of the oxalate complexes (i.e. the distribution of the elements within the crystal formation, localization of the oxalates in the waste, determination of soluble species).

In this work, the limiting rate mechanism is identified by finding the most suitable models describing dissolution reactions, and the activation energy is calculated, which can help industrialize the process. Additionally, modeling is performed to determine the speciation of the dissolvable elements, and purification methods are discussed on this basis. Finally, a detailed solid characterization is conducted to determine the residue's composition and assess the impact of the leaching temperature on the oxalate precipitate.

3. Materials and methods

3.1. Black mass preparation

The black mass utilized in this research was obtained after disassembling 150 kg of battery packs from Volvo Cars AB (Sweden). Packs were discharged by Volvo Cars AB and disassembled by Stena Recycling AB (Sweden). Then, the 120 kg collected cells (chemistry NMC 111) underwent a three-step process consisting of crushing, mechanical sieving, and magnetic separation, conducted by Akkuser Oy (Finland), all at temperatures below 50 °C. The resulting fine fraction (58.5 % of the initial weight) contains a mixture of active materials from the cathode and anode, along with current foils and separators. This fraction was further sieved to under 500 μ m at the Industrial Materials Recycling group at Chalmers University of Technology (Sweden) to achieve a highly concentrated homogeneous powder the so-called black mass (BM). This last step was carried out using a sieve shaker (Retsch) for 5 min in interval mode at an amplitude of 1.2 mm with a sieve aperture of 500 μ m at room temperature. Using industrial waste is important to monitor the behavior and impact of impurities in the process.

3.2. Characterization of solid samples

For analyzing the metal composition in a solid matrix, aqua regia (HCl/HNO3: vol %3/1 - Merk Millipore Chloric acid 37 % w/w and Merk Millipore Nitric acid 65 % w/w) was employed to digest the solid samples at 80 °C for 4 hours. Sampling of the BM was conducted using the coning and quartering technique, dividing the initial sample into halves until the desired sample weight was attained. This method aids in minimizing uncertainties associated with grabbing a sample from a container (Retsch GmbH Haan, 2015). The resulting slurry was then allowed to cool overnight. After filtration (Filter VWR 516-0811 - 11 μ m particle retention), and subsequent dilution in 0.5 M HNO₃ (Merk Suprapure Nitric acid 69 % w/w), the metal content was analyzed using inductively coupled plasma optic emission spectroscopy (ICP-OES, Thermo Fisher).

The carbon content in the BM was determined using a LECO CS744 instrument. X-ray powder diffraction (XRPD, Bruker D8 Twin-Twin diffractometer) was used to characterize the solid samples using a Cu ($\lambda = 1.54184$ Å) radiation source, in a 20 range of 10 °–80 ° with a rotational speed of 15 rpm. The operating current and voltage used were 40 mA and 40 kV respectively. Analysis of the X-ray diffraction data was carried out using the Pawley method in the TOPAS software (Coelho, 2018). The morphology was analyzed using scanning electron microscopy (SEM). Imaging was performed with a Phenom Pro X microscope (Thermo Fisher Scientific, USA), equipped with an energy-dispersive X-ray spectroscopy (EDS) analyzer for elemental identification. The SEM was operated in BSD FULL mode at an accelerating voltage of 15 kV. The particle size distribution of the solid residue was measured by laser diffraction technique with the MasterSizer 300 (Malvern Instrument – ms2000, UK), where the solid was dispersed in water.

3.3. Characterization of liquid samples

The concentration of elements was measured using an inductively



Fig. 1. Flowsheet of the proposed process: 1) Oxalic acid leaching – Recovery of Li and Al in oxalic acid solution, 2) Sulfuric acid leaching – Recovery of Co, Ni, Mn, and Cu in the acidic solution, 3) Solvent extraction of Cu 4) Recovery of Co, Ni, and Mn in the raffinate and direct synthesis of the cathode material. The article covers the investigation of Leaching I.

coupled plasma-mass spectrometer (ICP-OES, Thermo Fisher Scientific, Model iCAPTM 6000 Series). The samples were diluted with 0.5 M HNO₃ in the linear calibration range from 0.625 to 20 ppm. An approximate 0.3 ppm limit of detection was estimated for the method used. The pH of the solution was monitored during the operation using a pH electrode (Metrohm 6.0258.600) connected to the Tiamo software to record the data. The electrode was calibrated with buffer solutions at pH 2, 4, and 7 before each experiment at 20 °C. The titration of oxalic acid was done by redox titration using KMnO₄ in the presence of H₂SO₄. When there is an excess of MnO₄, the leachate solution becomes purple as no oxalic acid is left to be oxidized into carbon dioxide.

3.4. Leaching

Leaching was performed in a PVDF closed double-jacketed reactor; the initial volume of 60 mL of 0.6 M oxalic acid solution was inserted and heated up to the desired temperature. Once the temperature was reached and stabilized, three grams of BM sample were inserted, conforming to a solid-liquid ratio of 50 g/L. Mechanical stirring was provided at 400 rpm. All experiments were carried out in triplicates. During the leaching, 1 mL samples were taken and immediately filtered (Syringe filter PTFE - Restek – 0.45 μ m). The metal content of each liquid sample and the final leachate solution were analyzed using ICP-OES. Leaching experiments were all performed for 7 h, to ensure the system achieved dissolution equilibrium. Once this time passed, the reactors were cooled down to room temperature (25 °C \pm 1 °C), and the slurry was filtered to obtain the final leachate solution and resulting solid residue.

The leaching yield (Yi), defined as the chemical conversion of a given element i from solid to liquid, is expressed in Eq. (13):

$$Y_{i}(\%) = \frac{m_{i,BM,0} - m_{i,Res,t}}{m_{i,BM,0}} = \frac{m_{i,liq,t}}{m_{i,BM,0}} = \frac{C_{i,liq,t} * V_{liq,t}}{wt \%_{i} * m_{BM,0}}$$
(13)

In which $m_{i,sol,0}$ is the initial mass of the element, i, in the black mass, and $m_{i,Res,t}$ is the mass of the element left in the leaching residue after a certain time, t, while $m_{i,liq,t}$ is the mass of the element transferred in the leaching solution after a certain time, t.

3.5. Thermodynamic diagrams

Predominance and species distribution diagrams for metal-oxalate systems, used to determine which oxalate species can coexist in aqueous solution, were generated using the HYDRA (Hydrochemical Equilibrium- Constant Database) and MEDUSA (Make Equilibrium Diagrams Using Sophisticated Algorithms) programs (Puigdomenech, 2020).

4. Results and discussion

4.1. Black mass characterization

The black mass used for this study was obtained after sieving at 500 μ m; its elemental composition is given in Table 2. This work also monitors major metallic impurities such as Fe, Si, or P. The X-ray diffraction pattern of the black mass powder is depicted in Fig. 2a. It shows that the black mass primarily consists of NMC 111, graphite, and Cu. The particle size distribution of the black mass, presented in Fig. 2b highlights the existence of three groups of particles: the first one around 5–30 μ m, then

from approximately 30 to 110 μ m, and finally from 110 to 140 μ m. Associated with the SEM images and EDS analysis (seen in Fig. 2c), each group can be associated with the different components of the black mass: the smaller particles correspond to graphite particles from the anode, the second group consists of active cathode material, and the largest group comprises the current collector foils, Al, Cu, and separator. Supplementary material (Fig. S2) is provided to see the detailed distribution of each element. Moreover, the round morphology of the cathode material particle is seen with a smooth and flat surface; particles seem closely bound together with the binder. The EDS analysis shows the even distribution of all transition elements through the CAM (right image). The mapping (left image) reveals the presence of fluorine in the sample, homogeneously distributed, which can be seen as the binder footprint or electrolyte salt (Qing et al., 2023). Similar observations were made by Mousa et al. (Mousa et al., 2023).

4.2. Black mass dissolution

In the conducted leaching experiments, solid-liquid ratios and oxalic acid concentration were fixed (Rouquette et al., 2023) at 50 g/L and 0.6 M, while temperature (from 30 °C to 80 °C) and time (up to 7 hours) were varied to assess their impact on the dissolution kinetics of the black mass and the oxalate residue produced. The variation of all significant components in the system is illustrated in Fig. 3. To complement the discussion on the dissolution behavior of different metals in oxalic acid, predominance and species distribution diagrams were generated using Medusa. It is important to highlight that only pure species are considered in such modeling, and the final molar concentrations are considered to align with those observed in the leachate. The resulting plots are shown in Fig. 4. Additionally, Table 3 presents solubility constants of mono-elemental simple oxalate complexes that can be produced.

As depicted in Fig. 3a, the higher the temperature, the faster Li dissolves. At 80 °C, only 30 min is needed to reach a plateau of dissolution (lithium concentration of 2.5 g/L in the final leachate). In comparison, more than 6 h is required when the leaching is performed at 30 °C, corresponding to 1.8 g/L of lithium in the solution. For all temperatures (except 30 °C), the maximum recovery of Li is 90 %. Hence, a limitation in the dissolution is observed for this set of experiments. Different phenomena could induce this limitation. The produced oxalates could coat the unreacted NMC particle, blocking the leaching reagent access, hence limiting Li dissolution. On the other hand, Li (dissolved) could get trapped in the crystal formed during the oxalate precipitation.

For Al, a total dissolution is observed after 60 min for most studied temperatures (except 30 °C), corresponding to an approximative final concentration of 0.5 g/L in the leachate. The different soluble Al oxalate species can be seen in the species distribution diagram (Fig. 4a). At an approximative pH of 2, two anionic complexes coexist $Al(C_2O_4)_2^3$ and $Al(C_2O_4)_3^3$. This diverges from the findings in the literature; for instance, Zeng et al. (Zeng et al., 2015) suggest that at a molar ratio OA:LCO of 2.5 (similar to the molar ratios used in this study but for OA:NMC), a mixture of $Al(HC_2O_4)_3$ and $Al_2(C_2O_4)_3$ is formed, although the latter is reported insoluble.

While Al shows very fast dissolution, Cu behaves differently in the oxalic acid solution (Fig. 3c). Again, the temperature has a positive effect on the dissolution rate, after 7 h, only 5 % of the Cu is dissolved at 30 °C (final concentration of approximately 50 ppm), while 15 % or 25 % are dissolved at 50 °C and 80 °C respectively (approximately 570 ppm when leaching at 80 °C). In addition, for all observed temperatures, the

Table 2

Elemental composition of the black mass powder (obtained after aqua regia digestion + ICP measurement and TOC analysis for the carbon - STD given out of triplicate measurement).

Element	Р	Со	Ni	Si	Mn	Fe	Cu	Al	Li	С
wt % (g _{element} /g _{sample}) (%) ± STD (%)	0.4 0.0	11.6 0.2	8.7 0.2	0.2 0.0	7.5 0.2	0.1 0.0	2.4 0.1	0.8 0.1	3.4 0.1	32.0 0.2



Fig. 2. Black mass characterization: a) X-ray diffraction pattern (Graphite PDF 00-056-0159, NMC PDF 04-013-4379), b) Particle size distribution, and c) SEM image and element composition from EDS data.

operation can be divided into three steps, raising questions regarding the reaction of Cu with oxalic acid. Cu can be initially dissolved as Cu^{2+} and precipitated as simple CuC_2O_4 (negative slope), with the latter continuing to react with oxalic acid to form a soluble oxalate complex (again positive slope). The most probable copper oxalate complex in the solution is the $Cu(C_2O_4)_2^2$ as seen in Fig. 4b along with some small portion of the simple copper oxalate as it has a low solubility (see Table 3). To achieve higher dissolution of Cu, more oxidative conditions could be needed (Guimarães et al., 2022; Petranikova et al., 2023).

Regarding the transition metals from the cathode material (Co, Ni, and Mn), they present the same dissolution behavior. The two-step mechanism is particularly visible at lower temperatures (30 and 40 $^\circ \mathrm{C}$), indeed in the very first minutes, their dissolution can be observed (positive slope) followed by a negative slope indicating precipitation of some kind. This highlights that the release of metals into solution is initially faster than complexation, but complexation seems to take over the reaction rate, becoming the limiting factor of the operation. For all the temperatures investigated, the final recovery is equivalent; less than 0.5 % for Co and Ni and 2 % for Mn (for a respective concentration of 15, 5, and 100 ppm). For these three metals, the anionic oxalate complexes $Me(C_2O_4)^{\frac{3}{2}}$ can be found in the solution, as seen in Figures 4c, 4d, and 4e, along with the simple oxalate compounds. For Ni and Co, their simple oxalates are expected to be found in the solution, as their final concentrations are below the solubility limits (see Table 3). In the case of manganese, its concentration exceeds the solubility limit, suggesting that the neutral simple oxalate and the anionic species, $Mn(C_2O_4)^{2-}_{2-}$, coexist in the solution.

If we consider only the pure (mono-metal) oxalate complexes, the dissolved species in the solution are mostly anionic for all impurities. That knowledge is essential when developing a purification method for the solution. Traditional alkaline precipitation methods do not seem recommended as it would require substantial neutralization (up to pH 8). The authors recommend ion exchange as a fast and selective method for the removal of these impurities.

Another essential element to track in the operation is the evolution of the proton's concentration in the solution (Fig. 3g). The starting pH of the 0.6 M oxalic acid solution is 0.8, and the final value is 2 for all temperatures, with a solution potential of 300 mV. Protons actively participate in the dissolution of the CAM, and the pH naturally rises during the operation. The evolution of the pH was followed but not controlled, as a higher pH in solution can facilitate the solution's handling in terms of equipment (i.e., less corrosion potential or no addition of the acidic solution simplifying the leaching reactor setup). Additionally, it reduces the need for a neutralization agent during the purification stages (typically hydrolysis with NaOH in the recycling process) (Chernyaev et al., 2021). Finally, a higher pH promotes the dissociation of oxalic acid, providing more oxalate anions in the bulk to precipitate the transition metals oxalates (which are less soluble at higher pH) (Krishnamurty et al., 1960).

The proton consumption rate varies with the temperature; the higher the temperature, the higher the consumption rate. Above 50 °C, the proton concentration does not evolve after 60 min. This can indicate that in these conditions after 60 min, the protonation of the metal oxide from the cathode material is no longer happening and that only complexation reactions are occurring. It is important to compare this to the evolution of oxalate ions in the solution. As seen in Fig. 3h, the oxalate concentration keeps evolving after 60 min, this highlights that oxalate ions keep reacting with the remaining metals in solution or with the solidproduced oxalate compounds. The final concentration of oxalate is approximately 0.3 M for all leachate solutions. Half the initial molarity of oxalic acid remains in the solution; the regeneration of the acid will be investigated in future studies to increase the cost-efficiency and the sustainability of the process (Verma et al., 2022).



Fig. 3. Leaching yield of a) Li, b) Al, c) Cu, d) Mn, e) Co, f) Ni, g) proton consumption, and h) total oxalate concentration throughout the leaching. Error bars represent the standard deviation of the triplicate.

4.3. Characterization of the solid residue

4.3.1. Size and morphology of the particle in the residue

The different morphological characterizations operated on the residue are depicted in Fig. 5, this is essential for the definition of the dissolution mechanism of the black mass.

First, a simple observation can be made regarding the size distribution of the particles in the sample. Indeed, compared to the initial sample (see Fig. 2b) the overall particle size has decreased, seen by the decreased d50, from 29.8 µm to 17.5 µm. A new particle size group of around 1µm can be observed on the size distribution graph, while the peak of the 2nd group of particles (defined previously from 30 to 110 µm) has decreased. This primary observation could support the hypothesis that the NMC particle size decreases with the leaching and that the precipitation of the metal oxalates occurs in the bulk. However, as some particles are still visible around 100 µm it is also possible that some NMC unreacted particles are still trapped inside the structure. It is also worth mentioning that the group of particles around 10 µm seems untouched



Fig. 4. Species distribution diagram based on thermodynamic modeling with Medusa software for a) Al (20 mM), b) Cu (10 mM), c) Mn (1 mM), d) Co (1 mM), e) Ni (1 mM), and f) Fe (1 mM) at 25 $^{\circ}$ C and with oxalate concentration of 0.3 M and potential of 300 mV.

Table 3 Solubility and K_{sp} of pure simple oxalate compounds (data from literature (David, 2004)).

	CuC ₂ O ₄	MnC_2O_4	CoC_2O_4	NiC_2O_4
Solubility (g/L) at 18 °C	0.003	0.059	0.035	0.003
K _{sp}	4.4.10 ⁻¹⁰	1.70.10 ⁻⁷	5.7.10 ⁻⁸	4.2.10 ⁻¹⁰

by the operation, which supports the hypothesis that it is the group of graphite particles.

Secondly, SEM is used to observe the morphology of each particle after leaching at 60 °C as seen in Fig. 5a. The rounded particles of NMC are less prominent and are replaced by smaller agglomerates of cubic particles, which can be identified as metal oxalate structures. This differs from the observation made by He et al., who leached NMC532 cathode material with 0.6 M oxalic acid at a S/L of 20 g/L at 70 °C for 30 min. The resulting residue exhibits particles of irregular shapes with very rough surfaces and an increased size (He et al., 2022). Moreover, EDS analysis indicates the composition of the different particles. No Al foil could be found in the sample studied, which supports ICP results regarding its complete dissolution. Similarly, fluorine content has drastically decreased. Cu remains in the sample and can be found in a

similar foil shape as previously, primarily as metallic Cu and possibly CuO. Images of the residues after leaching at 30, 60, and 80 $^{\circ}$ C are provided in the supplementary material (Fig. S3), and no significant difference can be observed.

4.3.2. Composition and speciation of the residue

The X-ray diffraction patterns of the residue obtained after leaching at 30, 60, and 80 °C are shown in Fig. 6a, and the exact composition of the residue is given in the supplementary material (Table S1). It can be seen that they show comparable diffraction peaks regardless of the leaching temperature, indicating that in all cases, similar crystalline phases are present in the leaching residue. A difference within the temperature series is that the diffraction peak at 42.2 ° 20 (marked by arrow) is only present in the leachate obtained at 30 °C and disappears when higher temperatures are used. This peak is also present in the BM (Fig. 2a) and is thus assigned to unidentified impurities, which are temperature-dependently leached. As they seem soluble in aqueous media, it could potentially be some fluorine soluble impurity from the electrolyte salt or some decomposition products that dissolve at higher temperatures, the hypothesis that is supported by the EDS data as reported in the previous section.

The diffraction peaks at 26.6, and 44.6 $^\circ$ 20 (marked with *) reveal the



Fig. 5. a) SEM image and EDS report for the residue obtained after leaching at 60 °C and b) the particle size distribution for the residues obtained after leaching at 30, 60, and 80 °C.

presence of a graphite phase (PDF 04-016-6937) remaining in the residue from the BM, agreeing with our previous study (Rouquette et al., 2023). The other peaks in the diffraction pattern can be assigned to a transition metal oxalate phase, particularly the Co(C2O4) · 2 H2O (PDF 04-016-6937). The main question regarding the formed oxalate phase is if a common oxalate phase containing the different transition metals precipitates or if a phase separation occurs. In a study by Wang et al. (Wang et al., 2019), a Co-Ni mixed oxalate was prepared. They show that the formation of a solid solution between the Co and Ni oxalate phases leads to a single diffraction peak at 35.1 $^{\circ}$ 2 θ , whereas peak splitting would indicate the formation of a hybrid phase. No peak splitting can be observed for our leaching residues, indicating that a single oxalate phase containing Co, Ni, and Mn must be formed. Hence, Mn and Ni seem to act as dopants and occupy the same crystallographic site as Co ions in the oxalate framework. Nonetheless, when comparing the expected diffraction lines of $Co(C_2O_4) \cdot 2 H_2O$ with the observed pattern, it is visible that some diffraction lines are missing, i.e. the ones corresponding to the (11l) lattice planes (21.2, 24.7 29.1, 33.6 and 38.8 ° 20).

In previous reports on the structure of transition metal oxalates containing Ni or Mn, it was shown that oxalates are prone to the formation of disordered structures, which is accompanied by the extinction of certain diffraction peaks (Puzan et al., 2018; Puzan et al., 2018). This disorder is caused by a displacement of the one-dimensional oxalate chains with respect to one another.

To further characterize the formed leaching residues, the unit cell parameters and the space groups are determined using a Pawley fit; the refinement results are reported in Table 4. As the starting point, the oxalate phase is based on the reported structure by Puzan et al. for the disordered nickel oxalate (Puzan et al., 2018).

Fig. 6b-d shows that a description with the disordered oxalate structure and a graphite contribution allows the observed diffraction patterns to be reproduced. Even though the model well fits the data, it

has to be mentioned that the used model also accounts for more amorphous contributions around 24.7 and 33.8 $^{\circ}$ 20, which can be indexed and correspond to the (11*l*) and (11*-l*) lattice planes. With increasing temperature, these broad diffraction peaks become more pronounced, suggesting a disorder-order transition of the oxalate phase.

Regarding the lattice parameters within the temperature series (Table 4), they are close to the reported parameters for the single-phase α '-Mn, Co, or Ni oxalates (Puzan et al., 2018). The obtained values can be seen as the mean of the different lattice parameters of the individual oxalate phases. This confirms that Co, Ni, and Mn coprecipitate and form a solid solution.

Hence, the XRD analysis reveals that the leaching residue mainly comprises a solid solution consisting of a disordered (Co,Ni,Mn)C₂O₄ · 2 H₂O phase and graphite. Additionally, some residual impurities of unidentified BM components are present. No residual NMC111 can be evidenced (all intense peaks are gone). If any, only very little of the NMC could be left, up to a maximum of 1 % corresponding to the LOD of the machine in the case of highly crystalline materials. This indicates that the reaction is going toward a complete conversion. Finally, as the XRD analysis has revealed the presence of disordered (Co,Ni,Mn)C₂O₄ · 2 H₂O phase and not single (mono-metal) oxalate complexes. It is worth mentioning that this phase has physical properties different from those of single metal oxalate complexes. Hence, the solubility mentioned earlier (Table 3) has to be adapted, and it is a probable linear combination of the single oxalates.

4.4. Kinetics modelling on lithium dissolution

To gain a deeper understanding of the leaching mechanism, various kinetic models have been applied to the Li dissolution (Eqs. (1) to (10)). These models are explicitly used for this element, as the authors believe it best represents the dissolution behavior of the CAM. Fig. 7 illustrates



Fig. 6. a) X-ray diffraction patterns of the sample residues obtained after the leaching at 30, 60, and 80 °C with the expected diffraction lines for the $Co(C_2O_4)\cdot 2H_2O$ phase (PDF 04-016-6937). The asterisk indicates the peaks corresponding to the graphite phase (PDF 04-016-6937), b) Pawley fitting T = 30 °C, c) Pawley fitting T = 60 °C, and d) Pawley fitting T = 80 °C.

Table 4
Pawley fitting results. The angles α and γ were fixed to 90 $^\circ$ and only β was refined.

Sample Residue		Lattice parameters					R _{wp}
	a (Å)	b (Å)	c (Å)	α =γ (°)	β (°)		
30 °C	11.956(1)	5.460(1)	9.860(1)	90	126.89(1)	C12/c1	5.08
60 °C	11.939(1)	5.466(1)	9.843(1)	90	126.98(1)	C12/c1	4.93
80 °C	11.938(1)	5.464(1)	9.838(1)	90	126.94(1)	C12/c1	4.87

the experimental data points and the fitted models at 30 and 60 °C, showing leaching conversion as a function of time, along with the calculated kinetic constants for all models (k in min⁻¹). The determination coefficient (R²) is also provided, indicating the linear model's goodness of fit. A value close to 100% reveals that the model fits the experimental data points well. Fig. 7d depicts the linearized Arrhenius law (log(k) as a function of 1/T) plotted for the best-fitted models; the energy of activation (E_a) is calculated from the slope value (Eq. (12)).

The best R^2 values are obtained for Eqs. (6), (7), and the Avrami model. With higher fit at low temperature with a R^2 of about 98-99 % in the 3 cases, while at 60 °C, a R^2 of 96 % is obtained for Eq. (7) and about 90 % for Eq. (6) and the Avrami model. This deviation can be explained experimentally; running leaching at a higher temperature could lead to more experimental errors, which are considered neglectable. Hence, diffusion models (Eqs. (1) to (4)) are not selected as appropriate model, while the standard SCM model does not fit best (Eqs. (8) and (9)). However, it is worth mentioning that Eqs. (1) to (4) also have a reasonably good fit at 30 °C, indicating that at lower temperatures, diffusion is also limiting the reaction rate and that both could be considered in this case.

Eqs. (6) and (7) describe homogeneous or pseudo-homogeneous reactions (respectively, second and third order). Hence, particles are considered to be uniformly distributed in the leaching solution, and thereby, the slurry can be seen as a liquid. The order typically determines how the reactant concentration affects the leaching rate. This highlights that the black mass dissolution is chemically controlled, and it does not show any dissolution resistance due to some product layer around the unreacted lithium metal oxide particle. On the other hand, the Avrami model also fits the data correctly; this model typically defines the phase transformation. The order of the model is 0.5 at 30 $^\circ$ C and decreases when the temperature increases. Generally, an order lower than 0.5 shows that the leaching is governed by diffusion through the product layer, which contradicts previous considerations. The presence of both phenomena explains this; indeed, throughout our solid analysis characterization, we could see both products formed in bulk and products formed around unreacted particles.

Based on the kinetic rate constant obtained at each temperature for the best-fitted models, the energy of activation is calculated (Fig. 7d). This parameter is essential for understanding and optimizing the process toward its industrialization.



Fig. 7. Fitting of the Eqs. (1) - (9) to the experimental data at a) T = 30 °C, b) T = 60 °C, c) Fitting for the Avrami model with their rate constant associated and R², and d) the fitting for the Arrhenius Eq. 12 (for the best fitted models Eqs. (6), (7), and Avrami).

The highest R^2 (99.5 %) is obtained for the Avrami model, giving an energy of activation of 76 ± 3 kJ/mol. While 55 ± 4 kJ/mol and 63 ± 10 kJ/mol are determined with the 2nd and 3rd order kinetics models with a R^2 of 98 and 90 %, respectively. These values are concordant with the ones obtained by Verna et al. when they leached LCO with oxalic acid (Verma et al., 2021). It is important to highlight that the values obtained (between 55 and 76 kJ/mol) are relatively high compared to processes using inorganic acids (Wang and Friedrich, 2015; Chen et al., 2015). This is not abnormal for organic acids, as they typically require more

energy for reaction completion and have lower reaction rate (Tembo et al., 2024; Porvali et al., 2020). Additionally, it emphasizes again the chemically controlled nature of the dissolution, as the value is higher than 40 kJ/mol (Faraji et al., 2022; Habashi, 1993). Chemically controlled reactions are more sensitive to temperature, as the energy of activation of a reaction is usually higher than the diffusion during a leaching operation. Hence, tight temperature control will be needed, which may lead to higher operational costs and energy. Moreover, at high temperatures, diffusion can become the rate-controlling step (Faraji et al., 2022). Furthermore, it is important to remember that a sequence of consecutive reactions involves steps with varying activation energies, an increase in temperature can lead to the step with the lowest activation energy becoming the rate-determining step (Rosenqvist, 1974).

5. Conclusion

This study explores the dissolution of CAM from the black mass, along with the metallic impurities Al and Cu. From our previous work, the concentration effect was already investigated, and only optimal conditions were tested: S/L ratio of 50 g/L, 0.6 M of oxalic acid (Molar ratios OA:NMC of 2.5) under 400 rpm agitation for 7 h. The metal concentrations in the solution were monitored throughout the leaching, and the temperature varied from 30 to 80 °C. A Li recovery of 90 % was observed for all temperatures once dissolution equilibrium was achieved without reducing agent usage or special pre-treatment, which is high and comparable with inorganic acid recovery. Only Al is fully codissolved, and its speciation is demonstrated to be a mixture of Al $(C_2O_4)^{\frac{1}{2}}$ and Al $(C_2O_4)^{\frac{3}{2}}$. Cu is the other element sensibly dissolved in oxalic acid, and temperature influences the dissolution rate. The most probable Cu oxalate complex in the solution is the Cu(C_2O_4)²/₂ along with some small portion of the simple Cu oxalate as it has a low solubility. By stopping the leaching operation (under 60 minutes) and operating at 60 °C, its dissolution can be avoided at a rate lower than 5 %. Regarding the transition metals from the CAM material, low dissolutions are observed: 0.5 % for Co and Ni and 2 % for Mn, and they are expected as anionic species $Me(C_2O_4)^{2^-}$ in the solution. The identification of solvable species is essential to selecting the appropriate purification method. Based on this result, an anionic exchange operation is suggested as it would remove all impurities and yield a very pure lithium oxalate solution.

Moreover, the analysis of the XRD pattern reveals that the leaching residue mainly comprises a disordered (Co,Ni,Mn)C₂O₄ \cdot 2 H₂O phase and graphite mix. Additionally, no residual NMC111 can be evidenced, indicating a complete transformation during the leaching process. SEM reveals a new cubic type of particle corresponding to the oxalate mix. The images do not depict if the oxalate precipitates are coating the unreacted CAM particles. However, the particle size distribution supports that part of the oxalate is formed in the bulk, and the other part is formed at the surface of the NMC particle.

Lastly, the Avrami and 2^{nd} and 3^{rd} reaction models best fit the empirical leaching conversions (with the highest degree of correlation, R^2), excluding diffusion and SCM models. The selected models demonstrate that the dissolution is chemically controlled, enhancing our understanding of the process. The respective activation energies are 76 ± 3 kJ/mol, 55 ± 4 kJ/mol, and 63 ± 10 kJ/mol. This magnitude order also supports a chemically controlled operation. The recycling process is under development, and more work is ongoing to optimize the chemistry and parameters for the rest of the process. These first results are auspicious and have a high potential for industrialization later. One challenge remains in the regeneration of oxalic acid, which will be the subject of our future research.

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CRediT authorship contribution statement

Léa M.J. Rouquette: Writing – original draft, Methodology, Investigation. Laura Altenschmidt: Writing – review & editing, Methodology, Investigation. Matea Culina: Writing – review & editing, Investigation. William R. Brant: Writing – review & editing, Supervision. **Burçak Ebin:** Writing – review & editing, Supervision. **Martina Petranikova:** Writing – review & editing, Supervision, Funding acquisition.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Martina Petranikova reports financial support was provided by Swedish Energy Agency. Martina Petranikova reports a relationship with Sweden's Innovation Agency that includes: funding grants. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.hazadv.2025.100750.

Data availability

Data will be made available on request.

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