



Comparative environmental and economic assessment of emerging hydrometallurgical recycling technologies for Li-ion battery cathodes

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ABSTRACT

The growing demand for electric vehicles has led to a growing concern for battery recycling, particularly for critical raw materials. However, there is insufficient investigation into the environmental and economic impacts of hydrometallurgical recycling methods. In this study we explored emerging hydrometallurgical technologies in economic and environmental perspective to establish conceptual routes to recover Co, Ni and Mn oxides from waste $\text{LiNi}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2$ cathode materials from spent Li-ion batteries. After, life cycle assessment and costing techniques were utilized to compare the environmental and economical performances of each conceptual route. Recovery efficiency of metal oxides through each route was also considered as a key factor. Results suggested that deep eutectic solvent-based leaching produces the highest impact under many impact categories while electrolysis-based leaching showed the least. Under purification technologies assessed, ion-exchange based purification showed significantly lower impact under many categories except stratospheric ozone depletion. Solvent based purification has been identified as the worst technology for purification. Hydroxide based calcination has been identified as the most environmentally sustainable calcination method compared to oxalate calcination. The route consists with inorganic leaching, ion-exchange based purification and hydroxide calcination showed the lowest environmental impact (emission effect at 33.8 kg CO_2 eq), with lower economic impact (\$ 119) and the highest recovery efficiency (78 %) per 1 kg of cathode active materials. However, using electrolysis-based leaching can slightly increase the impacts with lower recovery efficiency (75 %) and better economic performance (\$104/kg of cathode active materials). Terrestrial ecotoxicity was identified to be the most affected impact category for the recovery processes. It is recommended that technologies like deep eutectic solvent-based leaching, solvent extraction and environmentally sustainable technologies like supercritical fluid extraction need further studies prior to industrial applications.

1. Introduction

The development of electric vehicles (EVs) aims to reduce CO_2 emissions and fossil fuel consumption in the transport sector, primarily using lithium-ion batteries. The transition to a wireless era is causing a surge in battery demand across sectors, with projections showing a surge in Li-ion battery (LiB) power requirements from 700 GWh in 2022 to 4.7 TWh in 2030 (IEA, 2023). Policy adaptations, such as incentives and reduced battery prices, and countries planning to impose restrictions on

fossil fuel-governed vehicles also influence this trend (IEA, 2023). For instance, China aims to sell 20 % of zero-emission vehicles by 2025, while the European Union has implemented measures to reduce transportation carbon footprint, leading to increased EV usage. California's policies, for instance, have decreased state-wise CO_2 emissions in many US states, influencing worldwide demand for LiBs and increasing battery waste over time (Akasapu and Hehenberger, 2023).

Currently, 57 % of total worldwide LiB production is carried out by Asia-Pacific regions. Moreover, more than half of this production is

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coming from China. America and Europe are only responsible for approximately 22 % and 21 % of production as Statista reports (Statista Research Department, 2024). In addition, this distribution will last until 2030, and total manufacturing capacities will be increased from 1.57 TWh (in 2022) to 6.79 TWh (in 2030) (Statista Research Department, 2023). This increase in the production facilities is expected to boost the demand for raw materials. For instance, the demand for Cobalt, Nickel, graphite and Lithium is expected to increase by 256 %, 1237 %, 530 % and 575 % respectively. In the case of mining of these materials, around 76 % of total Co mining is carried out by DR Congo followed by Indonesia (8 %). Graphite is largely mined by China which is responsible for the production of 77 % of the world requirement, being Madagascar and Mozambique the second largest suppliers at 6 % production each. Nickel is mainly mined by Indonesia which produce around 50 % of world Ni consumption (Jaganmohan, 2024). Since most of these countries follow less stringent environmental laws for mining, increasing demand can produce an enormous quantity of emissions in future. Perhaps, moving towards urban mining of spent batteries can lower this pressure exerted on mining industry, lowering the overall emissions. Moreover, it is a solution for the handling of high battery waste generation expected.

However, implementing new laboratory-identified technologies on a pilot or industrial scale presents challenges owing to uncertainties in recycling methods. Prior knowledge of the tested technologies from environmental and economic perspectives is advantageous. Decision-making of the core of the recycling process is crucial as it determines the quality of the material recovered and can also lower the overall environmental and economic pressure significantly. However, studies undertaken specifically to address this issue are not to be found.

To overcome this research gap, the current study employed a novel approach by simulating and arranging different emerging hydrometallurgical treatment steps into alternative conceptual treatment sequences that had already been tested at laboratory or pilot scales. The study aimed to evaluate the environmental and economic performance of trending and emerging technologies used to recycle $\text{LiNi}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2$ -cathode (NMC 111) material from waste LiBs through these simulations. The technologies were assessed based on recent applications at the laboratory/pilot level that showed promising recovery levels suitable for industrial application.

Life Cycle Assessment (LCA) and Life Cycle Costing (LCC) were used to assess the environmental and economic performance focusing exclusively on the hydrometallurgical treatment for extracting the critical raw materials (CRM) present in the cathode. The study also examined and compared various hydrometallurgical steps, such as leaching, purification/separation, and calcination, which extract Co-, Mn-, and Ni-based oxides from cathode active materials. Although Li was not considered for extraction as an oxide, it was accumulating in the solution for later production. The refining of metals in each study focused on Co, Ni, and Mn, and material flow was determined with an emphasis on these three metals.

The study also included recent inorganic acid (H_2SO_4)-based leaching experiments performed at the laboratory level for comparison. A novel aspect of this leaching method involved reducing the amount of oxidant (H_2O_2) used. It is from the knowledge of the authors that H_2O_2 is not mandatory for the recycling (de Castro et al., 2024; Martins et al., 2023) but it was considered based on literature of the novel technologies evaluated.

The study focuses on the target audience of battery manufacturers, recyclers, researchers, and policymakers to enhance their future recycling routes and amendments to existing routes.

2. Literature review

Since the introduction of more efficient Ni-Mn-Co (NMC)-type cathodic LiBs in 2010, LCO (LiCoO_2 cathode) production has led to a decrease (Vieceli et al., 2023). Though the new cathode material has

lower fraction of Cobalt than LCO cathode types the overall material contribution for NMC type cathodes are higher (Kallitsis et al., 2024). However, currently the highest market share (79 % of total LiB battery market) is occupied by NMC type LiBs due to their high performance. It is expected that after 10 more years the market share of NMC type cathode would be 100 % (Mathilde Carlier, 2023). This suggests that future LiB waste generation would highly contain NMC type cathode active materials as researchers should be more focused on recycling of NMC type cathode active materials. Nevertheless, among the NMC type cathodes the NMC-111 battery type had the highest material contribution than the rest and it is the first introduced NMC type cathode material (Kallitsis et al., 2024). Hence, much attention should be given to recycling of NMC 111-type batteries. Moreover, given the similar chemistries in all NMC type cathodes, researchers on NMC 111 cathode materials can be easily applied on other NMC type cathodes as well.

He et al. (2024) conducted a comparative review of new hydrometallurgical and direct LiB recycling methods, discussing advancements and future commercialization pathways. However, numerical comparison is unavailable, hindering the adaptation of the best technologies for future applications (B. He et al., 2024). Kallitsis et al. (2022) discuss the environmental impact of different recycling routes in another LCA study for NMC-type LiB recycling. This study focused on the total battery life cycle and compared hydrometallurgical and pyrometallurgical treatment options. The experiment concluded that hydrometallurgy has less environmental impact than alternative methods (Kallitsis et al., 2022). Therefore, hydrometallurgical recycling is gaining popularity owing to the efficient recovery of high-purity metals while reducing gas emissions and energy consumption. However, there is a lack of environmental and economic evaluation and comparison of the various hydrometallurgical recycling methods, leading to a lack of definitive determination of the most efficient approach (Ambaye et al., 2020).

LCA and LCC are practical tools that can compare technologies from environmental and economic perspectives. Castro et al. (2022) employed these methods to assess the potential enhancement of the entire treatment route developed. However, the higher impacts generated by the pretreatment steps used in the study hindered the impacts embedded in the hydrometallurgical steps. Fahimi et al. (2022) and Wu et al. (2022) have also conducted a study and compared the performance of various treatment routes used in treating LCO-type batteries. They performed a comparative analysis using the ESCAPE (embodied energy and carbon footprint) approaches for the total treatment processes, which impedes the identification of more effective leaching or purification methods (Fahimi et al., 2022). This is mainly because pretreatment is typically responsible for most emissions and energy utilization (Castro et al., 2022). Wu et al. (2022) discussed and compared various hydrometallurgical and purification methods using an LCA based approach. However, as the study focused on LCO-type batteries, the applicability of these technologies in NMC-type batteries is problematic (Wu et al., 2022).

Rinne et al. (2021) carried out a study to evaluate the possibilities of synergistic recovery of cathode metals from NMC-LiBs and nickel metal hydride (NiMH) batteries. However, the study discusses only one hydrometallurgical route with and without using NiMH battery materials and suggests that synergistic recycling is environmentally beneficial. Nevertheless, the study fails to compare other viable hydrometallurgical options that can be utilized to enhance the benefits. Moreover, economic evaluation is not done (Rinne et al., 2021). The study carried out by Du et al. (2022) compares the use of virgin and recycled NMC cathode metals to produce power batteries in China through LCA approach. The study reveals that using recycled NMC lowers the environmental impacts than using virgin materials. However, this study also used only one hydrometallurgical route hindering the possibility of comparing various technologies applicable for the same (Du et al., 2022). Finally, Zhou et al. (2021) elaborated comparative LCA of LiB recycling methods through merging different treatment segments such as pretreatment,

pyrometallurgy, hydrometallurgy etc. Consideration of different cathode chemistries of LiBs and focusing on the total recycling line in the study hinders the importance of the hydrometallurgical refining part. This is mainly due to the higher environmental impact given by the pretreatment or pyrometallurgy method utilized. Other than that, hydrometallurgical material consumption varies largely on the cathode chemistries and using of a single hydrometallurgy route for various cathode materials can provide misleading information (Zhou et al., 2021).

3. Methodology

3.1. Technology identification

This investigation utilized the Scopus database to identify NMC cathode recycling technologies based on laboratory studies published between 2015 and 2024. The keywords “cathode”, “NMC”, “recycling”, “black mass”, “hydrometallurgy”, and “metal extraction” were employed with the Boolean operator “or” between terms. Articles were subsequently ranked based on their citation frequency. Initially, 250 articles were considered for the preliminary assessment, and manual filtering was conducted based on novelty and data availability. Ultimately, nine distinct emerging technologies were identified from 20 articles. Further surveys were conducted to identify studies that converted the end products to Ni, Co and Mn oxides while Li being left in the final solution. References older than 2015 were used only if more details were required to confirm the corresponding technology. Pretreatment steps were not considered in this study, as they are well-established technologies (Premathilake et al., 2023). The identified technologies are briefly summarized in Section 4.1 to provide a prior idea of the technology assessed in the next stage (Section 4.2). Among the identified technologies, three different purification technologies were incorporated for the analysis. Namely, oxalic acid-based purification, adsorbent (ion-exchange resin) based purification and solvent extraction-based purification. In order to provide a broader clarity, the flow diagrams for each purification technology were given under Supplementary materials (SI) 1, Figs. S1, S2 and S3.

3.2. Life cycle assessment: goal and scope definition

The goal of the LCA study is to provide an extensive comparison between the emerging technologies used and those identified in Section 3.1. The technologies used in this study are all on laboratory scales with potential usage at industrial level. The possibility of using the technology on a larger scale was determined through the assessment of future recommendations of the studies referred. Recovery efficiencies, simplicity in adapting the technology, scalability and cost of materials were also considered to determine the applicability of the technology at the industrial level. As the technologies used in the study have a higher potential to be used soon, a critical analysis of their pros and cons is compulsory. Hence, the LCA and LCC based approach, and hotspot and scenario analyses were used as tools for this investigation. The LCA study will be an attributional ex-ante analysis to predict industrial level material requirement and emissions.

A treatment/extraction sequence based on NMC 111 type cathode material was used for LCA/LCC analysis to keep the consistency. Adjustments were made where necessary with assumptions to calculate the raw material requirements and products. The study was conducted according to ISO 14040 and 14,044 standards. Sima Pro 9.5.0.1 software and Eco-invent 3.91 V database were used to develop the model to evaluate the impacts of each theoretical route. All calculations were performed using the ReCIPE 2016 v1.1 midpoint (H) calculation method.

In the current study all the 18 impact categories: Global warming, Ozone formation (Terrestrial ecosystems), Terrestrial acidification, Freshwater eutrophication, Terrestrial ecotoxicity, Mineral resource

scarcity, Fossil resource scarcity, Water consumption, Land use, Human non-carcinogenic toxicity, Human carcinogenic toxicity, Marine ecotoxicity, Freshwater ecotoxicity, Marine eutrophication, Fine particulate matter formation, Ozone formation (Human health), Ionizing radiation, Stratospheric ozone depletion were used. Special attention was given to global warming potential impact category as it will be used for the benchmark analysis and for comparison with literature values as it represents the process emission effect. Nevertheless, freshwater eutrophication, marine eutrophication and stratospheric ozone depletion impact categories were not shown in results tables as these categories mostly showed damages $<10^{-3}$ in corresponding units. However, they were shown in the damage assessment graphs in percentages for better clarity.

3.2.1. Functional unit

The functional unit of the study was selected as the treatment of 1 kg of NMC 111 cathode active material (where the oxide amounts of Co \approx 0.33 kg, Ni \approx 0.33 kg, and Mn \approx 0.33 kg is assumed based on the formula of the cathode material $\text{LiNi}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2$). The recovery of Co_3O_4 , NiO, and MnO throughout the treatment process was considered as the final product. The total Li available in the cathode is assumed to be passed through each step and accumulate in the final solution where further refining can be done, and it was not used for mass balance calculations mainly due to the lack of focus on Li in most of the studies utilized and inconsistencies of the final form of Li. We identified each treatment route's emissions, recycling efficiencies, and outputs based on 1 kg of cathode active material input. In addition, 1 kg of NMC 111 input makes it easy to compare different routes and treatment segments.

3.2.2. System boundary

This study focuses solely on the specific hydrometallurgical treatment steps for the cathode materials of EoL LiBs. Therefore, we disregarded the steps such as production, transportation, and use that do not affect the treatment/recovery of materials (Fig. 1). For the LCA study, leaching, purification, and calcination (treatment for active materials) were only investigated since the study is focusing on the recovery of CRM from used LiBs cathodes. Also, unaffected treatment segments such as LiB collection of spent batteries, pretreatment, and final use of recovered materials were not considered, as they could be considered same for all the routes (Castro et al., 2022).

3.2.3. Life cycle assessment: inventory and modelling

Inventories for four different leaching mechanisms (Deep eutectic solvent (DES) based leaching, Inorganic acid based leaching, Supercritical fluid (SCF) based leaching and Electrowinning (EC) based leaching), three different purification/separation mechanisms (Ion exchanged (IE) based separation, Solvent extraction (SE) based purification, Oxalate based (OP) precipitate separation), and two different calcination mechanisms (Hydroxide based calcination (HC), Oxalate based calcination (OC)) were extracted from the secondary sources. At least two or more studies were used for each technology to calculate the chemical consumption, energy requirements, and emissions. Whenever no more than one study was found for a particular technology, other studies on NMC (811, 622, etc.) or LCO cathodes-based studies were utilized with necessary approximations. Stoichiometric calculations were performed to identify the products produced in each treatment step. However, the product quantity identified from stoichiometry was multiplied by the recovery efficiency at each step according to the literature. The ratio between the input and output metal oxides was used to calculate the efficiency of each treatment sequence. Since all the technologies evaluated were at the laboratory level, inventory analysis was performed for ~ 1 g of NMC 111 cathode active material treatment. LCA analysis was done for the 1 kg (default) NMC 111 treatments.

Chemical and energy usage and emissions identified were modelled in Sima Pro 9.5.0.1 using the Eco-invent 3.91 V database (allocation cut-off, unit). The global average (GLO) eco-invent processes were selected

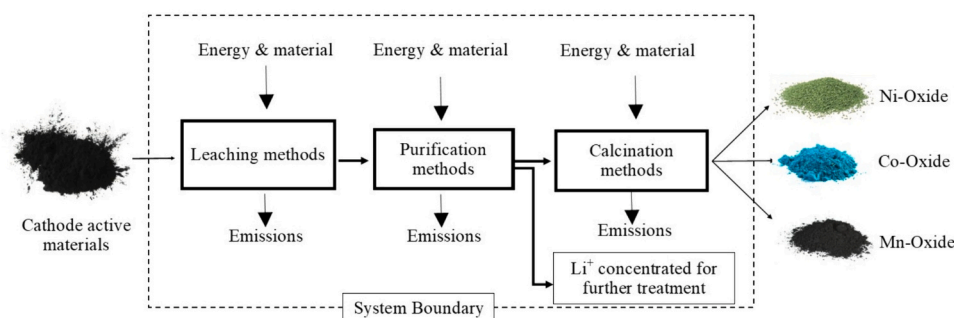


Fig. 1. Depiction of the system boundary based on one treatment sequence.

for modelling. Whenever GLO processes were unavailable in the database, rest-of-world (RoW) processes were chosen for standardization. The unavailable process in the Eco-invent database was modelled separately using literature values. For example, DES chemicals (oxalic acid and choline chloride) were not found in the database; hence, they were modelled using the process described by Zaib & Vahibi and Zhao and collaborators (Vahidi and Zhao, 2017; Zaib et al., 2022). The process for oxalic acid production was not available in the Eco-invent database; instead, acetic acid production was used because both acids have similar production procedure as depicted by Vahidi and Zhao (2017).

The energy consumption for each step was determined by assuming an average power consumption of the laboratory instruments for the corresponding steps. The total capacity of the instrument was used for pre-heating, and a 30 % working potential was used for the rest of the working period. The average instrumental power consumption is shown in the complete inventory analysis under the Supplementary materials. However, for EC-based leaching, the energy requirement was calculated using data from the corresponding articles (Diaz et al., 2020; Strauss et al., 2021). Consequently, Eq. (1) was utilized to calculate the electricity consumption of the process.

$$P = IV \quad (1)$$

where, P; power, I; current used and V; voltage applied. The energy consumptions were identified first for the total NMC 111 active materials utilized in the study. Later, the energy consumption for 1 g of the NMC 111 cathode material was calculated by dividing the total energy consumption by the amount of cathode materials treated. Nevertheless, under result and discussion section (Section 4) energy consumptions were given as the Simapro-network diagram calculates for the treatment of 1 kg of cathode active materials. In addition, for materials that can be used more than once, such as resins, their shelf life was used according to their data sheets to calculate the amount required for the treatment of 1 g of NMC 111. However, 20 usage cycles (standard scenario-without improvements) were assumed for the electrodes used in the EC leaching study as per the lack of data.

Finally, in addition to the eco-invent and modelled processes, dummy variables were used to link the technologies to arrange the treatment sequences. With nine technologies identified, seven treatment sequences that could be utilized to treat NMC 111 cathode active materials were elaborated.

3.2.4. Technology comparison

Each technology under different treatment steps were discussed as per the output given by the LCA studies. Accordingly, comparison of the impacts of leaching technologies, purification steps and calcination possibilities were done based on the chemical usage, energy requirements, and emissions for treating 1 kg of NMC 111 cathode active materials. Moreover, through the analysis, hotspots were identified for each technology where high impacts are generated.

3.2.5. Standard scenario comparison

The treatment sequences were simulated using technologies identified for each treatment segment, such as leaching, purification, and calcination. Only the possible sequences were considered (further elaborated under Section 4.3). For example, the leaching solutions resulting from DES-based leaching contain oxalates; hence, using adsorbent materials or organic extractants is incompatible (Chang et al., 2022). Therefore, purification based on precipitation (oxalates) was used for DES-based leaching followed by calcination. Moreover, the ion exchange resin-based purification or solvent extraction-based purification might be not compatible when oxalate anions are present in the leaching solution as it may produce flocs of precipitates and can block or reduce dissolving. Hence, these two technologies were not connected after the DES based leaching, instead oxalate-based precipitation and oxalate-based calcination was used. The identified treatment sequences are provided in the Results and Discussion section (Section 4.3). The impact of each treatment sequence was analyzed based on the recovery efficiency of critical metals. Thus, the best treatment sequences for recovery efficiency and low environmental impact can be distinguished according to the standard scenario. The LCA inventory utilized for the standard scenario analysis is given under SI 2, Section 1 along with methods, assumptions, process and data sources. A sensitivity analysis using a Monte Carlo simulation with 1000 runs was also conducted to understand the uncertainty of the impact assessment. Result of the sensitivity analysis carried out for standard scenario is provided in SI 1, Fig. S4.

3.2.6. Improved scenario comparison

Improved scenarios for each treatment sequence (route) were established by improving the standard scenarios. For improvement, the factors identified during hotspot analysis were incorporated. Accordingly, an improved energy mix and low-voltage electricity generation by photovoltaic panels (Switzerland Energy Mix for Low Voltage) was used. The recycling rates were increased from 50 % to 80 % under improved scenarios for the organic acids/solvents used (e.g., DES, D2EHPA, or Cyanex 272), as suggested in the literature (Vahidi and Zhao, 2017; Zaib et al., 2022). In SCF-based leaching, the CO₂ recycling rate was assumed to be 80 % in the improved version to prevent underestimation, although the literature shows that 100 % recycling is possible in industrial lines (Kelly Leitch et al., 2005). Furthermore, the electrodes used in EC-based leaching were assumed to be used 50 times instead of 20 times. The organic solvents (DMSO) used in the DES-based leaching were reduced by 30 %, assuming higher recycling at industry level (Chang et al., 2022).

Moreover, according to the findings of Guimarães et al. (2022), the reducing agent usage was reduced by 50 % for conventional inorganic acid leaching, although the authors mentioned leaching without reducing agents (de Castro et al., 2024; Guimarães et al., 2022). The adsorbent materials (ion-exchange resin) used in adsorbent-based purification are determined to have a shelf life of 10 years instead of the 8 years used in the standard scenario (Dow chemical company, n.d.). The

hazardous waste resulting from each purification step was reduced by 10 %, assuming an industrial-level treatment (Castro et al., 2022). SI 2, Section 2 presents the complete LCA inventory of the improved scenario. The life-cycle impact of each treatment sequence was assessed with these improvements to approximate the industrial-level impact assessment. A sensitivity analysis is conducted to understand the uncertainties involved in the improved scenarios. Fig. S5 in the SI 1 provides the result obtained for the sensitivity analysis for improved scenario.

3.3. Life cycle costing study

As Villares et al. (2017) reported, material and energy efficiencies in industrial scale is significantly higher than laboratory scale estimations. Hence, Economic analyses were performed using the material consumption at improved scenario of the LCA study (Villares et al., 2017). Using the improved scenario, it is reasonable to assume industrial-scale consumption.

The chemical consumption and waste generation for each route were calculated using the “process contribution” using the Sima-Pro software. The Ali-Baba trading, chem world and Intratec websites were consulted regarding the industrial level chemical prices (Alibaba trading, 2024; ChemWorld trading, 2024; Intratec, 2024). World average electricity prices were taken from “Thunder said energy” research website (Thunder Said Energy, 2024). Further, the costs for hazardous waste incineration and treatment of used ion exchange resin were taken from the “Boulder County” website (Boulder County, 2024). The disposal costs for scrap metals were taken from Castro et al. (2022). The complete inventory set for the LCC analysis is given under each route in SI 2, Section S3. In the Supplementary materials it was given maximum and minimum values of the prices of various raw materials required for the specific treatment routes. Since the cost of materials is hidden trading information, receiving multiple values to work out the standard deviations was not possible. Hence, the highest and lowest prices given by websites had to be used for the calculation of standard deviations and variance. The following equation was utilized for the standard deviation under the assumption of uniform distribution of prices (Coskun and Oosterhuis, 2020).

$$\text{Standard deviation} = \frac{(\text{Maximum price} - \text{Minimum price})}{\sqrt{12}} \quad (2)$$

Additionally, when the valuable spent products were received during the process, those were indicated with a negative price to show a potential income during the economic evaluation. As the literature proposed, this step was conducted only for organic products (DES solution and spent solvent mixtures) that could be recycled.

4. Results and discussion

4.1. Technology analysis

Three emerging technologies were identified through recent secondary sources with promising scale-up potential. Moreover, inorganic acid-based leaching was also considered as an emerging technology as per the recent advancement achieved by many researchers in the field. Sulfuric acid-based leaching is well-reported in literature for LiBs recycling, and advancements can be observed in the reduced usage of hydrogen peroxide as a reducing agent and the reduced usage of acids (de Castro et al., 2024; Guimarães et al., 2022). Different concentrations, leaching times, temperature and solid to liquid ratios are reported depending on various cathode active materials studied.

DES-based leaching is a recent technology that has emerged for cathode material leaching. DES was made from hydrogen bond acceptors, and donors to dissolve the metal oxides available in the cathode (HBA-HBD type). This is because such solutions provide the required properties for leaching, such as low pH range, reducibility, and the ability to coordinate. According to the literature, the use of DES has

environmental benefits, but recyclability is still a challenge (Chang et al., 2022). Once the DES is made, the leaching is carried out like the inorganic acid based leaching mechanisms optimizing temperature, pH level, solid-liquid ratio and leaching time. Most recent studies show longer leaching hours for the DES based leaching as the acidic media is not corrosive as the inorganic acids (Chang et al., 2022; Tran et al., 2019).

Supercritical fluids (SCF) are also used to leach metals from cathode active materials. In this emerging technology, the cathode active material will react with inorganic acid inside a pressurized reactor with the availability of CO₂. CO₂ will be inserted to the pressurized reactor via a high-pressure dosing pump in the liquid form. Due to the pressure and the heat inside the reactor the CO₂ will achieve its supercritical state enhancing the speed of metal leaching. This method is highly effective because of its extremely high solubility and high stability provided by CO₂ and inorganic acid (Bertuol et al., 2016; Calgaro et al., 2015). The method is also seemingly convenient for low energy use due to reduced reaction time and fast kinetics. It is reported that the leaching time can be reduced to 5–30 min using SCF based leaching (Preetam et al., 2023).

Electrochemical (EC)-assisted leaching is an innovative technology recently used to leach NMC cathode active materials. The method is also reported as a green approach because it produces fewer toxic products and has lower energy use, with a comparably higher yield of recovered metals (Diaz et al., 2020). In this method the leaching will be carried out in a dual chamber electrochemical cell which is separated by a bi-polar membrane. For the anode, a foam made of nickel will be used while the cathode will be a stainless-steel electrode. The cathode compartment will contain the cathodic powder along with H₂SO₄ and FeSO₄, while the anode compartment uses KOH. As the current is passing through the cell, the metals will be leached to the solution (Diaz et al., 2020; Strauss et al., 2021).

As the first purification technology, oxalate-based precipitation of metals considered as discussed by Chang et al. (2022). Accordingly, when DES based leaching is used additional oxalic acid addition is not required to obtain the precipitates as the DES already contain oxalates. Hence, this method was only compatible when DES based leaching is done. Once the leachate is received, it will undergo dilution step with addition of dimethyl sulfoxide (DMSO) as the leachate has very low water solubility. After, leachate will be subjected to centrifugation at 10000 rpm for 5 min. This will separate Ni-oxalate dehydrate from the rest of the cations. The supernatant will be then diluted with DI water and heated up to 70 °C for 3 h. Once filtered, the residue will contain Co-oxalate dehydrate while the filtrate will contain Mn metal ions. Then the pH of the filtrate will be adjusted to 12 using NaOH and the solution will be filter for the second time. Here the residue will be Mn-Oxalate dehydrates (Chang et al., 2022; Tang et al., 2022). A flow diagram for the steps is given in Supplementary materials under Fig. S1 in SI 1.

Adsorbent material (ion-exchange resin)-based separation/purification is also an emerging technology that widely used in recent studies and most commercial chelating resins focus on Ni, Co, Mn, and Fe as iminodiacetate (Lewatit TP 207 and Amberlite IRC748), amino-phosphonic acid (Purolite S950, Amberlite IRC-747, and Lewatit TP 260), and bis-picolylamine groups (Dowex M4195 and Lewatit TP 220) (Strauss et al., 2021; Virolainen et al., 2021). The technology is applied once the metal ions are leached into the solution. The solution will be forced into a vessel that contains the target ion exchange resin. The flow rates must be adjusted to increase the efficiency of the metal ion exchangeability. Often, the pH of the carrier solution will be adjusted, and the carrier media will be fine-tuned to give out only the targeted metal ion to maximize efficiency. For instance, low pH carrier solution will give out Ni²⁺ ions to the resin while, addition of ammonium acetate and diluted ammonium hydroxide will make Co²⁺ to be attached to the cation exchange resin. Later, Mn can be separated from the Li using solvent extraction method. Further, the solution might be required to pass through the ion exchange resin multiple times depending on the concentration of metal ions. Once the ion exchange resins are rich with

targeted metal ions, the media will be backwashed with diluted inorganic acids (H_2SO_4) to release the metal ions back into a solution separately. Finally, the pH of the solutions will be increased up to 11 using NaOH to precipitate the metal ions as their hydroxides (Strauss et al., 2021). Supplementary Fig. S2 in SI 1 shows the flow diagram of the precipitation steps.

Organic solvent-based extraction is the third purification method identified. The technology uses the leached solution resulted from the leaching step. Firstly, liquid-liquid extraction can be utilized to extract Co from the leached solution towards Mn by 0.4 M Alamine 336 organic extractant which is combined with kerosene at the organic to aqueous (O/A) ratio of 0.5. The extracted Co may be contaminated with minor amounts of Mn (around 5.4 %). This can be further purified by extracting Co from the Mn using D2EHPA extractant. The resulting Co rich solution can be used to precipitate Co in its hydroxide form at pH around 10 by adding NaOH. The Co depleted solution after the first extractant can be utilized to extract Ni by enriching the organic fraction with 0.7 M Alamine 336 diluted with kerosene at O/A 2. This can effectively extract Ni which can be precipitated with addition of NaOH at pH of 8. This will also result in effluent rich with Li ions that may be extracted using an organic solvent of Cyanex 936. However, for the easiness of the study and for the standardization with other purification technologies, Li-ion is assumed to be left in the solution state. Mn in the organic fraction will be taken to aqueous fraction using inorganic acid (HCl) with 0.1 M concentration which can be then precipitated as Mn (OH)₂ with the addition of NaOH at pH 8 (Omelchuk et al., 2017; Xuan et al., 2022). The extraction steps are represented in the flow diagram given in Supplementary materials (SI 1, Fig. S3).

In addition to the three separation/purification methods, two calcination methods (hydroxide calcination and oxalate calcination) were used to convert the purified product into metal oxides. Accordingly, the precipitated metal hydroxides or metal oxalates will be heated to higher temperatures (~500–800 °C) in a vacuum furnace to eliminate water vapor or gases derived from thermal decompositions of hydroxide or oxalates. As per the studies found in secondary sources, both methods use longer calcination times (~24 h) (N. Zhang et al., 2018; Zhu et al., 2019). These seven technologies, categorized into three main parts, as shown in Table 1, will be evaluated regarding environmental and economic impacts using LCA and LCC studies in the next sections.

4.2. Technology comparison

The technologies identified in Section 3.1 were compared according

Table 1
Summary of technologies used in the study.

Process	Technology	References used
Leaching technologies	Conventional leaching	(Chen and Ho, 2018; Guimarães et al., 2022; Vieceli et al., 2023)
	Deep eutectic solvent-based leaching	(Chang et al., 2022; He et al., 2023; S. Wang et al., 2020)
	Supercritical fluid-based leaching	(Bertuol et al., 2016; Zhang and Azimi, 2022)
	Electrolysis based leaching	(Diaz et al., 2020; Strauss et al., 2021)
Purification/separation technologies	Oxalate based purification	(Chang et al., 2022)
	Absorbent material-based purification	(Strauss et al., 2021; Zhang et al., 2023)
	Organic solvent extractant based purification	(Omelchuk et al., 2017; W.-Y. Wang et al., 2020; Xuan et al., 2022)
Calcination technologies	Oxalate calcination	(Wu et al., 2021; Yang et al., 2014; Yao et al., 2019; Zhu et al., 2019)
	Hydroxide calcination	(Eilers-Rethwisch et al., 2018; Li et al., 2017; Xu et al., 2018; Zhang et al., 2018)

to their usage. For instance, the four identified leaching methods were compared with each other based on their environmental impacts. For comparison, the inputs and outputs required to treat 1 kg of NMC 111 cathode materials were considered. Similarly, the three purification methods and two calcination methods were compared. Through the comparison, hotspots for each treatment step were also identified.

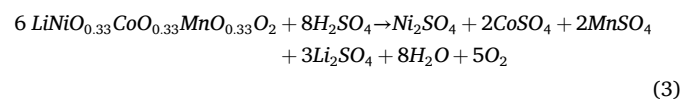
4.2.1. Leaching methods

Table 2 shows the impacts received under significant impact categories for leaching technologies assessed. To compare the different leaching mechanisms studied, “leaching of 1 kg of NMC 111 cathode active material” was chosen as the functional unit. Results show that the highest contribution comes from electricity usage for inorganic and DES based leaching mechanisms. However, SCF and EC have very little impact from energy consumption. Highest environmental degradation had occurred through DES based leaching and the lowest environmental impacts were reported by EC based leaching. The complete list of impacts under all 18 impact categories was given under SI 1, Table S1.

A comparison of the percentage impact of each leaching method under different impact categories is shown in Fig. 2.

DES-based leaching causes more impacts under different impact categories studied, mainly due to electricity use. The total process emission effect (PEE) of DES-based leaching is 2.80×10^2 kg CO₂ eq. per 1 kg of NMC 111 cathode material. The technique requires prolonged leaching hours, forcing the method to use more electricity in stirring and heating. The leaching of 1 kg of NMC 111 cathode active material requires approximately 1.04×10^3 MJ of electricity which caused approximately 78 % of the impact of DES-based leaching. The rest (~22 %) of the impacts were due to DES production. It seems that the use of choline chloride (ChCl) in DES has a great impact due to the high amount of ethylene oxide used in ChCl production. Despite that, most recovery mechanisms studied with DES-based leaching have repeatedly used ChCl as DES’s hydrogen bond donor (HBD) (Chang et al., 2022; X. He et al., 2023; Tran et al., 2019). It has been identified that the leaching of metal oxide strongly depends on the HBD of the DES, and ChCl is a good candidate for this purpose (Binnemans and Jones, 2023). Hence, the substitutability of ChCl with a chemical with less impact is not convenient, and many authors mentioned higher recyclability rates for DES, although we used 50 % recyclability for the LCA analysis. Nevertheless, if very high recycling rates and considerable cut-off of electricity are used in the process, the impacts related may decrease which will be analyzed under the improved scenario (Section 3.2.6).

The conventional leaching (inorganic) mechanism reported the second highest emission at 2.14×10^1 kg CO₂ eq. among the techniques evaluated, considering 1 kg of cathode active material input. 87 % of the reported impacts of conventional leaching by H₂SO₄ are also due to the high energy usage for heating, and the total electricity was 88.2 MJ. Moreover, 10 % of the impact was generated through the production of H₂O₂. However, Guimarães et al. reported that it is possible to carry out the metal leaching process using inorganic acids such as H₂SO₄ without a reducing agent (H₂O₂), which can reduce the impact of the overall leaching process (de Castro et al., 2024; Guimarães et al., 2022). The expected reaction with NMC 111 is given under Eq. (3).



The third highest emission was reported by SCF-based leaching, which amounted to 1.34×10^1 kg CO₂ eq. per 1 kg of the active cathode material. The major part (~64.3 %) of the reported impacts were from the use of NaOH for the treatment of CO₂ derived from the process. Electricity does not play a major role in SCF treatment because of the lower energy requirement for the reduced leaching time (approximately 5 min.) at slightly lower temperatures than those of conventional or DES-based leaching. This is a key energy-saving step in the technology

Table 2
Impacts of leaching technologies under significant impact categories differentiated into contributed materials.

Inorganic leaching									
Impact category	Unit	Total	Sulfuric acid	Hydrogen peroxide	Electricity				
Global warming	kg CO ₂ eq	21.36	0.53	2.22	18.62				
Ionizing radiation	kBq Co-60 eq	2.35	0.03	0.08	2.24				
Ozone formation, Human health	kg NO _x eq	0.05	0.00	0.00	0.04				
Fine particulate matter formation	kg PM2.5 eq	0.05	0.01	0.00	0.04				
Ozone formation, Terrestrial ecosystems	kg NO _x eq	0.05	0.00	0.00	0.04				
Terrestrial acidification	kg SO ₂ eq	0.10	0.02	0.01	0.06				
Terrestrial ecotoxicity	kg 1,4-DCB	53.00	14.01	9.30	29.69				
Freshwater ecotoxicity	kg 1,4-DCB	1.58	0.27	0.16	1.16				
Marine ecotoxicity	kg 1,4-DCB	2.01	0.35	0.20	1.46				
Human carcinogenic toxicity	kg 1,4-DCB	1.08	0.06	0.25	0.77				
Human non-carcinogenic toxicity	kg 1,4-DCB	25.39	5.18	3.04	17.17				
Land use	m ² a crop eq	0.33	0.03	0.03	0.27				
Mineral resource scarcity	kg Cu eq	0.15	0.12	0.01	0.02				
Fossil resource scarcity	kg oil eq	5.63	0.33	0.66	4.64				
Water consumption	m ³	0.32	0.07	0.11	0.14				
Supercritical fluid-based leaching									
Impact category	Unit	Total	Sulfuric acid	Hydrogen peroxide	Carbon dioxide	Sodium hydroxide	Water	Electricity	
Global warming	kg CO ₂ eq	13.42	0.30	0.93	3.53	8.63	0.00	0.03	
Ionizing radiation	kBq Co-60 eq	1.12	0.02	0.03	0.12	0.95	0.00	0.00	
Ozone formation, Human health	kg NO _x eq	0.03	0.00	0.00	0.00	0.02	0.00	0.00	
Fine particulate matter formation	kg PM2.5 eq	0.03	0.00	0.00	0.00	0.02	0.00	0.00	
Ozone formation, Terrestrial ecosystems	kg NO _x eq	0.03	0.00	0.00	0.00	0.02	0.00	0.00	
Terrestrial acidification	kg SO ₂ eq	0.06	0.01	0.00	0.01	0.03	0.00	0.00	
Terrestrial ecotoxicity	kg 1,4-DCB	72.97	7.94	3.90	25.71	35.37	0.00	0.04	
Freshwater ecotoxicity	kg 1,4-DCB	1.04	0.15	0.07	0.22	0.61	0.00	0.00	
Marine ecotoxicity	kg 1,4-DCB	1.35	0.20	0.09	0.28	0.79	0.00	0.00	
Human carcinogenic toxicity	kg 1,4-DCB	0.65	0.03	0.10	0.10	0.41	0.00	0.00	
Human non-carcinogenic toxicity	kg 1,4-DCB	19.39	2.94	1.27	3.48	11.67	0.00	0.02	
Land use	m ² a crop eq	0.28	0.02	0.01	0.05	0.20	0.00	0.00	
Mineral resource scarcity	kg Cu eq	0.12	0.07	0.00	0.01	0.04	0.00	0.00	
Fossil resource scarcity	kg oil eq	3.21	0.19	0.28	0.60	2.14	0.00	0.01	
Water consumption	m ³	0.33	0.04	0.04	0.02	0.22	0.00	0.00	
Deep eutectic solvent-based leaching									
Impact category	Unit	Total	Deep eutectic solvent				Electricity		
Global warming	kg CO ₂ eq	280.27	60.98				219.29		
Ionizing radiation	kBq Co-60 eq	28.76	2.34				26.42		
Ozone formation, Human health	kg NO _x eq	0.60	0.12				0.48		
Fine particulate matter formation	kg PM2.5 eq	0.57	0.09				0.49		
Ozone formation, Terrestrial ecosystems	kg NO _x eq	0.61	0.13				0.48		
Terrestrial acidification	kg SO ₂ eq	0.94	0.18				0.76		
Terrestrial ecotoxicity	kg 1,4-DCB	491.82	142.07				349.74		
Freshwater ecotoxicity	kg 1,4-DCB	15.97	2.36				13.61		
Marine ecotoxicity	kg 1,4-DCB	20.26	3.07				17.18		
Human carcinogenic toxicity	kg 1,4-DCB	10.79	1.69				9.10		
Human non-carcinogenic toxicity	kg 1,4-DCB	246.76	44.51				202.25		
Land use	m ² a crop eq	3.83	0.64				3.19		
Mineral resource scarcity	kg Cu eq	0.37	0.15				0.22		
Fossil resource scarcity	kg oil eq	87.85	33.18				54.67		
Electrolysis based leaching									
Impact category	Unit	Total	Sulfuric acid	Iron sulfate	Electrolyte, KOH	Steel	Nickel	Electricity	Scrap steel
Global warming	kg CO ₂ eq	0.11	0.00	5.43	0.53	0.32	0.00	0.00	0.11
Ionizing radiation	kBq Co-60 eq	0.01	0.00	0.54	0.02	0.02	0.00	0.00	0.01
Ozone formation, Human health	kg NO _x eq	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00
Fine particulate matter formation	kg PM2.5 eq	0.00	0.00	0.01	0.00	0.02	0.00	0.00	0.00
Ozone formation, Terrestrial ecosystems	kg NO _x eq	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00
Terrestrial acidification	kg SO ₂ eq	0.01	0.00	0.02	0.00	0.06	0.00	0.00	0.01
Terrestrial ecotoxicity	kg 1,4-DCB	2.92	0.00	22.90	17.07	14.86	0.00	0.02	2.92
Freshwater ecotoxicity	kg 1,4-DCB	0.06	0.00	0.37	0.04	0.30	0.00	0.32	0.06
Marine ecotoxicity	kg 1,4-DCB	0.07	0.00	0.48	0.06	0.39	0.00	0.39	0.07
Human carcinogenic toxicity	kg 1,4-DCB	0.01	0.00	0.30	0.20	0.05	0.00	0.01	0.01
Human non-carcinogenic toxicity	kg 1,4-DCB	1.08	0.00	7.63	0.79	4.49	0.00	0.27	1.08
Land use	m ² a crop eq	0.01	0.00	0.15	0.02	0.01	0.00	0.00	0.01

(continued on next page)

Table 2 (continued)

Electrolysis based leaching									
Impact category	Unit	Total	Sulfuric acid	Iron sulfate	Electrolyte, KOH	Steel	Nickel	Electricity	Scrap steel
Mineral resource scarcity	kg Cu eq	0.03	0.00	0.37	0.06	0.09	0.00	0.00	0.03
Fossil resource scarcity	kg oil eq	0.07	0.00	1.34	0.12	0.08	0.00	0.00	0.07

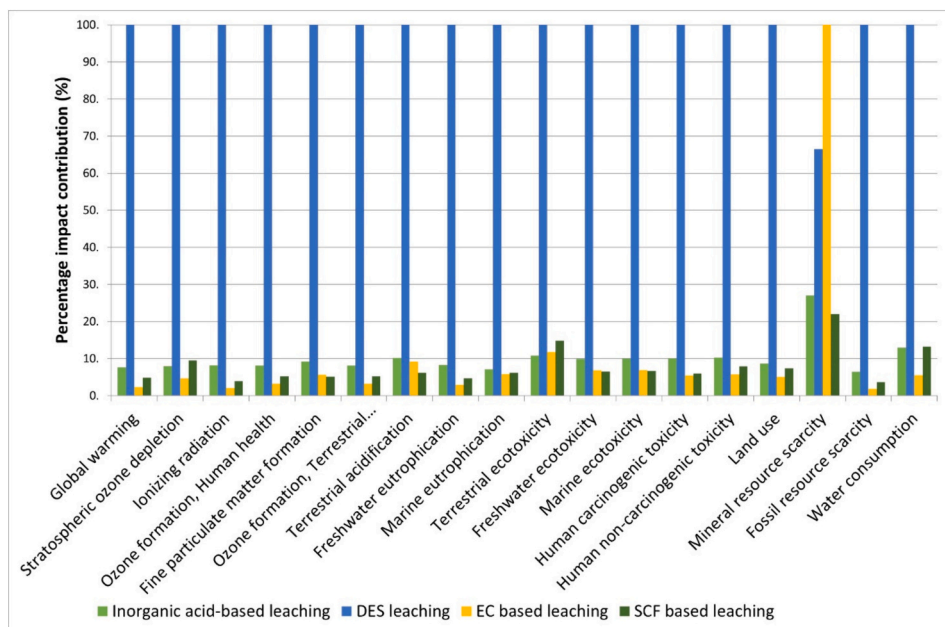


Fig. 2. Percentage impacts of each leaching method under different impact categories (DES = deep eutectic solvent, EC = electrolysis, SCF = supercritical fluid).

considered.

Moreover, 26.3 % of the total impact of the process was due to CO₂ usage. Although it is required to release CO₂ under laboratory conditions after treatment, in industrial supercritical extractions, CO₂ can be recirculated in higher percentages (Kelly Leitch et al., 2005). Hence, these emissions can be drastically lowered in actual SCF-based treatment lines. This can be further analyzed under the improved scenario.

The lowest impact was demonstrated by EC-based leaching at 6.39×10^0 kg CO₂ eq. per 1 kg of cathode materials because of the lowest energy requirement for the electrolysis and the reusability of the electrodes. Impacts due to the energy usage are minimum as the electricity consumption is very low in the technique. So, a major part (~85 %) of the impact is derived from using electrolyte materials for electrolysis. The process uses approximately 2.5 kg of KOH electrolyte to treat 1 kg of the active materials. Approximately 9 % of the impacts were derived from steel usage for the electrodes.

Additionally, EC-based leaching had the highest impact under the mineral resource scarcity impact category because steel and Ni-based minerals used for electrode manufacturing. DES-based leaching is the second highest under the same impact category because of the higher chemical and energy requirements for leaching. For the SCF and Conventional leaching methods, relatively lower amounts of mineral resources were used to prepare inorganic acids (e.g. H₂SO₄).

4.2.2. Purification/separation methods

Three different separation and purification methods were compared based on the environmental impact of each method. Moreover, for standardization, the functional unit of this part was adopted as the “purification/separation of 1 kg of NMC 111 leached metal ions”. Table 3 represents the impacts resulted by various purification methods under significant impact categories. In addition, Table S2 in the SI 1 contains the complete list of impacts of each technology analyzed under

different impact categories.

As per the results, the highest impact contribution is given by solvent extraction-based purification and the lowest is reported by ion-exchange resin-based purification. Unlike in leaching technologies, in purification process the highest contribution is given by the material usages rather than the energy usage. To compare the impact contribution by various mechanisms used for purification, Fig. 3 illustrates the percentage of each technology’s impact across various categories.

The solvent extraction has a high impact across many impact categories, except for stratospheric ozone depletion. The total PEE of the solvent extraction of leached metals is 2.18×10^2 kg CO₂ eq. per 1 kg of leached metal. The main contributor to the impacts generated in this category was the high use of organic solvents. It was observed that approximately 31.4 % of the PEE was due to the use of organic solvents. Increasing the recyclability of organic solvents can reduce this impact. However, it is important to note that, in this analysis, we used a recycling rate of 50 % for organic solvents, which suggests that a recycling rate higher than 50 % is required to lower the impact of organic solvents. Another 10 % impact was attributed to the HCl used in the aqueous part when extracting metals from the organic fraction. The waste and by-products produced in the process also contribute to PEE significantly. For instance, hazardous waste from solvent extraction contributes approximately 28.6 % of the overall emissions and 26.4 % of the impact in the PEE caused by the heat used to treat these wastes and by-products. However, increasing the recycling rate can also reduce hazardous waste resulting from this method, thereby enhancing the overall environmental friendliness of the technology. Energy use is not playing a major role in this procedure. In summary, the total sustainability of solvent-based extraction depends heavily on the recycling rate. Using organic solvents for extraction has a greater impact than inorganic solutions. However, under stratospheric ozone depletion, solvent extraction showed the lowest impact compared to the other mechanisms. The main

Table 3
Impacts under significant impact categories for purification methods differentiated into contributed materials.

Ion exchange-based purification									
Impact category	Unit	Total	ion-exchange resin	Sulfuric acid	Water	Hazardous waste	Ammonium hydroxide	Ammonium acetate	Electricity
Global warming	kg CO ₂ eq	19.86	14.25	0.07	0.01	4.71	0.28	0.50	0.03
Ionizing radiation	kBq Co-60 eq	0.47	0.38	0.00	0.00	0.06	0.00	0.02	0.00
Ozone formation, Human health	kg NO _x eq	0.03	0.02	0.00	0.00	0.00	0.00	0.00	0.00
Fine particulate matter formation	kg PM2.5 eq	0.02	0.02	0.00	0.00	0.00	0.00	0.00	0.00
Ozone formation, Terrestrial ecosystems	kg NO _x eq	0.03	0.02	0.00	0.00	0.00	0.00	0.00	0.00
Terrestrial acidification	kg SO ₂ eq	0.05	0.03	0.00	0.00	0.01	0.00	0.00	0.00
Terrestrial ecotoxicity	kg 1,4-DCB	46.26	35.79	1.85	0.03	4.55	1.58	2.40	0.04
Freshwater ecotoxicity	kg 1,4-DCB	0.72	0.55	0.04	0.00	0.10	0.01	0.02	0.00
Marine ecotoxicity	kg 1,4-DCB	0.94	0.72	0.05	0.00	0.13	0.01	0.03	0.00
Human carcinogenic toxicity	kg 1,4-DCB	1.12	0.60	0.01	0.00	0.49	0.00	0.01	0.00
Human non-carcinogenic toxicity	kg 1,4-DCB	16.20	12.28	0.69	0.01	2.71	0.13	0.37	0.02
Land use	m ² a crop eq	0.20	0.13	0.00	0.00	0.05	0.00	0.01	0.00
Mineral resource scarcity	kg Cu eq	0.06	0.04	0.02	0.00	0.00	0.00	0.00	0.00
Fossil resource scarcity	kg oil eq	5.64	4.84	0.04	0.00	0.40	0.11	0.24	0.01
Global warming	kg CO ₂ eq	0.20	0.14	0.01	0.01	0.02	0.01	0.01	0.00
Oxalate based purification									
Impact category	Unit	Total	Dimethyl sulfoxide	Water	Sodium hydroxide	Electricity	Spent solvent mixture		
Global warming	kg CO ₂ eq	74.95	33.42	0.01	0.01	0.02	41.50		
Ionizing radiation	kBq Co-60 eq	2.00	1.83	0.00	0.00	0.00	0.17		
Ozone formation, Human health	kg NO _x eq	0.10	0.08	0.00	0.00	0.00	0.02		
Fine particulate matter formation	kg PM2.5 eq	0.09	0.08	0.00	0.00	0.00	0.01		
Ozone formation, Terrestrial ecosystems	kg NO _x eq	0.10	0.08	0.00	0.00	0.00	0.02		
Terrestrial acidification	kg SO ₂ eq	0.24	0.22	0.00	0.00	0.00	0.03		
Terrestrial ecotoxicity	kg 1,4-DCB	154.77	140.50	0.03	0.03	0.03	14.18		
Freshwater ecotoxicity	kg 1,4-DCB	2.76	2.58	0.00	0.00	0.00	0.18		
Marine ecotoxicity	kg 1,4-DCB	3.57	3.32	0.00	0.00	0.00	0.24		
Human carcinogenic toxicity	kg 1,4-DCB	1.33	1.07	0.00	0.00	0.00	0.26		
Human non-carcinogenic toxicity	kg 1,4-DCB	44.60	39.20	0.01	0.01	0.02	5.37		
Land use	m ² a crop eq	0.70	0.55	0.00	0.00	0.00	0.15		
Mineral resource scarcity	kg Cu eq	0.19	0.17	0.00	0.00	0.00	0.02		
Fossil resource scarcity	kg oil eq	26.64	25.39	0.00	0.00	0.00	1.23		
Global warming	kg CO ₂ eq	0.67	0.61	0.01	0.00	0.00	0.05		
Solvent extraction-based purification									
Impact category	Unit	Total	Hydrochloric acid	Extractant Solvent	Sodium hydroxide	Water	Electricity	Hazardous waste	Spent solvent mixture
Global warming	kg CO ₂ eq	217.73	22.37	68.33	4.40	0.17	2.79	62.30	57.37
Ionizing radiation	kBq Co-60 eq	7.14	1.59	3.70	0.48	0.01	0.34	0.79	0.23
Ozone formation, Human health	kg NO _x eq	0.52	0.06	0.37	0.01	0.00	0.01	0.05	0.03
Fine particulate matter formation	kg PM2.5 eq	0.29	0.06	0.15	0.01	0.00	0.01	0.04	0.01
Ozone formation, Terrestrial ecosystems	kg NO _x eq	0.61	0.06	0.46	0.01	0.00	0.01	0.05	0.03
Terrestrial acidification	kg SO ₂ eq	0.71	0.11	0.43	0.02	0.00	0.01	0.10	0.03
Terrestrial ecotoxicity	kg 1,4-DCB	593.22	129.47	360.58	18.04	0.84	4.45	60.23	19.60
Freshwater ecotoxicity	kg 1,4-DCB	9.28	2.37	4.86	0.31	0.02	0.17	1.29	0.25
Marine ecotoxicity	kg 1,4-DCB	12.21	3.06	6.42	0.40	0.02	0.22	1.75	0.33
Human carcinogenic toxicity	kg 1,4-DCB	10.62	1.14	2.31	0.21	0.01	0.12	6.48	0.36
Human non-carcinogenic toxicity	kg 1,4-DCB	173.67	41.31	80.31	5.95	0.29	2.58	35.82	7.42
Land use	m ² a crop eq	3.39	0.57	1.82	0.10	0.00	0.04	0.65	0.21
Mineral resource scarcity	kg Cu eq	0.73	0.27	0.36	0.02	0.00	0.00	0.06	0.03
Fossil resource scarcity	kg oil eq	118.12	6.05	103.30	1.09	0.04	0.70	5.24	1.71
Global warming	kg CO ₂ eq	2.30	0.51	1.01	0.11	0.36	0.02	0.21	0.08
Ionizing radiation	kBq Co-60 eq	217.73	22.37	68.33	4.40	0.17	2.79	62.30	57.37

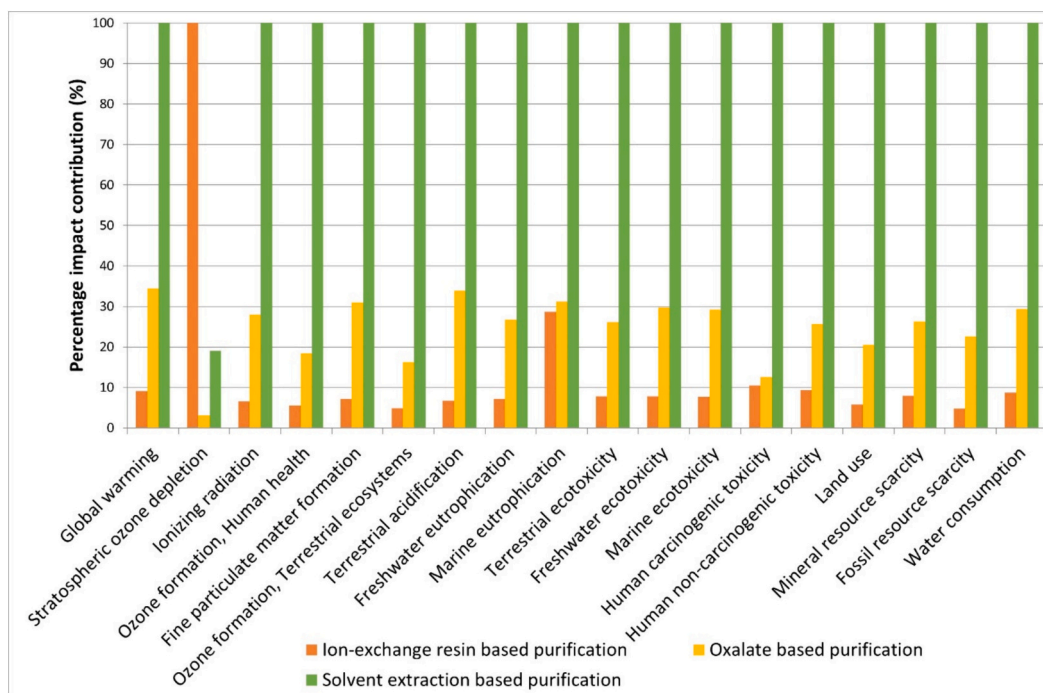


Fig. 3. Percentage impact of each separation or purification method under different impact categories.

reason for this could be the use of organic materials for the treatment. Organic solvents do not contain halogens, whereas inorganic acids or solvents are composed of halogens that can be easily released during the reaction, further impacting stratospheric ozone depletion.

Oxalate-based purification methods were designed to purify the metals derived from the DES-based leaching process as the metals leached would not be used in solvent-based or adsorbent material-based extraction as explained under Section 3.2.3. Moreover, to keep the metals in the suspension until further separation, DMSO is needed due to the addition of DES, which made the solutions less soluble in water. When oxalate-based purification was used, adding DMSO had the largest effect (approximately 99 %) on the total emissions (7.50×10^1 kg CO₂ eq. per 1 kg of leached metal). This impact was divided into two categories: 1) direct DMSO (44.6 %) and 2) spent solvent mixture (55.4 %). However, there is a higher possibility of recycling these solvents back into the process, lowering the overall impact. In the current study, we used 50 % recycling, which is not sufficient to lower the overall impact generated by the solvents used. Compared with other contributors, the impact of electricity was negligible for oxalate-based purification.

Metal extraction based on adsorbent materials has the lowest impact on separation and purification treatment methods. The total emission of this mechanism is reported to be 1.99×10^1 kg CO₂ eq. per 1 kg of leached metal. The primary contributor was ion-exchange resin usage, which accounted for approximately 71.7 % of the PEE. The production and transportation of ion-exchange resins directly contribute to this impact. Moreover, the incineration of hazardous waste and the disposal of spent ion-exchange resin and waste chemicals accounted for 23.8 % of the generated impact. Additionally, the adsorbent material-based purification showed the highest impact under stratospheric ozone depletion. The “ion-exchange resin usage” primarily generates 99 % of the impact in this category. This originates from the use of trichloromethane to produce ion-exchange resins. Energy usage is again negligible for this process.

4.2.3. Precipitate calcination methods

Because the purification and separation methods provide different

Table 4

Impact contribution for significant impact categories from main components of calcination methods.

Oxalate calcination			
Impact category	Unit	Total	Electricity
Global warming	kg CO ₂ eq	94.71	93.74
Ionizing radiation	kBq Co-60 eq	11.29	11.29
Ozone formation, Human health	kg NO _x eq	0.20	0.20
Fine particulate matter formation	kg PM2.5 eq	0.21	0.21
Ozone formation, Terrestrial ecosystems	kg NO _x eq	0.21	0.21
Terrestrial acidification	kg SO ₂ eq	0.32	0.32
Terrestrial ecotoxicity	kg 1,4-DCB	149.50	149.50
Freshwater ecotoxicity	kg 1,4-DCB	5.82	5.82
Marine ecotoxicity	kg 1,4-DCB	7.35	7.35
Human carcinogenic toxicity	kg 1,4-DCB	3.89	3.89
Human non-carcinogenic toxicity	kg 1,4-DCB	86.45	86.45
Land use	m ² a crop eq	1.36	1.36
Mineral resource scarcity	kg Cu eq	0.09	0.09
Fossil resource scarcity	kg oil eq	23.37	23.37

Hydroxide calcination			
Impact category	Unit	Total	Electricity
Global warming	kg CO ₂ eq	60.60	60.60
Ionizing radiation	kBq Co-60 eq	7.30	7.30
Ozone formation, Human health	kg NO _x eq	0.13	0.13
Fine particulate matter formation	kg PM2.5 eq	0.13	0.13
Ozone formation, Terrestrial ecosystems	kg NO _x eq	0.13	0.13
Terrestrial acidification	kg SO ₂ eq	0.21	0.21
Terrestrial ecotoxicity	kg 1,4-DCB	96.65	96.65
Freshwater ecotoxicity	kg 1,4-DCB	3.76	3.76
Marine ecotoxicity	kg 1,4-DCB	4.75	4.75
Human carcinogenic toxicity	kg 1,4-DCB	2.51	2.51
Human non-carcinogenic toxicity	kg 1,4-DCB	55.89	55.89
Land use	m ² a crop eq	0.88	0.88
Mineral resource scarcity	kg Cu eq	0.06	0.06
Fossil resource scarcity	kg oil eq	15.11	15.11
Global warming	kg CO ₂ eq	0.45	0.45

precipitates, a calcination step was used to convert the precipitates to oxides of the corresponding metals. In this study, we analyzed two calcination methods: hydroxide and oxalate calcination. The functional unit used for the analysis was 1 kg of metal oxide (Co, Mn, and Ni oxides) produced via calcination. The initial literature analysis shows that both methods used longer calcination times. However, gaseous emissions depend on the anion (–hydroxide or –oxalate) present in the precipitate. Table 4 shows the results of impact contribution from components for significant impact categories. SI 1 (Table S3) also provides the complete environmental impacts reported for the two calcination methods for different impact categories.

Results suggest that electricity usage is the main component for the impact generation. Hydroxide based calcination has lower impact than oxalate-based calcination under different impact categories.

Fig. 4 compares the impacts generated by the calcination of each anion-based precipitate.

According to the analysis, oxalate-based calcination has a greater environmental impact than hydroxide-based calcination because it requires more oxalate salts and requires more energy than hydroxides to produce 1 kg of metal oxide. According to stoichiometry, to produce 1 kg of mixed metal oxides it would require 1.935 kg of mixed metal oxalates (Eq. (4)). However, the same amount of metal oxides can be made by using only 1.215 kg of mixed metal hydroxides (Eq. (5)). Moreover, about 444 MJ of electricity is required to produce 1 kg of metal oxide through oxalate calcination. However, GHG emissions have a minimal impact compared to the energy requirement for the calcination process. In contrast, hydroxide-based calcination is environmentally friendly and requires less energy (287 MJ) to produce 1 kg of metal oxide. In both calcination methods, the impact was almost completely generated by the electricity consumption because calcination processes lasting longer than 28 h. Hence, Fig. 4 shows a similar pattern of impact under different impact categories.



Furthermore, the thermal breakdown of cobalt oxalate produces GHG emissions, whereas cobalt hydroxide produces only water vapor.

This also reduced the total impact generated by hydroxide calcination.

4.3. Standard scenario comparison

Standard scenarios were established using alternative possibilities of leaching, purification, and calcination technologies. Seven routes were designed using different combinations of the identified technologies and the compatibility of the resulting solutions in each step with the next combined technology was considered. For example, DES-based leaching is incompatible with adsorbent materials and solvent extraction-based purification because of the availability of oxalate (Chang et al., 2022). Furthermore, oxalate-based precipitation and hydroxide-based calcination are incompatible methods. Only sulfate-based leaching solutions were compatible with solvent or adsorbent material extraction (Strauss et al., 2021; Xuan et al., 2022). And hydroxide-based precipitation or extraction is only compatible with hydroxide-based calcination. This also applies to oxalate-based precipitation. Therefore, these technologies have led to the design of a limited number of routes. Fig. 5 shows each route with the corresponding hydrometallurgical steps involved.

The CRM mass transfer from the active material to the leaching solution was calculated considering the leaching efficiency reported in the literature. The mass of CRM in the purified solution or semi-precipitate was calculated by multiplying the mass of CRM in the leachate by the average recovery efficiency of the purification or separation method. Similarly, the calcined oxide mass for each metal was calculated by multiplying the CRM mass in the precipitates by the recovery efficiency of the calcination method. Stoichiometric calculations were also incorporated when the metal oxide changed to metal ions, metal oxalate/hydroxide, and finally to oxide again. Table 5 provides these mass transfer values based on 1 g of the cathode active material.

4.3.1. Life cycle assessment of standard scenario

Mass transfers, efficiencies (Table 2), and inventory collection (SI 2, Section S1) were employed for the life-cycle comparison of the different conceptual routes established. The analysis used the recovery of 1 kg of cathode active material from NMC 111 LiBs as its functional unit. Table 6 shows the impacts generated by each CRM extraction route for different impact categories.

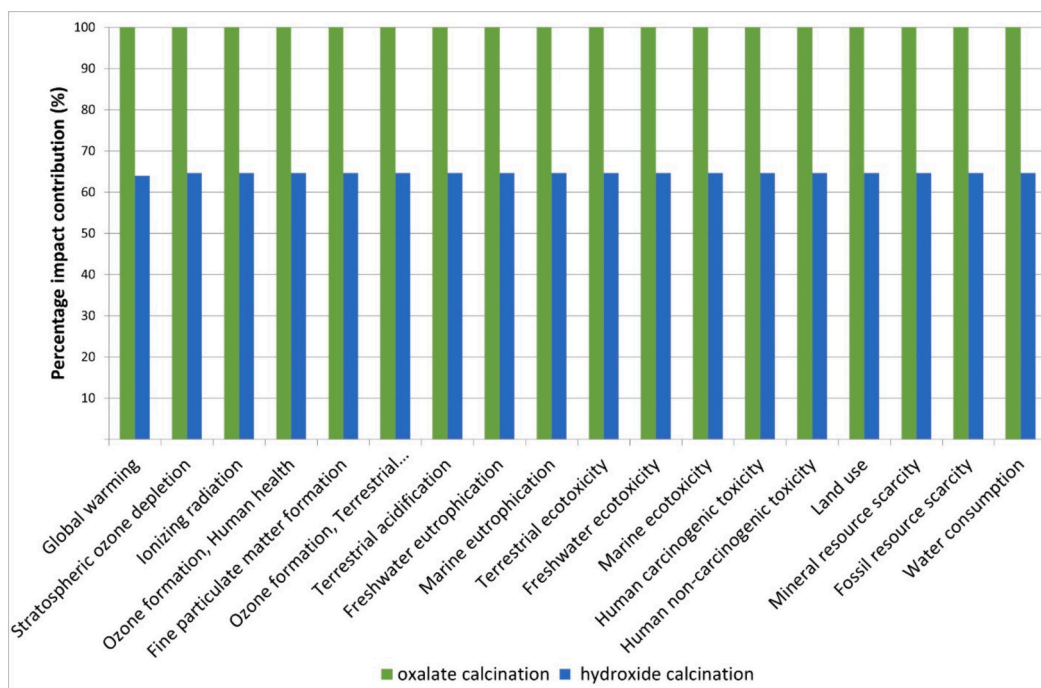


Fig. 4. Percentage impact of the two calcination methods under different impact categories.

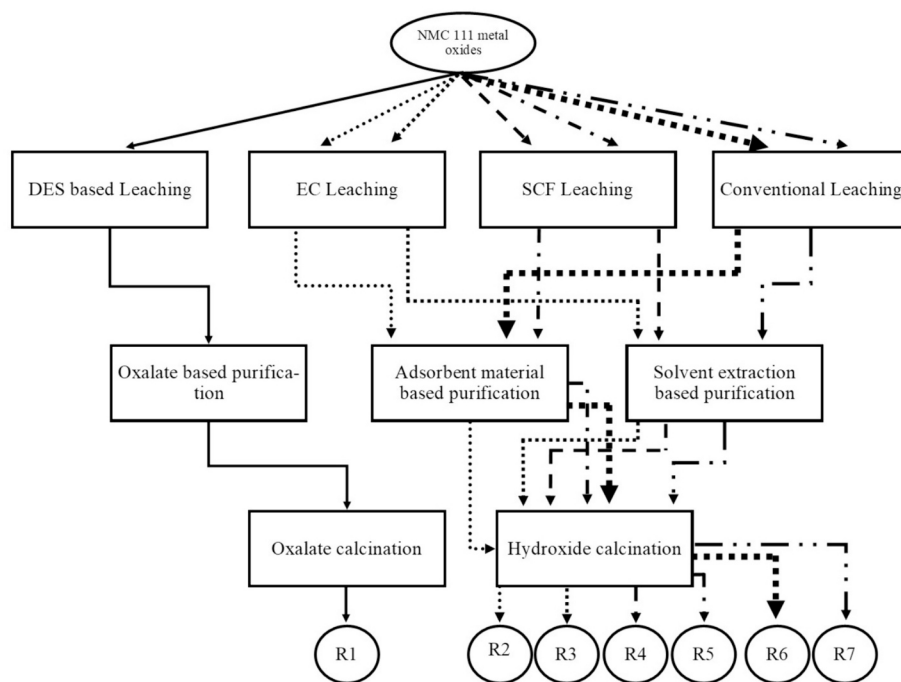


Fig. 5. The flow chart of technologies used for each recovery route (DES = deep eutectic solvent, EC = electrolysis, SCF = supercritical fluid).

Table 5

Mass transfer of elected critical raw materials in each conceptual route with the final recovery efficiency.^a

NMC 111 oxide		After leaching		After purification		After calcination		Total recovery efficiency (%)
Metal oxide	Mass (g)	Metal ion	Mass (g)	Metal oxalate/hydroxide	Mass (g)	Metal oxide	Mass (g)	
Route 1 NMC 111 → DES leaching → Oxalate purification → Oxalate calcination → Metal oxide								
Co oxide	0.33	Co ²⁺	0.19	CoC ₂ O ₄	0.43	Co ₃ O ₄	0.23	70 %
Ni oxide	0.33	Ni ²⁺	0.20	NiC ₂ O ₄	0.49	NiO	0.25	76 %
Mn oxide	0.33	Mn ²⁺	0.18	MnC ₂ O ₄	0.47	MnO	0.23	71 %
Route 2 NMC 111 → EC leaching → Adsorbent mat. purification → Hydroxide calcination → Metal oxide								
Co oxide	0.33	Co ²⁺	0.19	Co (OH) ₂	0.31	Co ₃ O ₄	0.26	80 %
Ni oxide	0.33	Ni ²⁺	0.19	Ni (OH) ₂	0.30	NiO	0.25	74 %
Mn oxide	0.33	Mn ²⁺	0.18	Mn (OH) ₂	0.29	MnO	0.23	71 %
Route 3 NMC 111 → EC leaching → Solvent extr. purification → Hydroxide calcination → Metal oxide								
Co oxide	0.33	Co ²⁺	0.19	Co (OH) ₂	0.29	Co ₃ O ₄	0.25	76 %
Ni oxide	0.33	Ni ²⁺	0.19	Ni (OH) ₂	0.30	NiO	0.24	73 %
Mn oxide	0.33	Mn ²⁺	0.18	Mn (OH) ₂	0.26	MnO	0.20	62 %
Route 4 NMC 111 → SCF leaching → Solvent extr. purification → Hydroxide calcination → Metal oxide								
Co oxide	0.33	Co ²⁺	0.15	Co (OH) ₂	0.23	Co ₃ O ₄	0.19	59 %
Ni oxide	0.33	Ni ²⁺	0.15	Ni (OH) ₂	0.23	NiO	0.19	57 %
Mn oxide	0.33	Mn ²⁺	0.14	Mn (OH) ₂	0.21	MnO	0.16	50 %
Route 5 NMC 111 → SCF leaching → Adsorbent mat. purification → Hydroxide calcination → Metal oxide								
Co oxide	0.33	Co ²⁺	0.15	Co (OH) ₂	0.24	Co ₃ O ₄	0.21	62 %
Ni oxide	0.33	Ni ²⁺	0.15	Ni (OH) ₂	0.23	NiO	0.19	57 %
Mn oxide	0.33	Mn ²⁺	0.14	Mn (OH) ₂	0.23	MnO	0.19	57 %
Route 6 NMC 111 → conventional leaching → Adsorbent mat. purification → Hydroxide calcination → Metal oxide								
Co oxide	0.33	Co ²⁺	0.20	Co (OH) ₂	0.32	Co ₃ O ₄	0.27	83 %
Ni oxide	0.33	Ni ²⁺	0.20	Ni (OH) ₂	0.32	NiO	0.26	77 %
Mn oxide	0.33	Mn ²⁺	0.19	Mn (OH) ₂	0.30	MnO	0.24	74 %
Route 7 NMC 111 → conventional leaching → Solvent extr. purification → Hydroxide calcination → Metal oxide								
Co oxide	0.33	Co ²⁺	0.20	Co (OH) ₂	0.30	Co ₃ O ₄	0.26	79 %
Ni oxide	0.33	Ni ²⁺	0.20	Ni (OH) ₂	0.31	NiO	0.25	77 %
Mn oxide	0.33	Mn ²⁺	0.19	Mn (OH) ₂	0.27	MnO	0.21	65 %

^a NMC = LiNi_{0.33}Mn_{0.33}Co_{0.33}O₂, DES = deep eutectic solvent, EC = electrolysis, SCF = supercritical fluid.

Table 6 shows that route 1 has the most significant effect on all types of impacts, such as DES-based leaching, oxalate-based purification, and metal-oxalate calcination. The high impact stemmed from the high electricity consumption of the leaching and calcination sections (around 2000 MJ). The percentage contributions of the two processes to the PEE were 53.3 % and 38.6 %, respectively. Moreover, the percentage contribution of Ni-oxalate calcination (13.7 %) was higher than that of

Mn and Co, where Co-oxalate calcination had the lowest (11.8 %). However, route 1 has a lower impact on stratospheric ozone depletion and mineral resource scarcity. This is because of the use of organic solvents and the low mineral intensity of the materials used for the treatment process.

Route 7, which involved conventional leaching, solvent extraction, and calcination of metal hydroxide, had the second-highest impact. This

Table 6
Impacts made by each route under different impact categories.^a

Impact category	Unit	Route 1	Route 2	Route 3	Route 4	Route 5	Route 6	Route 7
Global warming	kg CO ₂ eq	5.26 × 10 ²	1.53 × 10 ²	2.56 × 10 ²	2.09 × 10 ²	1.28 × 10 ²	1.74 × 10 ²	2.82 × 10 ²
Stratospheric ozone depletion	kg CFC11 eq	2.13 × 10 ⁻⁴	5.38 × 10 ⁻⁴	1.50 × 10 ⁻⁴	1.24 × 10 ⁻⁴	4.28 × 10 ⁻⁴	5.63 × 10 ⁻⁴	1.59 × 10 ⁻⁴
Ionizing radiation	kBq Co-60 eq	5.42 × 10 ¹	1.71 × 10 ¹	1.99 × 10 ¹	1.63 × 10 ¹	1.41 × 10 ¹	1.96 × 10 ¹	2.25 × 10 ¹
Ozone formation, Human health	kg NO _x eq	1.09 × 10 ⁰	3.29 × 10 ⁻¹	5.88 × 10 ⁻¹	4.77 × 10 ⁻¹	2.74 × 10 ⁻¹	3.71 × 10 ⁻¹	6.41 × 10 ⁻¹
Fine particulate matter formation	kg PM2.5 eq	1.07 × 10 ⁰	3.43 × 10 ⁻¹	4.75 × 10 ⁻¹	3.76 × 10 ⁻¹	2.73 × 10 ⁻¹	3.75 × 10 ⁻¹	5.13 × 10 ⁻¹
Ozone formation, Terrestrial ecosystems	kg NO _x eq	1.11 × 10 ⁰	3.32 × 10 ⁻¹	6.42 × 10 ⁻¹	5.20 × 10 ⁻¹	2.77 × 10 ⁻¹	3.75 × 10 ⁻¹	6.98 × 10 ⁻¹
Terrestrial acidification	kg SO ₂ eq	1.78 × 10 ⁰	5.80 × 10 ⁻¹	9.27 × 10 ⁻¹	7.17 × 10 ⁻¹	4.45 × 10 ⁻¹	6.10 × 10 ⁻¹	9.71 × 10 ⁻¹
Freshwater eutrophication	kg P eq	2.37 × 10 ⁻¹	7.41 × 10 ⁻²	1.02 × 10 ⁻¹	8.31 × 10 ⁻²	6.11 × 10 ⁻²	8.38 × 10 ⁻²	1.13 × 10 ⁻¹
Marine eutrophication	kg N eq	1.89 × 10 ⁻²	6.00 × 10 ⁻³	7.61 × 10 ⁻³	6.14 × 10 ⁻³	4.89 × 10 ⁻³	6.37 × 10 ⁻³	8.04 × 10 ⁻³
Terrestrial ecotoxicity	kg 1,4-DCB	9.02 × 10 ²	2.99 × 10 ²	5.96 × 10 ²	4.95 × 10 ²	2.62 × 10 ²	3.04 × 10 ²	6.14 × 10 ²
Freshwater ecotoxicity	kg 1,4-DCB	3.01 × 10 ¹	9.87 × 10 ⁰	1.42 × 10 ¹	1.13 × 10 ¹	7.93 × 10 ⁰	1.07 × 10 ¹	1.52 × 10 ¹
Marine ecotoxicity	kg 1,4-DCB	3.81 × 10 ¹	1.25 × 10 ¹	1.82 × 10 ¹	1.46 × 10 ¹	1.01 × 10 ¹	1.36 × 10 ¹	1.96 × 10 ¹
Human carcinogenic toxicity	kg 1,4-DCB	1.99 × 10 ¹	6.81 × 10 ⁰	1.19 × 10 ¹	9.49 × 10 ⁰	5.53 × 10 ⁰	7.57 × 10 ⁰	1.28 × 10 ¹
Human non-carcinogenic toxicity	kg 1,4-DCB	4.58 × 10 ²	1.48 × 10 ²	2.29 × 10 ²	1.88 × 10 ²	1.24 × 10 ²	1.65 × 10 ²	2.50 × 10 ²
Land use	m ² a crop eq	7.16 × 10 ⁰	2.27 × 10 ⁰	3.96 × 10 ⁰	3.23 × 10 ⁰	1.91 × 10 ⁰	2.49 × 10 ⁰	4.25 × 10 ⁰
Mineral resource scarcity	kg Cu eq	6.77 × 10 ⁻¹	7.18 × 10 ⁻¹	1.09 × 10 ⁰	5.45 × 10 ⁻¹	2.52 × 10 ⁻¹	3.22 × 10 ⁻¹	7.12 × 10 ⁻¹
Fossil resource scarcity	kg oil eq	1.53 × 10 ²	3.84 × 10 ¹	1.00 × 10 ²	8.05 × 10 ¹	3.21 × 10 ¹	4.40 × 10 ¹	1.08 × 10 ²
Water consumption	m ³	4.35 × 10 ⁰	1.26 × 10 ⁰	2.38 × 10 ⁰	2.09 × 10 ⁰	1.21 × 10 ⁰	1.49 × 10 ⁰	2.66 × 10 ⁰

^a Impacts made per 1 kg of cathode active material treatment.

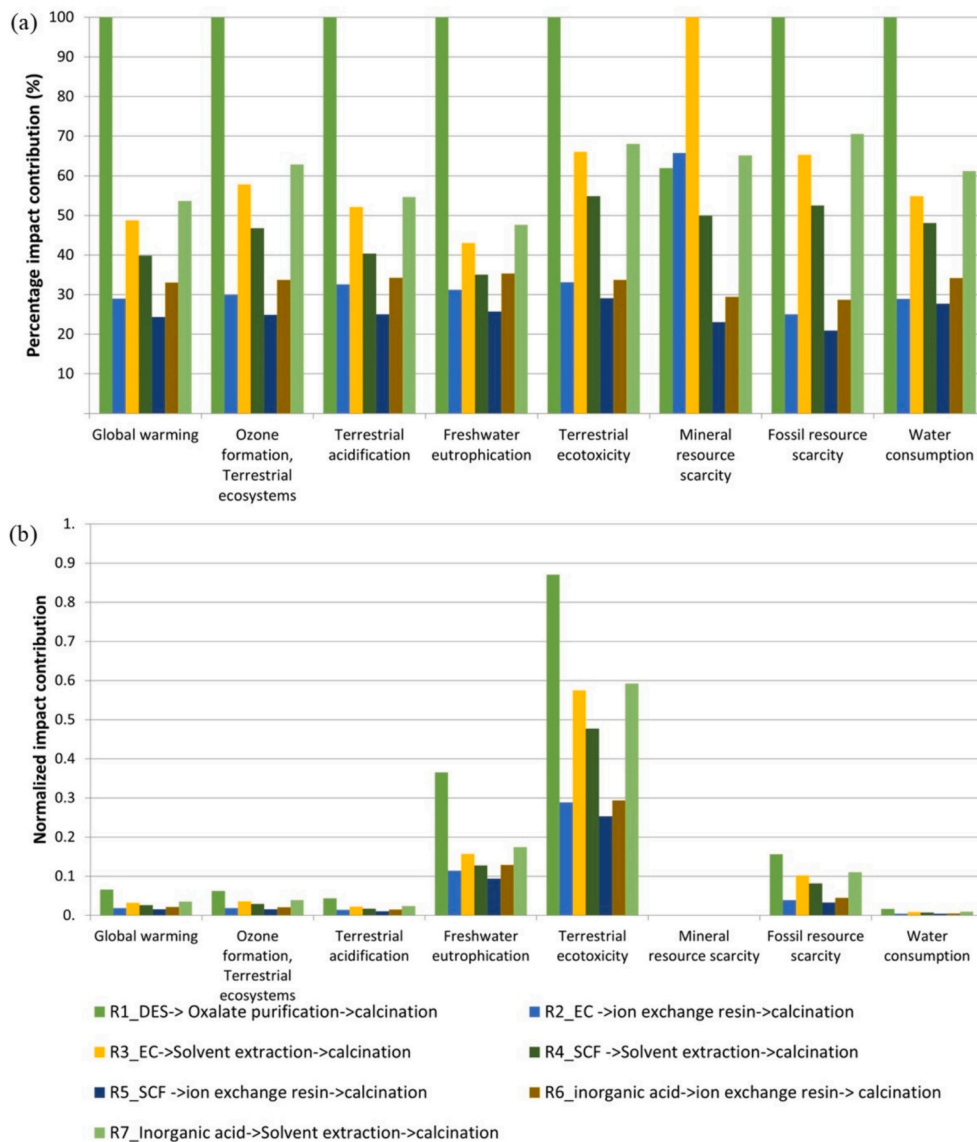


Fig. 6. Comparison of a) percentage impacts made by each route under various impact categories; b) normalized impacts made under different impact categories by route (*DES = deep eutectic solvent, EC = electrolysis, SCF = supercritical fluid).

is because the solvent extraction-based purification method significantly impacts the total emissions - 45.6 %. Furthermore, the calcination of metal hydroxides accounted for approximately 46.6 % of the impact in the same category. Among the calcination processes, Ni-hydroxide was the highest contributor (16.6 %), followed by cobalt-hydroxide (16 %) and Mn-hydroxide (14.2 %). Compared with these, the contribution of the leaching step was negligible (7.5 %). Nevertheless, route 7 showed less stratospheric ozone depletion impact because of the organic solvent-based purification process. The total energy requirement for route 7 is 721 MJ and major part of this is used by calcination process.

Routes 3 and 4 provide the third- and fourth-highest contributions, respectively. Both methods use solvent-based extraction for purification, followed by hydroxide-based calcination. Further analysis of the two routes revealed that these two steps, not the leaching method used, were responsible for the highest contribution (48 % contribution for route 3 and 46.2 % for route 4) for the PEE. Nevertheless, route 3 had the greatest impact on mineral resource scarcity due to electrolyte materials' high contribution to EC leaching (50.5 %) and the hydrochloric and organic solvents used in purification (38 %). Organic extractants from petroleum-based raw materials (such as Cyanex 272) can contribute significantly to mineral resource scarcity. The energy requirement for route 3 was 607 MJ and for route 4 was 476 MJ.

Routes 5, 2, and 6, ranked from lowest to highest, had the lowest impacts. Although the reported routes had a lower impact in many categories, they had the highest impact on stratospheric ozone depletion. This is because the adsorbent material-based purification system utilizes ion-exchange resins. Given that all three routes share the same calcination process, we can conclude that route 5 experienced the least impact owing to the SCF-based leaching process. However, it should be noted that SCF has lower material recovery efficiency (~58 %). This characteristic of SCF leaching provides lower mass of material to the next steps lowering the overall material consumption of the treatment mechanism which can ultimately lower the environmental impact of the route. This was followed by hydroxide-based calcination, which had the least environmental impact under calcination methods. Moreover, EC-based leaching lowers the impact compared with conventional leaching method which shows supremacy of the route even with high material recovery. The route 2, 5 and 6 consumed 639, 501, and 754 MJ respectively. We normalized the impact categories by converting all impacts into a single unit to identify those that contributed more significantly than the others. Fig. 6-a and b shows the selected impact categories for each treatment route before and after normalization. Categories that give broader outlook were manually selected over the 18 impact categories to keep the clarity of the figure.

The results in Fig. 6 indicate that terrestrial ecotoxicity, freshwater

eutrophication, and fossil resource scarcity have the highest significance among all impact categories. Hence, the identified treatment procedures have a significantly higher impact on these categories. However, the order of the routes according to the highest-to-lowest impact generation remains unchanged, suggesting that Route 1 has the highest environmental impact while Route 5 has the lowest.

As the final part of the standard scenario analysis, a Monte Carlo analysis was performed with 1000 iterations, considering routes 1 and 5. This was performed to evaluate the sensitivity of the model. SI 1, Fig. S4 presents the results of the analysis. Accordingly, Route 5 is certainly better under many impact categories than Route 1, with 1000 adjustments of values within the standard deviation. Under the water consumption impact category, it is unclear whether Route 5 is always better than route 1. However, under stratospheric ozone depletion, Route 5 has an exceptionally low probability of lowering the impact.

4.4. Life cycle assessment for the improved scenario

For the improved version, industrial-level recycling rates, material usage, and waste material handling were used as specified in Section 3.2.6. SI 2, Section S2 presents the comprehensive assessment of inventory. Table 7 shows the impacts produced by each improved route version under different impact categories.

According to the findings, all the routes reduced their impacts under the improved scenario. Nevertheless, the order of the emissions from the highest to the lowest route remains unchanged, with the highest impact from route 1 and the lowest from route 5. Furthermore, Route 2 had a similar impact as Route 6, but considering only the total emissions. The emissions decreased almost five-fold on Route 1 with the improved scenario. Considering Route 1, impacts were significantly reduced in many categories, such as stratospheric ozone depletion, ozone formation and fine particulate matter. However, with the improved version, the ionizing radiation, land use, and water consumption impact categories had a higher impact on Route 1. All three categories have increased the impacts because of adapting solar energy for electricity generation under improved scenario. Thin films used in solar photovoltaic (PV) cells, which may contain cadmium- or gallium-like radioactive elements, can elevate ionizing radiation. Furthermore, it employs copper or silicon which can emit radiation during refinement. Solar farms use more land than other energy sources, which can affect natural habitats and ecosystems. Producing PV cells requires cooling sources for thermal power plants which can also lead to increased water consumption. In addition, refining minerals such as silicon requires more water during many steps (Luderer et al., 2019; Zahedi et al., 2022).

Route 2 reduced its emissions by almost 78 % compared to the

Table 7
Impacts made by each improved route under different impact categories.^a

Impact category	Unit	Route 1	Route 2	Route 3	Route 4	Route 5	Route 6	Route 7
Global warming	kg CO ₂ eq	1.07×10^2	3.43×10^1	9.95×10^1	7.85×10^1	2.74×10^1	3.38×10^1	1.02×10^2
Stratospheric ozone depletion	kg CFC11 eq	9.77×10^{-5}	4.11×10^{-4}	7.85×10^{-5}	6.23×10^{-5}	3.23×10^{-4}	4.27×10^{-4}	8.10×10^{-5}
Ionizing radiation	kBq Co-60 eq	1.11×10^2	3.58×10^1	3.63×10^1	3.09×10^1	3.05×10^1	4.16×10^1	4.22×10^1
Ozone formation, Human health	kg NO _x eq	2.08×10^{-1}	7.02×10^{-2}	2.08×10^{-1}	1.62×10^{-1}	5.41×10^{-2}	6.69×10^{-2}	2.11×10^{-1}
Fine particulate matter formation	kg PM2.5 eq	1.73×10^{-1}	6.45×10^{-2}	1.52×10^{-1}	1.16×10^{-1}	4.70×10^{-2}	5.92×10^{-2}	1.50×10^{-1}
Ozone formation, Terrestrial ecosystems	kg NO _x eq	2.14×10^{-1}	7.15×10^{-2}	2.30×10^{-1}	1.80×10^{-1}	5.51×10^{-2}	6.82×10^{-2}	2.33×10^{-1}
Terrestrial acidification	kg SO ₂ eq	4.30×10^{-1}	1.58×10^{-1}	3.65×10^{-1}	2.78×10^{-1}	1.16×10^{-1}	1.52×10^{-1}	3.67×10^{-1}
Freshwater eutrophication	kg P eq	7.26×10^{-2}	2.49×10^{-2}	4.61×10^{-2}	3.66×10^{-2}	2.00×10^{-2}	2.59×10^{-2}	4.81×10^{-2}
Marine eutrophication	kg N eq	7.34×10^{-3}	2.97×10^{-3}	4.09×10^{-3}	3.05×10^{-3}	2.17×10^{-3}	2.78×10^{-3}	3.94×10^{-3}
Terrestrial ecotoxicity	kg 1,4-DCB	6.05×10^2	2.17×10^2	3.88×10^2	3.10×10^2	1.76×10^2	2.26×10^2	4.05×10^2
Freshwater ecotoxicity	kg 1,4-DCB	1.12×10^1	3.97×10^0	6.83×10^0	5.42×10^0	3.17×10^0	4.17×10^0	7.15×10^0
Marine ecotoxicity	kg 1,4-DCB	1.44×10^1	5.11×10^0	8.88×10^0	7.05×10^0	4.09×10^0	5.37×10^0	9.30×10^0
Human carcinogenic toxicity	kg 1,4-DCB	6.88×10^0	2.79×10^0	6.84×10^0	5.41×10^0	2.23×10^0	2.90×10^0	7.13×10^0
Human non-carcinogenic toxicity	kg 1,4-DCB	2.02×10^2	7.22×10^1	1.27×10^2	1.02×10^2	5.94×10^1	7.80×10^1	1.35×10^2
Land use	m ² a crop eq	7.32×10^0	2.45×10^0	3.42×10^0	2.79×10^0	2.03×10^0	2.71×10^0	3.73×10^0
Mineral resource scarcity	kg Cu eq	5.21×10^{-1}	6.12×10^{-1}	8.57×10^{-1}	4.03×10^{-1}	2.12×10^{-1}	3.03×10^{-1}	5.58×10^{-1}
Fossil resource scarcity	kg oil eq	3.88×10^1	8.94×10^0	3.66×10^1	2.89×10^1	7.22×10^0	9.09×10^0	3.79×10^1
Water consumption	m ³	6.19×10^0	2.02×10^0	2.75×10^0	2.32×10^0	1.75×10^0	2.34×10^0	3.09×10^0

^a Impacts made per 1 kg of cathode active material treatment under the improved scenario.

standard scenario. Three impact categories—ionizing radiation, land use, and water consumption—have increased their impacts due to the usage of solar energy-based electricity. In contrast, Route 3 reduced the total impact on the emissions approximately by 62 % with the improved scenario, while the ionizing radiation and water consumption categories exhibited increased impacts. The land-use impact category still demonstrated a decreased impact under the improved scenario. The increase in ionizing radiation and water consumption was due to solar-based energy utilization. However, reduced use of organic solvents and higher recycling rates led to a decrease in the impact of land use. Higher organic solvent usage significantly increased the impact of land use in the standard scenario. This is because of the extraction and production facilities required for the process of crude oil (Hugo Valin et al., 2015). With the improved version, these impacts significantly decreased, such that the increased impacts due to solar energy use is negligible. Route 4, which also employed solvent extraction-based purification, exhibited a similar pattern for all three impact categories. However, this route also showed a significant 60 % decrease in its emissions.

The improved processes of routes 5 and 6 follow the same pattern as routes 1 and 2, which did not use solvent extraction-based purification. However, route 7 again follows the pattern of routes 3 and 4, with increasing impacts only under ionizing radiation and water consumption. Moreover, routes 5, 6, and 7 decreased the emission impacts by 78 %, 80 %, and 63 %, respectively. Therefore, routes 1 and 6 report the highest decrease in PEE, whereas route 3 reports the lowest decrease. This explains that using solar-based electricity and recycling DES up to 80 % in route 1 can significantly reduce the impacts. In addition, solar-based electricity, along with a reduced amount of reducing agents, can significantly lower the impact of Route 6. Moreover, 80 % of the recycling of organic solvents may not reduce the related impacts of Route 3. However, the reduced impacts of Route 1 were still higher than those of the other treatment processes.

As Routes 1 and 6 reported the highest reduction in impact under the improved scenarios, a Montecarlo-sensitivity analysis was performed for these two routes with 1000 iterations. SI 1, Fig. S5 displays the results of the analysis. Accordingly, Route 6 was certainly better than Route 1, even after considerably reducing impacts in many categories. However, in the stratospheric ozone depletion category, route 1 was superior to route 6 for each value within the standard deviation. Moreover, in the water consumption category, both routes have a similar tendency to perform better.

4.5. Life cycle costing analysis

The LCC analysis was carried out considering the improved version of each route. This is primarily because of the high environmental impact observed in laboratory studies. An improved version can denote the industrial or at least pilot-scale emissions, which is much more reliable for analyzing the economic impact. Moreover, for the costing analysis only direct costs related to the treatment of 1 kg of cathode active materials were considered. Other operational costs (laborer costs or transportation costs) were assumed to be the same for all the treatment routes and hence not considered a major factor. Table 8 represents the main results of LCC assessment with mean prices and standard deviation. Further, SI 2, Section S3 provides a comprehensive list of mean costs for each chemical with the standard deviation of prices, treatment costs, income from byproduct and the quantities of the same required to treat 1 kg of the active cathode material.

As per the results, the highest cost was shown by route 3 and the lowest reported by route 5. Routes 2 and 3 have the highest deviations. SI 1, Fig. S6-a, b and c shows the total treatment cost, average recovery efficiency and process emission effect per 1 kg of cathode active material under each route respectively.

Fig. 7 generated to make a comparison between the costs, environmental impacts and efficiency of the routes. Hence, the figure shows the relative costs, the relative recovery efficiency and environmental impact

Table 8

Cost of treatment for each route studied with standard deviation.

Treatment route	Cost of treatment (\$/kg of cathode material)	Standard deviation (\pm \$)
Route 1: DES leaching → Oxalate precipitate purification → Oxalate calcination	191.16	1.90
Route 2: EC leaching → adsorbent based purification → Hydroxide calcination	103.94	24.38
Route 3: EC leaching → Solvent extraction-based purification → Hydroxide calcination	364.37	24.42
Route 4: SCF leaching → Solvent extraction-based purification → Hydroxide calcination	303.35	3.60
Route 5: SCF leaching → adsorbent based purification → Hydroxide calcination	99.10	3.33
Route 6: Conventional leaching → Adsorbent material-based purification → hydroxide calcination	118.50	0.71
Route 7: Conventional leaching → Solvent extraction-based purification → hydroxide calcination	389.76	1.53

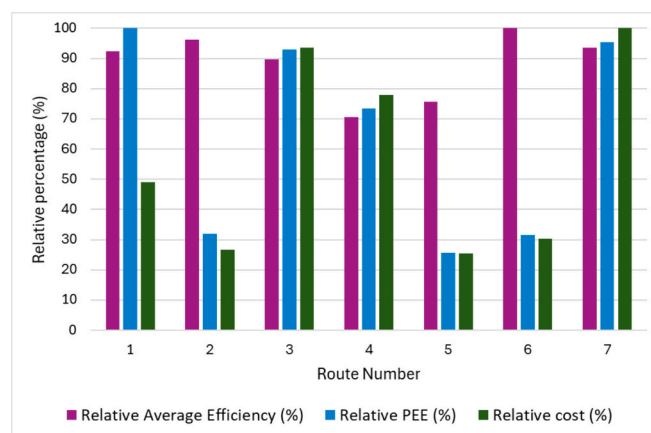


Fig. 7. Comparison of each treatment route in terms of treatment cost efficiency, PEE, and recovery efficiency (PEE = process emission effect).

(in terms of process emission effect) per 1 kg of cathode active material recovery. Moreover, Fig. 7 was generated based on the percentage effect of each three parameters to enhance the clarity and ease of comparison. Though the environmental impacts were analyzed through various categories, only emissions effect derived through global warming potential (GWP) was selected to include in Fig. 7. The main reason for this decision is that ReCipe 2016 calculation method brings GWP as a holistic comprehensive indicator over the other parameters.

As per Figs. 7 and S6 (SI 1) the treatment costs vary from ~\$ 100–400 per 1 kg of cathode treatment under different routes considered. The highest costs were obtained when the solvent extraction technology is involved in the treatment sequence (Route number 3, 4 and 7). This is mainly due to the high unit cost of organic solvents (~\$5.5/kg) and the quantity of materials required. Most of these costs can be recovered through obtaining used organic solvents which can be recycled or reused effectively. However, it seems that 80 % of recycling is not sufficient for the reduction of overall costs resulted by using the organic solvents. The highest cost was reported by route 7 (\$ 390), due to the high quantity of organic solvent required for the extraction of higher amount of metal ions leached through inorganic acid leaching. Hence, PEE of the route is also elevated (at 102 kg CO₂) according to Fig. S6-b (SI 1). However, the average efficiency (73 %) of the route is

also reported to be high compared to other technologies. Route 4 has the lowest cost (\$ 303) among the routes that used organic solvents for purification. However, average efficiency (55 %) and the PEE (27.4 kg CO₂) is also reduced as per the reduced quantity of organic solvents used.

Route number 1 has a slightly higher cost (~\$190) than route 6 (~\$120) considering 1 kg of cathode material treatment. Though the material requirement and unit cost of materials is higher for DES manufacturing, most of these costs are covered through recycling possibility of DES. Moreover, using DES has other advantages like not having to add oxalic acid separately. Hence the purification can be done at a lower cost as the DES itself is made using ChCl and Oxalic acid. However, when different DES is used, the purification technology should be determined accordingly. Nevertheless, these advantages have reduced the overall cost of the treatment. On the other hand, the major cost determinant factor for route 6 is the electricity and the usage of ion-exchange resins. It was identified that around \$ 88 cost needs to be spent for the ion-exchange resins considering the treatment of 1 kg of cathodic materials while for electricity \$ 98. Moreover, it should be identified that the usage of inorganic acid-based leaching in the technology has increased the quantity of leached metals in the solution which demands more ion-exchange materials for the purification step. This can be further identified by the higher average efficiency (78 %) of the route. In contrary route 1 showed an average efficiency of 72 %. Comparing the PEE of the two methods (Fig. 7) suggest that route 6 is far more efficient than route 1 which reports a lower scale PEE (33.8 kg CO₂) than the route 1 (107 kg CO₂) thanks to the lower impacts generated by inorganic acid-based leaching and ion-exchange based purification technologies.

The lowest costs were reported by route 2 and 5, being route 5 the most cost-effective treatment sequence. The main reason for the lowest cost received is due to the lower usage of material quantities due to the effective leaching resulted by EC and SCF based leaching mechanisms. Both the leaching techniques produce lower quantities of leaching solutions compared to DES or inorganic acid based leaching solutions which demand lower quantity of materials for purification steps. Moreover, route 5 has the lowest cost due to the lower average recovery efficiency reported (59 %) while route 2 shows 75 % overall average recovery efficiency. Both the routes can be identified as greener methods with lower PEE at around 34.3 kg CO₂ for route 2 and 27.4 kg CO₂ for route 5. A comparative values of recovery rate, PEE and cost of treatment were given under Fig. S6 for better understanding.

As the study provides information on the costs of the treatment for each route studied, it is possible to assume that lower the cost can increase the profitability of the treatment route in long term. However, the profitability of each route highly depends on the capital investment to establish the industrial treatment plants. For instance, supercritical fluid extraction or electrolysis-based extraction need a higher investment as the plants need specific instrument for the treatment. Moreover, frequent maintenance and work-related hazards can also play a major role in determining the overall profitability of the route, which needs to be extensively researched in future.

4.6. Benchmark analysis

Benchmarking is performed by comparing the results obtained in this study with those of other studies conducted to recycle and recover cathode active materials from EoL LiBs. This task is difficult, especially because of the lack of studies that have focused explicitly on cathode active materials. Moreover, differences in assumptions, functional units, and calculation methods made the analysis more problematic. Despite the limitations of available literature in the field, the results of the study were compared to the highest possible standard.

Castro et al. (2022) implemented a method to recover materials from EoL LiBs, justified by an LCA. This study revealed the impact of a 2.3–5.9 kg CO₂ eq. for the total emissions per cell (~ 500 g). According to the same study, the cathode material content was responsible for 28 %

of the battery, along with the aluminum current collector. Based on the study, cathode active material treatment may cause an overall emission of approximately 3.5 to 9.1 kg CO₂ eq. per 1 kg. The cathode mass in the cell is approximately 180 g. This study utilized organic acid-based leaching, and the LCA inventory included the avoided products. Given the use of avoided products, the impact may be very low compared to the current study. Interestingly, the authors reported that a higher citric acid recycling rate is required to make the process environmentally and economically sustainable, which is in line with the findings of the current study. Furthermore, a study reported a material recovery of approximately 44 % through hydrometallurgical steps (Castro et al., 2022). Wu et al. (2022) did another study that reports recycling of 1 kg of LCO-type cathode material released about 33–118 kg CO₂ eq. when only hydrometallurgical treatment was used. The values obtained by Wu et al. matched the results of the current study for various treatment mechanisms. Moreover, this study confirms that acid leaching has a comparably lower impact under different impact categories and that metal separation impacts the environment more, further justifying the findings of the current study (F. Wu et al., 2022).

Fahimi et al. (2022) conducted a similar study, which revealed that 1 kg of cobalt recovery from LCO-type LiBs results in GHG emissions of approximately 5.1 kg CO₂ equivalent under hydrometallurgical-based treatment. This study used several articles to calculate the average GHG emissions using the ESCAPE method. However, this does not include carbon emissions related to energy utilization, thus lowering the overall emissions. Moreover, it is not possible to compare these values with those of the current study because of the different calculation methods and functional units used. However, the authors reported that organic acid-based treatment tends to increase the total GHG emissions owing to the higher quantities used. Moreover, treating organic acids requires higher recycling rates to reduce total emissions (Fahimi et al., 2022). This finding further confirmed the results of this study. Different authors have reported different recovery rates for recycling procedures, with each hydrometallurgy step affecting the total recycling rate. A single process can significantly affect the final recovery rate. The amount of material transferred to the next step also significantly affects the environmental impact, making it a major uncertainty parameter affecting a recycling route's total sustainability (Oliveira et al., 2015; F. Wu et al., 2020).

5. Conclusions

Considering the various hydrometallurgical treatment steps, energy use has emerged as a hotspot. Second, there are concerns about the high material consumption for organic chemicals. Study found that SCF based leaching gives less efficiency in terms of recovery of materials though it gives better environmental performance when used in a route. However, other leaching methods, EC based, conventional and DES based leaching provide better efficiency in recovery of metals. Nevertheless, DES-based leaching can significantly increase the environmental impact, thereby limiting the use of this technology. It was identified that material recycling rates higher than 80 % are necessary to achieve better environmental and economic performance for DES based leaching. Consequently, conventional and EC-based leaching are better technologies for reducing the environmental impact while increasing the overall leaching of metals.

Adsorbent (ion-exchange)-based purification demonstrated better environmental performance when used in the route with a higher recovery rate (> 70 %) than other purification technologies. Solvent-based extraction significantly increases the emissions when incorporated in the route. Over 80 % recycling of materials is likely to reduce the impacts involved with solvent extraction-based purification. Regarding the calcination method, hydroxide-based calcination provides better performance compared to oxalate calcination in terms of emissions.

The best overall performance is shown by inorganic acid based leaching mechanisms followed by adsorbent-based purification with

hydroxide calcination (route 6) in terms of recovery efficiency (78 %), environmental impact in terms of emissions (33.8 kg CO₂ eq.) and economic performance (\$ 119) per 1 kg of cathode active material recovery. Under the other significant environmental impact categories identified, route 6 showed: terrestrial ecotoxicity; 176 kg 1,4-DCB, freshwater eutrophication; 0.02 kg P eq. and fossil resource scarcity; 7.22 kg oil eq. which only seconds to route 5 (SCF based leaching, adsorbent extraction and hydroxide calcination). Route that follows, DES-based leaching, oxalate precipitation and calcination (route 1) reported as the most polluting technology with high recovery rate (72.3 %) while route 3 (EC-based leaching, solvent based extraction and hydroxide calcination) reported as the worst treatment mechanisms considering both poor environmental and economic performances. This is mainly due to the use of extraction-based purification method. Accordingly, technologies such as DES-based leaching and solvent extraction-based purification, should undergo further experimentation in the long run under laboratory conditions. Specifically, the recycling mechanisms of organic solvents require extensive studies to enhance their sustainability. Moreover, SCF-based leaching is more environmentally sustainable across various impact categories and mildly economical. Hence, further studies on the optimization and 100 % CO₂ recirculation can increase the industrial applicability of this technology.

Finally, the limitations such as pricing variations, and limitations in study-oriented data can deviate the results from the accurate values. Moreover, using different data sources and databases can change the findings of the study significantly as well.

CRediT authorship contribution statement

Dilshan Sandaruwan Premathilake: Writing – review & editing, Writing – original draft, Software, Methodology, Formal analysis, Conceptualization. **Teklit Gebregiorgis Ambaye:** Writing – review & editing, Validation, Supervision, Conceptualization, Methodology. **Amilton Barbosa Botelho Junior:** Writing – review & editing, Supervision, Methodology. **Ana Teresa Macas Lima:** Writing – review & editing, Supervision. **Denise Croce Romano Espinosa:** Supervision, Resources, Project administration, Funding acquisition. **Mentore Vaccari:** Supervision, Resources, Project administration, Funding acquisition.

Declaration of competing interest

The authors 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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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.spc.2024.09.015>.

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