

Article



Critical Evaluation of the Potential of Organic Acids for the Environmentally Friendly Recycling of Spent Lithium-Ion Batteries

Eva Gerold *, Clemens Schinnerl and Helmut Antrekowitsch

Chair of Nonferrous Metallurgy of Montanuniversitaet Leoben, 8700 Leoben, Austria; clemens.schinnerl@stud.unileoben.ac.at (C.S.); helmut.antrekowitsch@unileoben.ac.at (H.A.) * Correspondence: eva.gerold@unileoben.ac.at; Tel.: +43-3842-402-5207

Abstract: The need to recover valuable metals from spent lithium-ion batteries (LIBs) is undisputed. However, the environment and the climate are also affected by emissions from the recycling processes. Therefore, the call for environmentally friendly recycling methods is currently louder than ever. In the field of hydrometallurgical recovery of metals from spent LIBs, inorganic acids have so far proved to be an effective, but environmentally problematic, leaching agent, since the pollution of wastewater by high salt loads and the emission of toxic gases cannot be avoided. This has recently led to a trend towards the application of organic acids, as these have significantly more environmentally friendly properties. In order to continue this approach, and to improve it even further from an environmental point of view, this work focuses on the utilization of low leaching temperatures in combination with organic acids for the recovery of valuable metals from spent lithium-ion batteries. This can drastically reduce the required energy demand. Furthermore, attention is paid to higher $(50-100 \text{ g}\cdot\text{L}^{-1})$ solid-liquid ratios, which are indispensable, especially with regard to the economic establishment of the tested process. The experimental verification of the feasibility using citric, oxalic, and formic acid showed the possibility of an efficient recovery of cobalt, nickel, and lithium. In particular, citric acid in combination with hydrogen peroxide as a reducing agent appears to be a suitable and environmentally friendly alternative to classical inorganic acids, even at low process temperatures, for the hydrometallurgical recycling of lithium-ion batteries.

Keywords: lithium-ion batteries; recycling; recovery of critical elements organic acids; green chemicals

1. Introduction

The definition of the European Union's climate policy targets and the need to minimize CO₂ emissions worldwide means that there is no way of avoiding a change in the transportation sector. Sales of plug-in hybrids and battery electric vehicles have therefore increased considerably in recent years (see Figure 1a), which will also be reflected in a rapid growth rate in the coming years. For 2021, all regions, and most countries, witness strong increases in EV sales, whereas Europe (EU, EFTA, and UK) leads with a 14% EV share for the first six months combined. Thus, the sales of 6.4 million EVs are expected in 2021, representing a growth of 98% compared to 2020 (see Figure 1b). Depending on the scenario assumed, sales of EVs will increase to between 13.1 and 20 million by 2025, while by 2030 they are already expected to reach between 25.8 and 46.8 million units [1,2].

Considering the increasing sales of electric vehicles and the composition of lithium-ion batteries, with a focus on the cathode and anode materials used, the need for sustainable and climate-friendly recycling processes becomes obvious. Due to the multitude of possible cathode systems (NMC, NCA, LTO, LFP, etc.), the difficulty of establishing a uniform recycling process for spent LIBs also becomes apparent [3,4].



Citation: 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. https://doi.org/10.3390/ recycling7010004

Academic Editor: Sascha Nowak

Received: 15 December 2021 Accepted: 26 January 2022 Published: 31 January 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 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/).



Figure 1. Global plug-in vehicle sales (**a**) from 2016 to 2020 including preliminary calculation for 2021 and (**b**) distribution across most important regions for 2020 and 2021 [2].

Based on published life cycle assessments for lithium-ion batteries, the generic composition for NMC batteries can be summarized in Figure 2. It is obvious that aluminum constitutes the largest proportion of the battery in terms of mass since it is used in the cathode, as well as in the battery system periphery, module periphery, and cell housing. The data presented also indicates that about 55 wt.-% of a battery system belongs to the battery cells, which contain the electrolyte, the separator, the cell housing, and the electrodes. While the anode is a copper foil (Cu) coated mainly with graphite, the cathode coating consists of transition metal oxides, in this case lithium nickel cobalt manganese oxide (LiNi_{0.33}Co_{0.33}Mn_{0.33}O₂). An average EV battery system weighs approximately 350 kg. It can be deduced that 3.5 kg of lithium, 10.9 kg of nickel, 10.9 kg of cobalt, and 9.8 kg of manganese are required for a system, which emphasizes the importance of recycling [5,6].



Figure 2. Generic composition of a NMC battery system in (**a**) total shares of materials and (**b**) divided into individual components [5,6].

With regard to the commodities required for the production of these systems, it is necessary to promote the most efficient recovery route, especially for the used, critical raw materials. In the European Union, these include cobalt and lithium, as well as graphite, which highlights the precarious situation in this industry. The Cobalt Institute [7] estimates

that about 50% of the cobalt mined worldwide is used in secondary batteries and, in particular, in lithium-ion batteries. However, cobalt is classified as a critical metal and is particularly problematic with regard to the origin of approximately 60% of the world's mine production from the Democratic Republic of Congo, as both geopolitical instability and unethical labor practices have been documented in this context [3,4,7,8].

Additionally, the US Geological Survey [8] estimates that 39% of the mined lithium is used in primary and secondary lithium-based batteries. Although the accurate estimation of the world's lithium reserves is very challenging and therefore fraught with uncertainty, the development of the recycling processes for this critical element must be accelerated. In particular, the uneven geographical distribution of reserves can lead to significant fluctuations in the lithium market [3,8].

The aim of this publication is to demonstrate sustainable ways of processing spent lithium-ion batteries and recovering the critical metals they contain. It is focused on the utilization of low leaching temperatures in combination with organic acids for the recovery of scarce metals from active materials. Therefore, the following chapter summarizes the current state of research as well as the technology, especially with regard to hydrometallurgical recycling routes and with a special focus on sustainable solutions.

2. Recycling Chains for Lithium-Ion Batteries

The currently applied recycling methods can be divided into pyrometallurgical and hydrometallurgical process routes, with the latter showing a higher potential, especially in the area of selective metal recovery. For this reason, the hydrometallurgical processes for the recycling of lithium-ion batteries will be examined in more detail in this publication.

The pretreatment steps applied have a major influence on the establishment of effective recycling processes. Spent lithium-ion batteries often consist of a metal casing, a plastic cover, and an electric control unit [9]. Due to the arrangement of the cathode and anode collectively with the separator foil, a shredding of these components is necessary prior to hydrometallurgical processes in order to achieve a corresponding volume reduction [10,11]. Classical pretreatment methods include mechanical and thermal process steps, which subsequently can optimize both the consumption of acid for lixiviation and the leaching efficiency. In addition, a decrease in impurities can already be realized at this stage and thus has a positive effect on the further treatment, cleaning effort, and cost [12–14].

The first stage is usually a deactivation step, since due to the high potential of lithiumion batteries for spontaneous combustion during the dismantling process, this is essential for increasing the safety of these practises [6]. This includes processes such as shortcircuiting, discharging, but also thermal deactivation [15]. In the latter process, the spent lithium-ion batteries are exposed to a temperature of at least 300 °C to vaporize and decompose the components of the electrolyte, respectively, resulting in the opening of the battery cell [6,15]. Another effective way of deactivation is the application of a sodium chloride solution with the battery contacted for 24 h [16]. Mechanical processes that follow the deactivation are crushing, sieving, magnetic separation, fine crushing, and classification [17]. After separation of all components of a spent lithium-ion battery (e.g., metal casing, plastic cover, cathode, and anode), thermal processes are typically used to separate the binder and carbon contents of the spent LIB from the cathode material [11,15]. In order to realize high efficiencies in the leaching process, an additional grinding step often follows prior to the application of the cathode material in hydrometallurgical procedures [16]. By increasing the specific surface area, an optimization of the leaching success can be guaranteed [16]. Finally, it should be mentioned that in most cases a combination of thermal and mechanical treatments is used for spent lithium-ion batteries in order to ensure an effective treatment tailored to the subsequent hydrometallurgical process [15,18].

2.1. Hydrometallurgical Recycling Routes

In order to recover the valuable transition metals cobalt and nickel, as well as lithium, from the cathode and anode coatings, hydrometallurgical processes such as leaching,

extraction, crystallization, or precipitation are often applicated [19]. Hydrometallurgical recycling processes for lithium-ion batteries require the use of large volumes of chemicals, which therefore result in a high volume of wastewater. In addition, hydrometallurgy is more complex and time-consuming in its process than pyrometallurgical methods. However, at the same time, there are enormous advantages, such as low energy requirements due to low temperatures, a high recovery rate of valuable materials, and a higher purity of these

recovered materials [19,20]. The first step in hydrometallurgical recycling represents leaching of the feedstock, which in the case of lithium-ion battery recycling is pre-treated cathodes. A variety of chemicals can be applied as leaching reagents, predominantly inorganic (HCl, H₂SO₄, HNO₃, H₃PO₄, etc.) or organic acids and ammonia–ammonium salt systems. In this context, the addition of H₂O₂ shows the possibility of significantly increasing the extraction of cobalt and lithium. This effect can be explained by the reduction of Co^{3+} to Co^{2+} , which becomes leached more easily. Each of these solvents is characterized by specific advantages and disadvantages, for example in cost, environmental impact, or their chemical behaviour [20]. These properties must be considered and compared specifically for each application. In addition to the differences in chemical inputs, parameters such as temperature, solid/liquid ratio, and holding period play a significant role. To meet very high-quality requirements, especially for the application in traction batteries, producers of EVs and their battery suppliers agree on strict material specifications. Therefore, the recycling processes to recover the raw materials in a high-quality condition must also be designed accordingly. The removal of contaminants from the material mixture and the reduction of impurities introduced by the recycling process represent a central objective of these methods in order to avoid downcycling of these high-tech materials [21]. Various hydrometallurgical methods, such as extraction, crystallization, or precipitation, are available for this purpose. These need to be optimally coordinated with each other in order to achieve a high recycling efficiency with an adequate quality of the secondary materials [19–22].

Companies that have established a purely hydrometallurgical recycling process for LIBs are currently rare. Worth mentioning here are Retriev Technologies from Canada and the USA, respectively, and Recuply Valibat from France [20,23].

2.2. Effect of Organic Acids in Leaching of Black Mass

The main reason for using organic acids for the recycling of lithium-ion batteries involves their high potential to transfer the valuable metals into solutions. In combination with the formation of complexes, a specific recovery of the elements processed in the active material is possible. Another aspect is the reactivity at low temperatures and short leaching periods, which makes it likely to establish organic acids in future sustainable industrial processes [24,25]. Due to the possibility of avoiding the salination of wastewater and the generation of toxic or problematic gases (e.g., chlorine gas) during the process, organic acids reveal themselves as an environmentally friendly alternative to their classical inorganic equivalents and leave a smaller environmental footprint. However, due to the lower acid strength, the addition of reducing agents and the extension of the leaching period are necessary in selected cases to reach efficient recovery rates [24,26].

When comparing organic and inorganic acids for the recycling of lithium-ion batteries, the energy requirements, as well as the greenhouse gas emissions caused by their production, must also be taken into account. The production of, e.g., citric acid requires $35 \text{ MJ} \cdot \text{kg}^{-1}$, which is about 10% of the energy consumption for the synthesis of sulfuric acid with the same concentration [22]. Furthermore, leaching with organic acids requires significantly lower process temperatures. This means that correspondingly lower process costs are incurred, and additional greenhouse gas emissions can also be avoided. For organic acids, there are promising possibilities for recovering the acid and thus limiting the consumption of resources. By avoiding inorganic chemicals at high temperatures, emissions of sulfuric, chloridic, and nitrous gases can additionally be avoided [22].

The wide range of potential organic chemicals opens up an almost unbelievable number of possibilities for leaching and recovering valuable metals from lithium-ion batteries. Various studies have shown that citric [27–29], oxalic [30], and formic acid [10] are among the representatives with a very high potential for industrial application in this case [25]. For this reason, this publication is limited to a closer look at these three organic chemicals, with hydrogen peroxide as a reducing agent also receiving attention. Table 1 accordingly lists the corresponding reaction equations for the selected lixiviates with selected metal cations.

Туре	Complexation Reaction (M = Co ²⁺ , Li ⁺ , Mn ²⁺ , Ni ²⁺)	Reaction No.
	$n[H_2C_6H_5O_7^-] + M^{n+} \to M[H_2C_6H_5O_7]_n$	(1)
Citric-metallic complexes [30]	$n[HC_6H_5O_7^{2-}] + 2M^{n+} \rightarrow M_2[HC_6H_5O_7]_n$	(2)
	$n[C_6H_5O_7^{3-}] + 3M^{n+} \rightarrow M_3[C_6H_5O_7]_n$	(3)
Ovalia matallia comployee [20]	$n[HC_2O_4^-] + M^{n+} \rightarrow M[HC_2O_4]_n$	(4)
Oxalic-metallic complexes [50]	$n[C_2O_4^{2-}] + 2M^{n+} \rightarrow M_2[C_2O_4]_n$	(5)
Formic-metallic complexes [10]	$n[HCO_2H] + M^{n+} \to M[CO_2H]_n^n$	(6)

Table 1. Complexation reactions of citric, oxalic, and formic acid.

Citric acid has been considered for several years as a potential alternative to inorganic acids for leaching valuable metals from lithium-ion batteries. Particularly with regard to the leaching of cobalt and lithium, there are several publications that attribute great potential to this chemical [29,31–33]. However, for efficient leaching success, the presence of hydrogen peroxide is indispensable, since in the absence of this chemical, Co_3O_4 is formed as an intermediate product, which is particularly difficult to transfer into a solution [32,34]. This results in the effect that a significant excess of citric acid would be necessary to realize a transfer to the citrate $(Co_3(C_6H_5O_7)_2)$ [31]. In addition, it can be seen that lithium is significantly worse extracted without H₂O₂, since both Co and Li are in the same compound $(LiNi_xMn_yCo_zO_2)$ [32]. In some studies, it could already be shown that with the addition of 1 vol.% of H_2O_2 , an optimization of the process is possible [32]. With regard to the other relevant process parameters, the leaching temperature in particular stood out as having a statistically significant effect on metal extraction [29]. This can be explained by the increased solubility of metal-organic acid complexes at higher temperatures. However, the application of H_2O_2 results in a necessary limitation of this parameter since the decomposition of hydrogen peroxide is significantly accelerated at higher temperatures [32]. In some cases, the concentration of the acid played only a minor role, with the best possible efficiencies already being obtained at 1.25 M (100% for Li and 90% for Co) [29,32]. The solid/liquid ratio was deliberately kept very low in these studies in order to achieve an optimum transfer of the valuable metals into the liquid phase [31,32]. It was found that a significant deterioration in the efficiency of the metal extraction was already detected above $30 \text{ g} \cdot \text{L}^{-1}$ [32].

In this context, oxalic acid may not only be treated as a classic leaching medium, but should already lead to the separation of cobalt and lithium in the same process step. Therefore, oxalic acid is classically used mainly for the recycling of LiCoO₂ cathodes [34]. On the one hand, poorly soluble cobalt oxalates are formed, which precipitate, and lithium passes into the solution as a readily soluble oxalate [35]. Nevertheless, it must be mentioned that oxalic acid has so far achieved only insufficient leaching success for nickel and manganese [34].

For the leaching of cathode materials with formic acid, it is reported in the literature that the leaching efficiency is significantly improved by the addition of hydrogen peroxide. By adding up to 6 vol.% H_2O_2 , a leaching rate of 100% can be achieved for lithium. Since formic acid is an aldehyde, it also has an additional reductive effect on metals with high oxidation potentials. Furthermore, it could be shown that aluminum hardly passes into a solution, and thus the selective separation of this metal is possible. Higher acid concentrations (up to 4.5 mol·L⁻¹) lead to an improvement in the leaching efficiency of

Li, Ni, Co, and Mn (98.22%, 99.96%, 99.96%, and 99.95%, respectively), with Al hardly passing into a solution (below 10%). When evaluating the optimum solid/liquid ratio for the best possible metal extraction, it was found that at a fixed reaction time of 120 min, a slight decrease in efficiency is observed at higher solid/liquid ratios (e.g., 90 g·L⁻¹). This indicates that the reaction requires a sufficient supply of formic acid to keep the reaction rate high. The leaching temperature shows an improvement in leaching efficiency up to 60 °C due to the improved reaction kinetics, but no longer exerts a significant influence above this temperature [10].

The available literature review on the recycling of spent LIBs indicates that mechanical treatment, pyrometallurgy, hydrometallurgy, and biotreatment are the main routes for the recycling of lithium-ion batteries, with hydrometallurgy dominating compared to the other recycling techniques because it is a feasible technology for recovering valuable metals from waste LIBs. Organic acids are effective and environmentally friendly leaching agents and have been proven to play an important role in the recovery of lithium, nickel, cobalt, and manganese [36]. Although they are weaker than inorganic acids, organic acids have been extensively studied for leaching active material, which contributes to avoiding the additional application of reducing or oxidizing agents, reducing the complexity of pregnant fluid management, and thus reducing energy loss. The GHG emissions to recover 90% of Co by an organic leaching process are close to 500 g/CO_2 eq per kg Co, while for an inorganic acid leaching process they are close to $4000 \text{ g/CO}_2\text{eq}$ per kg Co [37]. Efforts must be made to separate the leached metals from these organic acid media to create economic and environmental benefits. In organic acids, temperature was found to have a significant effect on the leaching rate. In this study, the use of low temperatures also kept the energy input to the process low, further improving the process from an environmental standpoint [14,29,36].

3. Materials and Methods

3.1. Sample Preparation and Analysis of the Input Material

To demonstrate the suitability as a leaching agent for spent lithium-ion batteries citric (99.5% p.a. Carl Roth, Karlsruhe, Germany), oxalic (Dihydrate, 99.5% p.a. Carl Roth, Karlsruhe, Germany) and formic acid (98% p.a. Carl Roth, Karlsruhe, Germany) were tested. Hydrogen peroxide (30%, Carl Roth, Karlsruhe, Germany) was employed as the reducing agent for selected experiments. The corresponding chemical structures of the organic acids employed are presented in Figure 3. For the conducted tests a thermally pre-treated active material was applied (pyrolysis at 550 °C), to exclude organic components that would interfere in the hydrometallurgical processes. The analysis of this material was carried out on the one hand by means of a scanning electron microscope (JEOL JSM-IT300, Freising, Germany) in order to investigate the morphology of the input. Furthermore, hydrometallurgical digestion and compositional determination was executed using a mass spectrometer with inductively coupled plasma.



Figure 3. Chemical structure of citric, oxalic, and formic acid [38].

3.2. Experimental Procedure

For the leaching tests a double-walled vessel was applied, which could guarantee a constant process temperature by employing a thermostat. The liquid chemicals used were added by a temperature-controlled drip funnel and the powdery substances by a powder funnel. In order to generate a defined atmosphere and thus no additional oxidation potential, the surface of the leaching vessel was rinsed with nitrogen. To ensure homogeneous mixing of the active material and optimum contact with the leaching solution, a magnetic stirrer was applied at a constant rotational speed of 350 rpm. For a better overview of the experimental setup, it is shown schematically in Figure 4 and the components used are labelled. For the final solid-liquid separation after the holding period, a vacuum filtration was implemented.



Figure 4. Schematic illustration of the experimental setup for the hydrometallurgical treatment of active material from spent lithium-ion batteries according to [39].

3.3. Analysis of the Obtained Product

The pregnant leaching solutions of the performed experiments were analyzed by an atomic emission spectrometer with microwave-induced plasma (4210 MP-AES, Agilent, Santa Clara, CA, USA). The evaluation was executed using the statistical experiment planning and evaluation program MODDE 12 (Sartorius AG, Göttingen, Germany). A linear fractional model design was applied to each tested acid to generate a statistical experimental plan in order to keep the experimental effort within reasonable limits. The leaching time [min] and temperature [°C] were specified as quantitative input factors within defined limits. Furthermore, the stoichiometric factor [-] for the leaching medium was specified as a constant parameter. As a qualitative factor, the addition of hydrogen peroxide was included in the experimental design. The concentrations of valuable metals (cobalt, nickel, and lithium) in the liquid solutions after the leaching process were defined as output parameters.

4. Results

Figure 5 shows SEM images at different magnifications of the active material obtained from the used LIBs. The irregular and agglomerated particles result from the thermal pretreatment of the material in the course of pyrolysis at 500 °C to remove organic compounds from the feedstock for the hydrometallurgical treatment. These can be clearly seen in the SEM images. The elemental composition by EDX shows the presence of Co, Ni, and Mn, where Li cannot be detected by the instrument used (JEOL JSM-IT300).



Figure 5. SEM images of the active material at different magnifications after pyrolytic pre-treatment.

The analysis of the active material by mass spectrometer with inductively coupled plasma (ICP-MS) also allows the measurement of the lithium content and is shown in Table 2.

Table 2. Composition of the used, active material for the leaching experiments measured by ICP-MS (Residual content to 100 mass% is graphite).

Element	Со	Ni	Li	Mn	Cu	Al	Zn	Fe
[Mass-%]	6.5	22.0	5.2	7.3	4.8	3.7	0.7	0.01

Table 3 shows the experimental and analysis data of the filtrates for the leaching experiments with citric (C1 to C5), oxalic (O1 to O5), and formic acid (F1 to F5). The leaching efficiency corresponds to the mean value of the three identical experiments and is calculated according to formula (1).

Leaching efficiency
$$[\%] = \frac{c_{\rm M}}{w_{\rm M,BM}} \cdot V_L \cdot 100 \, [\%]$$
 (1)

 c_M —Concentration of M in the filtrate (M = Co²⁺, Li⁺, Ni²⁺) [g·L⁻¹]

 $w_{M,BM}$ —Mass fraction of M in the black mass (M = Co²⁺, Li⁺, Ni²⁺) [-]

 V_L —Volume of the leaching solution [l]

In each case, an acid excess of a stoichiometric factor of 1.3 and a solid/liquid ratio of 100 g \cdot L⁻¹ were selected. For the experiments with an addition of hydrogen peroxide, a fixed amount of 5 vol.-% was defined in order to provide a sufficient supply of the reducing agent.

The results for the pregnant leaching solutions with citric acid indicate a clear influence of the hydrogen peroxide content on the efficiency of the process. This statement is particularly true for the leaching of cobalt (+40%) and nickel (+14%), while the efficiency of lithium hardly improved. A deterioration in leaching efficiency of 3.8% was observed for lithium at the maximum leaching duration of 4 h and a maximum temperature of 40 °C when H_2O_2 was used (cf. test results for C2 and C4).

In the conducted experiments with oxalic acid, the addition of H_2O_2 resulted in a significant deterioration of the leaching efficiencies at all tested temperatures. The dissolution was reduced by about 50% for both cobalt and nickel. The leaching of lithium with oxalic acid is hardly affected by the addition of reducing agents.

In general, leaching with formic acid showed by far the worst leaching efficiencies, although H_2O_2 was found to have no effect on them.

	Reducing Agent	Holding Period	Temperature	Leaching Efficiency Co	Leaching Efficiency Ni	Leaching Efficiency Li
Unit	[-]	[h]	[°C]	[%]	[%]	[%]
C1	Yes	1	40	80.5	31.5	100.0
C2	Yes	4	25	70.7	27.3	100.0
C3	No	1	25	33.5	15.0	100.0
C4	No	4	40	30.5	13.7	96.2
C5	Yes	1	25	44.6	17.0	88.0
O1	Yes	1	40	36.8	17.8	66.0
O2	Yes	4	25	23.4	12.2	72.8
O3	No	1	25	24.5	12.9	79.4
O4	No	4	40	55.4	23.1	71.9
O5	Yes	1	25	20.9	8.7	83.4
F1	Yes	1	40	10.3	10.7	48.5
F2	Yes	4	25	1.4	1.1	6.3
F3	No	1	25	3.7	6.0	68.7
F4	No	4	40	2.0	3.1	59.4
F5	Yes	1	25	8.3	10.1	56.0

Table 3. Experimental data for the leaching with citric (C1–C5), oxalic (O1–O5), and formic (F1–F5) acid (each reported leaching efficiency for Co, Ni, and Li corresponds to an average of three identical experiments).

5. Discussion

5.1. Influence of Operating Variables

Leaching tests were carried out to investigate the effect of temperature on the leaching process, especially at a low temperature level, and the results were used to decide whether temperature is a significant factor for further leaching experiments. The effect of temperature on Co, Ni, and Li recovery in citric, oxalic, and formic acid at a stoichiometric acid excess of 1.3, a pulp density of 100 g·L⁻¹ and the addition of 5 vol.-% of H₂O₂ is shown in Figure 6. Higher temperatures lead to faster leaching kinetics and higher metal concentrations in the pregnant leaching solution in general for the tests with citric and oxalic acid. A clearly opposite behavior can be observed for formic acid, leading to the statement that increasing temperature during leaching with formic acid results in a deterioration of dissolution for Li, Co, and Ni. From this, it can be concluded that the reaction kinetics cannot be accelerated accordingly by the temperature, but that other effects inhibit the dissolution.

The extension of the holding period from 1 to 4 h shows that only in a few cases can a significant improvement in the leaching efficiency be achieved. For the leaching experiments with formic acid, a decrease of up to 33% could be detected in each case considered, which can be attributed to redissolution processes. The highest increase over time is shown by the leaching efficiency of nickel in the tests with citric and oxalic acid.

In a previous study [31], it was reported that an increase in the leaching rates of Ni, Co, and Li is not determined by the leaching time or temperature but by the efficient supply of formic acid in order to maintain an appropriate reaction rate. This supports the statement that, above all, the acid concentration and not the temperature used is the limiting factor of the reaction.



Figure 6. Effect of (**a**) temperature and (**b**) holding period on cobalt, nickel, and lithium leaching with an stoichiometric acid excess of 1.3, a pulp density of 100 g·L⁻¹, and a 5 vol.-% of H_2O_2 (C ... Citric acid, O ... Oxalic acid, and F ... Formic acid) based on the concentration measured in the pregnant leaching liquid.

5.2. Statistical Test Evaluation

In addition to the evaluation of the leaching efficiency, a statistical evaluation was conducted for all tests carried out using MODDE 12. A linear fractional factorial design was applied in order to keep the experimental effort within reasonable limits.

In the following Figures 7 and 8, the results of the statistical test evaluation for citric and formic acid are shown in detail. As described in Section 3.3, this is based on the results of the analyses of the pregnant leaching solution. The diagrams show optimal parameter ranges for the elements cobalt, nickel, and lithium, which were desired to be recovered. The leaching duration is always plotted on the *x*-axis and the corresponding temperature on the *y*-axis. For all metals, the results have been presented both for the tests with and without reducing agent, as significant differences in the leaching efficiencies can be seen here. Linear, interactive, and quadratic terms were considered in the statistical evaluation. For the evaluation of leaching with citric acid, a confidence interval of 95% was used. This resulted in satisfactory statistical parameters for Li, Co, and Ni for the coefficient of determination (R²) and predictability (Q²). These were R² = 0.999 and Q² = 0.952 for lithium, R² = 0.998 and Q² = 0.953 for cobalt, and R² = 0.992 and Q² = 0.882 for nickel. The model construction was identical for all leaching media used and similar high statistical values for the coefficient of determination and predictability were obtained for all models.

Since the comparison of the test results for leaching with citric acid at a low temperature level revealed the most promising results so far, these will be considered in this section. For the metals cobalt and nickel, a very similar picture emerges, both with and without the application of a reducing agent. In principle, the use of H_2O_2 proves to be very advantageous, since significantly higher metal contents could be detected in the filtrates for Co and Ni. An increased temperature (resp. 40 °C) already allows a maximum possible leaching efficiency in the tested parameter field for short holding periods of one hour (see Figure 7a,b). However, the same results can also be achieved at 25 °C, whereby holding periods of at least three hours are necessary. For lithium, it can be seen in Figure 7c that the leaching duration is particularly decisive, while the H_2O_2 addition has hardly any influence on the maximum achievable leaching rate in the examined parameter field.



Figure 7. Statistical evaluation of the leaching tests with citric acid for the metal contents of (**a**) Co, (**b**) Ni, and (**c**) Li in the filtrates as a function of temperature, holding period, and concentration of reducing agent.



Figure 8. Statistical evaluation of the leaching tests with formic acid for the metal contents of (**a**) Co, (**b**) Ni, and (**c**) Li in the filtrates as a function of temperature, holding period, and concentration of reducing agent.

The statistical test evaluation for the leaching experiments with oxalic acid reveals very similar trends for all three metals considered as those of citric acid and is therefore not explicitly presented in this publication. However, clear differences can be seen in the assessment with formic acid, which will be discussed in more detail. For the evaluation of leaching with formic acid, a confidence interval of 95% was used. This resulted in satisfactory statistical parameters for Li, Co, and Ni for the coefficient of determination (R^2) and predictability (Q^2). These were $R^2 = 0.935$ and $Q^2 = 0.703$ for lithium, $R^2 = 0.997$ and $Q^2 = 0.900$ for cobalt, and $R^2 = 0.831$ and $Q^2 = 0.694$ for nickel. For further investigations and model creation, again, linear, interactive, and quadratic terms were considered.

For the entire parameter field (see Figure 8), the application of a short leaching time at low temperatures (resp. 25 °C) is particularly advantageous for the dissolution of Co, Ni, and Li. Figure 8c shows that lithium is particularly easily and rapidly leached and higher durations tend to lead to the redissolution of this metal. The use of H_2O_2 as a reducing agent at this low temperature level is also shown to be not absolutely necessary, since an improvement in efficiency can be achieved in only a few cases of the parameter field.

6. Conclusions

For all conducted organic leaching tests, temperature, in particular, is found to be a significant factor influencing the leaching rate. Generally, the solubility of metal-organic acid complexes increases with temperature, resulting in the better dissolution of the metals. However, it was also demonstrated that at a low temperature level (25–40 °C), the leaching time and the addition of a reducing agent can also exhibit an effect. The latter is only pronounced for the experiments with citric and oxalic acid, while when formic acid is used, the efficient supply of fresh chemicals to the reaction can evidently be considered as a limiting factor. Advantageously, the application of citric acid also results in the possibility of achieving the highest possible leaching efficiency in the tested parameter field after only 3 h at particularly low temperatures (25 °C). In a comparison of the three acids tested, the application of citric acid results in the best possible leaching efficiencies for Ni, Co, and Li in the defined parameter range.

Furthermore, the advantage of the low leaching temperatures should be particularly emphasized in this context. The leaching temperatures in the range of 25 to 40 °C allow the energy requirements of such processes to be significantly reduced compared with standard temperatures for leaching of between 60 and 80 °C. In addition, this also increases the controllability of the process, since even in the event of unforeseen changes in the material composition, the low temperatures make process control easier. This low temperature level also allows the decomposition rate of H_2O_2 (into oxygen and water) by the process heat to be reduced to a minimum, although the heavy metal ions present naturally also play a significant role in this context [40].

Nevertheless, the limitations of this study need to be pointed out. The constant changes in the compositions of the cathode materials affect not only the economic efficiency of these recycling processes, but also the chemical processes. Therefore, it is necessary to re-evaluate, and possibly adapt, the leaching system in the case of serious changes in composition. Although the low temperatures offer advantages, especially in the field of energy consumption of these methods, the correspondingly extended leaching durations have to be considered as well. Finally, it remains to be mentioned in this examination that hydrometallurgical processes often lead to increased procedural and process engineering efforts but grant the possibility of a targeted and efficient recovery of materials of high quality. In addition, further research is needed to recover the valuable metals in the pregnant leaching solution in high quality and quantity. For the industrial implementation of organic acids in the recycling processes described, however, trials on a larger scale are still necessary in order to ensure the stable operation of future recycling plants. Since the economic viability of such systems is not yet known, regulation on the part of politicians for this sector must force further research [41].

Despite the costs incurred for the production of organic acids, this methodology appears to be promising, as not only is the CO_2 footprint of these lixiviates significantly lower than those of inorganic acids when assessed over the entire process, but the wastewater is also less contaminated. In addition, their use allows the emission of toxic gases, such as SO_2 during the leaching process, to be avoided.

When comparing chemical properties, organic and inorganic acids each have specific advantages and disadvantages. In the case of certain organic acids (e.g., oxalic acid), limited solubility in water quickly reaches limits, as this means that larger volumes of liquid have to be applied for leaching and following precipitation. Classical inorganic acids used for the leaching of spent lithium-ion batteries, such as H₂SO₄, HCl, and HNO₃, have significantly higher solubilities in water. Furthermore, matrix effects of the liquid solution play a significant role, especially in subsequent recovery processes such as precipitation. Due to complex formation, reaction delays can occur, resulting in the hydrometallurgical process becoming more difficult to control. This effect can occur for both inorganic and organic acids. The subsequent further processing after an appropriate precipitation process offers great potential, especially when organic acids are used. Subsequent calcination makes it very easy to achieve thermal conversion into metal oxides, which is more difficult when inorganic acids are used due to the correspondingly adhering salts.

The sustainable recycling of spent lithium-ion batteries is still a challenging topic in research and industry. The further development of processes, especially with regard to environmentally friendly and climate-neutral methods, must be the goal of further research activities. Economic efficiency calculations may only play a subordinate role at the present, since the framework conditions in this context are constantly changing. Due to the processes used, which are also used industrially, profitability can be assumed for corresponding tonnages. At present, the focus has to be on the effective recycling and recovery of critical raw materials from these waste streams, as this can promote political independence and protect the climate in a sustainable way.

Author Contributions: Conceptualization, E.G. and H.A.; methodology, E.G.; software, E.G.; validation, E.G. and C.S.; formal analysis, E.G.; investigation, C.S.; resources, E.G.; data curation, E.G. and C.S.; writing—original draft preparation, E.G.; writing—review and editing, E.G. and H.A.; visualization, H.A.; supervision, H.A.; project administration, E.G.; All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

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

References

- 1. IEA. Global EV Sales by Scenario 2020–2030. Available online: https://www.iea.org/data-and-statistics/charts/global-ev-salesby-scenario-2020-2030 (accessed on 24 November 2021).
- Irle, R. Global EV Sales for 2021 H1. Available online: https://www.ev-volumes.com/news/global-ev-sales-for-2021-h1/ (accessed on 24 November 2021).
- Contestabile, M.; Panero, S.; Scrosati, B. A laboratory-scale lithium-ion battery recycling process. J. Power Sources 2001, 92, 65–69. [CrossRef]
- 4. Kanamori, T.; Matsuda, M.; Miyake, M. Recovery of rare metal compounds from nickel–metal hydride battery waste and their application to CH₄ dry reforming catalyst. *J. Hazard. Mater.* **2009**, *169*, 240–245. [CrossRef] [PubMed]
- Buchert, M.; Sutter, J. Aktualisierte Ökobilanzen zum Recyclingverfahren LithoRec II f
 ür Lithium-Ionen-Batterien; Öko-Institut e.V.: Freiburg, Germany, 2016.
- 6. Diekmann, J.; Hanisch, C.; Froböse, L.; Schälicke, G.; Loellhoeffel, T.; Fölster, A.-S.; Kwade, A. Ecological Recycling of Lithium-Ion Batteries from Electric Vehicles with Focus on Mechanical Processes. *J. Electrochem. Soc.* **2017**, *164*, A6184–A6191. [CrossRef]
- Cobalt Institute. Cobalt Mining. Available online: https://www.cobaltinstitute.org/about-cobalt/the-cobalt-value-chain/cobaltmining/ (accessed on 10 December 2021).
- 8. U.S. Geological Survey. Mineral Commodity Summaries 2021; U.S. Geological Survey: Reston, VA, USA, 2021.
- Zeng, X.; Li, J.; Singh, N. Recycling of Spent Lithium-Ion Battery: A Critical Review. Crit. Rev. Environ. Sci. Technol. 2014, 44, 1129–1165. [CrossRef]
- 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] [PubMed]

- 11. 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]
- Li, J.-H.; Li, X.-H.; Zhang, Y.-H.; Hu, Q.-Y.; Wang, Z.-X.; Zhou, Y.-Y.; Fu, F.-M. Study of spent battery material leaching process. *Trans. Nonferrous Met. Soc. China* 2009, 19, 751–755. [CrossRef]
- Liu, Y.-J.; Hu, Q.-Y.; Li, X.-H.; Wang, Z.-X.; Guo, H.-J. Recycle and synthesis of LiCoO₂ from incisors bound of Li-ion batteries. *Trans. Nonferrous Met. Soc. China* 2006, 16, 956–959. [CrossRef]
- 14. Meshram, P.; Pandey, B.D.; Mankhand, T.R. Recovery of valuable metals from cathodic active material of spent lithium ion batteries: Leaching and kinetic aspects. *Waste Manag.* 2015, 45, 306–313. [CrossRef]
- 15. Georgi-Maschler, T.; Friedrich, B.; Weyhe, R.; Heegn, H.; Rutz, M. Development of a recycling process for Li-ion batteries. *J. Power Sources* **2012**, 207, 173–182. [CrossRef]
- 16. Zhang, T.; He, Y.; Wang, F.; Ge, L.; Zhu, X.; Li, H. Chemical and process mineralogical characterizations of spent lithium-ion batteries: An approach by multi-analytical techniques. *Waste Manag.* **2014**, *34*, 1051–1058. [CrossRef] [PubMed]
- Shin, S.M.; Kim, N.H.; Sohn, J.S.; Yang, D.H.; Kim, Y.H. Development of a metal recovery process from Li-ion battery wastes. *Hydrometallurgy* 2005, 79, 172–181. [CrossRef]
- 18. 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. Sustain. Circ. Econ.* **2016**, *34*, 474–481. [CrossRef] [PubMed]
- Hanisch, C.; Diekmann, J.; Stieger, A.; Haselrieder, W.; Kwade, A. Recycling of Lithium-Ion Batteries. Handbook of Clean Energy Systems Online. Available online: https://www.researchgate.net/profile/Christian-Hanisch-2/publication/28064424 4_Recycling_of_Lithium-Ion_Batteries_from_Electric_Vehicles/links/55c0a82508ae092e9666d0ae/Recycling-of-Lithium-Ion-Batteries-from-Electric-Vehicles.pdf (accessed on 10 December 2021). [CrossRef]
- 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]
- Li, J.; Li, X.; Hu, Q.; Wang, Z.; Zheng, J.; Wu, L.; Zhang, L. Study of extraction and purification of Ni, Co and Mn from spent battery material. *Hydrometallurgy* 2009, 99, 7–12. [CrossRef]
- 22. Li, L.; Dunn, J.B.; Zhang, X.X.; Gaines, L.; Chen, R.J.; Wu, F.; Amine, K. Recovery of metals from spent lithium-ion batteries with organic acids as leaching reagents and environmental assessment. *J. Power Sources* **2013**, 233, 180–189. [CrossRef]
- Larouche, F.; Tedjar, F.; Amouzegar, K.; Houlachi, G.; Bouchard, P.; Demopoulos, G.P.; Zaghib, K. Progress and Status of Hydrometallurgical and Direct Recycling of Li-Ion Batteries and Beyond. *Materials* 2020, 13, 801. [CrossRef]
- 24. Gerold, E. Entwicklung Eines Hydrometallurgischen Recyclingkonzeptes für Lithium-Ionen-Batterien. Ph.D. Dissertation, Montanuniversität Leoben, Leoben, Austria, 2021.
- 25. Or, T.; Gourley, S.W.D.; Kaliyappan, K.; Yu, A.; Chen, Z. Recycling of mixed cathode lithium-ion batteries for electric vehicles: Current status and future outlook. *Carbon Energy* **2020**, *2*, 6–43. [CrossRef]
- 26. Golmohammadzadeh, R.; Faraji, F.; Rashchi, F. Recovery of lithium and cobalt from spent lithium ion batteries (LIBs) using organic acids as leaching reagents: A review. *Resour. Conserv. Recycl.* **2018**, *136*, 418–435. [CrossRef]
- Chen, X.; Zhou, T. Hydrometallurgical process for the recovery of metal values from spent lithium-ion batteries in citric acid media. Waste Manag. Res. J. Sustain. Circ. Econ. 2014, 32, 1083–1093. [CrossRef]
- Li, L.; Bian, Y.; Zhang, X.; Guan, Y.; Fan, E.; Wu, F.; Chen, R. Process for recycling mixed-cathode materials from spent lithium-ion batteries and kinetics of leaching. *Waste Manag.* 2018, *71*, 362–371. [CrossRef] [PubMed]
- 29. 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]
- Horeh, N.B.; Mousavi, S.M.; Shojaosadati, S.A. Bioleaching of valuable metals from spent lithium-ion mobile phone batteries using Aspergillus niger. J. Power Sources 2016, 320, 257–266. [CrossRef]
- 31. 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]
- 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]
- 33. Swain, B.; Jeong, J.; Lee, J.-C.; Lee, G.-H.; Sohn, J.-S. Hydrometallurgical process for recovery of cobalt from waste cathodic active material generated during manufacturing of lithium ion batteries. *J. Power Sources* 2007, *167*, 536–544. [CrossRef]
- 34. Yao, X.; Xu, Z.; Yao, Z.; Cheng, W.; Gao, H.; Zhao, Q.; Li, J.; Zhou, A. Oxalate co-precipitation synthesis of LiNi_{0.6}Co_{0.2}Mn_{0.2}O₂ for low-cost and high-energy lithium-ion batteries. *Mater. Today Commun.* **2019**, *19*, 262–270. [CrossRef]
- 35. Zhang, X.; Bian, Y.; Xu, S.; Fan, E.; Xue, Q.; Guan, Y.; Wu, F.; Li, L.; Chen, R. Innovative Application of Acid Leaching to Regenerate Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O₂ Cathodes from Spent Lithium-Ion Batteries. *ACS Sustain. Chem. Eng.* **2018**, *6*, 5959–5968. [CrossRef]
- 36. de Oliveira Demarco, J.; Cadore, J.S.; de Oliveira, F.D.S.; Tanabe, E.H.; Bertuol, D.A. Recovery of metals from spent lithium-ion batteries using organic acids. *Hydrometallurgy* **2019**, *190*, 105169. [CrossRef]
- 37. 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]
- 38. Fanghänel, E. Organikum; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2015.
- 39. Gerold, E.; Antrekowitsch, H. Potenzialabschätzung von Synergieeffekten zur simultanen Rückgewinnung von Wertmetallen aus komplexen, metallhaltigen Reststoffen. *Osterr. Wasser-Und Abfallwirtsch.* **2022**, *74*, 22–31. [CrossRef]

- 40. Gerold, E.; Luidold, S.; Antrekowitsch, H. Decomposition of hydrogen peroxide in selected organic acids. In Proceedings of the European Metallurgical Conference, Salzburg, Austria, 27–30 June 2021.
- 41. Marques, R.C.; Simões, P.; Pinto, F.S. Tariff regulation in the waste sector: An unavoidable future. *Waste Manag.* 2018, 78, 292–300. [CrossRef] [PubMed]