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Leaching the spent LIBs black mass with a synergistic system using H_2O_2 and dicarboxylic acids

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Abstract: Lithium-ion batteries are the primary energy source for modern electric mobility, making the processing of battery waste and the recovery of critical raw materials – particularly lithium, cobalt, manganese, and nickel – a major challenge for sustainable industrial development. The rapidly growing demand for energy storage technologies further intensifies the need for efficient and environmentally benign recycling processes. This study investigates the hydrometallurgical leaching of black mass derived from LCO-type lithium-ion batteries obtained exclusively through manual dismantling and mechanical processing, without any prior thermal or chemical pretreatment. Reductive leaching was performed using a ternary system consisting of sulfuric acid, adipic acid, and hydrogen peroxide at 85°C for one 120 minutes, with a liquid-to-solid ratio of 10. Under these conditions, the leaching efficiencies reached 83.91% for Co, 85.86% for Li, 76.98% for Al, 94.16% for Cu, 58.48% for Ni. The results demonstrate that synergistic organic-acid-based reductive leaching offers a promising alternative for the recovery of valuable metals from polymetallic lithium-ion battery waste, contributing to more sustainable and cleaner recycling practices.

Keywords: sustainable recycling, lithium-ion batteries, black mass, acidic leaching, organic reductants, critical raw materials

1. Introduction

The rising number of electric vehicles, along with growing demand for electronic devices, has intensified interest in the sustainable development of the lithium-ion battery (LIB) recycling industry across Europe (Guo et al., 2024). Simultaneously, the expansion of renewable energy sources and modern energy storage technologies also requires responsible raw material management, creating new opportunities for the recycling sector (Sobianowska-Turek et al., 2023). Within the framework of European circular economy regulations, Poland holds a strategically advantageous position to become a leader in the sustainable recycling of lithium-ion batteries. As a significant player in the European automotive and technology markets, Poland demonstrates substantial potential for dynamic growth - especially following the 2024 commissioning of two large-scale recycling facilities: Elemental Strategic Metals Sp. z o. o. in Zawiercie (Elemental Strategic Metals, 2026) and Eneris Batteries & Recycling in Żarki (Eneris, 2026). Moreover, Poland is well-positioned to be among the first in Europe to proactively address sector-specific challenges and capitalize on the benefits of developing a localized recycling infrastructure, which extends beyond industrial competitiveness to encompass environmental protection and support for local populations (Sobianowska-Turek and Urbańska, 2019). In this context, recycling lithium-ion batteries emerges not only as an environmental imperative but also as an economic necessity.

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The recovery of raw materials, such as cobalt, nickel, manganese, and lithium—essential components of LIBs —is becoming a crucial part of the transition toward a more sustainable circular economy (Bruno and Fiore, 2024; Pražanová et al., 2024). Recycling these metals aligns closely with key European Union strategies, as they are listed among 34 critical raw materials and are included in the group of 17 strategic raw materials under the Regulation of the European Parliament and Council on ensuring the secure and sustainable supply of critical raw materials, amending Regulations (EU) No. 168/2013, (EU) 2018/858, (EU) 2018/1724, and (EU) 2019/1020 of 11.04.2024 (Regulation (EU), 2024). Recycling waste LIBs and recovering the metals they contain directly relates to Chapter 3, Section 1, Art. 1, Point 1a, Sub-item (iii) of the mentioned regulation, which states that, to significantly increase the capacities of EU countries for each strategic raw material by 2030. Moreover, according to industry data, by 2034, demand for raw materials used in chemical energy sources (batteries and accumulators) will significantly exceed availability. It is estimated that by that year, the global deficit of key battery materials will reach approximately 572,000 tons of lithium (as lithium(IV) carbonate equivalent), 839,000 tons of nickel, 91,000 tons of cobalt, and 307,000 tons of manganese (Elements, 2026). Nevertheless, the supply of these materials is increasingly constrained not only by growing demand but also by technological and environmental challenges associated with their extraction. In particular, cobalt used in battery cathodes faces significant ethical and geological constraints (Haider, 2023). Simultaneously, lithium extraction is becoming increasingly complex and costly, as easily accessible high-grade deposits are being depleted and new projects must rely on lower-grade ores, more complex brines, and more demanding extraction and refining routes. These challenges collectively increase both technological complexity and production costs, further emphasizing the urgent need for efficient recovery strategies. Consequently, the development and implementation of advanced recycling technologies are essential, especially in the context of tightening legal regulations and the growing scarcity of primary raw materials for battery production. Within this framework, newly developed and innovative unit processes can play a significant role in improving the efficiency of battery material recovery and subsequent processing. Currently, chemical methods are the most suitable for extracting metals from polymetallic spent Li-ion batteries. Hydrometallurgical recycling typically involves acid or alkaline leaching of properly prepared battery waste (electrode powder obtained after mechanical processing). This is followed by a series of physicochemical operations to separate and concentrate valuable or problematic components into appropriate phases, producing commercial products and semi-finished products for further technological processing (chemical or thermal - pyrometallurgical) or waste. Hydrometallurgical processes are generally considered less energy-intensive than pyrometallurgical ones; however, their waste can be more environmentally burdensome due to the generation of large volumes of wastewater. Nonetheless, a key advantage of hydrometallurgical methods is their ability to process mixtures of different battery types simultaneously.

Additionally, this method allows for the recovery of metals with similar chemical properties from polymetallic wastes, such as used batteries and accumulators, which is practically impossible using pyrometallurgical methods (Sobianowska-Turek et al., 2025a). In Europe, the industrial processing of waste lithium-ion batteries using hydrometallurgical methods and vacuum distillation is currently carried out with technologies developed by AEA Technology (Great Britain), Recupyl (Spain), and Accurec (Germany) (Li et al., 2018). Due to the limited number of technologies capable of processing this waste, research aimed at developing new modular metallurgical processes for effective raw material recovery, primarily metals, from spent LiBs streams is critically important. Regarding waste Li-ion batteries, leaching studies have been conducted using both inorganic acids, such as sulfuric, nitric, or phosphoric acids, and organic acids, including citric, lactic, formic, priopionic, gluconic and acetic acids, with or without the addition of reducing agents (Aaltonen et al. 2017; Cerillo-Gonazalez et al., 2024; Vinayak et al., 2025; Gebeyehu et al. 2025,). Some examples of $LiCoO_2$ leaching are presented in Table 1.

A review of the literature (Table 1), shows that leaching efficiencies for cobalt and lithium frequently exceed 99%. However, such high recoveries are typically achieved only after energy-intensive pre-treatment, most commonly calcination, which is employed to remove organic binders and carbon to thereby enrich the metallic content of the black mass. This step significantly increases both energy consumption and process complexity.

Table 1. Examples of operating conditions for the acid leaching of valuable metals from spent $LiCoO_2$ material

LIBs material composition	**Pretreatment before leaching**	**Reagents**	**Reductant**	**Conditions**	**leaching efficiency**	**Ref.**
cathode powder Li 7.02%; Co 59.74%; Fe 0.0016% Ni 0.0008%	Calcination and grinding	3.0 M H_2SO_4	0.4 g/g glucose	95°C, 2 h	96.00% Li 98.00% Co	(Chen et al., 2018)
cell phone batteries Li 6.69%; Co 58.11%; Ni 0.39% Mn 0.14%	Thermal and mechanical treatment	0.7 M H_3PO_4	4.00 vol.% H_2O_2	40°C, 1h Ø< 0.075 mm	99.00% Co	(Chen et al., 2017)
cell phone batteries Li 4.8%; Co 41.5%; Mn 2.1%	Calcination at 573 K (300°C)	2.0% H_3PO_4	4.00 vol.% H_2O_2	90°C, 60 min Ø: 10 μm	88.00% Li 99.00% Co	(Pinna et al., 2017)
Nokia BL-5CA battery Li 5.77%; Co 58.03%	Calcination at 650°C	1.5 M H_3PO_4	1.5 M glucose	80°C, 2h, Ø: < 0.15 mm	100.0% Li 98.00% Co	(Meng et al., 2017)
various cell phone batteries Li 6.69%; Co 58.11%; Ni 0.39% Mn 0.14%	Calcination (700°C, 2h) and grinding to fine powder	0.6 M tartaric acid	3.0% H_2O_2	80°C, 30 min	98.00% Li 97.00% Co (as solid, pure cobalt tartrate)	(Chen et al., 2019)
(laptop batteries Composition after calcination: Co 46.06%; Li 5.60%; Cu 2.34% Ni 1.21%; Al. 0.24%	Thermal treatment (700°C, 6h) and sieving	2.0 M citric acid	1.25 vol.% H_2O_2	60°C, 2h, d90 = 55.90 μm	92.53% Li 81.50% Co	(Golmohammadzadeh et al., 2017)
Co 63%; Li 6.8%; Al. 10.2% Mn, Ni traces	Calcination (450°C, 1h; 800°C, 2h), grinding	5 M H_2SO_4	10% (v/v) methanol (CH_3OH)	90°C, 2h, S/L= 10 g/L	99% Co 99% Li	(Kong et al., 2023)
Various battery fractions Li 3-4% Co 17-25%; Mn 1.8-3%; Ni 3-4.5% Cu 0.4-20%	Fraction sorting	1.5 – 2 M H_2SO_4	Cu/Al (metals)	80°C, S/L =100 g/L Ø: 0.125 – 2 mm	55-95% Co 88-98.7% Li (depending on the material fraction)	(Peng et al., 2019)
Not provided	Pyrolysis (500oC, 20 min)	1M citric acid	0.2 M ascorbic acid	70°C S/L=1/12.5 Ø < 0.074 mm	un-pyrolyzed: 60.5% Co 60.6% Li Pyrolyzed: 94.5% Co 95.2% Li	(Jiang et al., 2024)
Mobile phones Not provided	Thermal treatment (700°C, 2h)	Mixture of 0.1 M citric acid, 0.1 M tartaric acid,	0.02 M ascorbic acid	80°C, 6h, S/L= 2 g/L	86% Co 98% Li	(Nayaka et al., 2018)

LIBs material composition	Pretreatment before leaching	Reagents	Reductant	Conditions	leaching efficiency	Ref.
Co 26.5%; Li 3.87%; Ni 2.74%; Mn1.67%; Al 1.64%; Cu 2.72%; Fe 0,.610%; P 0.45%; C 33%	Pre-roasting (600°C, 2h (Ar); 5h (Ar+O_2) Sulfation roasting (SO_2, 850°C)	H_2O	C	60°C, 1.5h, S/L= 100 g/L; Ø < 0.125 mm	61,2% Co 99.5% Li	(Biswas et al., 2023)

Consequently, a clear research gap exists regarding the development of direct, low-energy hydrometallurgical routes that eliminate the need for thermal pretreatment. The present study addresses this gap by investigating the direct leaching of $LiCoO_2$-rich black mass using organic acids, without any prior thermal or chemical processing.

While strong inorganic acids combined with hydrogen peroxide remain the most widely studied leaching systems, the application of organic acids – particularly in combination with organic reducing agents and and under elevated temperatures – remains insufficiently explored. Although organic acids generally exhibit lower leaching efficiencies than conventional inorganic reagents and often require process intensification, they offer important advantages, including biodegradability, lower toxicity, and reduced corrosivity toward industrial equipment (Willner et al., 2024). These features make them attractive candidates for more sustainable hydrometallurgical processing.

Current research on organic leaching systems has focused predominantly on citric, malic, and lactic acids, whereas their potential reducing capabilities remain poorly understood. To date, only a limited number of organic reductants – mainly ascorbic acid and glucose – have been systematically investigated (Chaudhary et al., 2023, Marchese et al., 2024; Mohanty and Devi, 2021). Given the critical role of the reducing agent in the dissolution of cobalt and lithium from lithium cobalt oxide, the identification of new organic reductants is essential for developing more selective and environmentally benign recycling processes (Domingues and de Souza, 2024).

In response to these limitations, the present study proposes and experimentally validates a hydrometallurgical leaching approach based on organic reductants under elevated temperature conditions. Specifically, glutaric and succinic acid—insufficiently addressed in the existing literature—as well as adipic acid, investigated for the first time in lithium-ion battery recycling, were evaluated in combination with sulfuric acid. The primary objective of this work was to assess the effectiveness of these organic compounds in enhancing the selective leaching of lithium and cobalt from spent lithium-ion black mass, obtained solely through manual dismantling and mechanical processing, without any thermal or chemical pretreatment. The investigated black mass originated from LCO-type lithium-ion batteries, and the scope of the study is limited to this battery chemistry. The novelty of this study lies in two aspects: first, the evaluation of direct leaching of $LiCoO_2$-rich black mass without thermal pretreatment; and second, the assessment of dicarboxylic acids—particularly adipic acid—as reducing components in sulfuric-acid leaching, including their synergistic interaction with hydrogen peroxide under intensified conditions. The rationale for combining these reagents was to separate their functional roles within the leaching system: sulfuric acid provided the acidic medium, the dicarboxylic acids were evaluated as reducing components capable of promoting the dissolution of $LiCoO_2$-bearing phases, and hydrogen peroxide was additionally tested as a reactive additive under intensified conditions. In doing so, the study aims to contribute of the development of more sustainable and diversified recycling strategies for lithium-ion batteries.

2. Materials and methods

2.1. Characteristics of tested spent Li-ion batteries

The studied material consisted of spent Li-ion batteries from portable computers/laptops, sourced from a company engaged in the recycling of electrical and electronic equipment in Poland (Lower

Silesia voivodeship). In the first step, the battery packs were manually removed from the devices. Next, the battery packs were manually dismantled step by step until individual cylindrical cells were obtained. The isolated cells were then subjected to manual mechanical processing in order to recover the black mass used in the subsequent leaching experiments. No chemical discharge procedure involving electrolyte solutions (e.g., NaCl solution) was applied prior to cell opening. All handling and mechanical processing steps were performed with appropriate safety precautions to minimize operational hazards associated with manual disassembly of spent cells. Waste Li-ion batteries with an average weight of 417 g were further separated into major components, including plastics, paper, metallic fractions, and polymetallic black mass (BM), which was used as the feed material in the acid leaching experiments (Fig. 1). The obtained black mass was not sieved or otherwise size-classified prior to leaching. The average particle size of the homogenized BM sample was approximately 35 μm. The particle size was determined by laser diffraction using a Mastersizer S analyzer (Malvern Instruments Ltd.).

The battery black mass (BM) obtained after manual separation and manual mechanical processing of the spent cylindrical cells was used for both phase and chemical characterization. XRD analysis was performed on a representative BM sample. The representative sample was homogenized and analyzed in powder form. Phase identification was carried out using a Malvern Panalytical Compact X-ray diffractometer (Aeris, 600 W), supported by HighScore Plus 5.3a software and reference patterns from the Crystallography Open Database (COD).

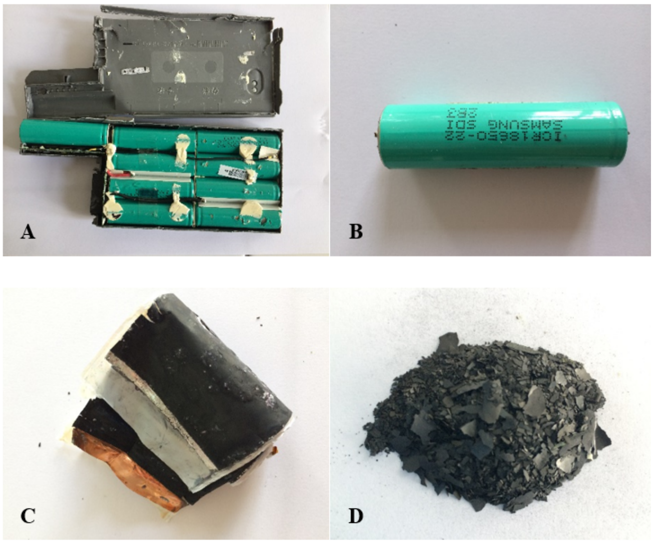

Fig. 1. Research material obtained from spent laptop LIBs after manual dismantling and manual mechanical processing; A: battery pack, B: single Li-ion cell, C: separated cell components (separator, foils and electrode powders), and D: polymetallic black mass (BM)

In addition, the representative BM sample was digested with aqua regia (3:1 v/v HCl/HNO_3) using an open-vessel system (DigiPREP Jr digestion block) at 120°C for 120 min. A sample mass of 0.5 g was digested in 10 mL of aqua regia. After digestion, the solution was filtered, and the solid residue was washed with deionized water. The filtrate was then diluted to a final volume of 50 mL. The concentrations of selected elements (Al, Cu, Co, Ni, Ca, Na, Mg, Cr, Fe, Mn, Zn) were determined by inductively coupled plasma optical emission spectrometry (ICP OES, Agilent 720, USA), using a 5-point calibration curves within the appropriate concentration range for each element. The analytical wavelengths (in nm) used for the determination of each element were as follows: Al (396.1), Cu (324.7), Co (230.7), Ni (230.2), Ca (317.9), Na (589.5), Mg (280.2), Cr (267.7), Fe (259.9), Mn (257.6), and Zn (213.8). The concentration of lithium was determined in all aqueous solutions using atomic absorption spectrometry with the Varian SpectrAA 20Plus instrument. Measurements were performed in absorption mode at a wavelength of 670.8 nm. Both standard and sample solutions were prepared by appropriate weight-based dilutions to minimize differences in solution density.

2.2. Leaching of the black mass

Acidic non-reductive and reductive leaching experiments were conducted in glass beakers using a WIGO ES 24 H magnetic stirrer equipped with a heating system. The black mass was added to the preheated leaching solution at the predetermined liquid-to-solid (l/s) ratios. After each leaching experiment, the slurry was filtered, and the pregnant leach solution (PLS) was analyzed for Co, Li, Al, Cu, Ni using ICP-OES. The metal content in the leach solutions was then determined and related to their initial concentrations in the black mass (BM), and the percentage recovery was calculated according to the following equation:

$$E = (C_{Me} \cdot V_{PLS})/(m_{BM} \cdot P) \cdot 100\%, \tag{1}$$

where: E - leaching recovery, %; C_{Me} – metal concentration in the PLS, g/dm^3; V_{PLS} – volume of PLS, dm^3; m_{BM}– mass of the BM sample, g; P – metal content in the BM sample, wt. %.

Non-reductive acidic leaching experiments were planned using the Design of Experiments (DoE) module in Minitab 16 to evaluate the main effects and interactions of key process variables. A 2^4 full factorial design with three center points was applied, based on the ranges reported in the literature (Sobianowska-Turek, et al., 2025b) to ensure clear estimation of all main effects and two-factor interactions (without aliasing). The inclusion of center points enables a formal test for curvature, providing insight into potential nonlinearity. The experimental design and resulting models were evaluated using ANOVA, R^2, adjusted R^2, and lack-of-fit tests. ANOVA assessed overall model significance and term contributions ($p < 0.10$), R^2 indicated the proportion of variance explained, adjusted R^2 accounted for model complexity, and lack-of-fit ($p>0.10$) tested residual error against pure experimental error. Collectively, these metrics confirmed model adequacy and design reliability. The Supplementary Material includes statistical results for all analyzed responses.

The investigated parameters included sulfuric acid concentrations of 1.50 M, 3.25 M, and 5.00 M H_2SO_4; initial leaching temperatures of 25.0°C, 40.0°C, and 55.0°C; leaching times of 30, 75, and 120 minutes; l/s ratios of 5.0, 7.5, and 10; and a constant stirring speed of 500 rpm.

In the present study, non-reductive leaching referred to acidic leaching carried out in sulfuric acid without the addition of an external reducing agent. In contrast, reductive leaching referred to acidic leaching performed in the presence of an added reductant, namely glutaric, adipic, or succinic acid, and in selected experiments also hydrogen peroxide. The non-reductive leaching stage was used to establish the baseline effect of sulfuric acid concentration, temperature, time, and liquid-to-solid ratio on metal extraction. The reductive leaching stage was subsequently designed to evaluate whether the addition of reducing agents could improve the dissolution of the $LiCoO_2$-bearing black mass, particularly by facilitating the reduction of cobalt species present in the cathode material to more soluble forms. The expected dissolution reactions of the main metal phases with H_2SO_4, as well as the reductive reaction of H_2O_2 with the cathode material were presented below (Qadir et al., 2024):

$$2LiCoO_2 + 3H_2SO_4 \rightarrow Li_2SO_4 + 2CoSO_4 + 1/2O_2 + 3H_2O \tag{2}$$

$$LiCoO_2 + 2H^+ + H_2O_2 \rightarrow Co^{2+} + Li^+ + 2H_2O + O_2 \tag{3}$$

Reductive leaching experiments were subsequently performed under the optimal conditions determined from the non-reductive DoE analysis namely: 1.50 M H_2SO_4, $T_{initial}$ = 55.0 °C, t = 120 min., l/s= 10. The selection of organic reducing agents was based on the thermodynamic calculations performed using HSC Chemistry v.9. These calculations (Table 2) indicated that glutaric acid ($C_5H_8O_4$), adipic acid ($C_6H_{10}O_4$), and succinic acid ($C_4H_6O_4$) – investigated for the first time in this context – exhibited lower standard oxide-reduction potentials than lithium-cobalt oxide, confirming their thermodynamic suitability for reductive acidic leaching of Li and Co from the investigated black mass. In this context, the reductive environment was intended to promote the reduction of cobalt species associated with the $LiCoO_2$ cathode phase, thereby enhancing its dissolution in the acidic medium. Analytically pure organic acids in solid form were added to the leaching system in the third minute of the experiment at a stoichiometric ratio with 25% excess.

Based on the metal recovery efficiencies obtained in the reductive leaching stage, adipic acid was identified as the most effective reducing agent. Consequently, an additional set of experiments was conducted to investigate the influence of an increased initial temperature (85 °C) and the addition of 3 vol. % hydrogen peroxide, while maintaining all other process parameters constant.

Table. 2. Standard redox potentials (pE^0) of selected reducers for the acidic leaching of $LiCoO_2$ materials

No.	Reducer	Reduction reaction	pE^0		
			25°C	40°C	55°C
1	Lithium-cobalt oxide ($LiCoO_2$)	$LiCoO_2 + 4H^+ + e^- = Li^+ + Co^{2+} + 2H_2O$	36.45	33.92	32.78
2	Hydrogen peroxide (H_2O_2)	$O_2 + 2H^+ + 26e- = H_2O_2$	11.75	10.94	10.21
3	Adipic acid ($C_6H_{10}O_4$)	$6CO_2 + 26H^+ + 26e^- = C_6H_{10}O_4 + 8H_2O$	1.69	1.39	1.13
4	Glutaric acid ($C_5H_8O_4$)	$5CO_2 + 20H^+ + 20e^- = C_5H_8O_4 + 6H_2O$	1.53	1.24	0.970
5	Succinic acid ($C_4H_6O_4$)	$4CO_2 + 14H^+ + 14e^- = C_4H_6O_4 + 4H_2O$	1.45	1.14	0.864

3. Results and discussion

3.1. Quantitative and qualitative characteristics of the tested black mass material

Through manual disassembly and separation, the constituents of the investigated Li-ion laptop batteries were isolated, specifically: external plastic casing (37.2 g), individual cylindrical cells (8 cells, each weighing 46.1 g), plastics, foils, paper (Σ 0.9 g), cables (1.2 g), metallic elements (4.8 g), and printed circuit boards (4.1 g). Then, the black mass fraction was directed to the acidic leaching experiments. The average content of the black mass (BM) in a single cell was 21.0 g (45.5%).

A representative sample of the black mass was analyzed by XRD, and the results indicated that the examined Li-ion batteries were of the LCO type, due to the presence of the cathode compound $LiCoO_2$, which is characteristic of this battery type. Carbon originating from the graphite anode was also detected (Fig. 2).

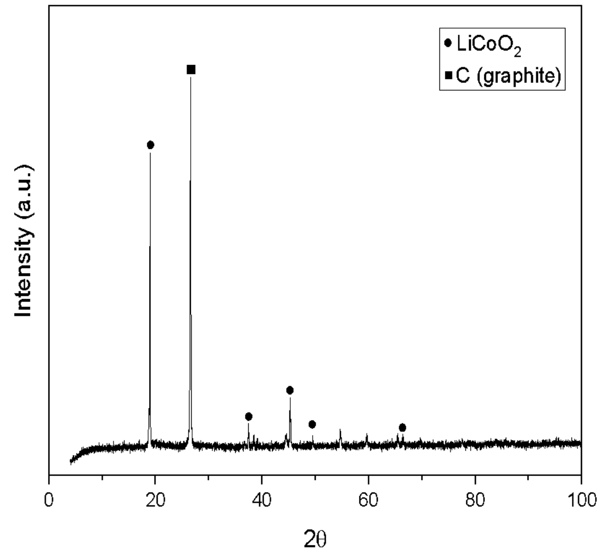

Fig. 2. XRD pattern of the black mass material

Given the chemical composition of the black mass, additional metallic phases — such as Cu, Al, or Ni — might be expected in the XRD pattern. However, these elements were present in relatively low concentrations, which likely places them below the typical detection limit of the XRD method. The black mass material was obtained through manual separation; therefore, small metallic particles originating from current collectors—most likely Cu and Al foils, possibly with surface oxide layers—can be expected. Nickel, in contrast, is typically present in the form of oxides (e.g., NiO) or as a component of layered oxide cathodes, depending on the battery chemistry (Chernyaev et al. 2021; Vanderbruggen et al. 2021; Dadé etal. 2022).

Quantitative and qualitative analysis by ICP-OES/ AAS performed on a solution obtained after digestion of the solid sample, revealed that the most valuable constituents of the black mass material were Co, Li, Al, Cu, and Ni (Table 3). The analysis also showed the presence of other metals, whose contents (mg/kg) were as follows: 10.70 ± 0.11 Cr, 66.65 ± 3.77 Fe, 96.3 ± 1.2 Mn, 43.06 ± 0.66 Zn, 4037 ± 23 Si. These minor elements should be regarded as trace impurities rather than primary constituents of the LCO cathode material. Chromium and zinc most likely originated from steel or galvanized components introduced during dismantling, while nickel was probably associated with battery casings or connectors rather than with the cathode chemistry itself. Sodium, calcium, magnesium, and silicone may derive from separator residues, ceramic coatings, mineral fillers, or incidental external contamination. Additional impurities could have been introduced during manual recovery of the black mass through cross-contamination from adjacent battery components, such as aluminum or copper foils, steel fixtures, or separator fragments, whereas others may originate from industrial cathode precursors used during cell manufacturing. Chemical analyses showed that these elements comprised approximately 30% of the total mass, with the remaining 70% consisting primarily of carbon/graphite, which is standard component of lithium-ion battery electrodes.

Table 3. Simplified composition of the black mass sample determined by ICP-OES/AAS. Co and Li content is given in wt.%; all other elements are expressed in mg/kg

Co	Li	Al	Cu	Ni	Mg	Na	Ca
%		mg/kg					
25.9 ± 0.1	2.59 ± 0.14	2727 ± 13	1333± 9	182.9 ± 1.6	898.4 ± 5.6	207.7 ± 1.6	256.1 ± 9.7

It should be noted that a small amount of undissolved solid residue was visually observed after the digestion procedure. However, the mass and composition of this residue were not determined, as the present study focused exclusively on the soluble fraction. Consequently, all reported recoveries referred to the fraction of elements released into the solution under the applied digestion conditions.

3.2. Non-reductive acidic leaching

The process of non-reductive acidic leaching using sulfuric acid proceeded rapidly, indicating a low activation energy threshold and favorable thermodynamic conditions. In all experiments, an increase in temperature was observed from the assumed initial temperatures of 25.0 °C, 40.0 °C, and 55.0 °C during the first 15 minutes of the process. Observed temperature variation was in the range of 2.0 °C to 5.0 °C. In addition, during the leaching process, the solutions foamed strongly, and the resulting foam remained throughout the process above the solutions, which appeared in light green-yellow or light pink colors. The experimental matrix and metal recoveries (E, %) were summarized in Table 4.

The results obtained for individual metals were analyzed using a DOE model implemented in Minitab 16. The analysis examined the variation in the transfer rates of Li, Co, Ni, Al, and Cu to the solution as a function of temperature (Factor A), time (Factor B), the solid-to-liquid ratio (Factor C), sulfuric acid concentration (Factor D), and their interactions. Although copper was included in the DoE study, no statistically significant model could be established within the investigated parameter ranges. The statistical analysis revealed no significant main effects or interactions for Cu. For all Pareto charts, the significance level was set to $\alpha = 0.10$, which corresponds to a standardized effect of 1.89 (vertical reference line). Factors whose standardized effects extended beyond this line were considered statistically significant for the acid leaching of LIBs black mass (Fig. 3, Tables 1.S.-4.S.). The DOE analysis showed that all main factors (A: temperature, B: time, C: l/s ratio, D: acid concentration) were statistically significant for the recovery of Li, Co, Ni, and Al. However, the relative importance of individual factors varied strongly depending on the metal considered, preventing the establishment of a universal parameter influence.

For cobalt recovery, temperature and time, as well as their two-factor interaction, were the most important factors, followed by acid concentration and its interaction with temperature (Fig. 4, left panel). The liquid-to-solid ratio had no statistically significant effect on the leaching yield. The temperature–time interaction plot (Fig. 4, right panel) revealed that at the effect of temperature was markedly stronger at shorter leaching times: increasing the temperature from 25°C to 55°C raised cobalt leaching yield by approximately 10% at 30 min, whereas at 120 min the increase was only about 3%.

Table 4. Experimental matrix of non-reductive leaching of the BM material and corresponding metal recoveries

Experiment number	**Parameters of leaching**				**E, %**				
	T, °C	**t, min**	**l/s, cm^3/g**	**C, mol/dm^3**	**Co**	**Li**	**Al**	**Cu**	**Ni**
1	25	120	10	5.00	24.61	62.15	31.76	83.87	52.87
2	25	120	5	1.50	21.36	58.87	30.32	89.53	47.62
3	25	30	5	5.00	19.44	53.30	14.53	81.84	40.93
4	55	120	10	5.00	26.13	66.92	29.35	74.89	66.44
5	25	120	5	5.00	24.38	60.55	24.77	63.92	60.03
6	55	120	5	1.50	25.85	66.57	30.84	80.10	67.41
7	55	120	10	1.50	26.77	69.80	26.78	85.67	69.11
8	25	120	10	1.50	22.10	61.05	31.03	81.05	56.84
9	25	30	10	1.50	10.39	38.97	9.75	87.87	30.07
10	55	30	10	5.00	26.66	68.62	20.26	77.20	56.25
11	25	30	10	5.00	17.35	49.74	13.74	76.77	41.04
12	55	30	5	5.00	26.36	69.72	44.73	79.86	51.47
13	25	30	5	1.50	11.24	38.02	15.32	77.08	32.80
14	55	30	10	1.50	25.44	61.49	21.78	76.47	58.39
15	40	75	7.5	3.25	23.98	59.82	21.67	78.45	55.51
16	40	75	7.5	3.25	24.91	61.29	24.97	81.65	60.40
17	40	75	7.5	3.25	24.07	60.40	23.84	78.72	56.93
18	55	120	5	5.00	26.34	61.46	26.55	72.00	65.39
19	55	30	5	1.50	25.30	60.31	33.91	75.60	56.43

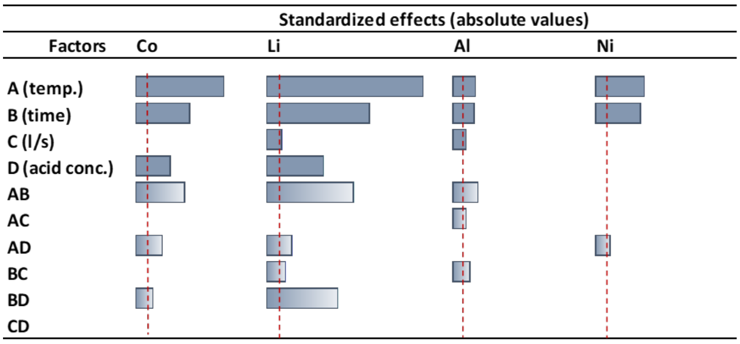

Fig. 3. Strength of main and interactions effects on the leaching efficiency of Co, Li, Al, and Ni based on Pareto charts. The vertical reference line indicates the critical value for statistical significance (α = 0.10)

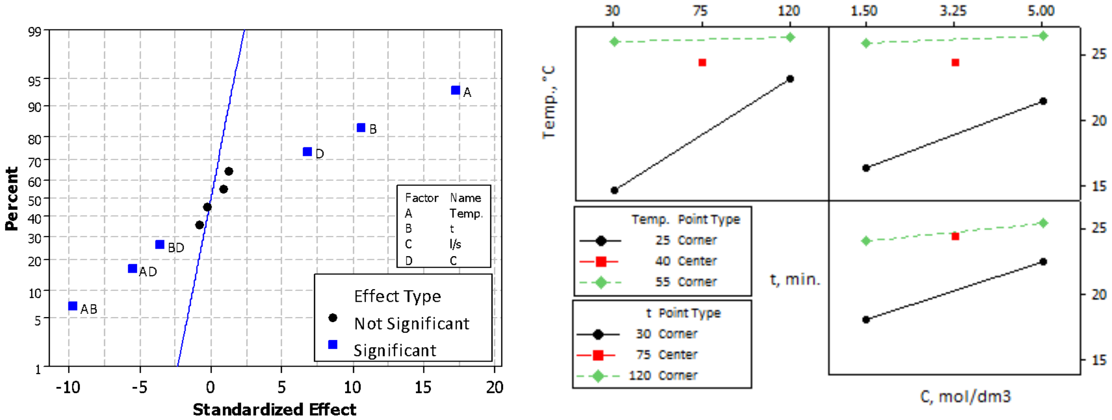

Fig. 4. Normal plot of the Standardized Effects (left)and interactions plot (right) for Co leaching. Y scale shows leaching efficiency, %

Acid concentration also influenced cobalt leaching efficiency, particularly through its interactions with temperature and time, with the effect being more pronounced at lower temperatures and shorter durations.

ANOVA performed on the model including main effects and two-factor interactions revealed a statistically significant curvature term for cobalt recovery (Table 1.S), indicating the presence of substantial nonlinearities within the investigated experimental region. Despite this, the fitted model describing the relationship between the process variables and Co extraction efficiency demonstrated high explanatory power, as confirmed by the statistical metrics (R-Sq = 98.87%, R-Sq(adj) = 97.09%):

$$E_{Co},\ \% = -8.60 + 0.573A + 0.184B + 3.59D - 0.00303AB - 0.0442AD - 0.00957BD + 1.84C_{CP} \quad (4)$$

where C_{CP} denotes the center-point indicator variable used to evaluate curvature.

The significant curvature term suggests that the current factorial model, although statistically robust, does not fully capture the nonlinear structure of the response surface. Therefore, the next stage of the study was planned to involve augmenting the current design with axial points to develop a full quadratic model within the Response Surface Methodology (RSM) framework. This would allow proper modelling of the observed curvatures and more accurate identification of the optimal process conditions.

The low cobalt recovery (20–25%) can be attributed to the absence of a reducing agent, which is necessary for the efficient dissolution of $LiCoO_2$. Without it, the leaching kinetics remain slow and the acid dosage becomes insufficient to drive the reaction to completion. These findings are consistent with the results reported by Cerrillo-González et al. (2022, 2024), who highlighted the critical role of time and temperature in the acidic leaching of $LiCoO_2$ and noted a shift from kinetic to diffusion control after approximately 2h due to the formation of a Co_3O_4 passivation layer. Similarly, Vieceli et al. (2023) observed limited cobalt extraction from LCO powder under comparable conditions without a reductant.

All tested factors affected lithium recovery (Fig. 5, left panel). However, the effect of the l/s ratio and its interactions with temperature and acid concentration was minimal (close to the reference line) and will therefore be excluded from further discussion. The most significant effects were observed for temperature and time, as well as their interaction (Fig. 5, right panel). This indicated that higher Li recovery was achieved under lower temperature (25°C) and longer leaching times. Specifically, at 25°C, increasing the leaching time from 30 to 120 minutes increased Li recovery by approximately 8%. At elevated temperature, neither leaching time nor acid concentration significantly affects Li recovery. Similarly to cobalt, acid concentration had no significant influence under elevated temperatures.

The statistical significance of the model terms was confirmed by ANOVA (Table 2.S), and the fitted model demonstrated high explanatory power (R-Sq = 99.47%, R-Sq(adj) = 98.65%). The regression equation describing lithium extraction efficiency as a function of the significant factors is given below:

$$\begin{aligned} ELi,\ \% = 4.05 + 0.891A + 0.369B - 0.645C + 6.66D - 0.00537AB + 0.0127AC - 0.0482AD + \\ + 0.00833BC - 0.0379BD \end{aligned}$$

The overall leaching efficiency for lithium reached on average 65%, which is approximately 10% higher than that achieved at 25°C. The higher recovery of lithium compared to cobalt was due to its better accessibility within the cathode material's crystal structure, as it is located in the oxide interlayers. Consequently, its extraction is more efficient even without a reductant. However, it remains limited because complete lithium release would require the breakdown of the host oxide structure.

The influence of the main and interaction effects on aluminum extraction (Fig. 6, left panel) was considerably weaker than that observed for lithium or cobalt. As confirmed by both the Pareto chart (Fig. 3) and ANOVA results (Table 3.S) six model terms were statistically significant at $\alpha=0.10$: temperature (A, $p < 0.01$), time (B, $p < 0.01$), l/s ratio (C, $p=0.045$), and their interactions AB ($p=0.002$), AC ($p=0.034$), and BC ($p=0.013$). Although the standardized effects of C, AC, and BC only marginally exceeded the significance threshold on the Pareto chart, their p-values consistently fell below the adopted α level, confirming their statistical relevance.

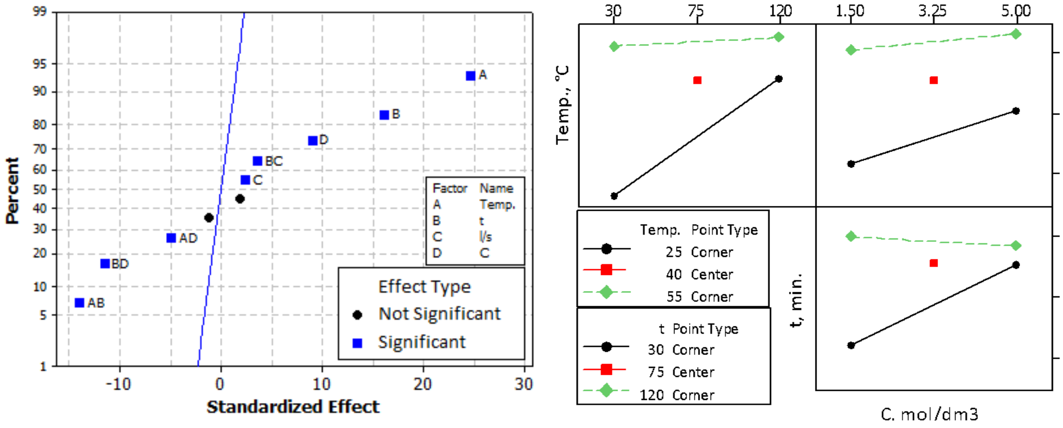

Fig. 5. Normal plot of the Standardized Effects (left)and interactions plot (right) for Li leaching. Y scale shows leaching efficiency, %

The regression equation describing aluminum extraction efficiency is:

$$E_{Al}, \% = -7.95 + 1.18A + 0.189B - 0.617C - 0.00664AB - 0.0653AC + 0.0274BC$$

The model exhibited good overall fit (R-Sq = 92.14%), while the adjusted coefficient of determination (R-Sq(adj) = 79.78%) was lower than those obtained for Co and Li, reflecting the inclusion of several marginally significant terms. Nevertheless, all retained terms were consistent with the physical behavior of aluminum in the leaching system and were therefore maintained in the final model.

As shown in Fig. 6 (right panel) aluminum extraction at 25°C was favored by longer leaching times, resulting in an approximate 15% increase. In contrast, leaching at elevated temperature is negatively affected by l/s ratio; specifically, a higher pulp density (l/s=5) yields about 7% higher Al extraction compared to l/s=10. Under these high-density conditions, leaching time becomes irrelevant. Conversely, at a lower pulp density (l/s=10), increasing the leaching time is beneficial, enhancing aluminum recovery to around 30%.

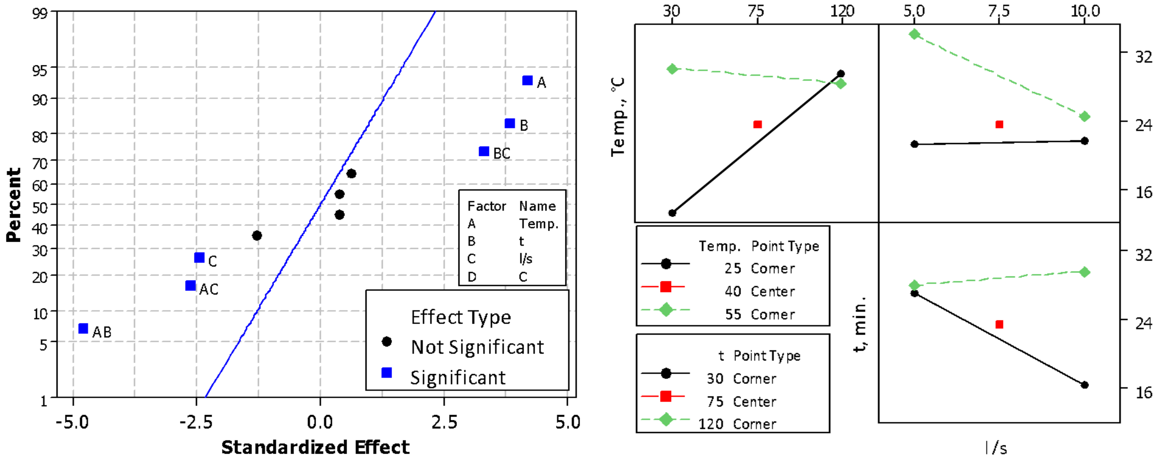

Fig. 6. Normal plot of the Standardized Effects (left)and interactions plot (right) for Al leaching. Y scale shows leaching efficiency, %

Statistical analysis for Ni (Figures 3 and 7, left panel, Table 4.S) identified temperature (A) and time (B) as statistically significant main effects influencing nickel recovery. The effect of acid concentration (D) was not statistically significant (p=0.311), however, it was retained in the model as it forms part of the significant interaction term AD (p=0.030). This indicates that the influence of acid concentration on Ni extraction is conditional upon temperature rather than purely additive.

The regression model demonstrated high explanatory power (R-Sq = 95.91%, R-Sq(adj) = 89.48%), and is expressed as:

$$E_{Ni},\% = -3.87 + 0.900A + 0.282B + 6.02D - 0.0936AD$$

As expected, increasing either temperature or time enhanced Ni leaching yield by nearly 20%, resulting in an average recovery of approximately 63% (Figure 7, right panel). This incomplete extraction of nickel was likely due to the presence of nickel in higher oxidation states (e.g., Ni^{3+}) within the cathode oxide structure, which are insoluble in non-reductive acidic media. Under the investigated conditions, only Ni^{2+} species were efficiently leached.

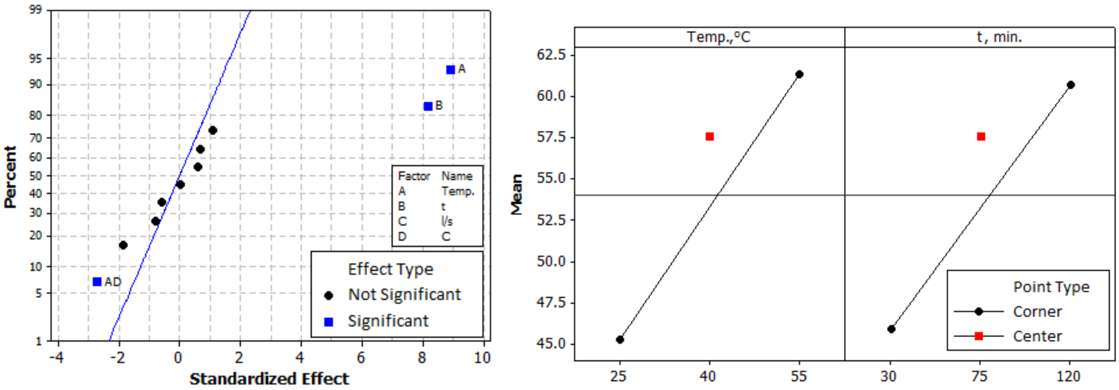

Fig. 7. Normal plot of the Standardized Effects (left) and interactions plot (right) for Ni leaching. Y scale shows leaching efficiency, %

Copper exhibited behavior distinct from that of the other investigated metals. Despite a relatively wide range of leaching efficiencies (64% to 89.5%), the statistical model explained none of the observed variance (R-Sq=0, R^2-adj=0). The high variability in Cu recovery is most likely attributable to material heterogeneity, particularly the uneven distribution of metallic and oxidized copper (and partially aluminum) phases in the black mass. Such heterogeneity may introduce substantial experimental noise, masking the influence of the investigated parameters on Cu extraction. In non-reductive leaching systems, the rate-limiting step is typically the reduction of Co^{3+} to Co^{2+}. This mechanism may explain the strong statistical significance of temperature and leaching time observed for Co, Li, Al, and Ni. However, residual metallic copper originating from current collector fragments may act as an internal reductant according to the reaction:

$$Cu^0 + 2Co^{3+} \rightarrow Cu^{2+} + 2Co^{2+}$$

$$(E^0\ Cu^{2+}/Cu = +0.34\ V\ \text{vs.}\ E^0\ LiCoO_2/Co^{2+} \approx +2.12\ V)$$

Although present in relatively low amounts, metallic copper may locally participate in redox reaction, introducing a secondary dissolution pathway independent of the externally controlled parameters. A similar contribution from residual metallic aluminum is theoretically possible; however, due to its low content in the investigated black mass, its effect was considered secondary.

The coexistence of two parallel mechanisms — (i) acid-driven dissolution of copper oxides and (ii) redox-mediated dissolution involving metallic copper — may account for the distinct statistical behavior of Cu and the lack of significant model fit. This interpretation is supported by literature reports indicating that metallic copper can act as an internal reductant in $LiCoO_2$ leaching systems. Peng et al. (2019) demonstrated that Cu and Al contents vary considerably across particle size-fractions of battery black mass, with coarser fractions enriched in metallic components exhibiting enhanced Co and li extraction. These findings are consistent with the hypothesis that residual metallic copper may influence local redox conditions and contribute to the observed variability in Cu recovery.

To summarize the factor effects on metal leaching, the necessity to elevate both temperature and time to maximize recovery was evident. Regarding acid concentration, the higher level (5.0 M) generally enhanced metal recoveries, with copper being the exception. However, the benefit was modest, as leaching with 1.5 M H_2SO_4 yielded results only slightly lower. A higher l/s ratio of 10 was selected to ensure sufficient contact between the leaching agent and the black mass. This choice was statistically justified: while the l/s ratio had a minimal positive effect on Li and Ni recovery and none on Co, it significantly reduced Al co-dissolution by approximately 10%. This selective suppression of Al leaching was a desirable outcome, as it helped concentrate the target metals (Co, Li, Ni, Cu) in the leachate while leaving more aluminum in the residue.

Beyond simple parameter optimization, the DoE analysis provided a structured comparison of factor significance for untreated LCO-rich black mass This information was useful for defining a rational baseline for reductive leaching systems applied directly to non-calcined black mass.

Consequently, the optimal leaching conditions were determined as follows: an acid concentration of 1.5 mol/dm^3, a temperature of 55°C, a duration of 120 minutes, and a liquid-to-solid ratio of 10. However, given the significant influence of temperature observed in preliminary tests (DoE) an additional leaching experiment was conducted at an elevated temperature of 85°C while keeping other parameters constant. The results presented in Table 5 showed that increasing the temperature raised the recovery of cobalt and lithium by only 5.83% and 1.78%, respectively. This confirmed that the temperature increase had a minor positive effect on the leaching efficiency of these metals.

Table 5. Non-reductive leaching parameters and metal recovery rates (E, %)

Leaching agent	**T, °C**	**t, min**	**l/s, cm^3/g**	**C, mol/dm^3**	**Co**	**Li**	**Al**	**Cu**	**Ni**
1.5M H_2SO_4	85	120	10	1.50	32.60	71.58	31.37	100.0	100.0

In contrast, the extraction of copper and nickel reached completion (100%), indicating that both metals were present in readily leachable forms under these conditions. For aluminum, only a slight improvement (4.6%) was observed, which can be attributed to slower dissolution kinetics or partial surface passivation.

Given that cobalt and lithium were the primary metals of interest in this study (with initial contents of ~26% and ~2.6%, respectively, compared to <0.5% for Cu and Ni), this modest improvement was considered insufficient to justify the use of elevated temperature as the baseline condition for subsequent reductant screening.

In summary, the non-reductive leaching results indicated that elevating the temperature to 85°C provided only a limited advantage for the target metals (Co and Li).

Therefore, 55°C was selected as the primary temperature for the subsequent reductive leaching experiments, allowing a systematic evaluation of the reducing agents without the confounding effect of high temperature.

3.3. Acidic reductive leaching and optimization of process parameters

The acidic reductive leaching processes using sulfuric acid proceeded less vigorously than in systems without the addition of $C_4H_6O_4$, $C_5H_8O_4$, and $C_6H_{10}O_4$, suggesting a higher activation energy barrier and less favorable thermodynamic conditions. In all experiments, no temperature increase was recorded from the initial setpoint of 55.0 °C, indicating that the reactions did not exhibit an exothermic character. Furthermore, between 1 and 3 minutes after the reducers were introduced, foaming ceased completely, suggesting the absence of gaseous product formation during the leaching processes. The measured pH of the filtrate ranged from 1.9 to 3.0.

In turn, in the process optimization experiments, increasing the initial temperature and adding a hydrogen peroxide reducer to the studied H_2SO_4 and $C_6H_{10}O_4$ system resulted in a large amount of thick, vitreous foam lasting for 120 minutes. Filtrates had an intense pink color and an acidic pH in the range from 1.5 to 3.0.

3.4. Effect of temperature and reducing agent on leaching efficiency

Adding organic acids, such as adipic, glutaric, or succinic acid, as reducers provided a new perspective on the acidic leaching of the black mass (BM) from spent lithium-ion batteries. Notably, adipic and succinic acids were tested as reducing agents for the first time in the literature. The obtained results showed that for all three acids used as reducers in leaching with sulfuric acid, the cobalt leaching rate increased by 12.86% for $C_6H_{10}O_4$, 8.70% for $C_5H_8O_4$ and 4.49% for $C_4H_6O_4$ (Table 6, experiments A1, A2, A3). In contrast, the lithium recovery rate improved only when adipic acid was applied, showing a 10.50% increase compared to the process conducted without a reducing agent, under the conditions of 1.50 M H_2SO_4, an initial temperature of 55.0°C, 120 minutes, and a solid-to-liquid ratio of 1:10 (Table 4, experiment No. 7). Additionally, it is worth noting that the leaching rates decreased significantly after the introduction of organic acids into the system for the other analysed metals: aluminium, copper, and nickel. This may suggest limited effectiveness of the reducing agents under the applied leaching conditions for these elements. However, while not optimizing the technological process, it is worth noting that these metals may remain in the battery mass. Only the main components with a small number of impurities were leached into the solution, which contributed to obtaining a final product with fewer impurities in the accompanying metals. The results of the first series of reductive leaching experiments in an acidic medium led to the selection of adipic acid ($C_6H_{10}O_4$) as the reducing agent for further research. To systematically assess the role of the reducing agent without the confounding effect of high temperature, the initial reductant screening was performed at 55°C. Subsequently, a direct comparison between 55°C and 85°C was carried out using the selected reducing agent (adipic acid) to evaluate the combined effect of temperature and reductant.

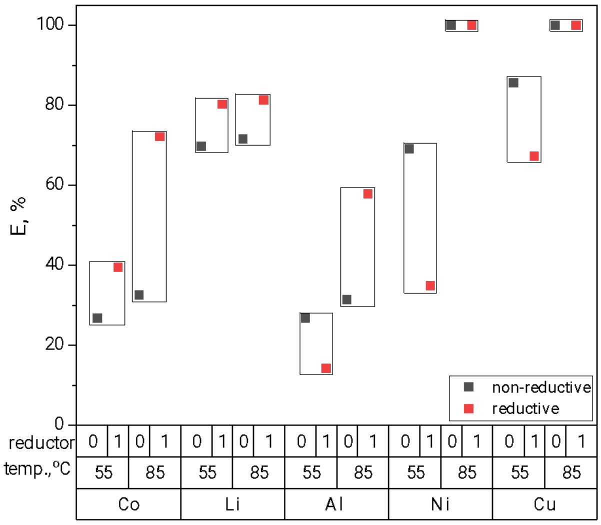

Fig. 8. Comparison of metal leaching efficiencies as a function of temperature and the presence of a reducing agent

To comprehensively evaluate the influence of both temperature and the presence of a reducing agent, the extraction efficiencies obtained under non-reductive and reductive conditions were compared. The data presented in Fig. 8 revealed distinct and metal-specific responses to these two factors.

For cobalt, a clear synergistic effect of temperature and reductant was observed. While increasing the temperature to 85°C in the absence of a reducer improved cobalt recovery only marginally (from 26.8 % to 32.6 %), the addition of adipic acid at 55°C raised it to 39.6 %. The combination of elevated temperature (85°C) and the reducing agent resulted in a substantial increase to 72.2 %, demonstrating that the reductant is most effective under thermally enhanced conditions.

Lithium extraction was consistently improved by the addition of adipic acid by approximately 10 percentage points at both temperatures, whereas the effect of temperature alone was negligible.

Aluminum showed an intermediate, temperature-dependent response to the reductant. At 55°C, adipic acid suppressed aluminum leaching (from 26.8 % to 14.3 %), whereas at 85°C it significantly enhanced it (from 31.4 % to 57.9 %). This behavior was likely related to kinetics effects. Nickel and copper exhibited a fundamentally different behavior. At 55°C, the use of a reducing agent markedly decreased their recovery – from 69.1 % to 34.9 % for Ni and from 85.7 % to 67.3 % for Cu. However, at 85°C, both metals were leached completely (100 %), regardless of the presence of a reductant. These results showed that high temperature enables full recovery of Ni and Cu regardless of the presence of a reductant; at 85°C the reducer is not required, while at 55°C it negatively impacts the extraction yield. This temperature-dependent behavior is consistent with adipic acid acting as an adsorbed organic inhibitor on metal-oxide/passive surfaces at 55 °C, where it stabilizes protective films and retards dissolution, while at 85 °C this film becomes unstable and oxide dissolution kinetics dominate, resulting in full Ni and Cu recovery and enhanced Al leaching.

Table 6. Results of the acidic reductive leaching of the battery mass

Experiment number	**Parameters of leaching**				**E, %**				
	T, °C	t, min	l/s, cm^3/g	C, mol/dm^3	Co	Li	Al	Cu	Ni
A1	55	120	1/10	1.50	**$H_2SO_4 + C_6H_{10}O_4$**				
					39.63	80.30	14.27	67.34	34.87
A2					**$H_2SO_4 + C_5H_8O_4$**				
					35.47	69.48	13.70	54.21	28.01
A3					**$H_2SO_4 + C_4H_6O_4$**				
					31.26	58.03	16.23	63.23	30.60
B	85	120	1/10	1.50	**$H_2SO_4 + C_6H_{10}O_4$**				
					72.20	81.32	57.91	100.0	100.0
C					**$H_2SO_4 + H_2O_2$**				
					31.32	69.89	54.45	100.0	100.0
D					**$H_2SO_4 + C_6H_{10}O_4 + H_2O_2$**				
					83.91	85.68	76.98	94.16	58.48

In the next step, the efficiency of a reference reducing system commonly reported in the literature – i.e. hydrogen peroxide combined with sulfuric acid – was evaluated (Table 6, experiment C). Previous studies have demonstrated that this mixture enables the leaching of over 90% of Li, Co, Ni and Mn from spent black mass (Sun & Qui, 2011; Gao et al., 2018). However, when applied to the material investigated in this work, no significant improvement was observed. On the contrary, the extraction yields of both cobalt and lithium decreased compared to the system containing adipic acid. This poor performance of the H_2SO_4–H_2O_2 system is most likely attributable to the catalytic decomposition of hydrogen peroxide at elevated temperature.

To further explore the role of the reducing environment, an additional experiment was conducted in which adipic acid was introduced together with hydrogen peroxide into the H_2SO_4 solution (Table 6, experiment D). The combination of these reducing agents at 85°C maximized the recovery of cobalt, lithium and aluminum, indicating the synergistic enhancement. The results indicated that adipic acid acted as the dominating reductant for $LiCoO_2$ leaching due to substantial electron-donating capacity ($C_6H_{10}O_4+8H_2O \rightarrow 6CO_2+26H^++26e^-$), whereas H_2O_2 played an auxiliary role with mixed redox character: it can assist interfacial redox processes while also oxidising metallic Cu/Al. In the combined H_2O_2–adipic acid system, competing side reactions may decrease the net Ni concentration in solution (passivation and/or removal via back-reduction or Ni–organic species formation), leading to a lower apparent Ni extraction. Given the low Ni content, minor losses manifest as substantial declines in extraction efficiency.

The findings of this study demonstrated that a synergistic system composed of sulfuric acid, adipic acid, and hydrogen peroxide enabled the leaching of cobalt and lithium with efficiencies of 83.91% and 85.68%, respectively, under optimized conditions (85°C, 120 minutes, l/s = 10). While these results were encouraging, they remained moderately lower than the highest efficiencies reported in the literature for systems based on sulfuric acid combined with hydrogen peroxide alone (Gebeyehu et al., 2025; Lee et al., 2025; Lim et al., 2025). For instance, Li et al. (2018) and Pražanová et al. (2024) achieved Co and Li leaching above 95% in carefully optimized H_2SO_4/H_2O_2 setups. Nearly complete recovery of these metals has also been reported using glucose as a reductant, both in a phosphoric acid media, and in 3 M H_2SO_4 at 95 °C, where Chen et al. (2017, 2018) obtained 96% Li and 98% Co after 2h. Other studies employing organic acids such as tartaric, citric, or formic acids similarly reported recovery rates exceeding 90% (Golmohammadzadeh et al., 2017; Zheng et al., 2017). From a process-integration perspective, the use of a ternary leaching system based on sulfuric acid, adipic acid, and hydrogen peroxide may complicate large-scale implementation compared with simpler binary systems. In particular, the presence of multiple reactive components may hinder direct recycling of the spent leaching solution and may require additional control of reagent consumption, decomposition, and solution conditioning prior to reuse. Therefore, although the present system showed favorable leaching performance under laboratory conditions, its practical applicability should be further evaluated in future studies with respect to reagent regeneration, solution recirculation, and process scale-up. Nevertheless, the environmental performance of the proposed reagent system could not be assessed solely on the basis of extraction efficiency and should be evaluated in future studies using broader sustainability criteria.

4. Conclusions

This study investigated the acidic leaching of spent lithium-ion battery black mass under both non-reductive and reductive conditions. Particular emphasis was placed on systems that do not involve any prior thermal or chemical pre-treatment of the feed material—an approach that clearly distinguishes this work from the majority of studies reported in the literature.

Based on the experimental results and comparative analysis of binary and ternary systems, the following conclusions could be drawn: (i) Temperature was identified as one of the most critical parameters governing leaching efficiency, regardless of whether non-reductive or reductive conditions were used. Statistically designed experiments and subsequent optimization confirmed its dominant influence. (ii) ANOVA analysis produced statistically valid linear models for Li, Co, Al, and Ni. Lithium showed excellent model fit, with high R^2 and adjusted R^2 values. In the case of cobalt, a significant curvature effect was observed under non-reductive conditions, indicating that a purely linear model was insufficient (although still practically acceptable). This finding supported the use of a quadratic model within a response surface methodology (RSM) framework for more accurate optimization of cobalt leaching. (iii) The addition of a reducing agent significantly enhanced the leaching efficiency of cobalt, lithium, and aluminum. However, at elevated temperatures, its effect on the dissolution of copper and nickel became negligible, suggesting different leaching mechanisms for these metals. (iv) Among the organic reductants tested, adipic acid proved to be the most effective, delivering the highest recoveries of both cobalt and lithium. Its superiority was particularly evident in cobalt leaching, where a strong interaction between temperature and the presence of the reductant was observed. (v) In the ternary leaching system (sulfuric acid + adipic acid + hydrogen peroxide), strong synergistic effects were observed, enabling highly efficient recovery of key metals from $LiCoO_2$-based black mass. Under optimized conditions, approximately 84% of cobalt and 86% of lithium were transferred into the leachate.

In a broader context, the results demonstrated that carefully designed synergistic acidic systems can offer an effective and potentially more sustainable alternative to conventional leaching approaches. The fact that no pre-treatment step was required highlights the practical relevance and process simplification potential of the proposed method. Despite the promising results, the environmental impact of the reagents employed requires further evaluation. Future studies should therefore include a comprehensive sustainability assessment of the proposed leaching system.

Future work should focus on: (i) further optimization of the ternary system to achieve an optimal balance between high Co/Li recovery and improved dissolution of Cu and Ni; (ii) integration of the leaching stage with downstream separation processes into a continuous, closed-loop flowsheet; (iii) pilot-scale validation to assess industrial feasibility and environmental performance within circular economy principles; and (iv) expansion of the experimental design toward advanced response surface methodology (e.g., central composite design – CCD) to enable more robust modeling and optimization of the process variables.

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References

AALTONEN, M., PENG, C., WILSON, B.P., LUNDSTRÖM, M., 2017. *Leaching of Metals from Spent Lithium-Ion Batteries*. Recycling, 2(20).

APTE, S., MUKHERJEE, A., MISHRA, P., 2025. *Sustainable metal recovery from spent lithium-ion battery using electrochemical technique: A comprehensive method review*. MethodsX, 15, 103506.

AQUAMETALS, *What Is Sodium Sulfate, and How Is It Relevant to Recycling? Lithium-Ion Battery Recyclopedia*. https://aquametals.com/recyclopedia/what-is-sodium-sulfate-and-how-is-it-relevant-to-recycling. Accessed on 22 April 2026.

BISWAS, J., ULMALA, S., WAN, X., PARTINEN, J., LUNDSTRÖM, M., JOKILAAKSA, A., 2023. *Selective sulfation roasting for cobalt and lithium extraction from industrial LCO-rich spent black mass*. Metals, 13, 358.

BRUNO, M., FIORE, S., 2024. *Review of lithium-ion batteries' supply-chain in Europe: Material flow analysis and environmental assessment*. Journal of Environmental Management, 358, 120758.

CERRILLO-GONZALEZ, M.M., VILLEN-GUZMAN, M., VEREDA-ALONSO, C., RODRIGUEZ-MAROTO, J.M., PAZ-GARCIA, J.M., 2022. *Acid leaching of LiCoO2 enhanced by reducing agent. Model formulation and validation*. Chemosphere, 287(Part 1), 132020.

CERRILLO-GONZALEZ, M.M., PAZ-GARCIA, J.M., MUNOZ-ESPINOSA, M., RODRIGUEZ-MAROTO, J.M., VILLEN-GUZMAN, M., 2024. *Extraction and Selective Precipitation of Metal Ions from LiCoO2 Cathodes Using Citric Acid*. Journal of Power Sources, 592, 233870.

CHAUDHARY, V., LAKHERA, P., KIM, K.H., DEEP, A., KUMAR, P., 2023. *Insights into the Eco-Friendly Recovery Process for Valuable Metals from Waste Lithium-ion Batteries by Organic Acids Leaching*. Separation and Purification Reviews, 53, 82–99.

CHARZEWSKA, K., ADAMEK, J., KATEUSZ, F., PIĄTEK, J., ZAJĄC, W., 2026. *Levulinic acid as a sustainable and selective leaching agent for hydrometallurgical recycling of commercial Li-ion batteries: Towards greener critical metal recovery*. Separation and Purification Technology, 380, 135196.

CHEN, X., GUO, C., MA, H., LI, J., ZHOU, T., CAO, L., KANG, D., 2018. *Organic reductants based leaching: A sustainable process for the recovery of valuable metals from spent lithium ion batteries*. Waste Management, 75, 459–468.

CHEN, X., KANG, D., CAO, L., LI, J., ZHOU, T., MA, H., 2019. *Separation and recovery of valuable metals from spent lithium ion batteries: Simultaneous recovery of Li and Co in a single step*. Separation and Purification Technology, 210, 690–697.

CHEN, X., MA, H., LUO, C., ZHOU, T., 2017. *Recovery of valuable metals from waste cathode materials of spent lithium-ion batteries using mild phosphoric acid*. Journal of Hazardous Materials, 326, 77–86.

CHERNYAEV, A., PARTINEN, J., KLEMETTINEN, L., WILSON, B.P., JOKILAAKSO, A., LUNDSTRÖM, M., 2021. *The efficiency of scrap Cu and Al current collector materials as reductants in LIB waste leaching*. Hydrometallurgy, 203, 105608.

DADÉ, M., WALLMACH, T., LAUGIER, O., 2022. *Detailed Microparticle Analyses Providing Process Relevant Chemical and Microtextural Insights into the Black Mass*. Minerals, 12(2), 119.

DOMINGUES, A.M., DE SOUZA, R.G., 2024. *Review of life cycle assessment on lithium-ion batteries (LIBs) recycling*. Next Sustainability, 3, 100032.

ELEMENTAL STRATEGIC METALS. https://elementalsm.pl, Accessed on 22 April 2026.

ELEMENTS, 2024. *Visualizing the Supply Deficit of Battery Minerals (2024–2034P)*. Accessed on 22 April 2026. https://elements.visualcapitalist.com/wp-content/uploads/2024/12/Benchmark-8_Mineral-Deficits_2034_Site-1-Elements.jpg

ENERIS, *Żarki – Eneris B&R: Zakład recyklingu baterii litowo-jonowych*. https://eneris.pl/zarki-br, Accessed on 22 April 2026.

GAO, W., LIU, C., CAO, H., ZHENG, X., LIN, X., WANG, H., ZHANG, Y., SUN, Z., 2018. *Comprehensive evaluation on effective leaching of critical metals from spent lithium-ion batteries*. Waste Management, 75, s. 477–485.

GEBEYEHU, K.B., CHEN, L., FAN, L., CHAO, Y., ZHU, W., 2025. *Recovery of high-value metals from the cathode of spent lithium-ion batteries via acid leaching: A review*. Journal of Environmental Chemical Engineering, 13, 116174.

GOLMOHAMMADZADEH, R., RASHCHI, F., VAHIDI, E., 2017. *Recovery of lithium and cobalt from spent lithium-ion batteries using organic acids: Process optimization and kinetic aspects*. Waste Management, 64, 244–254.

GUO, R., WANG, F., AKBAR RHAMDHANI, M., XU, Y., SHEN, W., 2024. *Managing the surge: A comprehensive review of the entire disposal framework for retired lithium-ion batteries from electric vehicles*. Journal of Energy Chemistry, 92, 648–680.

HAIDER, S.A., 2023. *The Ethical Dilemma of Green Economy: Examining the Human and Environmental Costs of Cobalt Mining in DRC*. Global Journal of Human-Social Science: B Geography, 23(2), 31–37.

JENIS, P., ZHANG, T., RAMASUBRAMANIAN, B., LIN, S., RAYAVARAPU, P.R., YU, J., RAMAKRISHNA, S., 2024. *Recent progress and hurdles in cathode recycling for Li-ion batteries*. Circular Economy, 3(2), 100087.

JIANG, S.-Q., LI, X.-G., ZHOU, W.-T., DENG, C.-Z., ZHU, X.-N., 2024. *Enhanced green leaching of spent lithium-ion batteries: Pyrolysis pretreatment combined with eco-friendly citric acid and ascorbic acid*. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 687, 133492.

LEE, C., ARBY, D.S., KIM, C., LIM, J., KWON, K., CHUNG, E., 2025. *Hydrometallurgical process of spent lithium-ion battery recycling. Part 1: Chemical leaching of valuable metals from cathode active materials: Review and case study*. Hydrometallurgy, 235, 106494.

LI, L., ZHANG, X., LI, M., CHEN, R., WU, F., AMINE, K., LU, J., 2018. *The Recycling of Spent Lithium-Ion Batteries: A Review of Current Processes and Technologies*. Electrochemical Energy Reviews, 1(4), 461–482.

LIM, J., JANG, Y., LEE, J., LEE, C., JBARI, O., KWON, K.E., 2025. *Hydrometallurgical process of spent lithium-ion battery recycling. Part 2: Recovery of valuable metals from the cathode active material leachates: Review and cost analysis*. Hydrometallurgy, 236, 106516.

MARCHESE, D., GIOSUÈ, C., STAFFOLANI, A., CONTI, M., ORCIONI, S., SOAVI, F., CAVALLETTI, M., STIPA, P., 2024. *An Overview of the Sustainable Recycling Processes Used for Lithium-Ion Batteries*. Batteries, 10(1), 27.

MENG, Q., ZHANG, Y., DONG, P., 2017. *Use of glucose as reductant to recover Co from spent lithium ions batteries*. Waste Management, 64, 214–218.

MOHANTY, A., DEVI, N., 2021. *A review on green method of extraction and recovery of energy critical element cobalt from spent lithium-ion batteries (LIBs)*. Mineral Processing and Extractive Metallurgy Review, 44, 52–63.

NAYAKA, G.P., ZHANG, Y., DONG, P., WANG, D., PAI, K.V., MANJANNA, J., SANTHOSH, G., DUAN, J., ZHOU, Z., XIAO, J., 2018. *Effective and environmentally friendly recycling process designed for LiCoO2 cathode powders of spent Li-ion batteries using mixture of mild organic acids*. Waste Management, 78, 21–57.

PINNA, E.G., RUIZ, M.C., OJEDA, M.W., RODRIGUEZ, M.H., 2017. *Cathodes of spent Li-ion batteries: Dissolution with phosphoric acid and recovery of lithium and cobalt from leach liquors*. Hydrometallurgy, 167, s. 66–71.

PRAŽANOVÁ, A., PLACHÝ, Z., KOČÍ, J., FRIDRICH, M., KNAP, V., 2024. *Direct Recycling Technology for Spent Lithium-Ion Batteries: Limitations of Current Implementation*. Batteries, 10(3).

QADIR, M.R., BRUCKARD, W.J., CHEN, M., 2024. *Leaching of Lithium-ion Battery Waste at Room Temperature using Controlled Reductant Addition*. SSRN.

REGULATION (EU) 2024/1252 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL, 2024. *Establishing a framework for ensuring a secure and sustainable supply of critical raw materials*. Official Journal of the European Union, L 2024/1252.

SOBIANOWSKA-TUREK, A., ŁOŚ, P., FORNALCZYK, A., ZYGMUNT, M., 2023. *Potential market value of electrolyte condensate recovered from LIBs mechanical treatment*. Gaz, Woda i Technika Sanitarna, 6, 21–22.

SOBIANOWSKA-TUREK, A., URBAŃSKA, W., 2019. *Future portable li-ion cells' recycling challenges in Poland*. Batteries, 5(4).

SOBIANOWSKA-TUREK, A., ZYGMUNT, M., FORNALCZYK, A., QIMING, T., 2025a. *Crystallization of Li2SO4·H2O salt from an aqueous solution obtained by solvent extraction of lithium ions using the new extractant Mextral 3938HDC*. Physicochemical Problems of Mineral Processing, 61(4).

SOBIANOWSKA-TUREK, A., ZIELIŃSKA, A., URBAŃSKA, W., MIELNICZEK, A., FORNALCZYK, A., PAWLAK, S., MAŁYSA, T., CEBULSKI, J., 2025b. *Optimizing Acidic Reductive Leaching for Lithium Recovery: Enhancing Sustainable Lithium Supply for Energy Markets*. Energies, 18(2), 398.

SOLEIMANI, A., KARIMI, G., PAYDAR, M.H., 2025. *A comprehensive study on reutilizing recovered Li2CO3 in the direct recycling of lithium-ion batteries*. Next Energy, 8.

SUN, L., QIU, K., 2011. *Vacuum pyrolysis and hydrometallurgical process for the recovery of valuable metals from spent lithium-ion batteries*. Journal of Hazardous Materials, 194, 378–384.

VIECELI, N., BENJAMASUTIN, P., PROMPHAN, R., HELLSTRÖM, P., PAULSSON, M., PETRANIKOVA, M., 2023. *Recycling of Lithium-Ion Batteries: Effect of Hydrogen Peroxide and Dosing Method on the Leaching of LCO, NMC Oxides, and Industrial Black Mass*. ACS Sustainable Chemistry & Engineering, 11, s. 9662–9673.

VINAYAK, A.K., MAJID, M., XIA, L., WANG, X., 2025. *Critical Review of Acid Leaching for Recovery of Valuable Metals from Spent Lithium-Ion Batteries*. Electrochemical Energy Reviews, 8, 25.

WILLNER, J., FORNALCZYK, A., GAJDA, B., FIGLUS, T., ŚWIEBODA, A., WĘGRZYŃSKI, D., MŁONKA, A., PERENC, B., KANDER, M., 2024. *Direct Sonochemical Leaching of Li, Co, Ni, and Mn from Mixed Li-Ion Batteries with Organic Acids*. Energies, 17(16).

ZHANG, Y., WANG, Y., HAN, Z., JIN, M., LI, X., LI, Y., KONG, X., ZHANG, Z., ZHANG, X., 2025. *Kinetic Optimization in Green Metal Recovery: Citric Acid vs Glycine for Sustainable Li-ion Battery Recycling*. Ecotoxicology and Environmental Safety, 302, 118746.

ZHENG, X., GAO, W., ZHANG, X., HE, M., LIN, X., CAO, H., ZHANG, Y., SUN, Z., 2017. *Spent lithium-ion battery recycling – Reductive ammonia leaching of metals from cathode scrap by sodium sulphite*. Waste Management, 60, 680–688.

ZHOU, B., SU, H., LIU, W., ZHU, Z., WANG, L., QI, T., 2025. *Solvent extraction of metal ions from the leaching solutions of waste lithium-ion battery materials: A review*. Separation and Purification Technology, 354, 129173.