recycling

MDPI

Article

Organic Acid Leaching of Black Mass with an LFP and NMC Mixed Chemistry

Marc Simon Henderson, Chau Chun Beh, Elsayed Oraby * and Jacques Eksteen

Western Australian School of Mines: Minerals, Energy and Chemical Engineering, Curtin University, Perth, WA 6102, Australia

* Correspondence: elsayed.oraby@curtin.edu.au

Abstract

There is an increasing demand for the development of efficient and sustainable battery recycling processes. Currently, many recycling processes rely on toxic inorganic acids to recover materials from high-value battery chemistries such as lithium nickel manganese cobalt oxides (NMCs) and lithium cobalt oxide (LCOs). However, as cell manufacturers seek more cost-effective battery chemistries, the value of the spent battery value chain is increasingly diluted by chemistries such as lithium iron phosphate (LFPs). These cheaper alternatives present a difficulty when recycling, as current recycling processes are geared towards dealing with high-value chemistries; thus, the current processes become less economical. To date, much research is focused on treating a single battery chemistry; however, often, the feed material entering a battery recycling facility is contaminated with other battery chemistries, e.g., LFP feed contaminated with NMC, LCO, or LMOs. This research aims to selectively leach various battery chemistries out of a mixed feed material with the aid of a green organic acid, namely oxalic acid. When operating at the optimal conditions (2% solids, 0.25 M oxalic acid, natural pH around 1.15, 25 °C, 60 min), this research has proven that oxalic acid can be used to selectively dissolve 95.58% and 93.57% of Li and P, respectively, from a mixed LFP-NMC mixed feed, all while only extracting 12.83% of Fe and 8.43% of Mn, with no Co and Ni being detected in solution. Along with the high degree of selectivity, this research has also demonstrated, through varying the pH, that the selectivity of the leaching system can be altered. It was determined that at pH 0.5 the system dissolved both the NMC and LFP chemistries; at a pH of 1.15, the LFP chemistry (Li and P) was selectively targeted. Finally, at a pH of 4, the NMC chemistry (Ni, Co and Mn) was selectively dissolved.

Keywords: battery recycling; mixed chemistry black mass; oxalic acid

check for updates

Academic Editor: Sascha Nowak

Received: 14 June 2025
Revised: 10 July 2025
Accepted: 16 July 2025
Published: 21 July 2025

Citation: Henderson, M.S.; Beh, C.C.; Oraby, E.; Eksteen, J. Organic Acid Leaching of Black Mass with an LFP and NMC Mixed Chemistry. *Recycling* **2025**, *10*, 145. https://doi.org/10.3390/recycling10040145

Copyright: © 2025 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

Current battery recycling technologies are geared towards the recycling of high-value battery chemistries, those containing large quantities of Co and Li (e.g., LCOs and NMC). However, as critical mineral prices increase, battery suppliers are reducing the quantity of Co used in their batteries, thus reducing the cost of battery production [1]. Manufacturers achieve this by developing new battery chemistries such as lithium nickel manganese cobalt oxides (NMCs) and lithium iron phosphates (LFPs), which require less Co [1,2] or, in the case of LFPs, no Co. As LFP chemistries gain market share in electric vehicles (EVs) and stationary energy storage, the resulting dilution of recycling feedstock will reduce the economic viability of spent lithium-ion battery (LiBs) recycling.

Prior to processing spent LiBs, they first require battery discharging and crushing/shredding stages [3]. The shredded battery material is a collection of the different battery components (foils, electrolytes, anode, cathode and separators) and is referred to as black mass (BM). This research is focused on developing green hydrometallurgical recycling routes for LFP-rich black mass. One of the most important steps in any hydrometallurgical process is the dissolution of the valuable metals into solution. When recycling battery materials, metal dissolution is achieved using either organic acids (e.g., citric acid, lactic acid, etc.) or inorganic acids (HCl, HNO_3, H_2SO_4, etc.) [4,5]. Traditionally, inorganic acids have been used, as they are able to effectively dissolve a range of metals [6]. However, these acids are corrosive, pose a safety risk to anyone handling them [4], and lead to the generation of toxic waste, which can damage the environment [6].

Organic acids offer a promising alternative to inorganic acids for leaching black mass [7]. One of the advantages is that organic acids are less toxic and offer more selectivity in terms of metal dissolution [7,8] when compared to similar inorganic acids. Metal selectivity is key when working with complex chemistries, such as those of LiBs. Some of the most common organic acids used for leaching NMC and LCO batteries include ascorbic [9], citric [6,10,11], malic [10], and lactic [12] acids. Researchers such as Esmaeili et al. [13] (citric + malic + ascorbic), Prasetyo et al. [4] (acetic + tannic), Nayaka et al. [14] (glycine and ascorbic), and Zhuang et al. [15] (H_3PO_4 + citric) have taken research on the organic leaching of NMC and LCO one step further by investigating the synergistic use of multiple inorganic and organic acids, and in doing so, they achieved higher metal dissolution efficiencies.

Despite the large amount of literature available on the use of organic acids for leaching high-value battery chemistries, little work has been conducted on low-value LFP chemistries. Thus, inorganic acids such as H_3PO_4 [16,17] and H_2SO_4 [18] remain the lixiviants of choice for LFP recycling. Among the limited research, oxalic acid [19,20], a mixture of citric acid and DL-malic acid [21], and formic acid [22] have been investigated for LFP leaching.

Kumar and coworkers [21] investigated leaching LFPs with organic acids derived from fruit. Their research found lemon juice to be the most promising, which is similar to Esmaeili and coworkers' [13] research, which used lemon juice to leach NMCs. In both studies, over 94% of Li was extracted. Kumar et al. [21] used a LFP black mass when conducting their research; thus, their work includes leaching efficiencies for contaminants such as Al and Cu. After 90 min of leaching at optimal conditions (100% lemon juice, 6% H_2O_2, a S:L ratio of 67 g/L at room temperature), 94.83%, 96.92%, and 47.24% of Li, Cu and Al were extracted, respectively. The dissolution of Fe was reported as 4.05%, which illustrates that their method is selective as it removes Li, Cu and Al while leaving behind most of the Fe. Equation (1), as proposed by Kumar et al. [21], who described the leaching of LFP using citric acid. This is a valid equation as the major acid in lemon juice is citric acid; however, it is important to note the presence of ascorbic and malic acid in the system as they too will influence the leaching of LFP.

$$2H_3Cit_{\,(aq)} + 3H_2O_{2\,(aq)} + 6LiFePO_{4\,(s)} \rightarrow 6FePO_{4\,(s)} + 2Li_3Cit_{\,(aq)} + 6H_2O_{\,(l)} \quad (1)$$

Impurities such as Al, Cu and Fe, along with dissolved Li in the leach liquor, were removed or recovered through evaporative concentration, followed by pH adjustment to precipitate $Al(OH)_3$, $Fe(OH)_3$ and $Cu(OH)_2$. Lithium was subsequently recovered as Li_2CO_3 through the addition of Na_2CO_3.

Li and coworkers [19] investigated the use of oxalic acid for the selective dissolution of Li from LFP cathode material. Lithium extraction efficiencies as high as 98% were achieved while 92% of the Fe was recovered as insoluble iron oxalate (FeC_2O_4). The optimal leaching

conditions were identified as follows: a solution of 0.3 M oxalic acid and an S–L ratio of 60 g/L at 80 °C for 60 min. The leaching process exhibited high selectivity towards Li, and the leaching rates and efficiencies could be increased through the addition of an appropriate reducing agent as demonstrated in previous studies involving LCO and NMC chemistries with organic acids. Equation (2), proposed by Li et al. [19], describes the leaching of LFP with oxalic acid.

$$\begin{aligned} &12LiFePO_{4\ (s)} + 6H_2C_2O_{4\ (aq)} + 2H_2O_{(l)} \\ &\rightarrow 3Li_2C_2O_{4\ (aq)} + 3FeC_2O_{4\ (s)} + 4H_3PO_{4\ (aq)} \\ &+ 3Fe_3(PO_4)_{2\ (aq)} + 2Li_3PO_{4\ (aq)} + 12H_2O_{\ (l)} \end{aligned} \quad (2)$$

The above equation illustrates that Fe precipitates out of solution as iron oxalate (FeC_2O_4). The main difference between the research conducted by Li and coworkers [19] and the organic leaching methods discussed earlier is that Fe is recovered as FeC_2O_4 rather than $FePO_4$. This is unique; however, FeC_2O_4 can still be used as a precursor material for the synthesis of new LFP cathode materials.

The majority of the reviewed literature focuses on either a single battery chemistry or, in some cases, a mixture of valuable chemistries [13]. However, none explores the recycling of low-value black mass (e.g., LFP-rich) contaminated with high-value materials (e.g., NMC). This represents a critical gap, as in practice, the recycling of spent LiBs as individual battery chemistries is limited. Different battery chemistries, due to misclassification, may be combined in the feedstock of a recycling facility. Thus, it is important to identify an organic acid capable of selectively extracting metals of interest from a mixed-chemistry black mass. While reviewing literature on different organic acids, it was evident that organic acids such as citric, ascorbic, malic, and lactic acids exhibit poor selectivity when extracting Li, Co, Ni and Mn. However, oxalic acid exhibits a high selectivity towards Li, and for this reason, the present paper evaluates the use of oxalic acid to selectively leach a mixed-chemistry black mass composed of LFP and NMC materials. Table 1 summarises the literature related to the use of oxalic acid for leaching various battery chemistries, including LCO, NMC, LMO, LCMO and LFP.

Table 1. Research dealing with the leaching of different battery chemistries with oxalic acid.

Battery Chemistry	Conditions	Extraction Efficiencies	Feed Materials	Reference
NMC	0.6 M Oxalic acid S:L ratio of 50 g/L 60 °C for 60 min	100% Al 98.8% Li <0.5% of Ni and Co 1.5% Mn	Dismantled electric vehicle LiBs (NMC 111)—they are crushed, sieved, and undergo magnetic separation to produce a NMC-, graphite-, Cu- and Al-containing black mass	[23]
NMC	0.6 M Oxalic acid S:L ratio of 20 g/L 30 min at 70 °C	>98.5% Co, Mn and Ni	Manually dismantled 18,650 NMC cells. Dimethyl carbonate is used to remove electrolyte and N-methyl-2-pyrrolidone to separate cathodic material from Al foil. The cathode material is calcined at 700 °C	[24]

Table 1. *Cont.*

Battery Chemistry	Conditions	Extraction Efficiencies	Feed Materials	Reference
NMC	1 M Oxalic acid S:L ratio of 10 g/L 95 °C for 12 h	NMC 111—100% Li, 0.26% Ni, 1.12% Co and 22.8% Mn NMC 532—95.4% Li, 0.12% Ni, 0.52% Co and 24% Mn NMC 811—89.6% Li, 0.13% Ni, 0.17% Co and 20.6% Mn.	Pristine cathode samples	[25]
LCMO		93.6% Li, 0% Ni, 1.8% Co and 30% Mn		
LMO		100% Li, 0% Ni, 0% Co and 26.2% Mn		
LCO	1M Oxalic acid S:L ratio of 50 g/L 80 °C for 120 min	>98% of $LiCoO_2$ Li in solution Co-oxalate in residue	Spent LiBs from phones—they are dismantled, and the cathodes undergo vacuum pyrolysis. Cathode material is separated from Al foil	[26]
LCO	1M Oxalic acid Stirring rate 400 rpm S:L ratio of 15 g/L 95 °C for 150 min.	98% Li 97% Co (insoluble oxalate)	Consumer electronics—crushed and sieved (−1.43 mm)	[27]
LFP	0.3 M Oxalic acid S:L ratio of 60 g/L 80 °C for 60 min	98% Li 92% Fe (precipitated as $FeC_2O_4 \cdot 2H_2O$)	Spent 123-18650 (LFP) batteries from electronics. The anode and cathode are manually separated, and then the cathodic material is pretreated using NMP, followed by calcination and a final grinding step	[19]
LFP	0.65 M H_3PO_4 0.33 M Oxalic acid S:L ratio of 40 g/L 70 °C for 51 min.	98.24% Fe 97.72% Li	Cathodic material from spent LFP batteries	[20]

Given the increasing variety of battery chemistries entering the end-of-life value chain, and the corresponding need to improve recycling rates, it is likely that battery sorting facilities will misclassify battery types. Consequently, there is a need to develop a greener and more robust recycling process capable of handling contaminated or mixed feedstocks. One of the most crucial stages in any hydrometallurgical process is leaching, as the ability to selectively dissolve target metals simplifies downstream processing and enhances overall process efficiency and economic viability.

To the best of the authors' knowledge, no existing research has investigated the use of an organic acid to selectively treat an LFP-rich feed material that is contaminated with LCO, NMC, NCA, or LMO battery chemistries. The closest studies involving mixed LFP and NMC feed materials are those by Zou et al. [28] and Xu et al. [29]. Zou and coworkers [28] examined the addition of LFP cathode material to NMC 111 black mass in an attempt to use LFP as a reducing agent. The idea behind their research is that in the NMC-H_2SO_4

leaching system, LFP dissolves and releases Fe^{2+} ions. The Fe^{2+} ions then act as reducing agents, converting transition metal oxides, specifically Co^{3+} and Mn^{4+}, into their more soluble species Co^{2+} and Mn^{2+}, respectively. Overall, Zou and coworkers [28] concluded that leaching with 2 M H_2SO_4 at 60 °C for 3 h using a 1:1.77 (wt/wt) ratio of LFP to NMC resulted in the extraction of 46.3%, 87.6%, 91.1%, 95%, 100%, 100% and 100% of Al, Ni, Mn, Cu, Co, Li, and Fe, respectively. Xu and coworkers [29] proposed a greener approach by employing ferric sulphate ($Fe_2(SO_4)_3$) for the dissolution of Li, Ni, Mn, Co, and Li from a mixed NMC-LFP feed. Xu and coworkers were able to extract 96.88%, 97.09%, 97.65%, 98.32%, and 0.21% of Mn, Ni, Co, Li, and P, respectively. The high dissolutions were achieved by reacting 7 g of the LFP-NMC mixture (LFP:NMC mass ratio of 1.33:1) with 240 g/L $Fe_2(SO_4)_3$ at 90 °C for 60 min. While the processes developed by Zou et al. [28] and Xu et al. [29] are effective, further research is needed to develop an organic acid-based leaching process capable of selectively targeting individual battery chemistries within a mixed-feed material rather than indiscriminately dissolving all constituent metals.

As discussed above, much research is available [9,30,31] around the use of organic acids to leach cathode materials such as NMC and LCO, followed by the selective separation of Li from Co, Ni, and Mn through oxalic acid precipitation. In theory, a similar approach can be applied to treating NMC-contaminated LFP feed materials. Thus, this research paper aims to develop a green selective organic leaching process suitable for treating LFP-rich, NMC-contaminated feed materials. A range of organic acids will be screened; however, based on the literature, oxalic acid appears to be the most promising candidate for selectively removing the NMC component from the LFP-rich mixture.

2. Method and Materials

2.1. Materials

The cathode material used for this research was purchased from MSE Suppliers, namely, pristine LFP ($LiFePO_4$, Batch: 05323A4, Tucson, AZ, USA) and NMC 111 ($Li_{1.05}Ni_{0.33}Mn_{0.33}Co_{0.33}O_2$, Batch: 23922A7, Tucson, AZ, USA). A range of organic and inorganic acids were explored for the screening experiments, namely, ascorbic (≥99% L-Ascorbic acid, Sigma-Aldrich, Shanghai, China), acetic (99.7% Glacial Acetic acid, Ajax Finechem Pty Ltd., Auckland, New Zealand), citric (≥99.5% DL-Malic acid, Sigma-Aldrich, Shanghai, China), malic (≥99% DL-Malic acid, Sigma-Aldrich, Shanghai, China), oxalic (≥99.5%, Oxalic acid Dihydrate, batch: 417178, Chem-supply, Gillman, Australia), and sulphuric (98% H_2SO_4, Ajax Finechem Pty Ltd., Auckland, New Zealand) acids. Finally, for the ICP-OES analysis, multi-element (1000 mg/L ICP multi-element standard solution IV, Merck, Darmstadt, Germany) and phosphorus (1000 mg/L P in 0.05% HNO_3, High Purity Standards) standard ICP solutions were used.

2.2. Methods

2.2.1. General Leaching Experiments

All leaching experiments were conducted in 250 mL three-necked round-bottomed flasks. The central neck was connected to a condenser, one of the side necks was used to house a thermocouple for temperature control, and the third neck was used as a sampling port. A heating mantle was used for temperature control and a magnetic stirrer for agitation. All experiments were conducted under atmospheric conditions, and although oxidative or reductive conditions were not specifically controlled, the Eh values of the leaching solutions were measured before and after leaching.

2.2.2. Screening Experiments

For the screening experiments, 200 mL of the respective acids were added to the round-bottom flask, along with 0.2 g and 3.8 g of the pristine NMC 111 and LFP, respectively. The leaching was conducted at 60 °C with an agitation speed of 600 rpm, and 5 mL samples were taken at 30, 60, 120 and 240 min intervals. After leaching, a Büchner funnel connected to an Erlenmeyer vacuum flask and a vacuum pump was used to separate the leach solution from the solid residue. The pH of the final leach solution was recorded, and the samples were prepared for ICP through further filtration and dilution (×10, ×100 and ×1000) using 5% HNO_3.

2.2.3. Optimisation Experiments

The above method was followed for all leaching experiments; the only difference would be in changing the leaching parameters (temperature, acid concentration, pH, and solid-to-liquid ratio). Initial stoichiometric calculations indicated that approximately 0.25 M of oxalic acid was required for the 2% solid leaching system, and this was confirmed by results from experiments in which the acid concentration was varied. It is worth noting that when the solid-to-liquid ratio was varied, the molar ratio of metals to oxalic acid was kept constant. As shown in Section 3.2.5, the concentration of oxalic acid increased from 0.25 M to 1.25 M as the solid-to-liquid ratio increased from 2% to 10%, with the concentration reaching 1.25 M at a 10% solid-to-liquid ratio.

2.3. Analytical Techniques

Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES):

The leach solutions were analysed using the PerkinElmer Optical Emissions Spectrometer Optima 8300. The calibration was performed using multi-element (Al, Cu, Co, Fe, Li, Mn and Ni) and P standards. Calibration standards of 1, 5, 10, 50, and 100 ppm were prepared using 5% HNO_3, which was made with ultra-pure water. The analyses were conducted using argon gas, with gas flow rates to the plasma and nebulizer of 15 and 0.6 L/min, respectively. The pump flow rate was set at 1.5 mL/minute, and the samples were analysed in triplicate. The software used for the ICP analysis was Syngistix (version 3.0) for ICP-OES.

SEM:

Solid samples were analysed using a Tescan Clara Field emission scanning microscope (FESEM) at the John De Laeter Centre at Curtin University. The SEM analyses were conducted using a beam current of 100 pA, a relatively low electron beam energy of 5 keV, and scanning speeds between 1 and 5 to produce secondary emission (SE) SEM images. Chemical mapping was performed using energy-dispersive X-ray spectroscopy (EDS) with the symmetry EBSD detector. The software used to analyse the SEM data was Aztec Synergy v6.1.

XRD:

Pristine NMC and LFP samples, along with leach residues, were sent out to ALS Metallurgy for analysis. The procedure that they followed involved packing the powdered samples into a backpacked sample holder and then analysing them using the Malven Panalytical Empyrean XRD instrument equipped with a PIXcel1D X-ray detector. The conditions used to analyse the samples were a radiation wavelength of Co Kα 1.789 Å, at 40 kV and 40 mA, with the data being collected over an angular range of 5 to 77°2θ for 118 s with a step size of 0.0131°2θ. When quantifying the minerals present in each sample, ALS Metallurgy used a combination of matrix flushing and reference intensity ratio-derived constants.

3. Results and Discussion

3.1. Lixiviant Screening

Screening experiments were conducted to determine whether an organic acid can replace conventional inorganic acid such as sulphuric acid, phosphoric acid and hydrochloric acid for leaching a mixed chemistry black mass. In this study, the synthetic black mass contains 95% LFP and 5% NMC (see Section 2). The conditions for the screening experiments were determined after reviewing the literature (see Table 1). The initial leaching conditions for each acid were determined to be 0.5 M acid, 2% solids, and 600 rpm agitation (magnetic stirred) at 60 °C for 4 h.

Figure 1A–F present the results of the screening experiments. Figure 1F corresponds to the H_2SO_4 leaching system. The high, non-selective metal dissolution observed is expected, as extensive research has demonstrated the effectiveness of H_2SO_4 in dissolving a range of metals. For instance, Vieceli et al. [32] reported that over 90% of Co, Li, Ni and Mn were leached within 15 min. In this research, no H_2O_2 was used, and a lower concentration of H_2SO_4 (0.5 M instead of 2 M) was applied, resulting in slightly lower metal dissolution compared to the results of Vieceli et al. [32]. Since H_2SO_4 is one of the most widely used lixiviants for metal dissolution in industry, the outcomes of this system will serve as the benchmark for evaluating the performance of the organic lixiviants tested. Leaching with H_2SO_4 resulted in complete dissolution of Fe, Li, and P within 30 min, while 91%, 90% and 82% of Ni, Co and Mn, respectively, were dissolved.

The strength of an acid is indicated by its pKa value, which is an indication of how easily the acid donates hydrogen protons. Among the acids screened, acetic and ascorbic acids have the highest pKa values—4.74 [33,34] and 4.16 [30], respectively—indicating that they are the weakest acids in this study. This correlates with their relatively poor metal dissolution capabilities observed in Figure 1A,B, especially in the case of acetic acid, which extracted less than 35% of the metals after 4 h. Citric (pKa_1 = 3.13, pKa_2 = 4.76 and pKa_3 = 6.40) and malic acid (pKa_1 = 3.40 and pKa_2 = 5.11) [35] are slightly stronger acids, and this is reflected in their improved metal dissolution efficiencies. However, their selectivity is similar to that of the H_2SO_4 leaching system, which exhibited no selectivity between the NMC and LFP chemistries.

On the other hand, the oxalic acid (pKa_1 = 1.23 and pKa_2 = 4.19 [23]) leaching system demonstrated a high degree of metal selectivity towards Li and P, with extraction efficiencies exceeding 97% after just 30 min, while 15.88%, 0%, 0% and 12.92% of Fe, Co, Ni and Mn, respectively, were co-extracted. The high selectivity towards Li was previously reported by Li and coworkers [19], in which LFP cathodic material was leached using 0.3 M oxalic acid at 80 °C for 30 min. It was determined that 98% of the Li was extracted, while Fe was left behind as an Fe-Oxalate ($FeC_2O_4 \cdot 2H_2O$). Other research such as Sun et al. [26], Rouquette et al. [23], and Schmitz et al. [11] investigated the use of oxalic acid as a selective lixiviant and precipitating agent. Sun and coworkers [26] determined that when leaching $LiCoO_2$ and CoO with 1 M oxalic acid and 5% solids at 80 °C for 2 h that 98% of the $LiCoO_2$ reacted, resulting in a Li-rich leach solution and Co-oxalate as a precipitate. Similar precipitation research was conducted by Schmitz and coworkers [11], in which citric acid was used to leach NMC 111; subsequently, oxalic acid was added as a precipitating agent to promote the formation of insoluble Co, Ni and Mn oxalates. Thus, it can be concluded that the low amounts of Fe, Ni, Co, and Mn being extracted in Figure 1E are attributed to the formation of insoluble metal–oxalates that form during the leaching process. A list of the most common oxalate complexes likely to form when leaching spent LiBs (LFP and NMC chemistry) is presented in Table 2.

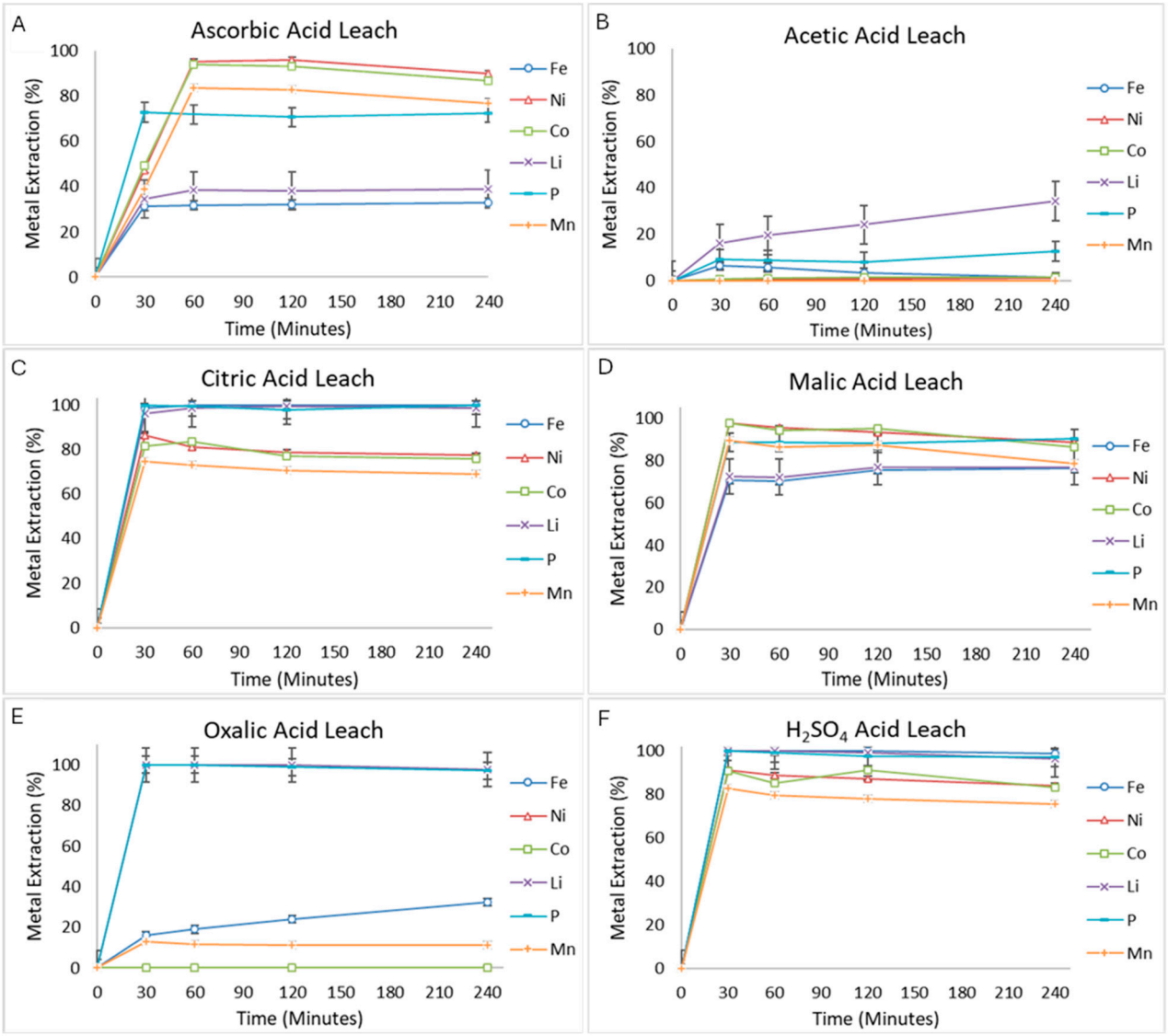


Figure 1. Organic acid screening experiments (0.5 M acid, 2% solids, 600 rpm, 60 °C, 4 h) using ascorbic acid (**A**), acetic acid (**B**), citric acid (**C**), malic acid (**D**), oxalic acid (**E**) and sulphuric acid (**F**).

Table 2. List of soluble and insoluble metal oxalates (adapted from [11,36]).

Compound	Solubility
$AL_2(C_2O_4)_3 \cdot H_2O$	Insoluble
$CoC_2O_4 \cdot 2H_2O$	Insoluble
$CuC_2O_4 \cdot 1/2H_2O$	Insoluble
$FeC_2O_4 \cdot 2H_2O$	Insoluble
$Fe_2(C_2O_4)_3$	Soluble
$Li_2C_2O_4$	Soluble
$MnC_2O_4 \cdot 2H_2O$	Slightly Soluble
$NiC_2O_4 \cdot 2H_2O$	Insoluble

When comparing the H_2SO_4 and oxalic acid-leaching systems, it is evident that oxalic acid offers a more selective route for targeting Li and P from mixed-chemistry (LFP and NMC) black mass. This is advantageous compared to the H_2SO_4 system, as it allows for

the separation of an already complex material. In this approach, Li can be recovered first, followed by Co, Ni and Mn in subsequent processing stages.

3.2. Optimisation of Oxalic Acid Leach—Synthetic Sample

3.2.1. Effect of Concentration

The concentration of the oxalic acid-leaching system was varied from 0.1 M to 1 M (see Figure 2A–D), while the temperature, leaching time, and stirring rate were kept constant. At 0.1 M, the extraction efficiencies for Li and P reached 65% and 60%, respectively. This extraction is significantly lower than those observed in the screening experiment (see Figure 1E). This reduction in extraction efficiency is attributed to the low oxalic acid concentration, which acts as the limiting reagent. When the oxalic acid concentration is increased to approximately the theoretical stoichiometric amount (0.25 M, see Figure 2B), the extraction of Li and P increases to between 90% and 100% after just 15 min. Further increases in oxalic acid concentration above 0.25 M (Figure 2C,D) have little effect on the extraction of Li and P. This trend is evident in Figure 2E, which presents the extraction curves for Li and P after 60 min at varying acid concentrations, showing a plateau after 0.25 M oxalic acid.

The co-extraction of Fe increases slightly when the oxalic acid concentration increases from 0.1 M to 0.25 M; and above 0.25 M, there is no significant change in the amount of Fe dissolved in the leach solution. However, a significant increase in the co-extraction of Mn is observed with increasing oxalate concentrations. When operating around the stoichiometric concentration (0.25 M), approximately 18% of Mn is extracted after 1 h, and this increases to between 38% and 44% (after 60 min) when the oxalate concentration is increased to 0.5 M and 1 M. This high Mn dissolution differs to that reported by Saleem et al. [37] and Rouquette et al. [23], who reported Mn extractions of only 1.5% and 2.4%, respectively, using oxalic acid-leaching systems. However, the findings in this research are similar to the results of Li et al. [25], who observed Mn co-extraction ranging from 20.1% to 32.9% as the oxalic acid concentration increased from 0.75 M to 2 M. When evaluating Figure 2C,D, it is evident that there is a decreasing trend observed for Mn, which aligns with the observations of Rouquette and coworkers [23]. This decline is attributed to the two-stage leaching mechanism associated with oxalic acid leaching of transition metals. As explained by Roquette and coworkers [23], the initial step involves the dissolution of Mn, followed by the precipitation of insoluble Mn-oxalates over time. However, as shown in Figure 2E, Mn concentration in the leach solution increases with higher oxalate concentrations. This observation is consistent with the findings of Georgeta et al. [38] and Roquette et al. [30], who reported that in the presence of excess oxalic acid, insoluble Mn-oxalate ($MnC_2O_4 \cdot H_2O$) can further react to form soluble complexes ($[Mn(C_2O_4)_2]^{-2}$). Consequently, an increase in Mn concentration with increasing acid concentration is to be expected.

Finally, variations in acid concentration had no observable effect on the presence of Co and Ni in the pregnant leach solution. This observation is consistent with the previous research, including those by Sun and Qiu [26], Mette and Yagmurlu [39], and Roquette and coworkers [23], who all reported minimal concentrations of Ni and Co in the leach solution. The low solubility of these compounds is reflected in their respective solubility product constant (Ksp), with values of 6.639×10^{-8} for Co-oxalate and 5.308×10^{-9} for Ni-oxalate, respectively [39].

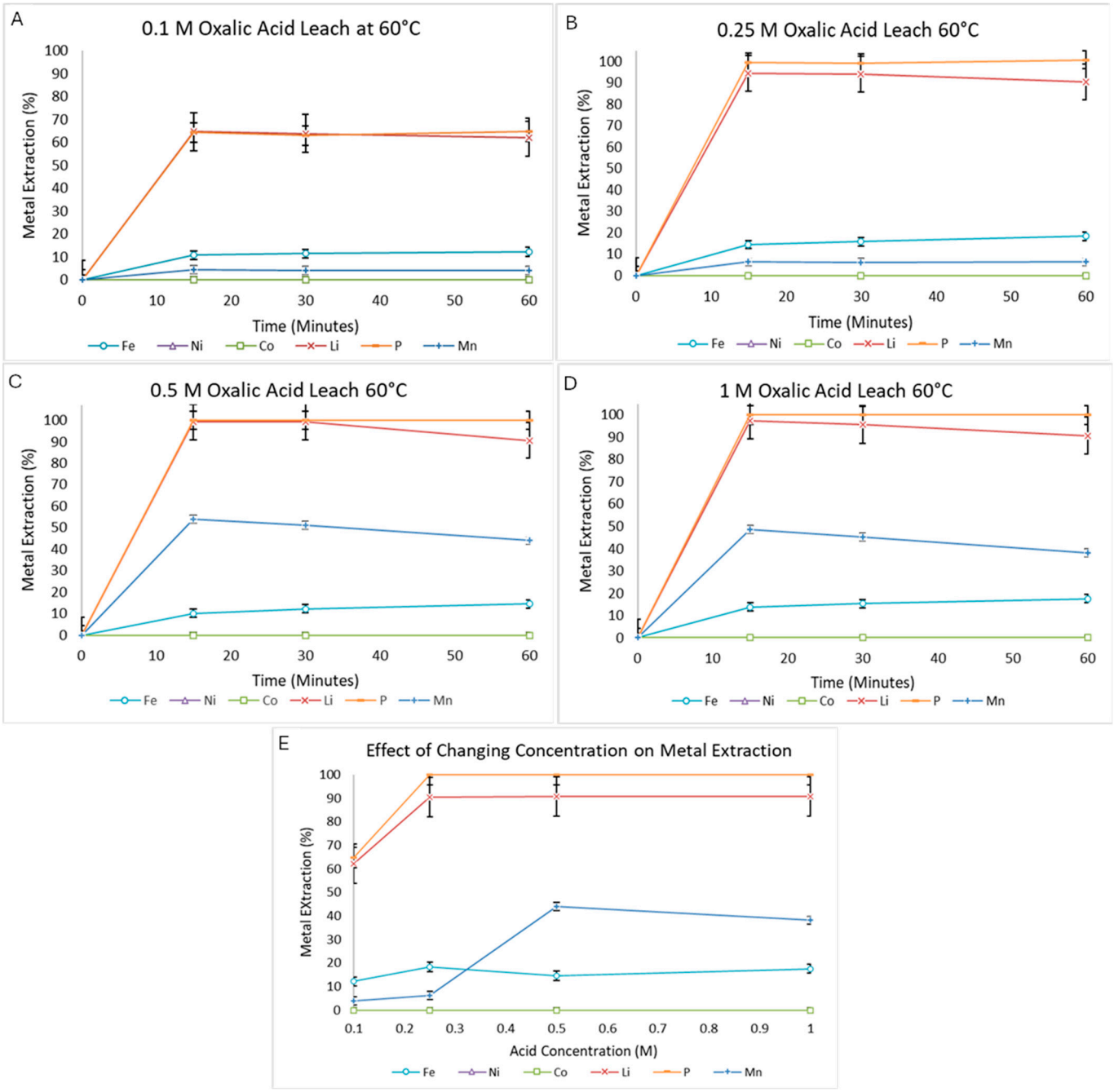


Figure 2. Effect of changing concentration on LFP-NMC leaching (2% solids, 60 min, 60 °C): 0.1 M oxalic acid (**A**), 0.25 M oxalic acid (**B**), 0.5 M oxalic acid (**C**), 1 M oxalic acid (**D**) and overall effect of changing concentration after 60 min (**E**).

3.2.2. Effect of Temperature

The temperature of the leaching system was varied between room temperature and 80 °C, while the solid–liquid ratio, agitation speed, acid concentration, and leaching time were kept constant. Figure 3A–D illustrate that increasing the leaching temperature does not significantly affect the leaching rates of Li and P. Overall, after 60 min, approximately 90% of Li and nearly 100% of P were leached. However, variations in temperature do impact the co-extraction of Ni, Mn and Fe. As shown in Figure 3A, Ni extraction reached approximately 10% after 15 min but decreased to 0% after 30 min. This observation can be attributed to the formation of insoluble Ni-oxalate with time, which precipitates out of the solution. The most significant effect of temperature was observed in Mn extraction

(Figure 3A–D). After just 15 min, as the temperature increased from 25 °C to 80 °C, the amount of Mn extracted increased from approximately 16% to 48%. This trend aligns with findings by Liu et al. [40], who reported that the solubility of oxalate in solution increases with temperature. This correlates with the results presented in Figure 3E, demonstrating increased Mn-oxalate solubility with temperature. Mn-oxalate, being slightly soluble at lower temperature, becomes more soluble at elevated temperature, explaining the observed increase in Mn leaching (Figure 3E). The increase in Fe dissolution can be attributed to a higher formation of Fe^{3+} ions at elevated temperature, as opposed to Fe^{2+}. This leads to the formation of Fe (III)-oxalate, which is more soluble than Fe (II)-oxalate, thereby enhancing Fe extraction at higher temperatures [37].

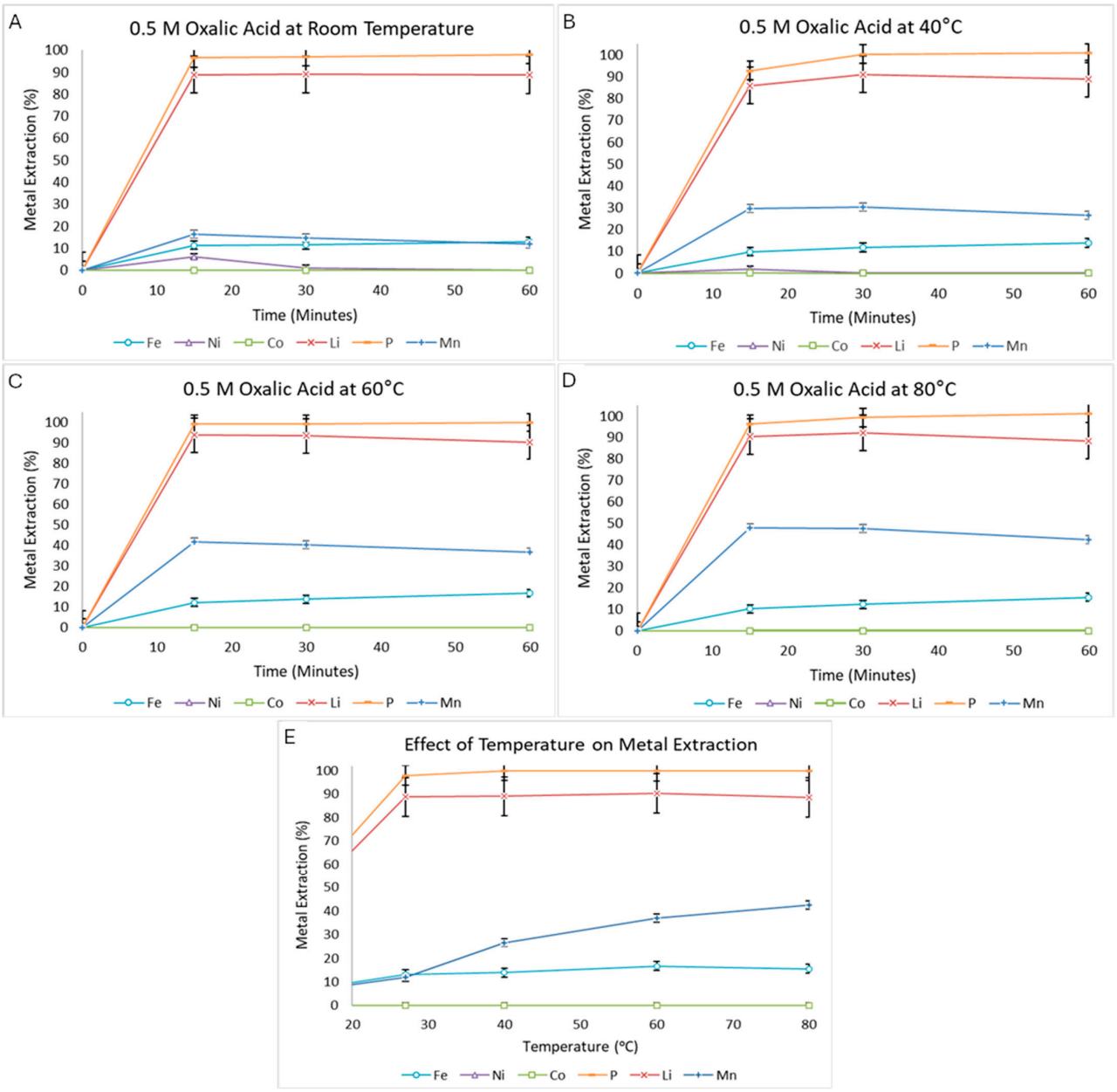


Figure 3. Effect of changing temperature on LFP-NMC leaching efficiency (2% solids, 0.5 M, 60 min). Oxalic acid leaching at room temperature (**A**), 40 °C (**B**), 60 °C (**C**), 80 °C (**D**), and a comparison of the effect of temperature (**E**).

3.2.3. Possible Leaching Reactions

The experimental data and literature discussed in Section 3, along with the Eh-pH diagrams (Figure 4), have been used to propose leaching equations (Equations (3) and (4) for the dissolution of NMC 111 and $LiFePO_4$ using oxalic acid. During the leaching of NMC 111, Li is observed in solution along with a small amount of Mn, while Co and Ni are not detected. According to the literature, this behaviour can be explained by the fact that Li dissolves as Li^+ and/or as soluble Li-oxalate, and Mn forms slightly soluble Mn-oxalate. In contrast, Co and Ni form insoluble oxalate complexes under the studied conditions, preventing their dissolution. This explanation is further supported by the Eh-pH diagrams for the various metal–oxalate systems (see Figure 4A–D). The leaching experiments were conducted at approximately pH 1.15, which corresponds to the regions in the Eh-pH diagrams where the formation of insoluble complexes with Mn, Co, and Ni is thermodynamically favoured. Based on this information, Equation (3) is proposed.

$$\begin{aligned} &3\ LiNi_{\frac{1}{3}}Mn_{\frac{1}{3}}Co_{\frac{1}{3}}O_{2\ (s)} + 5\ C_2H_2O_4\ .H_2O_{\ (aq)} \\ &\rightarrow\ LiH(C_2O_4)_{\ (aq)} + Li_2(C_2O_4)_{\ (aq)} + Ni(C_2O_4)_{\ (s)} + Co(C_2O_4)_{\ (s)} \\ &+ Mn(C_2O_4)_{\ (s)} + 14\tfrac{1}{2}\ H_2O_{\ (l)} + \tfrac{3}{4}O_{2\ (g)} \end{aligned} \quad (3)$$

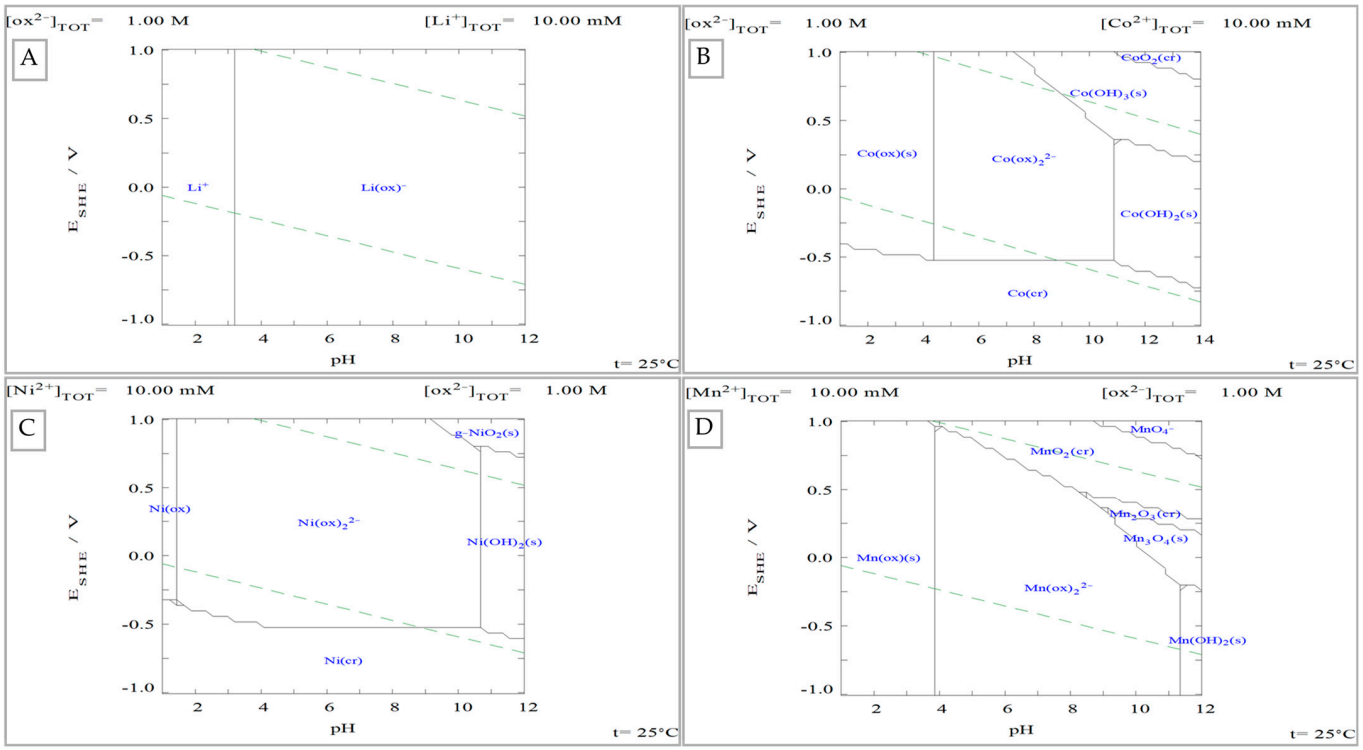


Figure 4. Eh-pH diagrams for different metal–oxalate systems (diagrams constructed using the Medusa software-32 bit version). Lithium–oxalate system (**A**), cobalt–oxalate system (**B**), nickel–oxalate system (**C**) and Mn-oxalate system (**D**).

The leaching of LFP with oxalic acid (see Equation (4)), as demonstrated in the results above, leads to the dissolution of large amounts of Li and P. Iron forms either a soluble Fe^{3+} oxalate complex or an insoluble Fe^{2+} oxalate complex (see Section 3.2.2 and Table 2), while

Li is present as soluble Li-oxalate species. Phosphorus occurs in solution either as a salt or in the form of phosphoric acid [41].

$$3\ LiFePO_{4\ (s)} + 6\ C_2H_2O_4\ .H_2O_{\ (aq)} \rightarrow\ Fe(C_2O_4)_{\ (s)} + Fe_2\,(C_2O_4)_{3\ (aq)} + Li_2\,(C_2O_4)_{\ (aq)} + LiH(C_2O_4)_{\ (aq)} + 3\ H_3PO_{4\ (aq)} + 12\ H_2O_{\ (l)} + 2\ H^+_{(aq)} \quad (4)$$

3.2.4. Changing pH

It is well established that the pH of a leaching system can be altered to promote the dissolution of specific metals. The Eh-pH diagrams for Co, Ni, and Mn (see Figure 4B–D) suggest the possibility of forming soluble metal–oxalate complexes at higher pH levels. Thus, leaching was investigated at approximately pH 4, using an oxalic acid concentration of 0.25 M, 2% solids, an agitation speed of 600 rpm, and room temperature for 2 h. Under these conditions, the extraction of Co, Ni and Mn increased significantly from 0%, 0% and 7.74% to 75.05%, 72.82% and 69.44%, respectively. As shown in Figure 5C, at pH 4, the selectivity of the oxalic acid-leaching system swung, favouring the extraction of Co, Ni and Mn over Li, P, and Fe. To the best of the authors' knowledge, this selective extraction behaviour has not been reported in the literature.

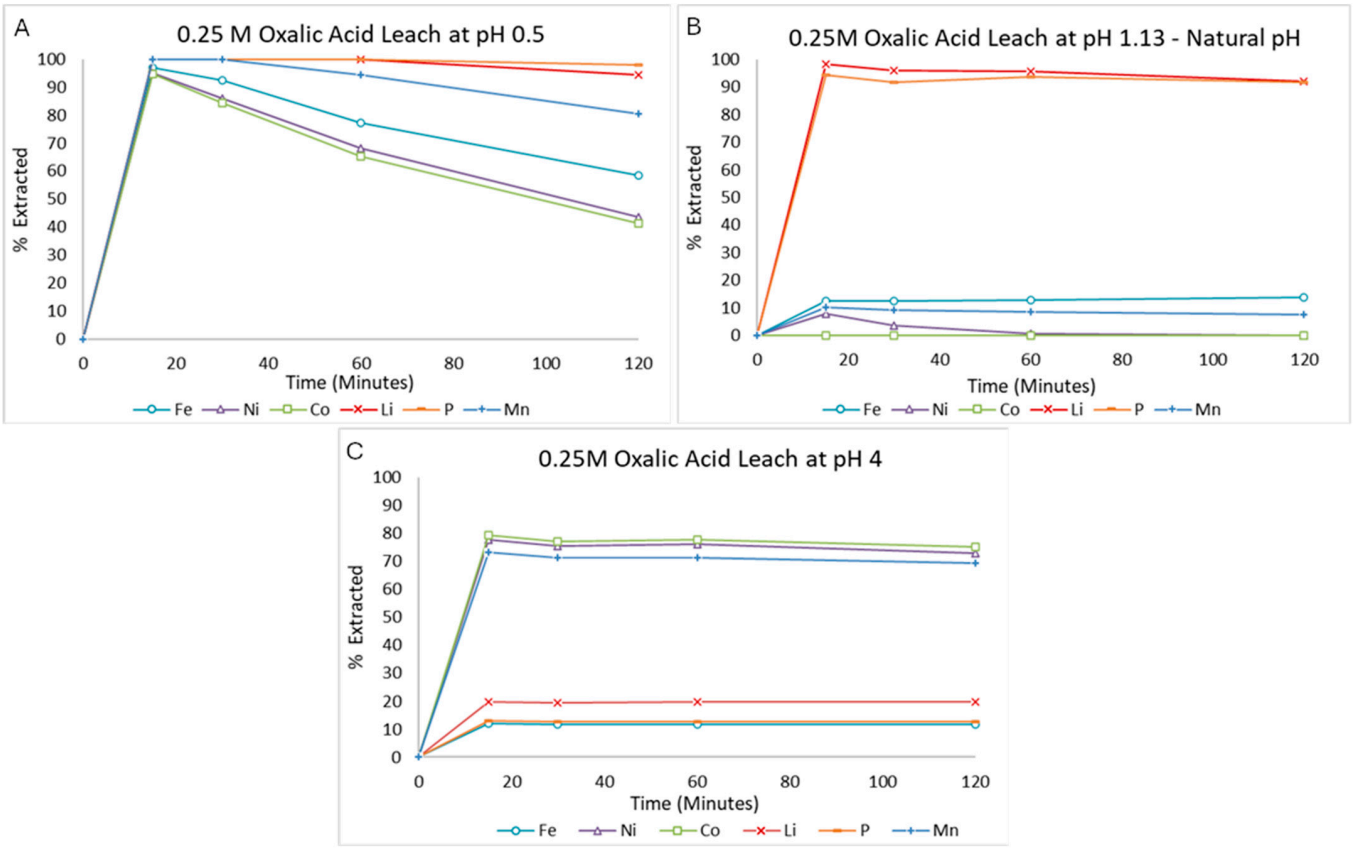


Figure 5. Effect of changing pH on LFP-NMC leaching efficiency (2% solids, 0.25 M, 25 °C, 120 min) at pH 0.5 (**A**), pH 1.13 (**B**), and pH4 (**C**).

On the other hand, at lower pH values (e.g., pH 0.5, see Figure 5A), selectivity is lost, and more than 94% of Co, Fe, Li, Mn, Ni and P are extracted after just 15 min. However, as observed previously, extended leaching time results in a decrease in the concentrations of Co, Ni, Fe and Mn in solution, due to the subsequent formation of insoluble metal–oxalate complexes. The initially high dissolution of Co, Ni and Mn at low pH can be attributed to

the formation of soluble metal sulphates, which subsequently react with oxalate ions in solution to form insoluble metal oxalates.

The findings from the above experiment provide the potential for multiple processing routes: indiscriminate dissolution of over 94% of all target metals; selective dissolution of over 90% of Li and P; or selective dissolution of over 70% of Co, Ni and Mn. However, further investigation is required to better understand the shift in metal dissolution behaviour with increasing pH, as this phenomenon has not yet been reported in the literature.

3.2.5. Effect of Solid–Liquid Ratio

Throughout this study, a solid-to-liquid ratio of 2% (20 g/L) was used due to the limited availability of sample material. However, in industrial applications, solid-to-liquid ratios are typically higher, around 10%. Thus, an experiment was conducted to evaluate the effect of a higher solid-to-liquid ratio on the leaching performance using synthetic black mass (see Figure 6A,B). The leaching was conducted using the optimal oxalic acid concentration (0.25 M), as identified in Section 3.2.1. At higher solid-to-liquid ratios, more solids are leached per mL of solution; thus, to maintain a consistent molar ratio of oxalic acid to target metals, the oxalic acid concentration was increased to 1.25 M. Comparing Figure 6A,B reveals that Li extraction increased from approximately 90.32% to 95.03%, while the co-extraction of Fe and Mn dropped from 18.33% to 10% and from 6.27% to 1.99%, respectively. The decrease in the co-extraction of Fe and Mn can be attributed to the greater consumption of oxalic acid during the initial leaching of Li and P, leaving less available for the co-extraction of other metals. Overall, these results are promising and suggest that the proposed process has the potential to be applied at an industrial scale for the treatment of mixed-chemistry black mass.

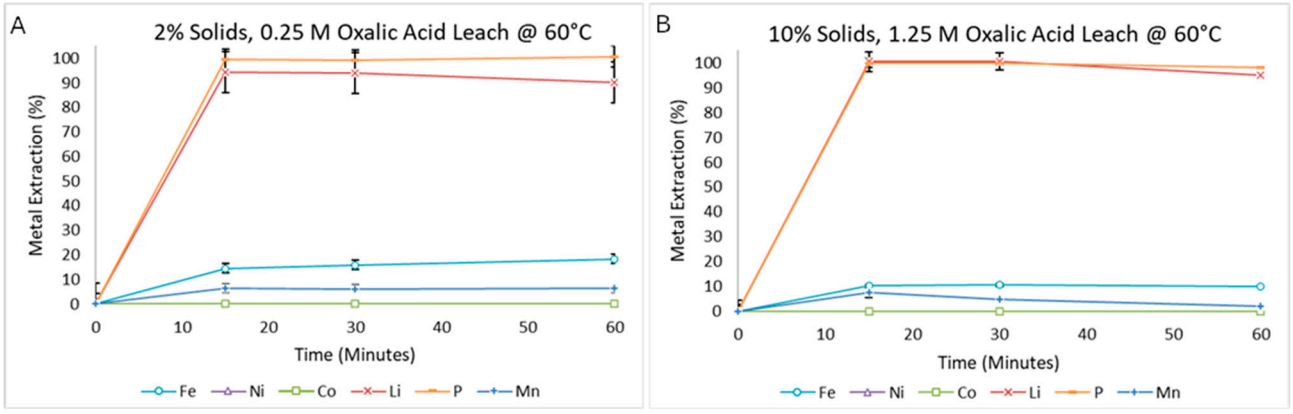


Figure 6. Effect of solid–liquid ratio on LFP-NMC leaching efficiency (2% solids, 60 °C, 60 min): leaching at 2% solids (**A**) and 10% solids (**B**).

3.2.6. Supersaturated Leaching System

The solubility of metal–oxalates complexes can vary depending on the concentration of oxalic acid in solution. Previous studies, such as those by Verma and coworkers [41], have stated that certain insoluble metal–oxalate complexes can react with excess oxalic acid to form more soluble oxalate complexes. Thus, a second stage leaching experiment was conducted using a supersaturated solution of 2.5 M oxalic acid to assess whether Co, Ni, and Mn could be recovered from the leach residue of synthetic black mass. From the onset, the solution proved difficult to work with and required temperatures above 40 °C to prevent oxalate precipitation. Leaching of the synthetic LFP-NMC material was conducted at 60 °C with agitation at 600 rpm for 1 h. The results, presented in Figure 7, show no significant change in the extraction of Co, Ni, and Mn. However, a significant decrease in Li and P

recovery was observed, reducing from >90% to 72% and 59%, respectively. The reduction in recovery is most likely due to the formation of large amounts of precipitated particles, which may have promoted further precipitation of oxalic acid and various metal–oxalate complexes from solution. These findings suggest that the use of highly concentrated oxalic acid leach solutions is not recommended at either laboratory or industrial scale, as this promotes the precipitation of oxalate and metal–oxalates that could hinder metal recovery. Similarly, Liu and coworkers [40] reported that oxalates can form low-solubility complexes with alkaline earth metals, contributing to scaling, an issue that can negatively affect process efficiency. This scaling effect, along with reduced metal dissolution, is important to keep in mind when designing and scaling up oxalic acid-leaching processes.

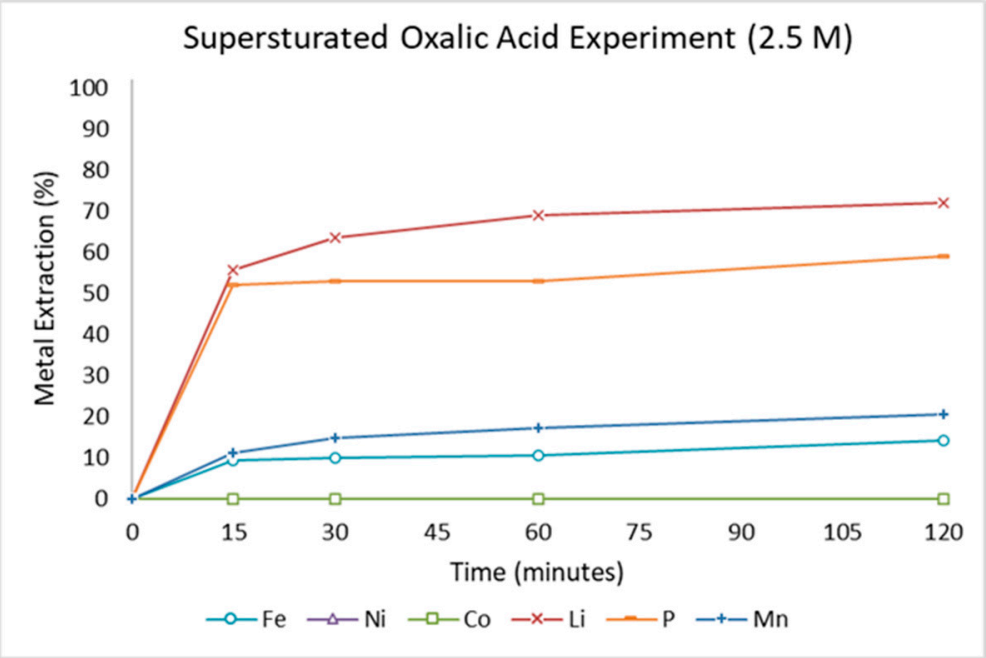


Figure 7. Supersaturated oxalic acid leaching of LFP-NMC (2% solids, 60 °C, 120 min).

3.2.7. Analysis of Residue Material

This paper has discussed the formation of various metal oxalates during the leaching process. To confirm the presence of these oxalates, SEM, SEM-EDS, and XRD were performed on the leach residues. The SEM images in Figure 8A,B depict the pristine LFP and NMC cathode materials, respectively. The NMC particles have a distinct spherical morphology with relatively uniform sizes ranging from 5 to 10 μm, while the LFP material is a mixture of very fine spherical particles (less than 0.5 μm) and larger irregularly shaped particles (3–5 μm).

XRD analysis was initially performed (see Figure 9A,B) on an LFP sample that had been leached using oxalic acid to determine whether oxalates had formed. The XRD results confirmed that almost all the LFP had dissolved, leaving behind a residue primarily composed of Fe-oxalates (humboldtine and iron oxalate hydrate).

After leaching the synthetic black mass with oxalic acid (see Figure 8C), a noticeable change in morphology was observed, with the formation of distinctive crystalline rod-like structures, a morphology characteristic of oxalates. Similar structures have been reported by researchers such as Li et al. [19], Li et al. [25], and Fan et al. [42]. The SEM-EDS results (see Figure 8D–F) showed that the oxalate crystals are composed of Co, Ni, and Mn, along with large amounts of Fe. This result is expected as the synthetic BM is LFP-rich, and thus Fe-oxalate is expected to constitute the majority of the residue, along with some Mn-, Ni-,

and Co-oxalates. To our surprise, the individual metal oxalates were not identifiable using SEM-EDS; rather, mixed-metal oxalates containing Fe, Mn, Co, and Ni were observed. This finding aligns with the work of Zhang et al. [43], who demonstrated through EDS and XRD analyses that attempts to precipitate Mn, Ni, and Co oxalates often result in the formation of mixed-metal oxalates.

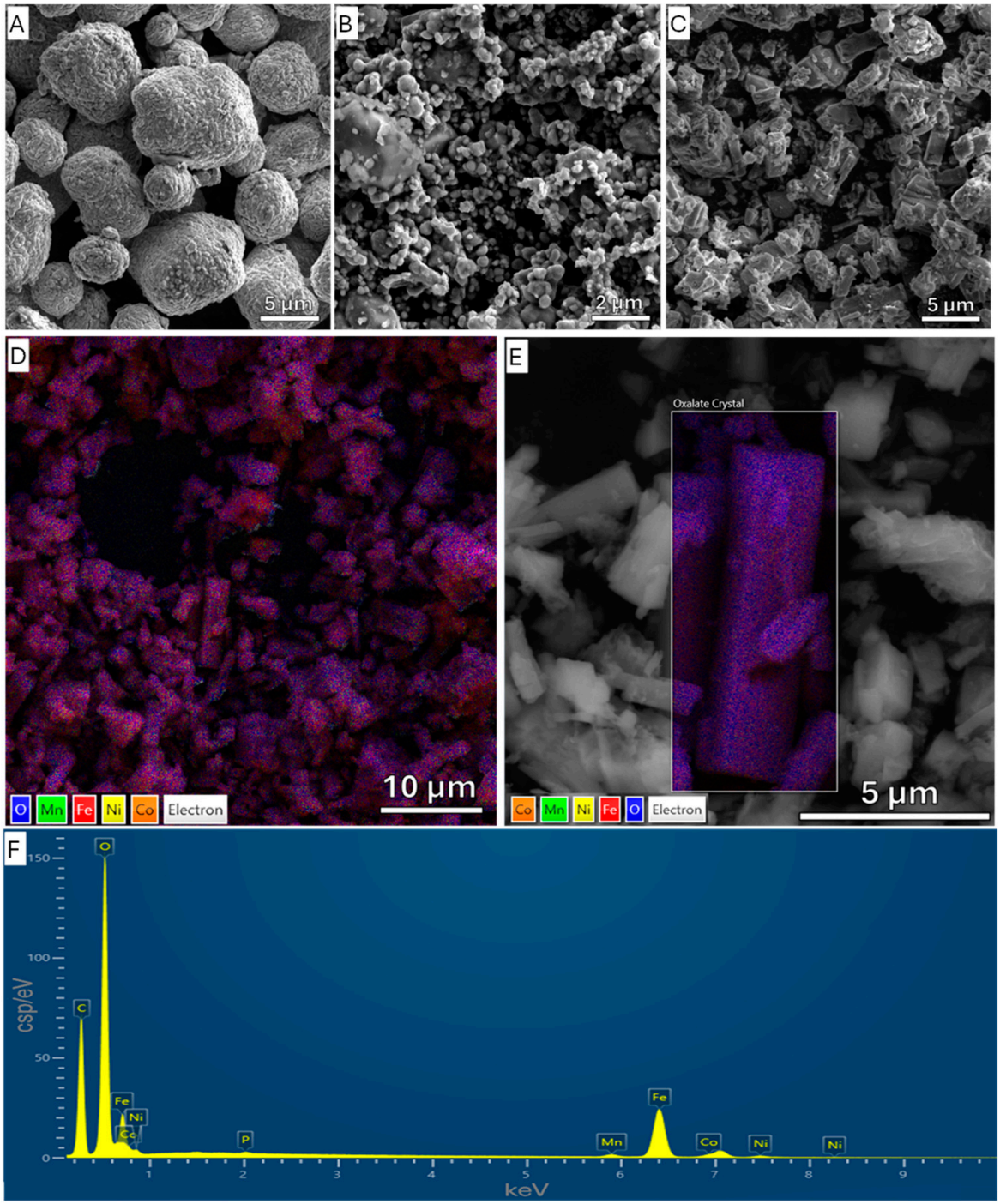


Figure 8. SEM image of pristine NMC (**A**), pristine LFP (**B**), and residue from oxalic leach (**C**). SEM-EDS chemical mapping and spectra of residue from oxalic leach (**D**–**F**).

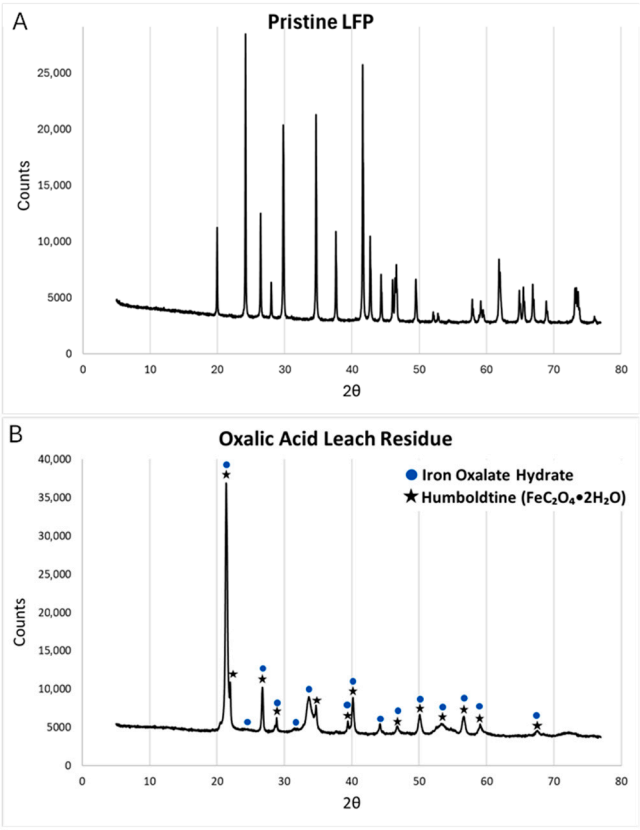


Figure 9. XRD spectra of pristine LFP sample (**A**); XRD spectra of residue from oxalic acid leached LFP (**B**).

3.2.8. Applications

The main aim of this research was to identify an organic acid capable of selectively separating different battery chemistries during the leaching of a mixed-chemistry feed. Oxalic acid has been identified as a suitable candidate, demonstrating the ability to selectively extract over 90% of Li and P while suppressing the dissolution of Co, Ni, Mn, and Fe under operating conditions of approximately pH 1.15, 2% solids, room temperature, and a contact time of just 15 min. However, this research also revealed that the selectivity of oxalic acid is highly sensitive to changes in pH. Thus, by controlling the pH of the leaching system, it is possible to swing the selectivity of metal dissolution, enabling targeted extraction of different elements. Given the use of pristine cathodic material, the results of this study are most applicable to the treatment of production scraps, particularly when they are processed as mixed streams. Based on the findings, two potential flowsheets for the leaching of NMC-contaminated LFP materials using oxalic acid are proposed (see Figure 10A,B). In Figure 10A, a pH 4 oxalic acid-leaching system is suggested as the first step, selectively extracting Co, Ni, and Mn from the BM. This leaves a residue enriched in Fe, Li, and P, effectively removing the NMC impurities from the LFP matrix. In the second step, the residue is treated with oxalic acid at pH 1.15 to selectively dissolve Li and P, producing a Li- and P-rich leachate while leaving Fe in the solid phase. Alternatively, as shown in Figure 10B, Li and P may be removed first using oxalic acid at pH 1.15, followed by a second leaching step at pH 0.5 to fully dissolve the remaining Fe, Co, Ni, and Mn. The main advantage of choosing Option B over Option A is that reduced reagents (in this case, H_2SO_4 and NaOH) are required to drop the pH from 1.15 to 0.5 as opposed to increasing it from pH 1.15 to 4. However, Option B is not as selective as Option A, which theoretically enables the production of three product streams, namely a Co-, Ni-, and Mn-rich solution, a Li-

and P-rich solution, and a Fe-oxalate-rich residue. This reduces the need for downstream separation processes to isolate Co, Ni, and Mn from Fe.

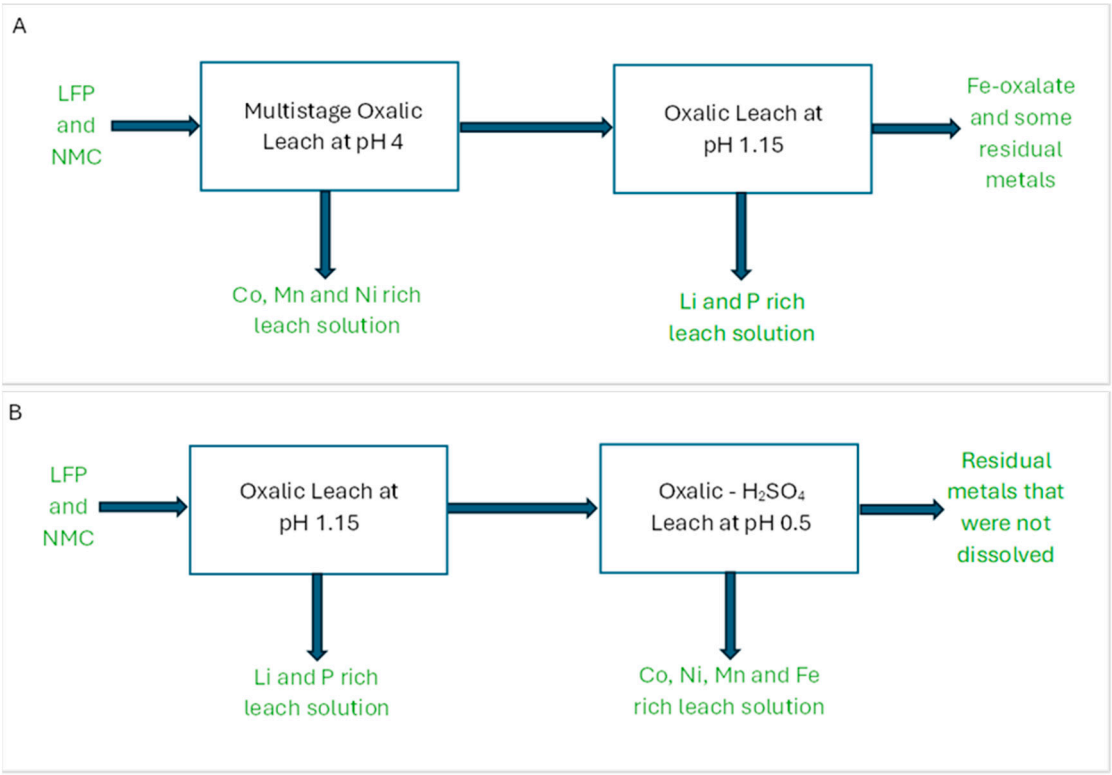


Figure 10. Possible leaching routes. Selective removal of Co, Ni and Mn impurities using a pH 4 oxalic acid-leaching system followed by pH 1.15 oxalic leach to remove Li and P (**A**). Selective removal of Li and P followed by non-selective oxalic-H_2SO_4 to remove Co, Ni, and Mn (**B**).

4. Conclusions

In conclusion, this study has identified oxalic acid as a promising organic leaching agent for the selective treatment of LFP black mass contaminated with other battery chemistries, such as NMC 111. Under the optimal leaching conditions (2% solids, 0.25 M oxalic acid, natural pH around 1.15, room temperature, 60 min), oxalic acid was shown to selectively dissolve approximately 95.58% and 93.57% of Li and P, respectively, while only co-extracting 12.83% of Fe and 8.43% of Mn. Notably, Co and Ni were not detected in the leach solution under these conditions. The study further demonstrated that increasing the temperature or the oxalic acid concentration led to greater co-extraction of Fe and Mn, suggesting that these parameters negatively impact selectivity. However, the most influential parameter was found to be the pH of the leaching system. At low pH values (0.5), the leaching system exhibited no selectivity, with over 94% of all metals dissolving after just 15 min. Nevertheless, extended leaching under these conditions resulted in the precipitation of Co, Fe, Mn, and Ni due to the formation of insoluble metal–oxalate complexes after 15 min. While when the pH was increased to approximately 4, the selectivity of the system shifted significantly. Under these conditions, 75.05%, 72.82% and 69.44% of Co, Ni and Mn, respectively, were selectively extracted into solution, while the co-extraction of Li, P, and Fe was limited to 19.83%, 12.70% and 11.71%, respectively. These results highlight the pH-dependent selectivity of the oxalic acid system. Finally, this research proposed a possible two-stage leaching circuit that could be implemented to selectively remove the NMC contaminants from the LFP material at pH 4. In the second stage, the residue is further leached at pH 1.15 to produce a Li- and P-rich pregnant leach solution

and a Fe-oxalate-rich residue. This sequential approach offers a selective and potentially scalable method for processing mixed battery materials.

Recommendations for future work:

- The proposed process should be applied to industrially sourced black mass, as it has so far only been demonstrated on a simplified system using pristine LFP and NMC materials. Testing with real-world samples is necessary to evaluate practical applicability.
- Further investigation is needed to better understand the observed shift in metal dissolution with changes in pH.
- Additives such as amine-based chelating agents could be explored to improve the dissolution of Co, Ni, and Mn in the oxalic acid-leaching system.

Author Contributions: Conceptualization, J.E., E.O., C.C.B. and M.S.H.; Methodology, M.S.H., E.O., J.E. and C.C.B.; Validation M.S.H.; Formal Analysis, M.S.H.; ICP-OES was conducted by M.S.H., and SEM imaging was conducted by M.S.H.; Investigation, M.S.H.; Resources, J.E., E.O. and C.C.B.; Data Curation, M.S.H.; Writing—original draft preparation, M.S.H.; Writing—review and editing, M.S.H., C.C.B. and E.O.; Data Visualization, M.S.H.; Supervision, J.E., E.O. and C.C.B.; Project Administration, J.E., E.O., C.C.B. and M.S.H.; Funding Acquisition, J.E., E.O. and C.C.B. All authors have read and agreed to the published version of the manuscript.

Funding: The Future Battery Industries CRC (FBI-CRC, as part of the Australian Government Cooperative Research Centres Program) and Curtin University funded the staff salaries and fee scholarships (for Mr Henderson). Part of this research was undertaken using the Tescan Clara FESEM with Oxford instrumentation (ARC LE 190100176) at the John de Laeter Centre, Curtin University.

Data Availability Statement: The data will be made available upon request to the corresponding author.

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

References

1. Mossali, E.; Picone, N.; Gentilini, L.; Rodriguez, O.; Perez, J.M.; Colledani, M. Lithium-ion batteries towards circular economy: A literature review of opportunities and issues of recycling treatments. *J. Environ. Manag.* **2020**, *264*, 110500. [CrossRef] [PubMed]
2. Vasconcelos, D.D.S.; Tenório, J.A.S.; Junior, A.B.B.; Espinosa, D.C.R. Circular Recycling Strategies for LFP Batteries: A Review Focusing on Hydrometallurgy Sustainable Processing. *Metals* **2023**, *13*, 543. [CrossRef]
3. Islam, M.T.; Huda, N.; Baumber, A.; Hossain, R.; Sahajwalla, V. Waste battery disposal and recycling behavior: A study on the Australian perspective. *Environ. Sci. Pollut. Res. Int.* **2022**, *29*, 58980–59001. [CrossRef] [PubMed]
4. Prasetyo, E.; Muryanta, W.A.; Anggraini, A.G.; Sudibyo, S.; Amin, M.; Al Muttaqii, M. Tannic acid as a novel and green leaching reagent for cobalt and lithium recycling from spent lithium-ion batteries. *J. Mater. Cycles Waste Manag.* **2022**, *24*, 927–938. [CrossRef]
5. Raj, T.; Chandrasekhar, K.; Kumar, A.N.; Sharma, P.; Pandey, A.; Jang, M.; Jeon, B.H.; Varjani, S.; Kim, S.H. Recycling of cathode material from spent lithium-ion batteries: Challenges and future perspectives. *J. Hazard. Mater.* **2022**, *429*, 128312. [CrossRef] [PubMed]
6. Choi, J.W.; Cho, C.W.; Yun, Y.S. Organic acid-based linear free energy relationship models for green leaching of strategic metals from spent lithium-ion batteries and improvement of leaching performance. *J. Hazard. Mater.* **2022**, *423*, 127214. [CrossRef] [PubMed]
7. 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]
8. 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] [PubMed]
9. 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]
10. 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]
11. 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. [CrossRef]

12. Roshanfar, M.; Golmohammadzadeh, R.; Rashchi, F. An environmentally friendly method for recovery of lithium and cobalt from spent lithium-ion batteries using gluconic and lactic acids. *J. Environ. Chem. Eng.* **2019**, *7*, 102794. [CrossRef]
13. Esmaeili, M.; Rastegar, S.O.; Beigzadeh, R.; Gu, T. Ultrasound-assisted leaching of spent lithium ion batteries by natural organic acids and H_2O_2. *Chemosphere* **2020**, *254*, 126670. [CrossRef] [PubMed]
14. Nayaka, G.P.; Pai, K.V.; Santhosh, G.; Manjanna, J. Recovery of cobalt as cobalt oxalate from spent lithium ion batteries by using glycine as leaching agent. *J. Environ. Chem. Eng.* **2016**, *4*, 2378–2383. [CrossRef]
15. Zhuang, L.; Sun, C.; Zhou, T.; Li, H.; Dai, A. Recovery of valuable metals from $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ cathode materials of spent Li-ion batteries using mild mixed acid as leachant. *Waste Manag.* **2019**, *85*, 175–185. [CrossRef] [PubMed]
16. Bian, D.; Sun, Y.; Li, S.; Tian, Y.; Yang, Z.; Fan, X.; Zhang, W. A novel process to recycle spent $LiFePO_4$ for synthesizing $LiFePO_4$/C hierarchical microflowers. *Electrochim. Acta* **2016**, *190*, 134–140. [CrossRef]
17. Yang, Y.; Zheng, X.; Cao, H.; Zhao, C.; Lin, X.; Ning, P.; Zhang, Y.; Jin, W.; Sun, Z. A Closed-Loop Process for Selective Metal Recovery from Spent Lithium Iron Phosphate Batteries through Mechanochemical Activation. *ACS Sustain. Chem. Eng.* **2017**, *5*, 9972–9980. [CrossRef]
18. Wu, D.-Y.; Wang, D.-X.; Liu, Z.-Q.; Rao, S.; Zhang, K.-F. Selective recovery of lithium from spent lithium iron phosphate batteries using oxidation pressure sulfuric acid leaching system. *Trans. Nonferrous Met. Soc. China* **2022**, *32*, 2071–2079. [CrossRef]
19. 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]
20. Li, P.; Luo, S.; Zhang, L.; Wang, Y.; Zhang, H.; Wang, J.; Yan, S.; Hou, P.; Wang, Q.; Zhang, Y.; et al. Study on efficient and synergistic leaching of valuable metals from spent lithium iron phosphate using the phosphoric acid-oxalic acid system. *Sep. Purif. Technol.* **2022**, *303*, 122247. [CrossRef]
21. Kumar, J.; Shen, X.; Li, B.; Liu, H.; Zhao, J. Selective recovery of Li and $FePO_4$ from spent $LiFePO_4$ cathode scraps by organic acids and the properties of the regenerated $LiFePO_4$. *Waste Manag.* **2020**, *113*, 32–40. [CrossRef] [PubMed]
22. Zhao, T.; Traversy, M.; Choi, Y.; Ghahreman, A. A novel process for multi-stage continuous selective leaching of lithium from industrial-grade complicated lithium-ion battery waste. *Sci. Total Environ.* **2024**, *909*, 168533. [CrossRef] [PubMed]
23. 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]
24. 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 $Li(NiCoMn)O_2$ Cathodes from Spent Lithium-Ion Batteries. *ACS Sustain. Chem. Eng.* **2018**, *6*, 5959–5968.
25. Li, Q.; Fung, K.Y.; Xu, L.; Wibowo, C.; Ng, K.M. Process Synthesis: Selective Recovery of Lithium from Lithium-Ion Battery Cathode Materials. *Ind. Eng. Chem. Res.* **2019**, *58*, 3118–3130. [CrossRef]
26. Sun, L.; Qiu, K. Organic oxalate as leachant and precipitant for the recovery of valuable metals from spent lithium-ion batteries. *Waste Manag.* **2012**, *32*, 1575–1582. [CrossRef] [PubMed]
27. Zeng, X.; Li, J.; Shen, B. Novel approach to recover cobalt and lithium from spent lithium-ion battery using oxalic acid. *J. Hazard. Mater.* **2015**, *295*, 112–118. [CrossRef] [PubMed]
28. Zou, Y.; Chernyaev, A.; Ossama, M.; Seisko, S.; Lundstrom, M. Leaching of NMC industrial black mass in the presence of LFP. *Sci. Rep.* **2024**, *14*, 10818. [CrossRef] [PubMed]
29. Xu, Z.; Dai, Y.; Hua, D.; Gu, H.; Wang, N. Creative Method for Efficiently Leaching Ni, Co, Mn, and Li in a Mixture of $LiFePO_4$ and $LiMO_2$ Using Only Fe(III). *ACS Sustain. Chem. Eng.* **2021**, *9*, 3979–3984. [CrossRef]
30. Choi, J.W.; Kim, J.; Kim, S.K.; Yun, Y.S. Simple, green organic acid-based hydrometallurgy for waste-to-energy storage devices: Recovery of $NiMnCoC_2O_4$ as an electrode material for pseudocapacitor from spent $LiNiMnCoO_2$ batteries. *J. Hazard. Mater.* **2022**, *424*, 127481. [CrossRef] [PubMed]
31. Nayaka, G.P.; Manjanna, J.; Pai, K.V.; Vadavi, R.; Keny, S.J.; Tripathi, V.S. Recovery of valuable metal ions from the spent lithium-ion battery using aqueous mixture of mild organic acids as alternative to mineral acids. *Hydrometallurgy* **2015**, *151*, 73–77. [CrossRef]
32. Vieceli, N.; Benjamasutin, P.; Promphan, R.; Hellström, P.; Paulsson, M.; Petranikova, M. Recycling of Lithium-Ion Batteries: Effect of Hydrogen Peroxide and a Dosing Method on the Leaching of LCO, NMC Oxides, and Industrial Black Mass. *ACS Sustain. Chem. Eng.* **2023**, *11*, 9662–9673. [CrossRef]
33. Zhang, J.; Ding, Y.; Shi, H.; Shao, P.; Yuan, X.; Hu, X.; Zhang, Q.; Zhang, H.; Luo, D.; Wang, C.; et al. Selective recycling of lithium from spent $LiNi_xCo_yMn_{1-x-y}O_2$ cathode via constructing a synergistic leaching environment. *J. Environ. Manag.* **2024**, *352*, 120021. [CrossRef] [PubMed]
34. Zhang, J.; Hu, X.; He, T.; Yuan, X.; Li, X.; Shi, H.; Yang, L.; Shao, P.; Wang, C.; Luo, X. Rapid extraction of valuable metals from spent $LiNi_xCo_yMn_{1-x-y}O_2$ cathodes based on synergistic effects between organic acids. *Waste Manag.* **2023**, *165*, 19–26. [CrossRef] [PubMed]
35. Gerold, E.; Kadisch, F.; Lerchbammer, R.; Antrekowitsch, H. Bio-metallurgical recovery of lithium, cobalt, and nickel from spent NMC lithium ion batteries: A comparative analysis of organic acid systems. *J. Hazard. Mater. Adv.* **2024**, *13*, 100397. [CrossRef]

36. Duarte, L.M.; Xavier, L.V.; Rossati, K.F.; Oliveira, V.A.D.; Schimicoscki, R.S.; Ávila Neto, C.N.D.; Mendes, G.D.O. Potassium extraction from the silicate rock Verdete using organic acids. *Sci. Agric.* **2022**, *79*, e20200164. [CrossRef]
37. Saleem, U.; Buvik, V.; Knuutila, H.K.; Bandyopadhyay, S. Recovery of lithium from oxalic acid leachate produced from black mass of spent electric vehicle Li-ion batteries. *Chem. Eng. J. Adv.* **2024**, *20*, 100648. [CrossRef]
38. Georgeta, G.; Marcela, S.; Delia, S.O.; Gratiela, P.A.I. Recovering Of Manganese Cations From Industrial Wastewater Using Oxalate Precipitation. *Ann. Univ. Oradea Fascicle Environ. Prot.* **2017**, *28*, 253–260.
39. Mettke, L.N.; Yagmurlu, B. *Optimizing Early-Stage Lithium Recovery: Investigating Oxalic Acid Leaching of Black Mass from End-of-Life NMC 622 Batteries*; Lazou, A., Meskers, C., Olivetti, E., Diaz, F., Gökelma, M., Eds.; REWAS; Springer: Cham, Switzerland, 2025.
40. Liu, Y.; Zhang, C.; Li, B.; Li, H.; Zhan, H. 2015. Extraction and Determination of Total and Soluble Oxalate in Pulping and Papermaking Raw Materials. *BioResources* **2025**, *10*, 4580–4587.
41. 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]
42. Fan, E.; Li, L.; Zhang, X.; Bian, Y.; Xue, Q.; Wu, J.; Wu, F.; Chen, R. Selective Recovery of Li and Fe from Spent Lithium-Ion Batteries by an Environmentally Friendly Mechanochemical Approach. *ACS Sustain. Chem. Eng.* **2018**, *6*, 11029–11035. [CrossRef]
43. Zhang, Y.Z.; Zhao, J.; Xia, J.; Wang, L.; Lai, W.Y.; Pang, H.; Huang, W. Room temperature synthesis of cobalt-manganese-nickel oxalates micropolyhedrons for high-performance flexible electrochemical energy storage device. *Sci. Rep.* **2015**, *5*, 8536. [CrossRef] [PubMed]

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.