



UNIVERSITY of the
WESTERN CAPE



LEACHING OPTIMIZATION NMC CATHODE MATERIAL USING ORGANIC ACID AND
REDUCING AGENT TO RECOVER AND RECYCLE VALUABLE METALS FROM
SPENT LI-ION BATTTERIES

BY

NONQABA DYONASHE

A partial thesis submitted in fulfilment of the requirements for

The

Diploma in Analytical Chemistry, Faculty of Applies Science

At

the Cape Peninsula University of Technology

Academic Supervisor and Industry Supervisor 1: Dr Zide (CPUT/ SAIAMC)

Industry Supervisor 2: Prof Bernard Jan Bladergroen (SAIAMC)

Industry Mentor: Tendai Tawonezvi (SAIAMC)

Bellville

Date submitted: 28 November 2023

SAIAMC/UWC copyright information

This partial thesis may not be published either in part (in scholarly, scientific or technical journals) or as whole (as a monograph) unless permission has been obtained from the University

ABSTRACT

In response to government regulations mandating the recycling of lithium-ion batteries (LIBs) to mitigate environmentally harmful waste, recycling has become a pivotal aspect of the life cycle of LIBs. This is especially crucial due to the growing demand for energy storage in applications such as renewable energy technologies and electric automobiles. Consequently, the dual objectives of LIB recycling technology should be to reduce the environmental impact of LIB waste and secure a backup supply of strategically rare materials like cobalt and lithium.

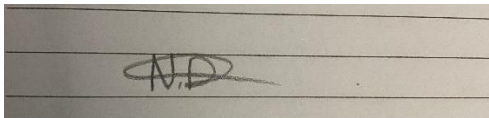
The surge in demand for lithium-ion batteries (LIBs) is driven by their appropriate electrochemical performance and widespread incorporation into electrical and electronic devices. In this study, a hydrometallurgical technique based on leaching is employed to recover cobalt and lithium from spent LIBs. Hydrogen peroxide and citric acid are introduced as leaching reagents to facilitate the leaching process. The leachate is characterized using X-ray diffraction (XRD) and scanning electron microscopy (SEM). The proposed method involves both a chemical leaching process and the mechanical separation of particles containing metal.

By optimizing the leachant's concentration, leaching time, and solid-liquid ratio, experimental conditions were established to achieve a recovery rate of over 90% for these metals. The combination of hydrogen peroxide in a citric acid solution was identified as an effective reducing agent, enhancing leaching efficiency. Specifically, leaching was carried out using 1.5 M citric acid and 6% volume hydrogen peroxide.

DECLARATION

I, Dyonashe Nonqaba, declare that:

- (i) The conclusions presented in this article are my own, unless otherwise specified or credited.
- (ii) I understand that this report has not been turned in in whole or in part for credit toward a degree or test to any other university.
- (iii) No data, images, diagrams, or additional information not explicitly recognized as coming from other persons are included in this partial thesis.
- (iv) This study does not include any graphics, typography, or tables that have been downloaded and pasted from the internet, unless specified otherwise. Information about the source is included in both this incomplete thesis and the References section.
- (v) Additionally, all of this work was done at the University of the Western Cape (UWC) under the direction of a representative of the South African Institute for Advanced Materials Chemistry (SAIAMC). Consequently, the supervisor of the SAIAMC must request and provide authorization before the work can be published or replicated.



Signed

06 November 2023

Date

Confirmation by external supervisor that the above student has completed the research project under my guidance and that I have seen the final submission.

Signed

Date

Signed

Date

ACKNOWLEDGEMENT

I would like to express my sincere gratitude and thanks to the following individuals and organizations:

1. My parents and other family members, without whose love and continuous support I would not have been able to finish my Diploma in Analytical Chemistry.
2. Dr. Zide, my supervisor, for your patience and faith in me. I've been inspired to go beyond what I could have imagined on my own and my curiosity has been piqued by your technical advice and guidance.
3. I would like to thank my co-supervisor, Prof. Bernard Bladergroen, for his extremely insightful feedback, which was instrumental in helping to resolve important issues during this project.
4. To my mentor, Mr. Tendai Tawonezvi, for his advice and contributions that inspired and kept me interested. The prompt completion of this project was made possible by your persistent availability to assist me with problem-solving and to answer my numerous questions.
5. Lastly, I want to acknowledge my sister (Noluvuyo Dyonashe) for constant support and understanding your love and encouragement have been the foundation of my success.

DEDICATION

This academic path has been motivated by my beloved family's consistent support, encouragement, and belief in my skills. Without you, this accomplishment would not have been possible. I also want to express my sincere gratitude to my supervisor, Dr. D. Zide, for all of her help, understanding, and insightful advice during this academic journey . Lastly, I express my gratitude to Tendai Tawonezvi, who served as my mentor.

Contents

ABSTRACT	6
DECLARATION	7
ACKNOWLEDGEMENT	8
DEDICATION	9
LIST OF FIGURES	12
CHAPTER 1	13
INTRODUCTION	13
Background	13
Research Aim and Objectives	14
CHAPTER 2	15
LITERATURE REVIEW	15
Background	15
LIB chemistry and structure	15
Hazards of spent LIBs	16
Mechanical processing	18
Pyro-metallurgical process	19
Hydrometallurgy process	19
LIB pre-treatment	21
Leaching	22
Lixiviant selection	23
Citric acid leaching	24
Hydrogen peroxide reductant	25
CHAPTER 3	26
MATERIALS AND METHODOLOGY	26
Citric acid leaching	Error! Bookmark not defined.
Leaching confirmation experiment	Error! Bookmark not defined.
Experimental procedure for the leaching process	26
CHAPTER 4	27
RESULTS AND DISCUSSION	27
NMC 523 material characterization	27
Effect of concentration	28
Effect of time	28
Effect of solid-liquid ratio	29

Reaction kinetics (Avrami model equation)	30
CHAPTER 5	32
RECOMMENDATION AND CONCLUSION	32
Recommendations	32
Optimizing the citric acid leach for larger material throughput	32
Conclusion	33
Citric acid leaching performance	33
REFERENCES	34

LIST OF FIGURES

Figure 1: Structure of 18650 Li-ion battery.....	16
Figure 2: Pyro-metallurgical process flowchart of spent LIBs.....	19
Figure 3: Hydrometallurgical recycling of lithium-ion batteries by reductive leaching	20
Figure 4: A process of leaching recovery for valuable metals from spent LIBs	23
Figure 5: Citric acid structure.....	24
Figure 6: X-ray diffraction (XRD) pattern of waste lithium, nickel, manganese, cobalt oxide (NMC 523) cathode material. (b)The scanning electron microscopy analysis of cathode material. (c) The energy dispersive X-ray spectroscopy EDX analysis of NMC	27
Figure 7: Effect of citric acid on the leaching of metals from cathode material	Error! Bookmark not defined.
Figure 8: Effect of time leaching of metals from cathode material ..	Error! Bookmark not defined.
Figure 9: Effect of soli-liquid ratio on the leaching of metals from cathode material	30
Figure 10: Avrami model equation.....	30

1. CHAPTER 1

1.1 INTRODUCTION

1.1.1 Background

Lithium-ion batteries (LIBs) have gained extensive usage in recent times as electrochemical power sources for portable electronic devices like laptops, smartphones, and digital cameras. This popularity is attributed to their notable characteristics, including high power and energy density, minimal environmental impact, prolonged storage life, absence of memory effect, and a broad operating temperature range (Bertuol et al., 2015; Chen et al., 2015; Georgi-Maschler et al., 2012; Hu et al., 2013). Every year, the amount of LIBs produced has increased quickly; in 2000, there were 500 million units produced globally; by 2005, there were 2.05 billion units, and by 2010 there were 4.6 billion (Nayaka et al., 2015; Xu et al., 2008). The goal of acid leaching is to transfer metals to the leaching solution and is a significant step in the hydrometallurgical processes. Strong inorganic acids like H_2SO_4 (Swain et al., 2007), HCl (Li et al., 2009), and HNO_3 (Leea and Rhee, 2003) are typically used as leaching agents when extracting LiCoO_2 from used LIBs. To convert Co (III) to Co (II) , hydrogen peroxide (H_2O_2) is typically added as a reducing agent in the interim. For example, Swain et al. (2007) studied the leaching of LiCoO_2 with sulfuric acid as a leaching agent; under ideal conditions, 94% Li and 93% Co may be leached.

The materials that are recovered during the recycling of spent LIBs are useful for producing new batteries and have the potential to reduce production costs. Recycling LIBs is a complex process that involves several obstacles both before and during the recycling process. These obstacles may prevent some recycling procedures from being economically feasible. The topic of whether recycling LIBs is a better financial decision than producing new batteries with raw materials is always raised by fluctuations in the price of virgin materials. Furthermore, the large range of battery chemistries and architectures makes the recycling procedure for LIBs complex.

1.1.2 Statement and Research Problem

The need for lithium-ion batteries (LIBs) is rising across a number of industries, which has raised questions about the energy storage systems' sustainability and resource efficiency. Important metals like nickel, manganese, and cobalt (NMC), which can be recovered and repurposed to lessen the financial and environmental costs associated with mining and producing these essential elements, are frequently found in spent LIBs. The issue statement in this instance seeks to address the efficient and sustainable leaching of NMC cathodes

using citric acid as a means of recovering important metals from used LIBs.

1.1.3 Research hypothesis

It was predicted that precious metals like nickel, manganese, and cobalt could be efficiently extracted from NMC cathode material by mixing hydrogen peroxide with citric acid. Variables include the concentration of hydrogen peroxide, the concentration of citric acid, the reaction temperature, and the leaching time will all have an impact on this leaching process. More metal recovery is anticipated as a result of higher temperatures, longer leaching times, and higher concentrations of hydrogen peroxide and citric acid. This is because the acidic solution will aid in the dissolving of metal ions from the NMC cathode material."

1.1.4 Research Aim and Objectives

Aim:

To recover valuable metals, such as nickel, manganese, and cobalt, from spent Lithium-ion Battery (LIB) NMC cathode material using an environmentally friendly leaching process with citric acid and hydrogen peroxide.

Objectives:

Metal Recovery: The primary objective is to recover valuable metals (nickel, manganese, and cobalt) from the spent NMC cathode material in a form suitable for subsequent processing and reuse in the battery industry or other applications.

Environmental Sustainability: Develop a sustainable and environmentally friendly leaching process that minimizes the generation of hazardous waste and reduces the environmental impact associated with metal recovery.

Chemical Selection: Investigate the effectiveness of citric acid and hydrogen peroxide as leaching agents. Determine the optimum conditions for their use, such as concentration, temperature, and reaction time.

Leaching Efficiency: Evaluate the efficiency of the leaching process by measuring the percentage of metal recovery from the NMC cathode material. This includes assessing the selectivity of the process to ensure that the desired metals are preferentially extracted.

Impurity Control: Develop methods to control and remove impurities, such as aluminum, lithium, and other elements that may be present in the NMC cathode material. This is essential to ensure the purity of the recovered metals.

Safety and Compliance: Ensure that the leaching process adheres to safety standards and environmental regulations. Minimize potential health and environmental hazards associated

with the chemicals and waste generated during the process.

2. CHAPTER 2

2.1. LITERATURE REVIEW

2.1.1 Background

Their advantageous qualities, such as their high energy density, extended life cycles, low self-discharge, and safe handling, rechargeable lithium-ion batteries (LIBs) are the preferred batteries in the consumer electronics market (Lupi et al., 2005, Swain et al., 2007). LIBs are used to manufacture popular portable electronic devices like cell phones, laptop computers, and camcorders. There are much more secondary batteries now than there were when these items were developed. More used batteries will need to be recycled due to the increased number of LIBs in use globally (Dorella and Mansur, (2007). Not only do spent LIBs contain large amounts of precious materials, but they also include toxic compounds. It is crucial to have a conversation about the release and fate (i.e., transit and transformation) of the metals included in these batteries, as well as the batteries themselves, into the environment. These batteries pose a serious risk to human health, the environment, and a substantial waste of finite resources when disposed of carelessly.

As previously mentioned, the focus of recycling operations is currently on cobalt recovery due to the high value of cobalt, which enables cost-effective operation, and the fact that existing LIB trash consists of many LCO batteries. Future LIB waste cobalt concentrations will be constrained as low-carbon materials like NCA, LFP, LMO, and NMC replace carbon-containing materials in the cathode chemistry of contemporary LIBs. Future procedures will have to change as a result in order to function properly on different metals like manganese, nickel, and lithium. The availability of lithium is crucial for energy security and for assisting us in lowering our carbon footprint as we transition to more environmentally friendly and sustainable energy sources, such as renewable energy, since LIBs depend on lithium for their unique qualities. Lithium is essential and its supply needs to be secured because of its unique qualities that give LIBs their remarkable capabilities.

2.1.2. LIB chemistry and structure

The components of a typical LIB include an anode, a cathode, a separator, an electrolyte

solution, protective shells, collectors (copper and aluminum foils), and containers (Gratz et al., 2014). A LIB's schematic representation is depicted in Fig. 1, and Table 1 lists each section's contribution (Horeh et al., 2016). According to Zeng et al. (2014), the cathode is an aluminum foil coated with cathode active materials, which are primarily oxide- and lithium-containing components.

A variety of compounds, including LiMPO_4 ($M = \text{Co, Mn, Fe}$), LiMO_2 ($M = \text{Co, Ni, Mn}$), and occasionally LiV_3O_8 and $\text{Li}_3\text{V}_2(\text{PO}_4)_3$, make up the cathode active materials (Chagnes and Pospiech, 2013; Etacheri, 2011; Gratz et al., 2014; Ordoñez et al., 2016). LiCoO_2 remains the most widely used cathode active material despite the introduction of novel cathode materials due to its stability and high specific energy density (Kang et al., 2006; Stephan, 2006; Zeng et al., 2014).

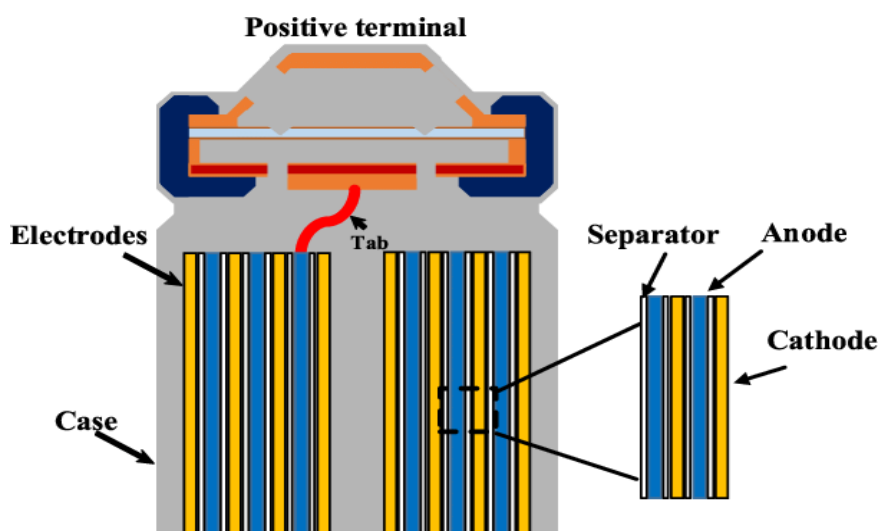


Figure 1: Structure of 18650 Li-ion battery

2.1.3. Hazards of spent LIBs

Spent LIBs contain poisonous compounds and hazardous heavy metals that pose a threat to ecosystem health as well as human health. Zheng and Partners (2018). It has been determined that the main elements causing waste lithium-ion batteries (LIBs) to be ecotoxic are cobalt and copper, while the main elements causing the LIBs to be potentially toxic to humans are aluminum, cobalt, copper, and nickel. Kang and associates (2013). One of the biggest issues surrounding LIBs is the disposal of spent batteries into general waste, as less than 10% of waste LIBs are currently gathered for appropriate disposal and recycling. Wang et al. (2014). Subterranean waterbodies can become contaminated with heavy metals like nickel and cobalt from the cathode material due to hazardous chemicals or the spontaneous combustion of LIBs in landfills. In addition, dangerous gases like CO_2 , HF,

and Cl₂ can be produced by heating the electrolyte and binders (PTFE and PVDF). Zheng and Partners (2018). When water encounters the solvent and electrolyte, hazardous gases may also be released. (2018) Winslow and associates.

When the temperature of LIBs rises above 90°C, the solid electrolyte interface (SEI), which covers the graphite anode, begins to degrade exothermically. Lu and associates, 2013. When the battery temperature reaches 120°C, the SEI layer ceases to protect the anode from corrosion. Combustible gases are produced as a result. Lu and associates (2013). The cathode becomes more effective at temperature thresholds where the metal oxide layer begins to form, disintegrating and releasing oxygen gas, depending on the cathode chemistry. While LFP cathodes function at 310°C, LCO cathodes operate at 150°C. Jiang et al. (2004) defined cathodes as electrodes that conduct electricity. When the combustible gas produced by the electrolyte reacts with the oxygen produced by the cathodes, a hazardous atmosphere is created.

2.1.4. LIB recycling

Recycling metals from LIBs offers a number of advantages, such as keeping hazardous waste centralized, minimizing the cost of landfilling, enabling the recycling of metals back into goods, minimizing reliance on natural resources, and conserving resources. One of the primary advantages of recycling LIBs is the decrease in waste. They contain hazardous waste, which can reduce the life cycle impact of LIBs by up to 51%. This waste includes reactive material, organic and inorganic compounds, and others. Wang and associates (2014). Large amounts of LIBs, like the batteries used in electric vehicles (EVs), which can be used as stationary energy storage systems in homes, businesses, and even cars, can benefit numerous power networks that are essential to the deployment of renewable energy sources

Recycling lithium-ion batteries (LIBs) not only contributes to a reduction in toxic waste but also plays a crucial role in lowering CO₂ emissions, typically associated with raw material extraction and production. Research indicates that efficient LIB recycling, with an 85% collection rate of LIBs in the European Union (EU), could mitigate over 218,000 tons of CO₂ by 2030 (Drabik et al., 2018).

However, the process of extracting nickel, cobalt, copper, lithium, and iron from LIBs generally incurs higher costs compared to mining for new metals (Hu et al., 2017). This cost

disparity can be attributed to the presence of organic binders and other chemicals in LIBs, complicating the separation and recovery of metals. Additionally, toxic components necessitate proper treatment. Moreover, the evolving chemistries in LIBs increasingly incorporate lower-value metals, resulting in reduced grades of valuable metals such as cobalt and nickel (Zheng et al., 2018).

For LIB recycling to be implemented successfully, it must consequently seek to improve both material recovery and economic effectiveness. The high processing costs associated with labor, collection, transportation, categorization, discharge, material separation, shredding, smelting, and purification are among the factors contributing to the current recycling rate of less than 5% of LIBs. et al., Natarajan (2018). Benefits including the development of jobs for battery collecting, disassembly, and recycling will also come from the commercial adoption of LIB recycling.

2.1. 5. Metal extraction

Metals and other materials can be separated from one another using a variety of extraction processes, each of which has benefits and drawbacks. Because so many different chemicals and materials go into making LIB cells, recycling LIBs usually involves combining various extraction techniques. In order to target specific LIB components like the cathode, anode, or casings, additional processing with hydrometallurgical or pyro-metallurgical processes is made possible by mechanical processing, which allows the various components to be separated and disassembled. Consequently, mechanical processing aids in enhancing the purity of the final metal extraction process and metal recovery for LIB recycling.

2.1.6. Mechanical processing

When recycling spent LIBs, mechanical separation procedures are typically used as a pretreatment to treat the outer cases and shells and to concentrate the metallic fraction. This metallic fraction is then processed using a hydrometallurgical or pyrometallurgical recycling process. To produce enriched particles of lithium cobalt oxide, a sequence of mechanical procedures including crushing, sieving, magnetic separation, fine crushing, and classification were used. The metal-bearing particles were satisfactorily separated from the waste after two steps of crushing and sifting. Steel casing fragments were extracted using a magnetic separator. A fine crushing was next performed to remove any little bits of aluminum foil that were sticking to the lithium cobalt oxide particles. Here, mechanical separation is prioritized over the metal

leaching procedure because it increases target metal recovery efficiency and does away with the requirement for a purification step.

2.1.7. Pyro-metallurgical process

Pyrometallurgy is the process of heat treating wasted LIBs by converting them chemically and physically. Utilizing pyrometallurgy, it is possible to recover and extract the desired metals from wasted LIBs, including Ni and Cd, which are valuable metals that are recycled. Lithium is typically retained in the slag of pyrometallurgical processes, making further treatment difficult. As a thermometallurgical technique to recover lithium and other precious metals, the carbothermic reduction method has drawn interest. The mixed wasted LIBs can be processed into lithium carbonate, pure metal, or metal oxide. In particular, water leaches lithium carbonate; the graphite in the leached slag burns and leaves behind metal oxides as the end byproduct. Next, wet magnetic separation is used to extract pure metals, graphite, and lithium carbonate. The pyrometallurgy process is intricate and requires a lot of energy, though. Consequently, it is necessary to improve pyrometallurgical technologies in order to lower energy consumption and loosen the constraints on processing equipment. (Zhang 2022)

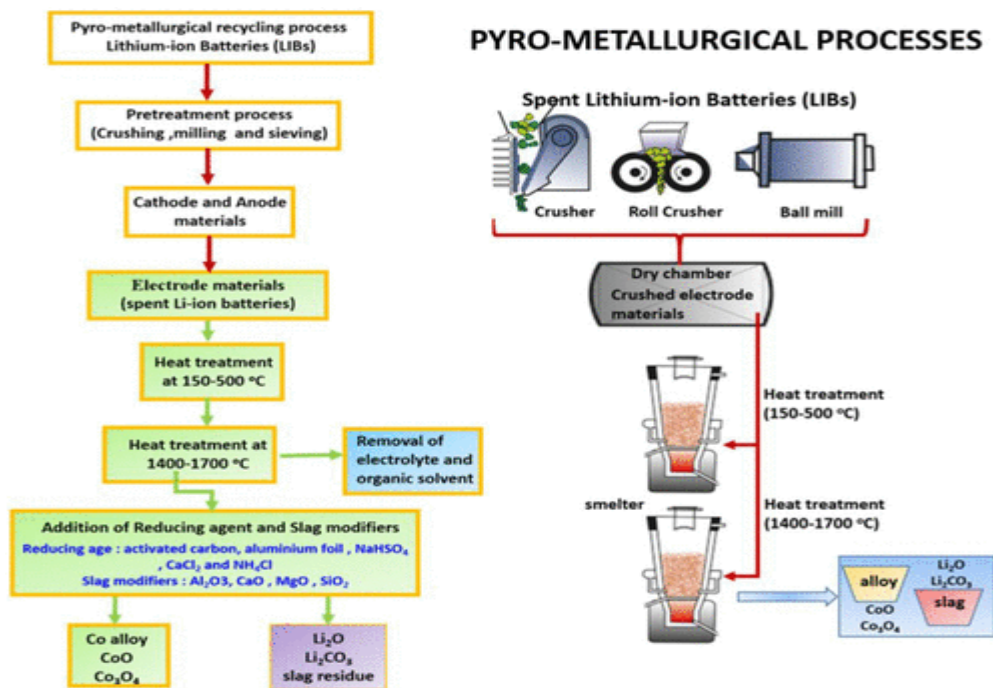


Figure 2: Pyro-metallurgical process flowchart of spent LIBs

2.1.7. Hydrometallurgy process

An easy and effective way to remove all the precious metals from wasted LIBs is hydrometallurgical processing. Several procedures are used in the hydrometallurgical technique to dissolve and extract metals from an aqueous medium. These procedures include solvent extraction. Yang et al., 2017; Paulino et al., (2008), chemical precipitation. Guzolu et al., (2017) Yang et al., 2017), acid leaching (Meshram et al., 2015; Paulino et al., 2008), and electrochemical separation. The first fundamental stage involves dissolving Co, Li, Ni, and Mn through acid leaching. These metals are then recovered using an appropriate technique from the solution, or leach liquor.

The impact of time on the efficiency of metal leaching was investigated using 1.5 M of citric acid. Throughout the leaching procedure, the solid-liquid ratio was maintained at 45 g/L, and the H₂O concentration was consistently kept at 6%. According to the results depicted in Figure 8, the efficiency for the initial half-hour was recorded at 75% for Li, 80% for Co, 70% for Mn, and 60% for Co. As the process progressed, reaching 180 minutes, the efficiency increased to 85% for Li, 90% for Co, and 80% for Mn. During the initial half-hour of the process, these metals exhibited low dissolubility, requiring a reducing agent for effective leaching. Subsequently, the efficiency significantly improved, reaching nearly 90% at the 180-minute mark.

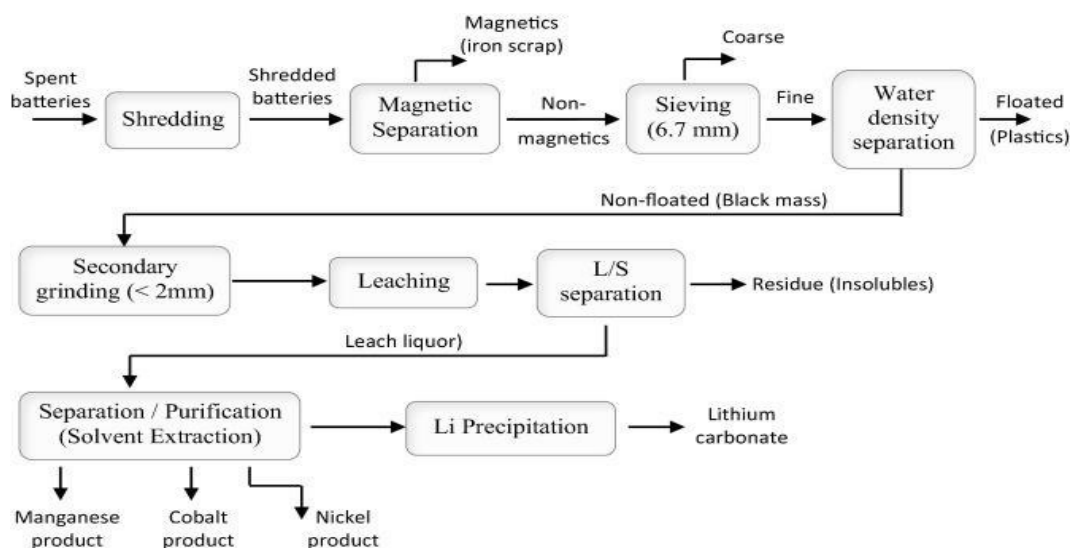


Figure 3: Hydrometallurgical recycling of lithium-ion batteries by reductive leaching

Table 1: Process summary for LIB recycling

Process	Advantages	Disadvantages
Mechanical	<ul style="list-style-type: none"> · Easy to use · Constant material composition 	<ul style="list-style-type: none"> · High energy requirements · Uniform feed composition · High explosion risk during shredding
Pyro-metallurgical	<ul style="list-style-type: none"> · Simple operation · Any feed composition · Large feed volumes 	<ul style="list-style-type: none"> High energy requirements · Lithium lost to slag · Plastics and organics form toxic gasses, not recovered
Hydrometallurgical	<ul style="list-style-type: none"> Low energy requirements · Minimal gas emissions · High recovery and purity for product streams 	<ul style="list-style-type: none"> · Aqueous waste effluents produced · Sensitivity to process input changes · Complex operation

2.1.8. LIB pre-treatment

The cathode material removed from the used battery should be the goal of the procedure, regardless of the technique utilized to recover it. Because there are currently no standard requirements for the production of LIBs, a higher barrier for end-of-life recycling arises from the battery products' various shapes, sizes, materials, and other characteristics that were tailored to diverse application scenarios. To get rid of these outdated battery products with inconsistent design criteria, the pre-treatment disposal process typically entails the following, which summarizes the current process flow that is suggested for recycling cathode materials. The method of releasing expended batteries' remaining capacity is not included in this work's classification of the pre-treatment step of the recycling process. However, as discharging should occur prior to scrapping, storage, and transportation, the discharge operation is required and the deactivated state must be employed as a safety precaution once the battery is stopped for the first time. The purpose of discharge is to safeguard property and human life throughout the recycling process in addition to preventing problems with spontaneous combustion of the battery. As a result, this part also includes a description of the results linked to discharge.

It has been determined that the liquid nitrogen stage is not necessary if the batteries are sufficiently discharged to less than 0.5V Musariri (2019). To make sure the batteries are depleted to less than 0.5V, the LIBs are often air dried after being discharged in a 5-weight percent NaCl solution for 48 hours. (2014) Chinese and others. As such, a band saw can be used to open batteries that are considered inactive when their voltage falls below 0.5V. The anode electrode, casings, cathode electrode, and other components are typically sorted by hand. Li et al. (2010);

2.1.9. Acid Leaching

Leaching is the process of applying a liquid solvent to a solid in order to extract one or more solutes from it. The solute or solutes used can diffuse from the solid to the liquid phase when both phases come into close contact, causing the solid's original constituents to separate. Using typical chemical leaching products, the lithium cobalt oxide employed as an active cathode is difficult to dissolve. The process of extracting lithium cobalt oxide from spent LIBs often involves the use of inorganic acids as leaching agents, such as sulphuric acid, HCl. Zhang et al.'s study [3] examined a number of leachates, including sulfurous acid, hydroxylamine hydrochloride, and hydrochloric acid, to extract lithium cobalt oxide.

It is possible to decrease the size of the solid input into a leaching reaction, which produces a large surface area that guarantees maximum contact between the mineral and the lixiviant and accelerates the dissolution process. Because size reduction processes are energy-intensive and inefficient, they are typically the most expensive phases of mineral processing; if necessary, this step must be used effectively. The undesirable materials must remain unreacted in the solid phase for the lixiviant to have no effect on them during the leaching process. Once the valuable metals have been extracted from the solid object, a filter is used to separate the solution containing the valuable metals from the unwanted solids. Thermodynamic phase diagrams are frequently used to calculate leaching conditions, which define the parameters under which the targeted minerals will be successfully extracted. Free (2013).

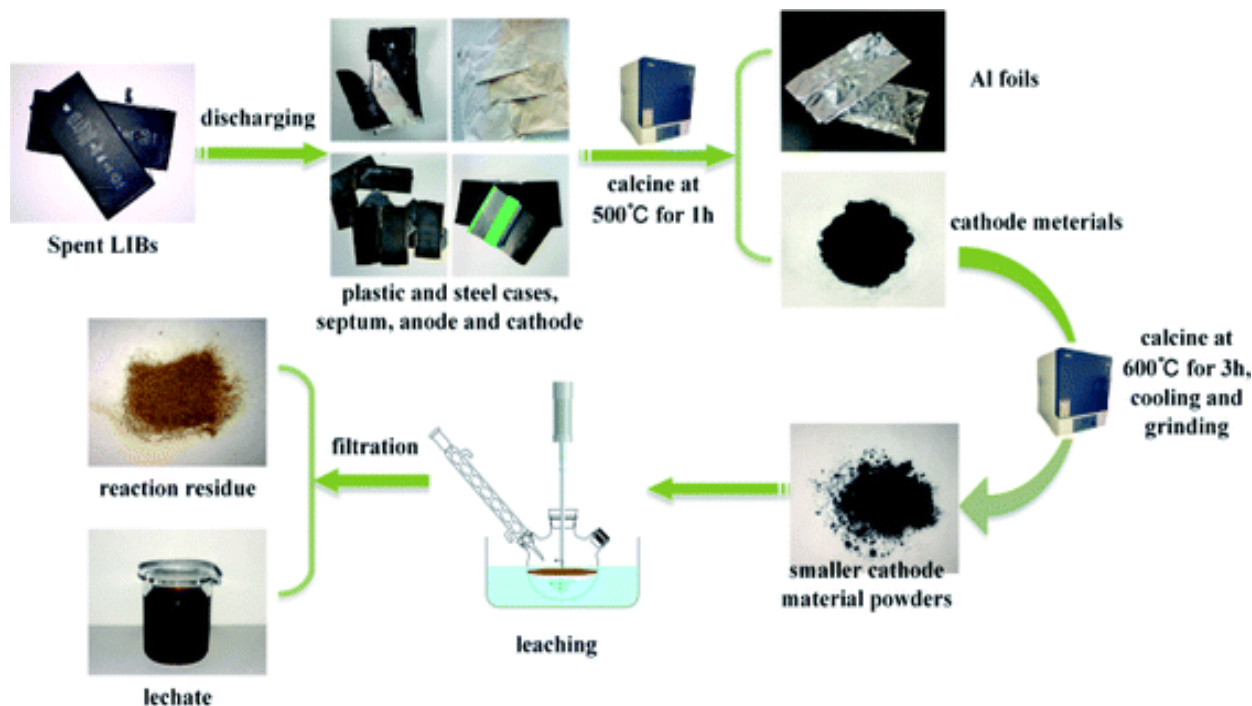


Figure 4: A process of leaching recovery for valuable metals from spent LIBs

2.1.10. Selection of lixivants

The choice of lixiviant has revealed variations in the leaching behaviour of different cathode materials, resulting in diverse leaching efficiencies. Chen and colleagues (2018) emphasized the critical role of cathode material in the leaching process. This importance is underscored by the fact that certain metals, such as manganese and nickel, can complicate cobalt separation due to their similar characteristics as transition metals. This similarity leads to comparable extraction behaviours and poor metal separation, amplifying the significance of selecting an appropriate cathode material for effective subsequent processing.

The consideration of co-extraction of unwanted metals becomes pivotal as it negatively impacts the purity of the desired metal in the end product, a crucial factor for reusability. The complexity of the separation process increases proportionally with the presence of distinct metals in the cathode material. In light of these challenges, the selection of a suitable lixiviant becomes paramount.

In evaluating lixiviant options, studies focusing on the leaching of NMC LIBs using citric and sulfuric acids were examined. Both acids exhibited excellent leaching performance while posing negligible hazards to the environment and human health.

Citric acid was selected by Musariri (2019) for his extensive study on organic acid leaching because

it is affordable and works well on LIBs with more modern cathode materials like NMC when paired with a reductant like hydrogen peroxide (H₂O₂). Despite having a higher pK_a value and being a weaker acid, citric acid can leach just as well as strong inorganic acids like sulfuric acid thanks to its potent chelating ability. et al., Golmohammadzadeh (2018). Organic acids are thought to have a minimal environmental impact and are frequently referred to as thermally stable. Golmohammadzadeh et al. (2018) state that these characteristics, in addition to their possible leaching capacities as a result of their chelating and acidic qualities, make them desirable replacements for mineral acids—which are typically hazardous and toxic—in hydrometallurgical processes. While both inorganic and organic acids carry some health risks, the risks associated with each are very different, so selecting an acid should be done on an individual basis.

2.1.11. Citric acid leaching

According to Golmohammadzadeh et al. (2018), fungi commonly produce citric acid, or (HA₆HA₈HAJ₇ or HA₃H_{AJ}), through the tricarboxylic acid cycle, which transforms a variety of hydrocarbon sources into citric acid. According to Theron and Lues (2010), citric acid is widely used in the food industry to create natural food flavors and in the pharmaceutical industry as a potent chelating agent. Citric acid's strong chelating ability makes it easy for metal citrate complexes to form in acidic media.. Because citric acid is the most widely used organic acid and the largest chemical obtained via This characteristic can be used to extract the metals from the cathode material during LIB leaching. Citric acid's potent chelating ability makes it simple to form metal citrate complexes in acidic media, a property that can be used to extract the metals from the cathode material during LIB leaching biomass fermentation, it is inexpensive to use as a lixiviant. . Pagliaro and Meneguzzo (2019).

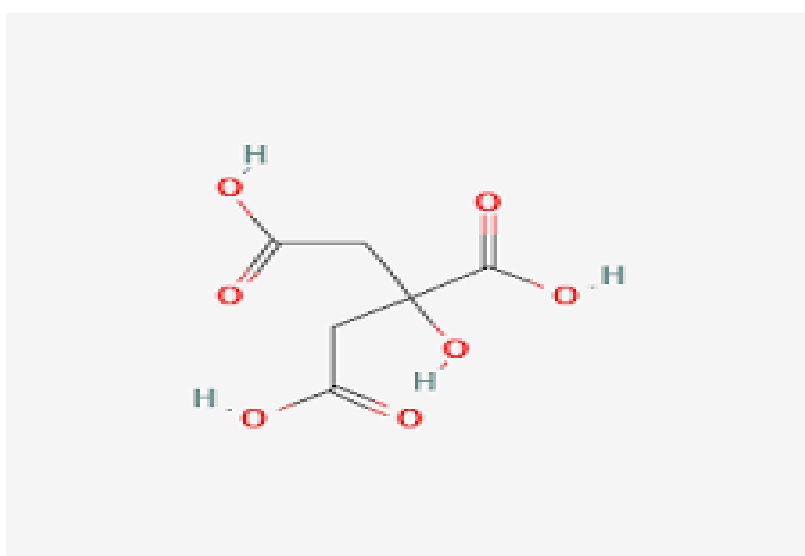


Figure 5: Citric acid structure

2.1.12. Hydrogen peroxide reductant

The advantage of adding a reductant to a lixiviant to increase its efficacy has been the subject of numerous studies, with sulphuric and citric acid being the most studied examples. In contrast to other reductants that have been studied in previous studies, like glucose and ascorbic acid, hydrogen peroxide is a relatively cheap and readily available molecule.

3. CHAPTER 3

3.1. MATERIALS AND METHODOLOGY

Raw materials description	Purity	Source
Citric acid	98%	Sigma Outreach LLC
Hydrogen peroxide	92%	Sigma Outreach LLC
NMC	523	In- house

3.2.2. Experimental procedure for the leaching process

A 100 mL thermostatic Pyrex reactor with three necks and a round bottom that has a temperature control facility was used for all batch-leaching tests. The reactor had an impeller stirrer, a thermometer, and a vapor condenser to lessen water loss by evaporation. Within the equipment, the leaching tests were carried out. An electric mantle with temperature control provided heating, while the reflux condenser prevented vapor loss at high temperatures. Citric acid of a known strength and volume was added to the reactor, and it was left to approach thermal equilibrium. With the magnetic stirrer providing agitation, a measured amount of powder and hydrogen solution were supplied to the reactor. Leaching tests were run in a variety of settings, including varying the concentration of citric acid, the S/L ratio, and the concentration of hydrogen peroxide, in order to determine the ideal circumstances. Samples were taken during the leaching experiment at prearranged intervals. A metal containing solution and a black residue were recovered following filtration and water washing. New samples of leached solids were treated using the leftover acid solution. To investigate how other organic acids, such citric acid acid, leach lithium, nickel ,manganese and cobalt from the cathodic material.

4. CHAPTER 4

4.1. RESULTS AND DISCUSSION

4.1.1. NMC 523 material characterization

The XRD depicted in Figure 6a shows that the valuable metals Ni, Co, Mn and Li in the cathode materials were present as $\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2$ (NMC 523). Figure 6b-c offers the microscopy and spectroscopy analysis of the cathode material by SEM and EDS, respectively.

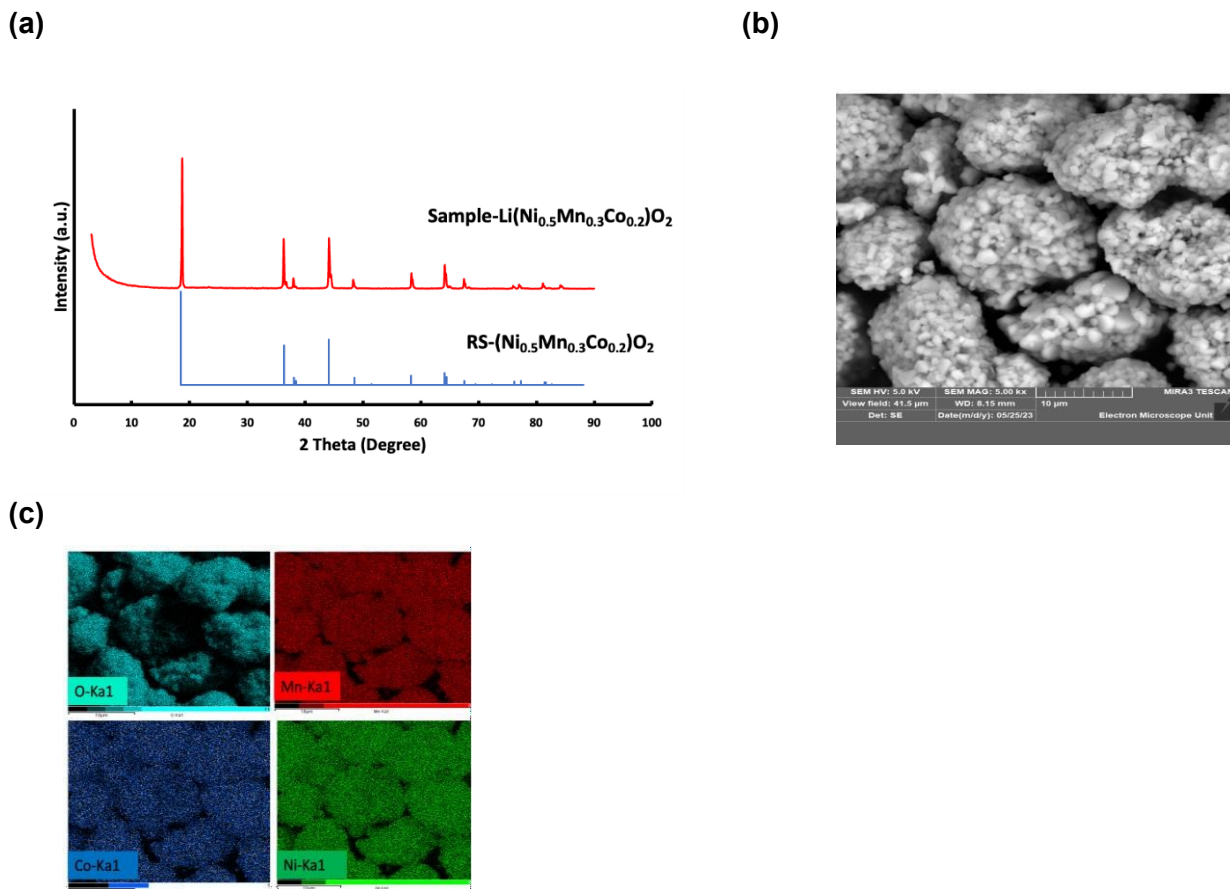


Figure 6: X-ray diffraction (XRD) pattern of waste lithium, nickel, manganese, cobalt oxide (NMC 523) cathode material. (b) The scanning electron microscopy analysis of cathode material. (c) The energy dispersive X-ray spectroscopy EDX analysis of NMC

The results of the analysis showed that the NMC 532 sample contained the metals Ni, Co, O, and Mn, as shown in Figure 6b-c. To sum up, the analysis was successful in finding valuable metals like Ni, Co, and Mn. ICP-OES, XRD, and EDS were used to analyze the chemical and material composition of the Li-ion cathode materials, which were found to contain primarily 18.24% Co, 44.78% Ni, 26.28% Mn, and 10.68% Li. The co-precipitation and co-extraction of cobalt (Co) and nickel (Ni) occur frequently due to the strong similarities in their physicochemical and electrochemical characteristics. However, because the traditional methods of separating Co and Ni are expensive, a different method of recovering the valuable Ni_xCo_y composite, $\text{Mn}(\text{OH})_2$ and Li_2CO_3 , is described in this work.

4.1.2. Effect of concentration

The effect of citric acid concentration in the range of 0.5–2M on the leaching efficiency of electrode material was examined under the following conditions: 45 g/L of solid-liquid ratio, 90°C temperature, 6% vol concentration of H_2O_2 , and 180 min reaction time. Figure 7 illustrates how the concentration of citric acid increased significantly with the leaching efficiency of metals. Cobalt, lithium, manganese, and nickel only had reaction efficiencies of 70%, 55%, 65%, and 52.33 with 1.5 M citric acid solution. The reaction efficiencies rose to 95%, 90%, 90%, and 85% as the nitric acid concentration rose to 1.5 M. Significant changes in the acid concentration did not affect the metal leaching rate when it was raised from 1.5 to 2 M. These findings indicate that the ideal starting concentration of nitric acid was 1.5 M.

4.1.3. Effect of time

The impact of time on the efficiency of metal leaching was investigated using 1.5 M of citric acid. Throughout the leaching procedure, the solid-liquid ratio was maintained at 45 g/L, and the H_2O_2 concentration was consistently kept at 6%. According to the results depicted in Figure 8, the efficiency for the initial half-hour was recorded at 75% for Li, 80% for Co, 70% for Mn, and 60% for Co. As the process progressed, reaching 180 minutes, the efficiency increased to 85% for Li, 90% for Co, and 80% for Mn.

During the initial half-hour of the process, these metals exhibited low dissolubility, requiring a reducing agent for effective leaching. Subsequently, the efficiency significantly improved, reaching nearly 90% at the 180-minute mark

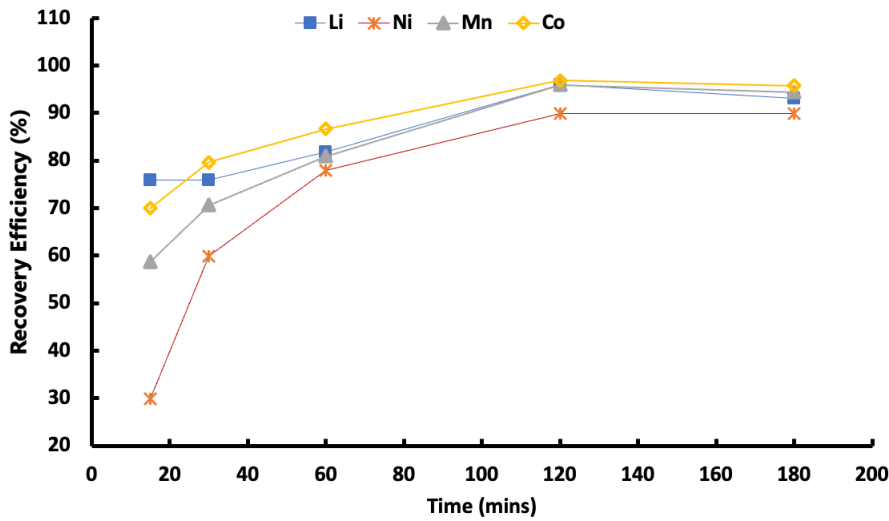


Figure 7: Effect of time on the leaching of metals

4.1.4 Effect of solid-liquid ratio

Figure 9 illustrates the variation in the metal leaching rate with an increase in solid-liquid ratio from 20 to 60 g/L. Under conditions of 90°C, 6% VOC concentration, 1.5 M citric acid, and a 180-minute reaction time, it was observed that the leaching rates of lithium, manganese, nickel, and cobalt decreased with an elevation in the solid-liquid ratio. Specifically, lithium, manganese, nickel, and cobalt exhibited reaction efficiencies of 95.5%, 95%, 94%, and 96%, respectively, with rates exceeding 90% when the solid-liquid ratio was 20 g/L.

At a lower solid-liquid ratio of 45 g/L, there was a sufficient amount of Ca^{2+} to almost completely react with the metal compound, resulting in the maximum leaching rate. Considering that a solid of 45 g/L can accommodate less electrode material and more electrode material was treated, a higher solid-liquid ratio proved to be more suitable. The optimal condition for leaching lithium, manganese, and cobalt from the cathode material was identified as 45 g/L, owing to lower chemical consumption and consistently favorable leaching efficiency.

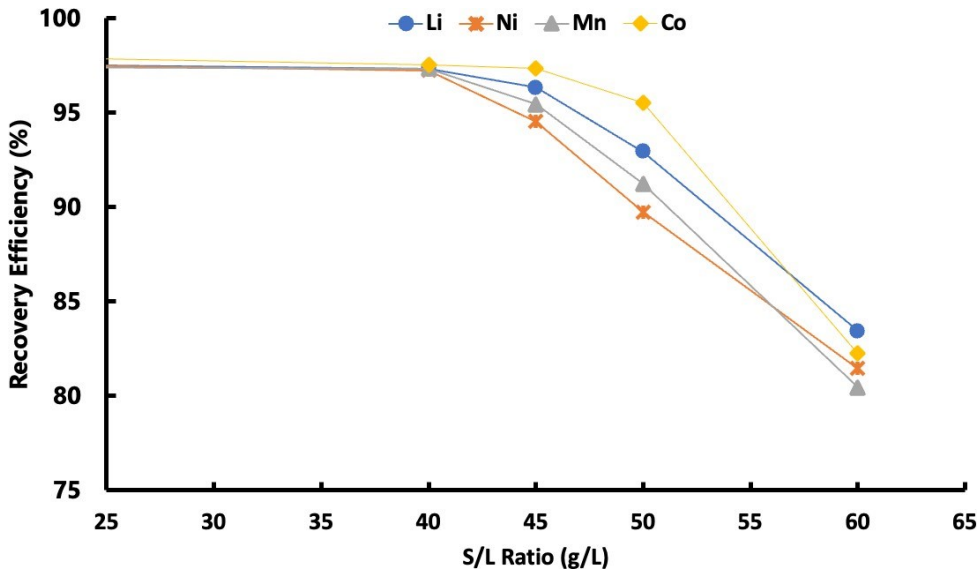


Figure 8: Effect of solid-liquid ratio on the leaching of metals from cathode material

4.1.5. Reaction kinetics (Avrami model equation)

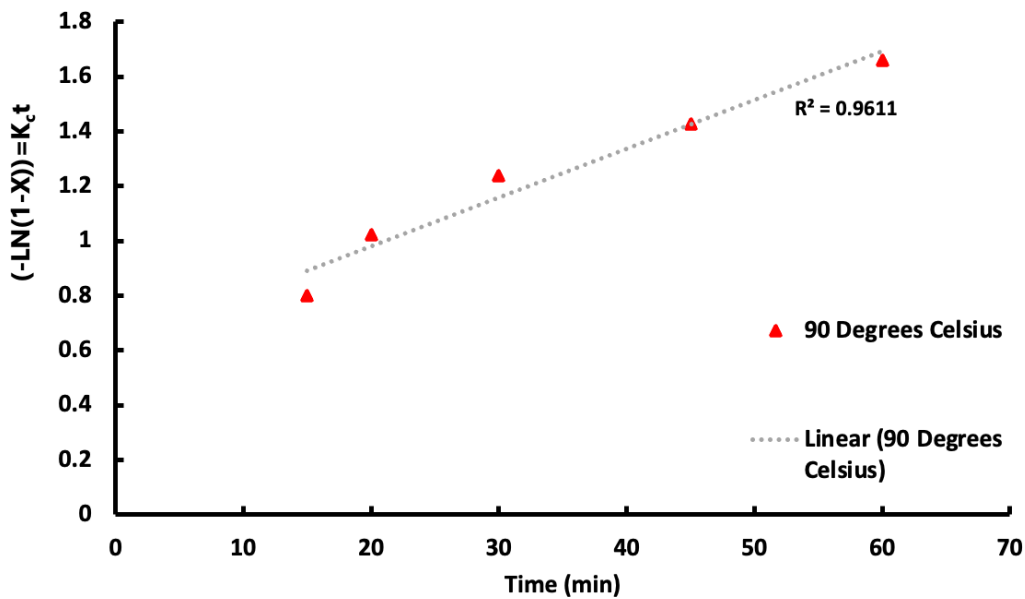


Figure 9: Avrami model equation

On a single set of NMC523 kinetic data, the Avrami model was fitted, and the fitted curve of $\ln [1 - X]$ vs. Int is shown in Figure 10. The pertinent results show that, in multiple trials, the kinetic data for Li, Co, Mn, and Ni matched well with Avrami, with a R^2 value of greater than 0.9. But for the purpose of fitting NMC523, the traditional shrinking core model was also used. Depending on the velocity limiting step, the model splits the leaching process into diffusion control through a liquid film layer. Even in the citric acid system with solid-phase residues, the leaching mechanism in this

study is expected to function similarly to the reverse crystallization mechanism suggested by the Avrami model.

5. CHAPTER 5

5.1. RECOMMENDATION AND CONCLUSION

Recommendations

5.1.1. Citric acid leach optimization for increased material throughput

It is recommended that future investigations into the effectiveness of citric acid leaching explore the optimization of the solid-to-liquid ratio. Industrial operations with high throughputs necessitate higher solid-to-liquid ratios, potentially reaching up to 200 g/L. Insufficient leaching at these ratios can lead to significant losses. Effective leaching at higher solid-to-liquid ratios will require substantially larger reductant dosages, as the reductant's role becomes crucial in reducing the metal content of the cathode powder.

In the course of this study, both the 40 g/L and 60 g/L leach solutions exhibited precipitation after a week of storage, underscoring the importance of citric acid concentration in the lixiviant for the stability of the metal citrate complex. Greater concentrations of citric acid can enhance the solubility of metal citrate in the leach solution, a factor that holds significance for lithium-ion battery recycling processes relying on citric acid.

5.1.2. Enhancing the performance outcomes of metal stripping

It is strongly recommended to conduct additional metal-stripping experiments utilizing citric acid as the stripping agent. Citric acid offers several advantages in terms of health and safety over sulphuric acid, and employing it aligns with a focus on ecologically benign and sustainable methods.

While previous studies have successfully used sulphuric acid to extract metals from a citrate medium, such as cobalt and lithium, the outcomes of this study, as indicated by Musariri (2019), were not as promising. Citric acid demonstrated a selective stripping performance for the target metals, leading to a notably better extraction of manganese and lithium from their respective loaded organics compared to other metals. The selective stripping characteristics of citric acid contributed to improved metal purities in the loaded stripping agents. However, partial stripping was observed in one stage for both the organics loaded with manganese and lithium.

As a result, it is suggested that future studies explore different counter-current stripping stages to determine if it is feasible to maximize the removal of lithium and manganese from the corresponding loaded organics.

5.2. Conclusion

5.2.1. Performance of leaching of citric acid

The leaching results showed that aluminium, nickel, manganese, cobalt, and lithium could be effectively leached from used LIB cathode material by citric acid. A reductive leach using 1.5M citric acid, 6 vol. % H_2O_2 , and 45 g/L for 30 minutes was found to consistently leach 75% Li, 80% Co, 70% Mn, and 60% Ni from the cathode powder. The average metal leaching should not differ by more than 1.5% for any of the metals, as the leaching effectiveness for each metal was demonstrated to be consistent with the standard error.

REFERENCES

1. Alonso, E., Sherman, A.M., Wallington, T.J., Everson, M.P., Field, F.R., Roth, R., Kirchain, R.E., (2012). *Evaluating Rare Earth Element Availability, A Case with Rev. Demand from Clean Tech.* Env. Sci. Tech. 46, 3406–3414.
2. Drabik, E., Rizos, V. (2018). *Prospects for electric vehicle batteries in a circular economy.* CEPS Res. 48, 123.
3. Gaines, L.L., Dunn, J.B., (2014). *Lithium-Ion Battery Environmental Impacts, in: Pistoia, G. (Ed.), Lithium-Ion Batteries*, Adv. and Appl. Elsevier, 23, 483–508.
4. Golmohammadzadeh, R., Faraji, F., Rashchi, F., (2018). *Recovery of lithium and cobalt from spent lithium ion batteries (LIBs) using organic acids as leaching reagents*, A rev. Resour. Conserv. Recycl. 46, 418–435.
5. Gruber, P.W., Medina, P.A., Keoleian, G.A., Kesler, S.E., Everson, M.P., Wallington, T.J., (2011). *Global Lithium Availability.* J. Ind. Ecol. 15, 760–775.
6. Li, L., Fan, E., Guan, Y., Zhang, X., Xue, Q., Wei, L., Wu, F., Chen, R., (2017). *Sustainable Recovery of Cathode Materials from Spent Lithium-Ion Batteries Using Lactic Acid Leaching System.* ACS Sustain. Chem. Eng. 5, 5224–5233.
7. Lu, L., Han, X., Li, J., Hua, J., Ouyang, M., (2013). *A review on the key issues for lithium-ion battery management in electric vehicles*, J. Power Sources 226, 272–288.
8. Musariri, B., Akdogan, G., Dorfling, C., Bradshaw, S., (2019). *Evaluating organic acids as alternative leaching reagents for metal recovery from lithium ion batteries.* Miner. Engin. 137, 108–117.
9. Natarajan, S., Aravindan, V., (2018). *Burgeoning Prospects of Spent Lithium-Ion Batteries in Multifarious Applications.* Adv. Energy Mater. 1445-1556.
10. Nishi, Y., (2014). *Past Present and Future of Lithium-Ion Batteries: Can New Technologies Open up New Horizons? In: Pistoia, G. (Ed.), Lithium-Ion Batteries*, Adv. and App. Elsevier, 56, 21–39.
11. Rinne, M., Elomaa, H., Porvali, A., Lundström, M., (2021). *Simulation-based life cycle assessment for hydrometallurgical recycling of mixed LIB and NiMH waste* Resour. Conserv. Recycl. 170, 105-586.
12. Wang, X., Gaustad, G., Babbitt, C.W., Richa, K., (2014). *Economies of scale for future lithium-ion battery recycling infrastructure*, Resour. Conserv. Recycl. 83, 53–62.
13. Warner, J., (2015). *The Handbook of Lithium-Ion Battery Pack Design: Chemistry, Components, Types and Terminology.* Elsevier, Midland.
14. Wilson, A.M., Bailey, P.J., Tasker, P.A., Turkington, J.R., Grant, R.A., Love, J.B., (2014). *Solvent extraction: the coordination chemistry behind extractive metallurgy*, Chem. Soc. Rev. 43, 123–134.

15. Winslow, K.M., Laux, S.J., Townsend, T.G., (2018). *A review on the growing concern and potential management strategies of waste lithium-ion batteries*, Resour.Conserv. Recycl. 129,263–277.
16. Yang, X., Zhang, J., Fang, X., (2014). *Rare earth element recycling from waste nickel-metalhydride batteries*, J. Hazard. Mater. 279, 384–388.
17. Yoshino, A., (2014). Development of the Lithium-Ion Battery and Recent Technological Trends, in: Pistoia, G. (Ed.), *Lithium-Ion Batteries: Adv. and App.* Elsevier, 67, 1–20.
18. Yu, M., Zhang, Z., Xue, F., Yang, B., Guo, G., Qiu, J., (2019). *A more simple and efficient process for recovery of cobalt and lithium from spent lithium-ion batteries with citric acid*, Sep.Pur. Tech. 215, 398–402.
19. Zhang, T., He, Y., Wang, F., Ge, L., Zhu, X., Li, H., (2014). *Chemical and process mineralogical characterizations of spent lithium-ion batteries: An approach by multi-analytical techniques*, Wast. Manag. 34, 1051–1058.
20. Zhao, J.M., Shen, X.Y., Deng, F.L., Wang, F.C., Wu, Y., Liu, H.Z., (2011). *Synergistic extraction and separation of valuable metals from waste cathodic material of lithium ion batteries using Cyanex272 and PC-88A*, Sep. Purif.Tech. 78, 345–351.
21. Zheng, X., Zhu, Z., Lin, X., Zhang, Y., He, Y., Cao, H., Sun, Z., (2018). *A Mini-Review on Metal Recycling from Spent Lithium Ion Batteries*. Engin. 4, 361–370.
22. Zou, H., Gratz, E., Apelian, D., Wang, Y., (2013). *A novel method to recycle mixed cathodematerials for lithium ion batteries*, Green Chem. 15, 1183–1191.
23. Li Li., Ji. Gea, F Wua, , R., Chena, S., Chena, B., Wu. (2009). Recovery of cobalt and lithium from spent lithium ion batteries using organic citric acid as leachant. a School of Chemical Engineering and the Environment, Beijing Institute of Technology, Beijing 100081, China. 176, 288-293.
24. S.M. Shin, N.H. Kim, J.S. Sohn, D.H. Yang, Y.H. Kim, Hydrometallurgy 79 (2005) 172–181.
- 25 . J.Zhang (2022). Pyrometallurgy-based applications in spent lithium-ion battery recycling. Nano Technology for battery Recycling. 171-182

