metals

MDPI

Article

Co-Precipitation of Metal Oxalates from Organic Leach Solution Derived from Spent Lithium-Ion Batteries (LIBs)

Dominik Schmitz [1,*], Hariaman Prasetyo [2], Alexander Birich [1], Rungsima Yeetsorn [2] and Bernd Friedrich [1]

[1] IME Process Metallurgy and Metal Recycling, RWTH Aachen University, Intzestrasse 3, 52056 Aachen, Germany; abirich@ime-aachen.de (A.B.); bfriedrich@ime-aachen.de (B.F.)
[2] The Sirindhorn International Thai-German Graduate School of Engineering, King Mongkut's University of Technology North Bangkok, Bangkok 10800, Thailand; s6409094860045@email.kmutnb.ac.th (H.P.); rungsima.y@tggs.kmutnb.ac.th (R.Y.)
* Correspondence: dschmitz@ime-aachen.de; Tel.: +49-241-80-95228

Abstract: Recent studies in hydrometallurgy are focused on developing eco-friendly and selective leach agents such as organic acids. These agents can extract metal ions, which are usually separated through precipitation methods. When traditional methods are used, the separation is complex and time-consuming, and each metal cation is required to be isolated separately. Moreover, extracted metal salts are subsequently recombined in the regeneration of cathode materials. To simplify this, a novel simultaneous precipitation approach has been developed, allowing the separation of metal salts that can directly contribute to regenerating novel cathode materials, bypassing the need for separate isolation. This study aimed to recover cobalt, nickel, and manganese from the organic leach solution of spent lithium-ion batteries (LIBs) through co-precipitation of metal oxalates. The investigation includes the selection of organic acids and the best parameters for the leaching process, as well as testing different molar ratios of the metals M^{2+} (M = Co, Ni, Mn) to oxalic acid (1:3, 1:4.5, 1:6, and 1:7.5) to examine the effects of the precipitating agent on the recovery percentages of the metals. The findings indicate that 2 M citric acid and 4 vol% H_2O_2 is the optimal parameter in the leaching process. Meanwhile, in the co-precipitation process, an increase in the molar ratio leads to a corresponding rise in the resulting metal recoveries. At the ratio of 1:7.5, cobalt, nickel, and manganese were recovered to the extent of 99.26%, 98.93%, and 94.01%, respectively. Nevertheless, at the increased molar ratio, the co-extraction of lithium and aluminum was observed, resulting in reduced selectivity and decreased precipitate purity.

Keywords: battery recycling; spent lithium-ion batteries; organic acid leaching; co-precipitation; oxalic acid; metal oxalate

check for updates

Citation: Schmitz, D.; Prasetyo, H.; Birich, A.; Yeetsorn, R.; Friedrich, B. Co-Precipitation of Metal Oxalates from Organic Leach Solution Derived from Spent Lithium-Ion Batteries (LIBs). *Metals* **2024**, *14*, 80. https://doi.org/10.3390/met14010080

Academic Editor: Felix A. Lopez

Received: 1 December 2023
Revised: 3 January 2024
Accepted: 5 January 2024
Published: 9 January 2024

Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/).

1. Introduction

Lithium-ion batteries (LIBs) are widely utilized in electric vehicles, mobile phones, computers, and other electronic devices due to their advantages, such as high energy density, small size, safety, and extended life cycle [1]. In the latest research report, the global LIBs market is forecast to grow from USD 44.5 billion in 2022 to USD 135.1 billion in 2031 at a compound annual growth rate (CAGR) of 13.1%. In 2022, Germany led the European market, and from that year to 2031, it is predicted to see the highest CAGR. One factor driving market expansion in the region is the country's reputation as one of the leading car manufacturers in Europe [2]. Environmental and economic aspects are the two main factors that describe how important and urgent LIB recycling is. The presence of cobalt and nickel as toxic-metal components has led to LIBs being considered typical hazardous waste. In addition, the critical metals, i.e., lithium, nickel, cobalt, and manganese, which are only produced in limited countries, will experience a sustained price increase as a result of the strong growth in demand. Lithium, nickel, cobalt, and manganese are part of the list of

34 critical raw materials (CRMs) that are of essential importance to the European Union's economy [3].

Two common recycling routes that can be used in LIBs are pyrometallurgy and hydrometallurgy. However, hydrometallurgy comes with its advantages. It allows the recovery of valuable and critical metals such as lithium, a task that pyrometallurgical methods cannot accomplish [4]. Additionally, it is distinguished by its minimal energy consumption and reduced gas emissions [4,5]. In general, a typical hydrometallurgical process consists of pre-treatment, acid leaching, and metal separation. A crucial step in the pre-treatment process, in addition to mechanical treatment, is pyrolysis. It removes organic compounds, such as binders and electrolytes, which enables easier hydrometallurgical processing of LIBs and a higher metal recovery efficiency [6].

Inorganic acids such as hydrochloric acid (HCl), sulfuric acid (H_2SO_4), and nitric acid (HNO_3) have been proven to be efficient solvents for leaching of LIBs. However, these particular acid types are not capable of selectively dissolving metals, exhibit higher corrosiveness towards equipment, present increased potential hazards to operators, and release undesired toxic gases such as SO_3, Cl_2, and NO_x, which are considered unacceptable from an environmental perspective. In addition, it is necessary to subject inorganic acids to expensive wastewater treatment [1,7,8]. Recent advancements in hydrometallurgical research have moved their focus toward the development of more selective, safer, environmentally friendlier, and sustainable leaching agents, such as organic acids. These agents can achieve comparable leaching performance to inorganic acids while employing reductive leaching methodologies [9].

Several investigations have focused on using organic acids to leach waste cathodic materials from spent LIBs. The most common organic leaching solutions are citric acid, DL-malic acid, and succinic acid. Li et al. [10] studied the recovery of lithium and cobalt from spent $LiCoO_2$ (LCO) batteries using succinic acid in the presence of H_2O_2. They achieved almost complete cobalt and substantial lithium leaching—nearly 100% and 96%, respectively, under optimal conditions of 1.5 M succinic acid concentration, 4 vol% H_2O_2, 15 g/L S/L ratio, 70 °C reaction temperature, and 40 min reaction time. In a separate study by Li et al. [9], lithium and cobalt were leached from cathodic LCO material using citric acid and H_2O_2. Under the best conditions of 1.25 M citric acid, 1 vol% H_2O_2, a 20 g/L S/L ratio, and 90 °C reaction temperature, they achieved a recovery of 93% for cobalt and 99% for lithium within 30 min. Li et al. [11] explored the extraction of cobalt and lithium from LCO cathodic material in spent LIB using DL-malic acid as a leaching agent. They achieved a recovery of 93% cobalt and 99% lithium after leaching with 1.5 M DL-malic acid and 2.0 vol% H_2O_2 at 90 °C and a 20 g/L S/L ratio within a 40 min reaction time.

Previous research findings highlight the significance of acid concentration and H_2O_2 in influencing the leaching process. Li et al. [11] studied the effect of DL-malic acid concentration on the extraction of lithium and cobalt. They found that an acid concentration of 1.5 M led to optimal results, with up to 93% cobalt and 99% lithium dissolution. Similarly, Li et al. [9] examined the effect of citric acid concentration on leaching and reported that the leaching efficiency increased by about 70% for cobalt and 63% for lithium when the citric acid concentration was increased from 0.3 M to 1.25 M. Comparable findings were reported by Li et al. [10,12] when using succinic acid or lactic acid as leaching agents. Additionally, investigations by Gao et al. [13], Li et al. [9–11], and Gerold [14] explored the impact of H_2O_2 addition, highlighting its role in aiding the dissolution of LIB cathodic materials. In particular, H_2O_2 facilitates the dissolution of compounds such as $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (NMC111), $LiCoO_2$ (LCO), or $LiMn_2O_4$ (LMO) by reducing Co^{3+} and Mn^{4+} into the more soluble Co^{2+} and Mn^{2+}. This process also promotes the dissolution of nickel and lithium, as these metals are part of the same oxide compound [9,13].

Compared to other methods for metal separation, co-precipitation is often regarded as the simplest, most effective, and cost-efficient technique. Various coprecipitating agents are known, including sodium hydroxide, sodium carbonate, and oxalic acid [15]. He et al. and Yang et al. documented the co-precipitation of Ni^{2+}, Co^{2+}, and Mn^{2+} ions

from the leach solution using sodium carbonate and sodium hydroxide [16,17]. Both co-precipitation methods require strict control of several factors, such as pH, temperature, and complexing agents, to achieve the desired materials. Furthermore, the hydroxide co-precipitation process must be carried out in an inert atmosphere to prevent the formation of inhomogeneous precipitates with varying crystal structures and compositions. In contrast, oxalic acid offers a simpler recovery process without the need for an inert atmosphere and strict control over co-precipitation parameters [15]. In the co-precipitation process, the metal ions are co-precipitated, resulting in the formation of water-insoluble metal compounds. In a typical precipitation process, each metal ion, namely lithium, cobalt, nickel, and manganese ions, are precipitated individually using different separation methods, resulting in the formation of diverse compounds. This traditional precipitation method is considered very complicated and time-consuming. Additionally, the isolated cobalt, nickel, and manganese salts are later recombined during the regeneration or resynthesis of cathode materials, such as NMC111 [18]. To avoid the need for individual separation, a novel approach by using oxalic acid co-precipitation has been devised to precipitate the valuable metal salts simultaneously. The resulting salts are suitable for subsequent calcination to form oxides or serve as precursors for the regeneration of the new cathode material [15,19,20].

Among organic acids, oxalic acid exhibits relatively strong acidity. At standard room temperature, the equilibrium constant (Ka) for the initial H^+ dissociation is 5.37×10^{-2} mol/L (pKa = 1.27). The subsequent loss of the second H^+ results in the formation of oxalate ions, governed by an equilibrium constant of 5.25×10^{-5} mol/L (pKa = 4.28). The dissociation process of oxalic acid can be depicted using the following reactions [19,21]:

$$H_2C_2O_4 \leftrightarrow HC_2O_4^- + H^+ \qquad K_{a1} = 5.37 \times 10^{-2}\ \text{mol/L} \tag{1}$$

$$HC_2O_4^- \leftrightarrow C_2O_4^{2-} + H^+ \qquad K_{a2} = 5.25 \times 10^{-5}\ \text{mol/L} \tag{2}$$

The oxalate ion (IUPAC: ethanedioate ion) is a bidentate anionic ligand with the capacity to donate two pairs of electrons to a metal ion. Due to its ability to bind to a metal cation at two different sites, this ligand is commonly referred to as a chelating ligand [22]. In historical contexts, oxalate has been used as a precipitating agent in rare earth extraction processes [23,24]. The solubility of oxalate compounds varies depending on the interactions between the metal and the ligand. Table 1 categorizes metal oxalate compounds in battery recycling into soluble and insoluble types. Compounds with a solubility of less than 1 g/L of water at 25 °C are considered qualitatively insoluble. The differences in the solubility among various metal oxalate species can be strategically utilized to achieve effective metal separation [25].

Table 1. Qualitative water solubility for relevant oxalate compounds in battery recycling at 25 °C data from ref. [26].

Compounds (Insoluble)	Compounds (Soluble)
$Al_2(C_2O_4)_3 \cdot H_2O$	$Fe(C_2O_4)_3$
$CoC_2O_4 \cdot 2H_2O$	$Li_2C_2O_4$
$CuC_2O_4 \cdot 0.5H_2O$	-
$FeC_2O_4 \cdot 2H_2O$	-
$MnC_2O_4 \cdot 2H_2O$	-
$Ni_2C_2O_4 \cdot 2H_2O$	-

Oxalate derived from organic sources has minimal to no impact on the environment and is generally safer to handle compared to conventional inorganic acids. Furthermore, it holds the promise of facilitating the development of a more energy-efficient process. Given these attributes, oxalate holds immense potential to establish a robust foundation for future advancements in metal separation [1,22].

The main aim of this study is to investigate the processes for recovering cobalt, nickel, and manganese from an organic leach solution of spent LIB (pyrolyzed black mass of $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$, NMC111) using co-precipitation of metal oxalates. "Black mass" refers to a mixture obtained from pre-treatment processing of spent batteries. In the initial stage, experiments will be conducted utilizing citric acid, DL-malic acid, and succinic acid as organic leaching agents with varying acid concentrations and amounts of H_2O_2. Once the optimal organic acid and experimental parameters are determined, these factors will be then employed as parameters in making a leach solution, which was subsequently utilized in the following process of co-precipitation. In the co-precipitation process, oxalic acid will be employed as the precipitating agent. Subsequently, experiments will be conducted, varying the oxalic acid-to-metal ratios to obtain the optimal recovery values for nickel, manganese, and cobalt.

2. Materials and Methods

The experimental method utilized in this study comprised three major stages—black mass preparation (pyrolysis and mechanical pre-treatment), organic acid leaching, and oxalate precipitation. The overview of the experiment can be seen in Figure 1.

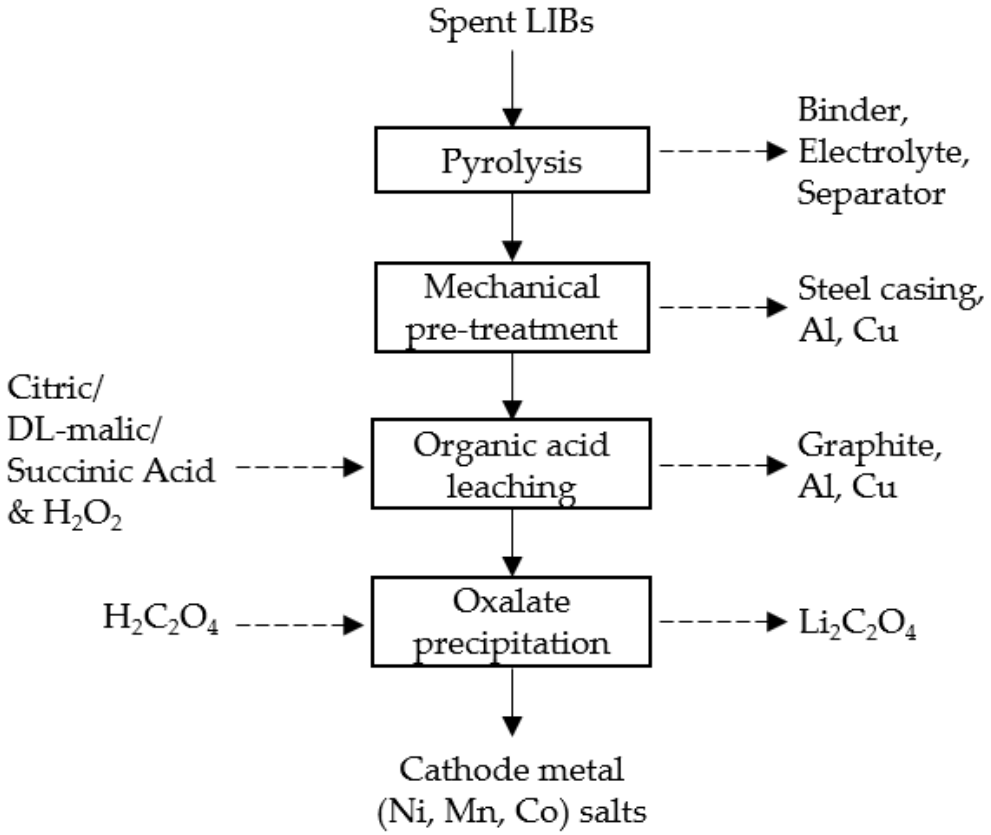


Figure 1. Process flow diagram of the experiment in this study.

2.1. Preparation of the Black Mass

NMC materials ($LiNi_xCo_yMn_{1-x-y}O_2$) sourced from spent LIBs (supplied by Litacells) were used in the experimental investigations. Initially, the batteries were disassembled into individual cells by the material supplier to initiate the investigation. Subsequently, the batteries were subjected to pyrolysis at a temperature of 550 °C [27] and operated for approximately three hours to facilitate the separation of organic compounds, particularly the binder that binds the aluminum foil and cathode. The bonding between the aluminum foil and cathode can potentially affect the extraction of valuable metals in subsequent processes [28]. After pyrolysis, the samples were passed through a series of mechani-

cal processes to decrease particle size, remove steel casing, aluminum, and copper, and attain uniformity before being used as feed material (black mass) in leaching and precipitation processes. Before being utilized in the next process, the composition of black mass was determined by inductively coupled plasma optical emission spectrometry (ICP-OES; Agilent 5900 SVDS, Waldbronn, Germany). For the sample, 50 mg of black mass was dissolved using 8 mL aqua regia (6 mL HCl and 2 mL HNO_3) in a microwave pressure digestion (Multiwave PRO; Anton-Paar, Graz, Austria; 30 min holding time, 200 °C and up to 50 bar). Table 2 shows the composition of the black mass resulting from this analysis. This analysis identified that the type of batteries used in the experiments is NMC111 ($LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$).

Table 2. Metal composition of the black mass.

Al	Cu	Co	Li	Mn	Ni	Fe	C
%	%	%	%	%	%	%	%
4.65	0.25	8.80	3.20	8.17	8.80	0.07	43.10

2.2. Organic Acid Leaching Procedure

Three organic acids, including citric acid, DL-malic acid, and succinic acid, were evaluated for their leaching performance to determine the appropriate leaching agent. The organic acid concentration and volume of H_2O_2 were varied, while the leaching temperature, S/L ratio, and reaction time were kept constant (see Table 3). The values for each parameter are based on the optimal values used in several previous studies [9,29–33]. The organic acid with the best leaching performance will be used as the leaching agent for the feed in the following precipitation procedure.

Table 3. Variable and fixed parameters for organic acid leaching experiment.

Variable Parameters	Fixed Parameters
Leaching agent (Citric acid, DL—Malic acid, Succinic acid)	Leaching temperature (80 °C)
Acid concentration (1 M, 2 M)	S/L ratio (20 g/L)
Volume of H_2O_2 (1 vol%, 4 vol%)	Reaction time (60 min)

Leaching with organic acid solutions of the desired concentration was carried out in a closed leaching reactor with a capacity of 1 L. The aqueous solutions of organic acids were prepared by dissolving appropriate amounts of pure citric acid (Merck, Darmstadt, Germany, >99.5%), DL-malic acid (Sigma Aldrich, ≥98%; Darmstadt, Germany), or succinic acid (Sigma Aldrich, ≥99%) in deionized water. After the acid was added to the leaching reactor, the impeller and the heater were set to 250 rpm and 80 °C, respectively. Once the actual temperature was 80 °C, the sample (black mass) with an S/L ratio of 20 g/L was inserted into the reactor slowly. The reaction time for the experiment was 60 min. During the experiment, H_2O_2 was gradually added. The leach solution was separated from the leaching residues by vacuum filtration. Afterward, samples of the leach solution were characterized using ICP-OES. The leaching efficiencies of metals were described according to Equation (3):

$$\text{Leaching efficiency } (\%) = \frac{L2}{L1} \times 100\% \quad (3)$$

where $L1$ represents the amount of metal present in the initial feed or black mass before leaching, while $L2$ denotes the amount of metal dissolved in the solution. All experiments were carried out three times to guarantee a high reliability of the obtained results.

2.3. Oxalate Precipitation Procedure

Oxalic acid ($H_2C_2O_4$) was used to separate the mixed cobalt, nickel, and manganese from the organic acid leach solutions. The oxalic acid solution (PanReac AppliChem, >99.50%; Bremen, Germany) was added to the leach solutions at 50 °C [34] at various molar ratios (see Table 4). This procedure took place on the magnetic stirring device (250 rpm) for 60 min before the suspension was filtrated by vacuum filtration. The color of the residue was light pink. The ICP-OES characterization was performed on filtrate samples. The calculation of metal recovery percentages was determined using Equation (4).

$$\text{Metal recovery } (\%) = \frac{M1 - M2}{M1} \times 100\% \quad (4)$$

where $M1$ stands for the quantity of metal in the solution before precipitation, whereas $M2$ signifies the amount of metal remaining in the solution after the precipitation process. All experiments were carried out three times to guarantee a high reliability of the obtained results.

Table 4. Parameters of the precipitation experiments.

Exp.	Precipitating Agent	Conditions			
		Temp.	Reaction Time	pH	Molar Ratio of M^{2+} to Oxalic Acid
		(°C)	(min)	-	-
1	Oxalic Acid	50	60	2 ± 0.1	1:3
2	Oxalic Acid	50	60	2 ± 0.1	1:4.5
3	Oxalic Acid	50	60	2 ± 0.1	1:6
4	Oxalic Acid	50	60	2 ± 0.1	1:7.5

3. Results

3.1. Organic Acid Leaching Results

The effect of organic acid used on cobalt, nickel, and manganese leaching with 1 M concentration and 1% H_2O_2 is shown in Figure 2. The figure shows that citric acid has the highest efficiency in leaching cobalt, nickel, and manganese with an efficiency range of approximately 97%. This is closely followed by DL-malic acid with an efficiency of around 95% and succinic acid with an efficiency ranging from 89% to 90%.

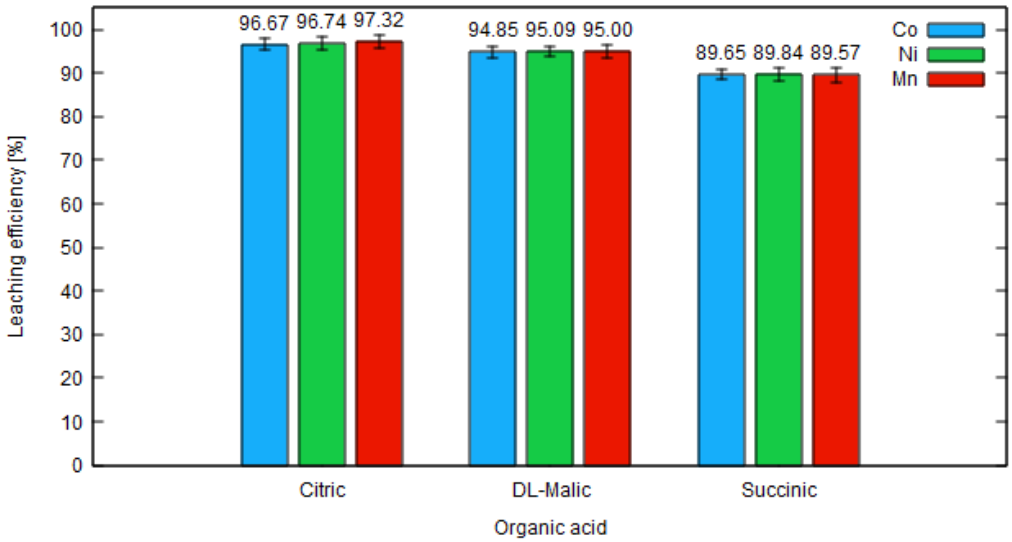


Figure 2. Effect of different organic acids on cobalt, nickel, and manganese leaching with 1 M concentration and 1 vol% H_2O_2.

Figure 3 demonstrates the effect of different citric acid concentrations on cobalt, nickel, and manganese leaching in 1 vol% H_2O_2. The graph indicates an increase in the leaching rate when the citric acid concentration increases from 1 M to 2 M. At a concentration of 1 M, the leaching percentages for cobalt, nickel, and manganese were 96.67%, 96.74%, and 97.32%, respectively. Increasing the concentration to 2 M led to an increase in the leaching percentage to 98.99% for cobalt, 98.91% for nickel, and 98.84% for manganese.

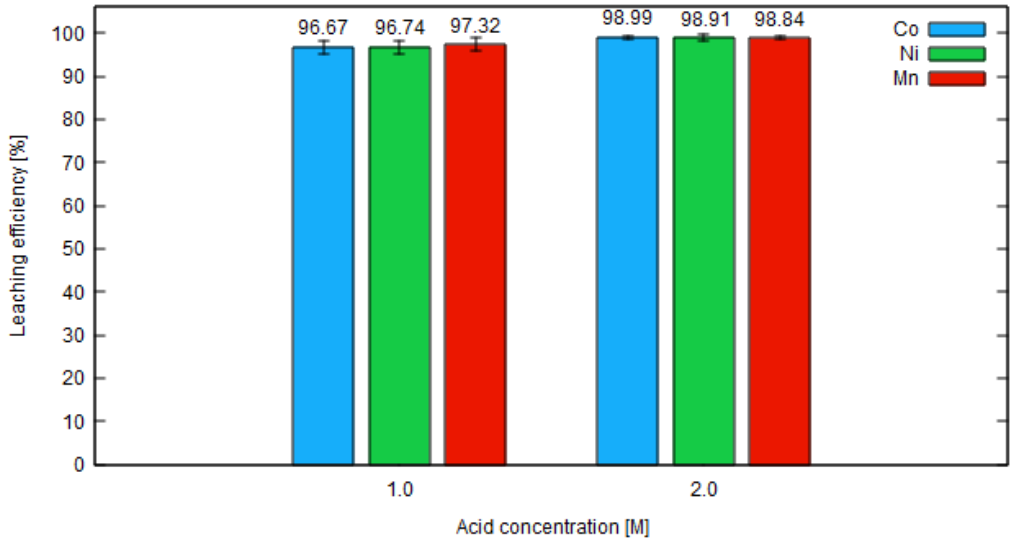


Figure 3. Effect of citric acid concentration on cobalt, nickel, and manganese leaching with 1 vol% H_2O_2.

Leaching investigations were also carried out to analyze the effect of adding H_2O_2 on the leaching process. The effect of H_2O_2 on cobalt, nickel, and manganese recovery in 1 M citric acid is shown in Figure 4. An increased addition of H_2O_2 resulted in a slightly faster leaching kinetic. At 1 vol% H_2O_2, the leaching percentages were 96.67% for cobalt, 96.74% for nickel, and 97.32% for manganese. When increasing to 4 vol% H_2O_2, the leached percentages for cobalt, nickel, and manganese increased slightly and reached 97.16%, 96.75%, and 97.77%, respectively.

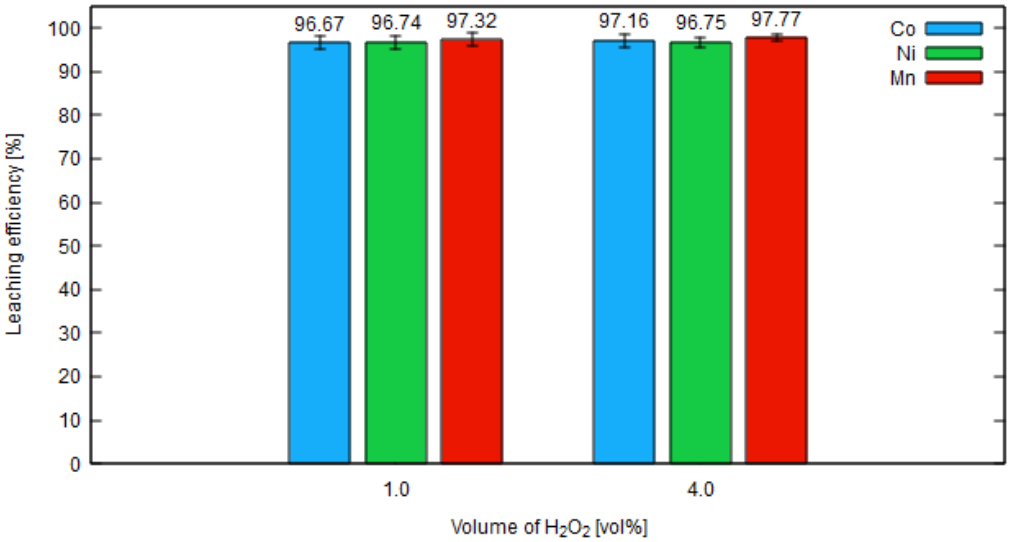


Figure 4. Effect of volume H_2O_2 on cobalt leaching with 1 M citric acid.

Throughout all conducted experiments, lithium and aluminum followed the same trend as the leaching cobalt, nickel, and manganese. This indicates that the trends observed are representative of the overall experimentation. From the collective trends observed, it is evident that the optimization of recovery values can be achieved by utilizing citric acid as the leaching agent at a concentration of 2 M and 4 vol% H_2O_2 volume. Figure 5 illustrates that when using 2 M citric acid and 4 vol% H_2O_2, the leaching efficiency of valuable metals such as cobalt, nickel, manganese, and lithium is around 99%, while aluminum, an impurity in the leach solution, has a recovery rate of about 33%. The metal concentrations in the aqueous solutions during the leaching process using citric acid 2 M and 4 vol% H_2O_2 are detailed in Table 5. Copper and iron are disregarded in the following stages of the process and are regarded as minor impurities due to their extremely low concentrations in aqueous solutions, specifically 1.81 ppm and 1.16 ppm, respectively.

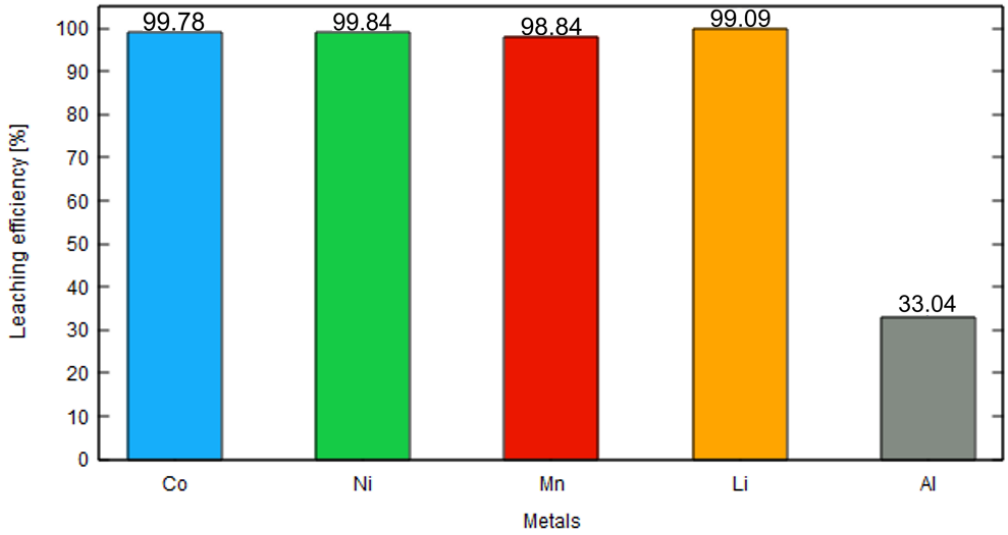


Figure 5. The leaching efficiency of metals with 2 M citric acid, and 4 vol % H_2O_2.

Table 5. Metal composition of the organic acid leach solution (2 M citric acid and 4 vol% H_2O_2).

Al	Cu	Co	Li	Mn	Ni	Fe
g/L	ppm	g/L	g/L	g/L	g/L	ppm
0.31	1.81	1.75	0.63	1.62	1.75	1.16

To obtain maximum efficiency in leaching and optimize the subsequent precipitation experiments, the following parameters were employed in the leaching process: a citric acid concentration of 2 M, H_2O_2 of 4 vol%, a leaching temperature of 80 °C, an S/L ratio of 20 g/L, and a reaction time of 60 min.

3.2. Oxalate Precipitation Results

The precipitation of metals from the leach solution was investigated by the addition of different molar ratios of oxalic acid. Figure 6 depicts the relationship between the molar ratio of M^{2+} to oxalic acid and the percentage recovery of metals. The diagram clearly shows that the addition of oxalic acid leads to a significant increase in metal precipitation. In the case of cobalt, the lowest ratio (1:3) yields a 97.69% recovery. Increasing the ratio to 1:4.5 leads to a significant improvement, reaching 99.22%, and further increases to 1:6 and 1:7.5 lead to cobalt recoveries of 99.27% and 99.26%, respectively. Nickel recovery exhibits a similar pattern, with an increase from 91.56% at the ratio of 1:3 to 98.55% at 1:4.5, at ratios of 1:6 and 1:7.5, the increase is comparatively lower at less than 0.5%. Manganese recovery follows a more gradual progression, starting at 63.70% at 1:3, increasing to 86.87% at 1:4.5, 91.23% at 1:6, and peaking at 94.01% at 1:7.5. Compared to cobalt and nickel, manganese

recovery is lower. This reduced recovery can be attributed to the higher solubility of manganese in the oxalate form when compared to cobalt and nickel [35].

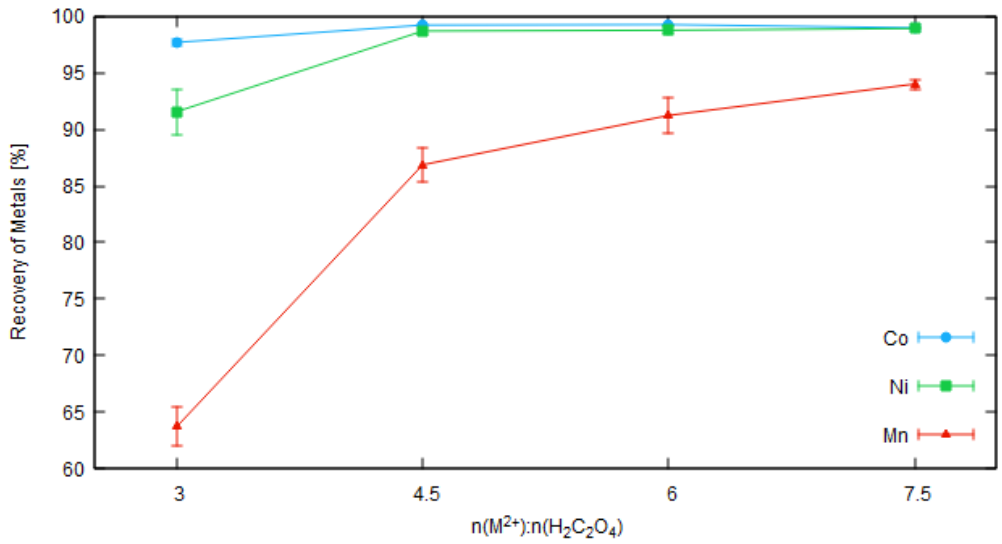


Figure 6. The effect of the molar ratios of M^{2+} to oxalic acid on the recovery of cobalt, nickel, and manganese.

As previously discussed, the addition of an oxalic acid ratio has an impact on the overall increase in metal recovery, including lithium and aluminum, which are not intended to be separated in this process. Figure 7 illustrates a gradual increase in lithium precipitation, starting from 12.25% at a ratio of 1:3 up to 37.60% at a ratio of 1:7.5. Similarly, aluminum shows an upward trend in recovery, from 22.82% at a ratio of 1:3 to 40.72% at a ratio 1:7.5. It should be emphasized that the increased recovery of these two metals is undesirable, as it would diminish purity and leads in losses during subsequent purification processes.

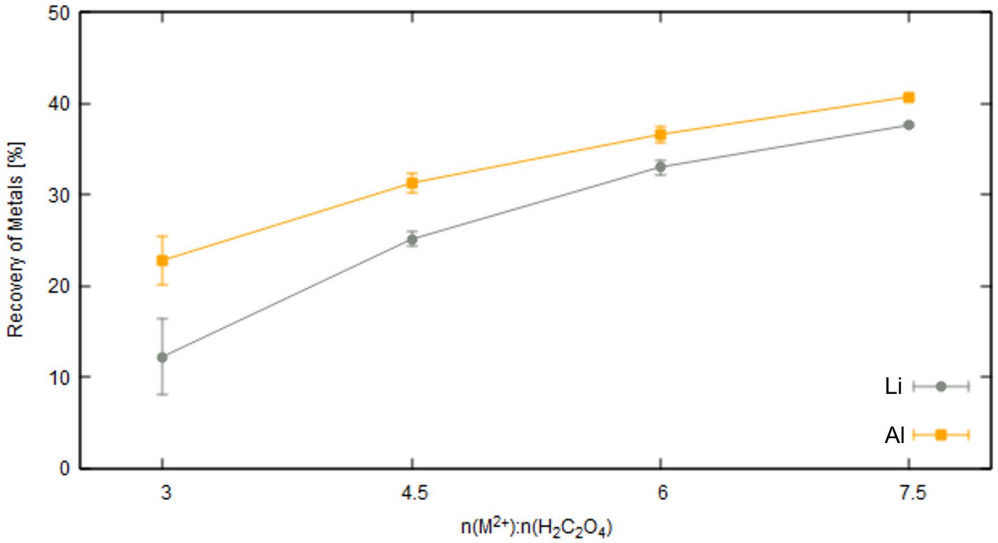


Figure 7. The effect of the molar ratios of M^{2+} to oxalic acid on the recovery of aluminum and lithium.

4. Discussion

4.1. Organic Acid Leaching

The leaching utilized agent can considerably affect leaching efficiency. The experiments showed that citric acid has the best leaching efficiency for the used black mass (Figure 2). Citric acid, being an eco-friendly organic acid, serves as an effective leaching agent because of its relatively high acidity compared to the other used organic acids. As a result, three moles of H^+ ions are released per one mole of citric acid. This differs from DL-malic acid

and succinic acid, which dissociate in two steps. Thus, it can be inferred that citric acid generates a higher quantity of H^+ ions in the solution compared to DL-malic acid and succinic acid [29]. In addition, citric acid can form complexes with valuable metals due to its three carboxylic acid groups, making it one of the best chelating agents [30]. This can support the following precipitation of the valuable metals as metal oxalate.

Further investigations also showed that increasing the concentration of citric acid from 1 M to 2 M improved the leaching efficiency. This demonstrates that the concentration of H^+ ions has a significant influence on the leaching efficiency of valuable metals. The use of citric acid as a leaching agent has a considerable advantage not only from a technical but also from an economic and ecological point of view. As a primary chemical, it is one of the most cost-effective organic acids produced by biomass fermentation [36].

Numerous researchers have looked into the potential of adding a reducing agent to a leaching agent to improve the leaching performance. Compared to other reducing agents such as ascorbic acid and glucose, hydrogen peroxide (H_2O_2) is a more affordable and widely accessible chemical. The addition of H_2O_2 was intended to increase the efficiency of leaching by reducing the oxidation state of valuable metal oxides such as cobalt and manganese (Co^{3+} and Mn^{4+}) to their more soluble form (Co^{2+} and Mn^{2+}), while nickel is also promoted as it is present in the same oxide compound [9]. In the conducted experiments, it was observed that 4 vol% H_2O_2 exhibits a higher leaching value compared to 1 vol% H_2O_2. The improvement in leaching efficiency with an increase in the amount of H_2O_2 can be associated with the fact that the quantity of H_2O_2 available when using 1 vol% H_2O_2 is insufficient for interaction with valuable metals, as it is prematurely consumed by other metals [37] or decomposes [9]. An increase in the quantity of H_2O_2 allows more H_2O_2 to interact with the valuable metals before it is consumed by other metals or decomposed by temperature, for example, resulting in increased leaching efficiency.

The leaching efficiency results of 99% with the best process parameters (2 M citric acid and 4 vol% H_2O_2) show that citric acid can be used as an efficient leaching agent in the extraction of valuable metals. These results can be compared with the results of inorganic leaching agents such as sulfuric acid with the same leaching efficiencies [32]. Besides its good effectiveness, the leaching has a significant degree of selectivity. The results demonstrate that the leaching efficiency of aluminum, which serves as a major impurity for subsequent stages, is only at 33%. This is in strong contrast to inorganic acids such as sulfuric acid, where the leaching processes normally exhibit a lack of selectivity (about 99.5% of aluminum leached) [32].

4.2. Oxalate Precipitation

In addition to the optimal process parameters for leaching, the optimization of the precipitation process is of major importance to achieve a high recovery rate of the valuable metals. Furthermore, economic considerations and the saving of resources should also be taken into account [38]. For this reason, a stoichiometric precipitation factor was determined to optimize the precipitation process. The scope of the study included a molar ratio of M^{2+} (M = Co, Ni, Mn) to oxalic acid ranging from 1:3 to 1:7.5, as defined by the reaction in Equation (5) [15,19].

$$M^{2+} - C_6H_6O_7\ (aq) + H_2C_2O_4\ (aq) \rightarrow MC_2O_4\ (s) + C_6H_8O_7\ (aq) \quad (5)$$

The comprehensive results of the experiments carried out showed that the 1:7.5 ratio gave the highest metal recovery (see Table 6). This outcome implies a direct relationship between the amount of oxalic acid added to the leach solution and the subsequent increase in metal recovery. The increase in the amount of oxalic acid results in a higher concentration of oxalate ions available in the solution, which form more precipitates with the desired metals. As the market values of cobalt and nickel are significantly higher than those of manganese, choosing the 1:4.5 ratio, which requires less oxalic acid consumption compared to the 1:6 and 1:7.5 ratios, is the more cost-effective option (see Table 6). While the amount of manganese recovered is not as low as the 1:6 and 1:7.5 ratios, the 1:4.5 ratio yields the

same percentage of cobalt and nickel recovery as the 1:6 and 1:7.5 ratios. Furthermore, not only is it less expensive, but using the 1:4.5 ratio also decreases the amount of impurities in the form of lithium and aluminum, increasing the purity of the precipitate.

Table 6. Metal recoveries at different molar ratios (M^{2+} to oxalic acid) during the co-precipitation process.

Molar Ratio	Co %	Ni %	Mn %	Li %	Al %
1:3	97.95	93.58	65.42	16.43	25.43
1:4.5	99.22	98.55	86.87	25.12	31.27
1:6	99.27	98.77	91.23	33.02	36.60
1:7.5	99.26	98.93	94.01	37.60	40.7

Increasing the molar ratio provides the system with an increased quantity of available oxalate ions. As a result, in addition to the valuable metals, more lithium and impurities such as aluminum react with the oxalate ions and form insoluble oxalate complexes, which are also precipitated. This reduces the purity of the precipitation product, which affects its quality for use as a precursor material for the production of battery-grade materials. To accomplish the separation of present impurities and obtain a high-quality product, further investigation is required. This may involve processes such as using formic acid to separate lithium [39] or employing NaOH to separate aluminum [40].

A quantitative analysis of the metal ion composition in the precipitate using ICP-OES (see Table 7) revealed that the proportions of nickel, manganese, and cobalt from the molar ratio of 1:7.5 were closest to the actual NMC111 ratio, which is 1:1:1. However, there was a slightly lower amount of manganese in the precipitate (Ni:Mn:Co = 1:0.86:0.97) due to the higher solubility of manganese oxalate. When utilized as a precursor for the resynthesis or regeneration of NMC111, this precipitate requires further processing, which involves high-temperature heating (about 800–950 °C) [15].

Table 7. The final composition of the solid precipitate in the different molar ratios after the co-precipitation process.

Molar Ratio	Co %	Ni %	Mn %	Li %	Al %
1:3	12.76	12.64	7.92	0.81	0.58
1:4.5	11.27	11.60	9.32	1.05	0.60
1:6	11.30	11.61	9.80	1.46	0.71
1:7.5	11.10	11.45	9.80	1.58	0.79

Author Contributions: Conceptualization, D.S., H.P., A.B., R.Y. and B.F.; methodology, D.S. and H.P.; validation, R.Y. and B.F.; formal analysis, D.S. and H.P.; investigation, D.S., H.P., A.B., R.Y. and B.F.; data curation, D.S. and H.P.; writing—original draft preparation, H.P.; writing—review and editing, D.S., A.B. and R.Y.; visualization, D.S. and H.P.; supervision, D.S., A.B., R.Y. and B.F.; project administration, D.S., A.B. and B.F.; funding acquisition, D.S., A.B., R.Y. and B.F. All authors have read and agreed to the published version of the manuscript.

Funding: The project on which this report/publication is based was funded by the German Federal Ministry of Education and Research within the Competence Cluster Recycling & Green Battery (greenBatt) under grant number 03XP0351A. The authors are responsible for the contents of this publication. H.P. was funded via a DAAD scholarship in the frame of the long-year TGGS-RWTH collaboration. The scholarship application was initiated by R.Y. All other costs were covered by the IME—RWTH Aachen University.

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Zheng, X.; Zhu, Z.; Lin, X.; Zhang, Y.; He, Y.; Cao, H.; Sun, Z. A Mini-Review on Metal Recycling from Spent Lithium Ion Batteries. *Engineering* **2018**, *4*, 361–370. [CrossRef]
2. MarketsandMarkets. A Lithium-Ion Battery Market by Type (Lithium Nickel Manganese Cobalt Oxide (Li-NMC), Lithium Iron Phosphate (LFP), Lithium Cobalt Oxide (LCO), Capacity, Voltage, Industry (Consumer Electronics, Automotive, Aerospace) Global Forecast–2031. 2022. Available online: https://www.marketsandmarkets.com/Market-Reports/lithium-ion-battery-market-49714593.html (accessed on 20 January 2023).
3. European Commision. Critical Raw Materials. 2023. Available online: https://single-market-economy.ec.europa.eu/sectors/raw-materials/areas-specific-interest/critical-raw-materials_en (accessed on 22 August 2023).
4. Punt, T. Selective Recovery of Metals from Citric Acid Leach Solutions during the Recycling of Lithium-Ion Batteries. Ph.D. Thesis, Stellenbosch University, Stellenbosch, South Africa, 2022.
5. Lie, J.; Liu, J.-C. Closed-Vessel Microwave Leaching of Valuable Metals from Spent Lithium-Ion Batteries (LIBs) Using Dual-Function Leaching Agent: Ascorbic Acid. *Sep. Purif. Technol.* **2021**, *266*, 118458. [CrossRef]
6. Sun, L.; Qiu, K. Vacuum Pyrolysis and Hydrometallurgical Process for the Recovery of Valuable Metals from Spent Lithium-Ion Batteries. *J. Hazard. Mater.* **2011**, *194*, 378–384. [CrossRef] [PubMed]
7. Meshram, P.; Mishra, A.; Abhilash; Sahu, R. Environmental Impact of Spent Lithium-Ion Batteries and Green Recycling Perspectives by Organic Acids—A Review. *Chemosphere* **2020**, *242*, 125291. [CrossRef]
8. Naseri, T.; Pourhossein, F.; Mousavi, S.M.; Kaksonen, A.H.; Kuchta, K. Manganese Bioleaching: An Emerging Approach for Manganese Recovery from Spent Batteries. *Rev. Environ. Sci. Biotechnol.* **2022**, *21*, 447–468. [CrossRef]
9. Li, L.; Ge, J.; Wu, F.; Chen, R.; Chen, S.; Wu, B. Recovery of Cobalt and Lithium from Spent Lithium-Ion Batteries Using Organic Citric Acid as Leachant. *J. Hazard. Mater.* **2010**, *176*, 288–293. [CrossRef]
10. Li, L.; Qu, W.; Zhang, X.; Lu, J.; Chen, R.; Wu, F.; Amine, K. Succinic Acid-Based Leaching System: A Sustainable Process for Recovery of Valuable Metals from Spent Li-Ion Batteries. *J. Power Sources* **2015**, *282*, 544–551. [CrossRef]
11. Li, L.; Ge, J.; Chen, R.; Wu, F.; Chen, S.; Zhang, X. Environmental Friendly Leaching Reagent for Cobalt and Lithium Recovery from Spent Lithium-Ion Batteries. *Waste Manag.* **2010**, *30*, 2615–2621. [CrossRef]
12. Li, L.; Fan, E.; Guan, Y.; Zhang, X.; Xue, Q.; Wei, L.; Wu, F.; Chen, R. Sustainable Recovery of Cathode Materials from Spent Lithium-Ion Batteries Using Lactic Acid Leaching System. *ACS Sustain. Chem. Eng.* **2017**, *5*, 5224–5233. [CrossRef]
13. Gao, W.; Zhang, X.; Zheng, X.; Lin, X.; Cao, H.; Zhang, Y.; Sun, Z. Lithium Carbonate Recovery from Cathode Scrap of Spent Lithium-Ion Battery: A Closed-Loop Process. *Environ. Sci. Technol.* **2017**, *51*, 1662–1669. [CrossRef]
14. Gerold, E.; Schinnerl, C.; Antrekowitsch, H. Critical Evaluation of the Potential of Organic Acids for the Environmentally Friendly Recycling of Spent Lithium-Ion Batteries. *Recycling* **2022**, *7*, 4. [CrossRef]
15. Refly, S.; Floweri, O.; Mayangsari, T.R.; Sumboja, A.; Santosa, S.P.; Ogi, T.; Iskandar, F. Regeneration of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ Cathode Active Materials from End-of-Life Lithium-Ion Batteries through Ascorbic Acid Leaching and Oxalic Acid Coprecipitation Processes. *ACS Sustain. Chem. Eng.* **2020**, *8*, 16104–16114. [CrossRef]
16. He, L.-P.; Sun, S.-Y.; Yu, J.-G. Performance of LiNi1/3Co1/3Mn1/3O2 Prepared from Spent Lithium-Ion Batteries by a Carbonate Co-Precipitation Method. *Ceram. Int.* **2018**, *44*, 351–357. [CrossRef]
17. Yang, Y.; Huang, G.; Xie, M.; Xu, S.; He, Y. Synthesis and Performance of Spherical $LiNi_xCo_yMn_{1-x-Y}O_2$ Regenerated from Nickel and Cobalt Scraps. *Hydrometallurgy* **2016**, *165*, 358–369. [CrossRef]
18. Wang, H.; Friedrich, B. Development of a Highly Efficient Hydrometallurgical Recycling Process for Automotive Li–Ion Batteries. *J. Sustain. Metall.* **2015**, *1*, 168–178. [CrossRef]
19. Kang, J.; Sohn, J.; Chang, H.; Senanayake, G.; Shin, S.M. Preparation of Cobalt Oxide from Concentrated Cathode Material of Spent Lithium Ion Batteries by Hydrometallurgical Method. *Adv. Powder Technol.* **2010**, *21*, 175–179. [CrossRef]
20. Refly, S.; Floweri, O.; Mayangsari, T.R.; Aimon, A.H.; Iskandar, F. Green Recycle Processing of Cathode Active Material from $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (NCM 111) Battery Waste through Citric Acid Leaching and Oxalate Co-Precipitation Process. *Mater. Today Proc.* **2021**, *44*, 3378–3380. [CrossRef]
21. Li, L.; Lu, J.; Zhai, L.; Zhang, X.; Curtiss, L.; Jin, Y.; Wu, F.; Chen, R.; Amine, K. A Facile Recovery Process for Cathodes from Spent Lithium Iron Phosphate Batteries by Using Oxalic Acid. *CSEE J. Power Energy Syst.* **2018**, *4*, 219–225. [CrossRef]
22. Verma, A.; Kore, R.; Corbin, D.R.; Shiflett, M.B. Metal Recovery Using Oxalate Chemistry: A Technical Review. *Ind. Eng. Chem. Res.* **2019**, *58*, 15381–15393. [CrossRef]
23. Royen, H.; Fortkamp, U. *Rare Earth Elements-Purification, Separation and Recycling*; Technical Report No. C211; IVL Svenska Miljöinstitutet: Stockholm, Sweden, 2016.
24. Lakshmanan, V.; Sridhar, R.; Halim, M.A. Process for Extraction of Rare Earth Elements. U.S. Patent 20130283977A1, 8 April 2013.
25. Hall, W.T. The Oxalate Method for Separating Calcium and Magnesium. *J. Am. Chem. Soc.* **1928**, *50*, 2704–2707. [CrossRef]
26. Haynes, W.M.; Lide, D.R.; Bruno, T.J. *CRC Handbook of Chemistry and Physics: A Ready-Reference Book of Chemical and Physical Data*, 97th ed.; CRC Press: Boca Raton, FL, USA, 2017.
27. Schwich, L.; Sabarny, P.; Friedrich, B. Recycling Potential of Lithium–Sulfur Batteries—A First Concept Using Thermal and Hydrometallurgical Methods. *Metals* **2020**, *10*, 1513. [CrossRef]
28. Zhang, G.; Du, Z.; He, Y.; Wang, H.; Xie, W.; Zhang, T. A Sustainable Process for the Recovery of Anode and Cathode Materials Derived from Spent Lithium-Ion Batteries. *Sustainability* **2019**, *11*, 2363. [CrossRef]

29. Golmohammadzadeh, R.; Rashchi, F.; Vahidi, E. Recovery of Lithium and Cobalt from Spent Lithium-Ion Batteries Using Organic Acids: Process Optimization and Kinetic Aspects. *Waste Manag.* **2017**, *64*, 244–254. [CrossRef] [PubMed]
30. Musariri, B.; Akdogan, G.; Dorfling, C.; Bradshaw, S. Evaluating Organic Acids as Alternative Leaching Reagents for Metal Recovery from Lithium Ion Batteries. *Miner. Eng.* **2019**, *137*, 108–117. [CrossRef]
31. Fan, B.; Chen, X.; Zhou, T.; Zhang, J.; Xu, B. A Sustainable Process for the Recovery of Valuable Metals from Spent Lithium-Ion Batteries. *Waste Manag. Res. J. A Sustain. Circ. Econ.* **2016**, *34*, 474–481. [CrossRef] [PubMed]
32. Gao, W.; Liu, C.; Cao, H.; Zheng, X.; Lin, X.; Wang, H.; Zhang, Y.; Sun, Z. Comprehensive Evaluation on Effective Leaching of Critical Metals from Spent Lithium-Ion Batteries. *Waste Manag.* **2018**, *75*, 477–485. [CrossRef] [PubMed]
33. Yang, L.; Xi, G.; Xi, Y. Recovery of Co, Mn, Ni, and Li from Spent Lithium Ion Batteries for the Preparation of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ Cathode Materials. *Ceram. Int.* **2015**, *41*, 11498–11503. [CrossRef]
34. Nakajima, A.; Zheng, Q.; Ogawa, T.; Hirama, S.; Watanabe, M. Metal Recovery of $LiCoO_2$/$LiNiO_2$ Cathode Materials by Hydrothermal Leaching and Precipitation Separation. *ACS Sustain. Chem. Eng.* **2022**, *10*, 12852–12863. [CrossRef]
35. Rouquette, L.M.J.; Petranikova, M.; Vieceli, N. Complete and Selective Recovery of Lithium from EV Lithium-Ion Batteries: Modeling and Optimization Using Oxalic Acid as a Leaching Agent. *Sep. Purif. Technol.* **2023**, *320*, 124143. [CrossRef]
36. Pagliaro, M.; Meneguzzo, F. Lithium Battery Reusing and Recycling: A Circular Economy Insight. *Heliyon* **2019**, *5*, e01866. [CrossRef]
37. Chernyaev, A.; Zou, Y.; Wilson, B.P.; Lundström, M. The Interference of Copper, Iron and Aluminum with Hydrogen Peroxide and Its Effects on Reductive Leaching of $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$. *Sep. Purif. Technol.* **2022**, *281*, 119903. [CrossRef]
38. Gerold, E.; Luidold, S.; Antrekowitsch, H. Selective Precipitation of Metal Oxalates from Lithium Ion Battery Leach Solutions. *Metals* **2020**, *10*, 1435. [CrossRef]
39. Hou, J.; Ma, X.; Fu, J.; Vanaphuti, P.; Yao, Z.; Liu, Y.; Yang, Z.; Wang, Y. A Green Closed-Loop Process for Selective Recycling of Lithium from Spent Lithium-Ion Batteries. *Green Chem.* **2022**, *24*, 7049–7060. [CrossRef]
40. Ferreira, D.A.; Prados, L.M.Z.; Majuste, D.; Mansur, M.B. Hydrometallurgical Separation of Aluminium, Cobalt, Copper and Lithium from Spent Li-Ion Batteries. *J. Power Sources* **2009**, *187*, 238–246. [CrossRef]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.