Bachelor's thesis

NTNU
Norwegian University of Science and Technology
Faculty of Natural Sciences
Department of Chemical Engineering

Anna Minguet Lopez

Lithium recovery from battery recycling stream

Bachelor's thesis in Chemical Engineering

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Supervisor: Sulalit Bandyopadhyay
Co-supervisor: Erik Prasetyo
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Abstract

In this research the lithium recovery from battery recycling stream was studied. The purpose was to analyse all the routes as well as the recycling processes of lithium-ion batteries, with special emphasis on the recovery of Lithium.

The main goal of this Bachelor thesis is to explain the whole recycling process in an understandable way for anyone who has never been in direct contact with the field of chemistry.

Carrying out some experiments in the laboratory in order to better understand some of the steps of the recycling process.

KEYWORDS: Lithium-ion batteries (LIBs), Electric vehicles, Hydrometallurgy, Lithium recovery, Leaching, Precipitation

Preface

The completion of this work has been possible thanks to two entities, firstly to my home University, UPC, for having given me the opportunity to study abroad, and to the destination University, NTNU, for having given me the opportunity to live this experience.

This Bachelor thesis has been carried out in the research group of Environmental Engineering and Reactor Technology (EEART) at the Department of Chemical Engineering. The research work has been carried out between February 2023 - June 2023.

First of all, I would like to thank my supervisor, Sulalit Bandyopadhyay, for having accepted me as a student to carry out this Bachelor thesis.

I would like to express my gratitude to Erik Prasetyo, postdoctoral fellow of the Department of Chemical Engineering, to help me at all times from the beginning to the end of the work, for their patience in the laboratory and for always finding a moment to meet me despite having a lot of work.

I also want to thank the other members of the department who have helped me during my work.

Finally, I also want to thank my family for their unconditional support they have been giving me from a distance every day and for giving me the opportunity to study abroad. This thesis would not have been possible without them.

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Abbreviations

LIB	Lithium-ion batteries
SO_2	Sulfur dioxide
PVDF	Polyvinylidene fluoride
Mn_2O_3	Manganese oxide
MQ Water	Milli-Q Water
CO_2	Carbon dioxide
NaOH	Sodium hydroxide
H_2O_2	Hydrogen peroxide
$H_2C_2O_4$	Oxalic acid
$(NH_4)_2S$	Ammonium sulfide
MP-AES	Microwave Plasma Atomic Emission Spectrometer
$(NH_4)_2CO_3$	Ammonium carbonate
NTNU	Norwegian University of Science and Technology

1. Introduction

Nowadays batteries are so important in our daily routine. Constantly, we are in touch with them. Are used in almost every portable electronic device. From laptops to drones, phones, automobiles, and tablets one common electronic component you will find there is a battery. [1]

On the other hand, the climate emergency in which we live has to rethink the way we are doing things. A great improvement in terms of the use of batteries, think about their recycling process once their useful life is over.

In the manufacture of many types of batteries, the raw materials used and the materials used in the manufacturing process are pollutants and have a considerable impact on the environment and the human body.

This Bachelor Thesis pretends to investigate the entire recycling process of one type of batteries from the point at which a battery is disused until, thanks to the whole process, its materials are again useful for its operation.

More specifically, I will investigate the process of Lithium recycling from Lithium-ion Batteries (LIB).

This thesis will expose two different parts, the theoretical one and also the experimental one which will include all the explanations of the experimental process which involve leaching, separation and purification. There will be attempts to recover Li from leach or purified solutions using precipitation and crystallization.

2. What are batteries?

A general description of batteries could be that batteries are devices that store electric energy in chemical form and then release it as a direct current in a controlled manner.

All kinds of batteries contain a positive electrode and a negative electrode submerged into an electrolyte, and the whole set is in a container. [2]

When a battery is supplying energy, his positive electrode is called cathode and the negative electrode is called anode. The terminal marked as a negative is the source of electrons that will flow through an external electrical circuit to the positive terminal.

When a battery is connected to an external electrical load, a redox reaction converts high-energy reactants to lower-energy products, and the difference in free energy is sent to the external circuit as electrical energy. [3]

One of the important components which batteries contain is the electrolyte, which is any substance that contains in its composition free ions, which makes it behave as an electrical conductor. The electrolyte allows ions to move between the both electrodes. [4]

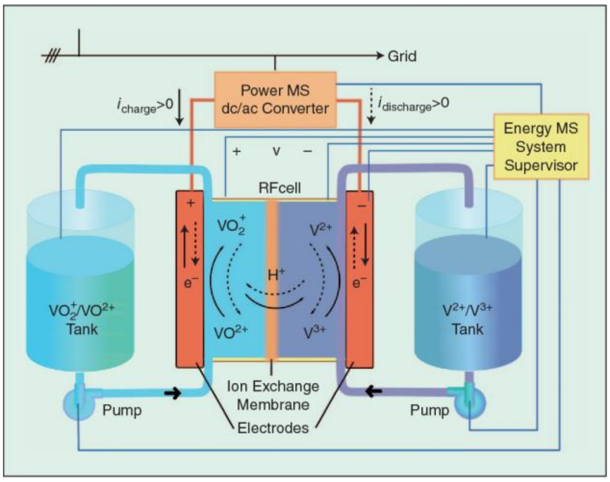


Figure 1. Chemical function of batteries

3. Types of batteries

To start with, the main classification of batteries is in two types, primary and secondary batteries.

3.1. Primary batteries

The first group, primary batteries, are the ones that are single use and non-rechargeable. We can say that they are single-cycle batteries because once fully drained, primary cells can’t be recharged. His function consists of a chemical inside it that gets consumed with use and time and once it is fully drained, you need to dispose of it. The chemical reaction is irreversible. [1]

Different types of disposable batteries have different ways of use, but they are limited to single use.

3.2. Secondary batteries

This group of batteries are the ones that are reusable and can be continuously charged and discharged.

The secondary battery is converted into electrical energy through chemical energy, but the electrical energy can be converted into chemical energy through the loading method, which can cause the battery to be reused. And the number of uses varies according to the material and design. [5]

The different types of secondary batteries have different uses because of their nominal tension, the working temperature and also the safety.

3.2.1. Li-Ion batteries (LIBs)

I will put special emphasis on these types of secondary batteries since they are the ones I will work on throughout my Bachelor Thesis.

The commercialization of this type of battery began in 1991 and since then they have had a great growth in sales. The main factors that have influenced the penetration of these batteries in the market have been the growing preference for hybrid and electric vehicles together with the rapid technological development.

The rise in the use of lithium batteries must be mainly due to their high energy density, their high energy efficiency, their prolonged life times and high-power applications such as stationary storage and transportation.

Lithium-ion batteries are the most commonly used types of rechargeable batteries nowadays. We use them constantly on devices like our mobile phones and electric vehicles.

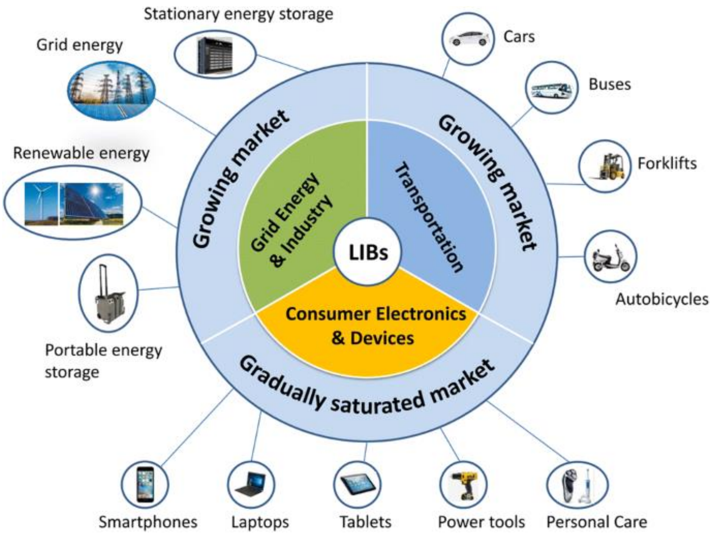


Figure 2. Emerging applications demanding LIBs

As I have previously mentioned, one of the main applications where this type of battery plays an important role is in electric vehicles. This industry has had a significant increase in recent years thanks to the different policies implemented by governments to reduce gas emissions. [6]

On the other hand, LIBs in electrical vehicles are commonly based on precious metals, such as Cobalt (Co), Nickel (Ni), Lithium (Li) and Manganese (Mn) which have a significantly high cost and also they are valuable metals. Due to this demanding growth of the industry, the significant cost of their materials and also because the presence of these valuable materials in spent LIBs they are found as an important secondary resource for the extraction of such valuable metals, various efforts have been made by the scientific community to improve the performance and safety of lithium-ion batteries. [7]

Table 1 presents the distribution of chemical compositions of lithium-ion batteries.

Distribution (wt%)	Chemical compounds and metals
5-7	Li
5-20	Co
5-10	Ni
15	Organic compounds
5-10	Other metals (Cu, Fe, Al, etc.)

Table 1. Distribution of the chemical compositions of LIBs

The term LIB covers a range of different battery chemistries, each with different performance attributes. The basic concept of a LIB is that lithium can intercalate into and out of an open structure, which consists of either ‘layers’ or ‘tunnels’. Generally, the anode is graphite but the cathode material may have different chemistries and structures, which result in different performance attributes and there are trade-offs and compromises with each technology.

A LIB comprises an anode and a cathode, a separator, an electrolyte solution (aluminum and copper foils), protective shells and containers. [8]

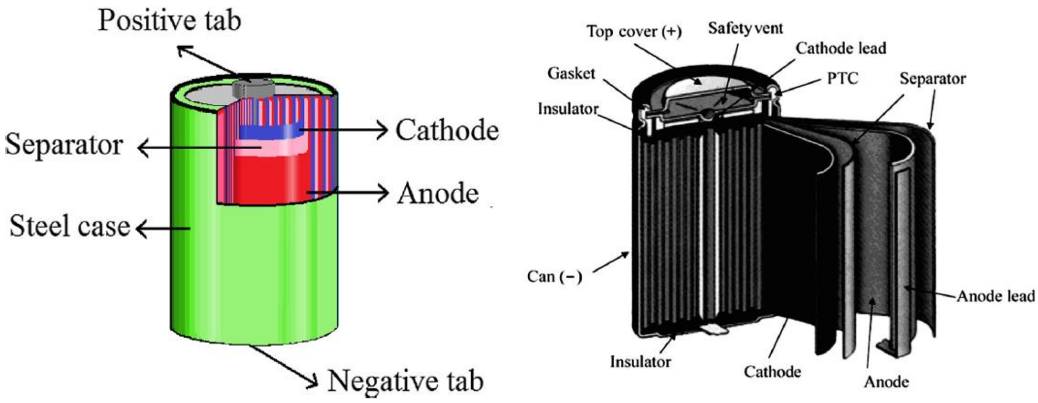


Figure 3. Shape and components of a conventional LIB

The operation of the cells of this type of batteries is as follows:

Lithium ions (+) move between the cathode and anode internally while the electrons are moving with the opposite direction in the external circuit. This migration is the reason the battery powers the device, because it creates the electrical current.

As the battery discharges, the anode releases lithium ions to the cathode which generates the electron spin that uses the energy of the corresponding device.

When we charge the battery, the exact opposite happens. Lithium ions are released by the cathode and received by the anode. [7]

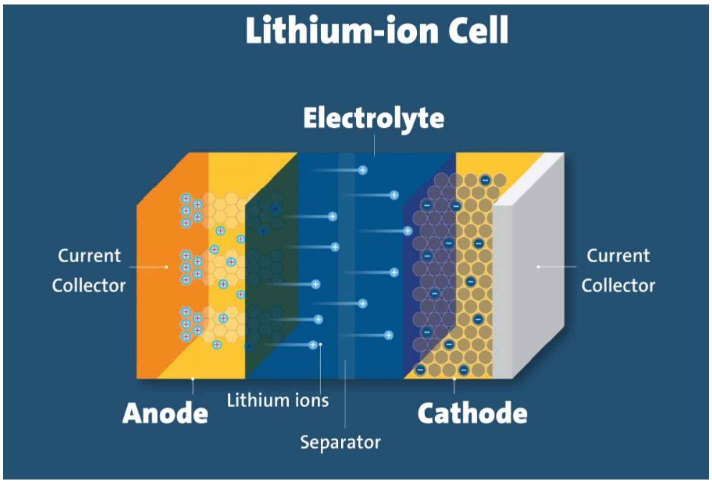


Figure 4. Lithium ion cell

3.3. Main differences between primary and secondary batteries

The main difference can be seen with “primary” and “secondary” words, that is to stay, a primary battery can only be used once and the battery will disappear once the charge runs out. A secondary battery is recycled many times and can be used again when the battery is fully charged.

The common differences are as follows:

- The specific mass capacity and specific volume capacity of the primary batteries are larger in front of the ordinary rechargeable batteries, but the internal resistance is much higher than that of the secondary batteries, which means that the charging capacity is lower.

- From a structural point of view, the secondary battery undergoes reversible changes between the volume of the electrode and the structure during discharge, while the interior of the primary battery is much simpler because it doesn’t need to accommodate these reversible changes.

- The internal resistance of the primary battery is huge, and the high current discharge performance of the primary battery is not as good as that of the secondary battery.

- The secondary battery is more respectful with the environment than the primary battery. A primary battery must be discarded after its use and rechargeable batteries can be used repeatedly.
  New generation rechargeable batteries that accomplish national standards are often used repeatedly more than 1000 times, which means that the waste generated by rechargeable batteries is less than 1/1000 of that of a primary battery.
  Regardless of the perspective of waste reduction, resource utilization and economics, the advantages of secondary batteries are very clear.

- Self-discharge of primary batteries is much smaller than that of the secondary batteries. A battery can only be discharged once, for example, alkaline and carbon batteries fall into this category, and secondary batteries can be recycled repeatedly.

- Under the condition of low current and intermittent discharge, the specific mass capacity of the primary battery is larger than that of the secondary battery, but when the discharge current is more than 800mAh, the capacity advantage of the primary battery will be significantly reduced. [5]

4. LIBs

The structure and operation of Lithium-ion batteries has been explained in section 3.2.1. In this section, I will focus on the explanation of why we recycle this type of batteries, the benefits that recycling brings us, and finally, the existing methods of recycling LIBs.

4.1. Why we recycle LIBs

Lithium ion batteries contain Fe, C, Al, Cu, Li, Co and Ni as valuable materials. Due to the presence of some strategic metals such as Cobalt and Lithium, spent LIBs are an important secondary resource for the extraction of these valuable materials.

The presence of these metals would affect the environment and threaten life on the planet if not treated properly. [9]

4.2. Environmental impacts of improper LIBs management

Strict worldwide regulations have been legislated on hazardous waste in the manufacture, accumulation, use, recycling and disposal of waste. Spent LIBs are a considerable waste stream that requires sufficient management due to the proliferation of LIB use and the increasing number of waste LIBs.

The incorrect disposal of spent LIBs causes environmental impacts. The main pillars in the management of spent LIBs are reuse, recycling, incineration and landfill. Due to the high concentrations of toxic metals that make up LIBs, these can be considered hazardous for the environment. [10]

Hence, improper disposal of these LIBs in a landfill could lead to adverse environmental pollution and soil and water contamination due to the leakage of toxic substances and heavy metals from them. Where disposal in a specialist landfill is envisaged, this could become prohibitive due to the limited number of accredited sites. In case of combined incineration of LIBs with other solid wastes, toxic gasses will be released into the environment.

For all these reasons, it is important to recycle LIBs waste mainly to protect the environment, not only from an economic point of view. To avoid the excess storage costs of spent LIB in special places and the environmental pollution caused by its improper disposal, selective leaching and recovery of the contained metals could be beneficial not only in terms of environmental impact but also to the sustainable use of secondary resources. [11]

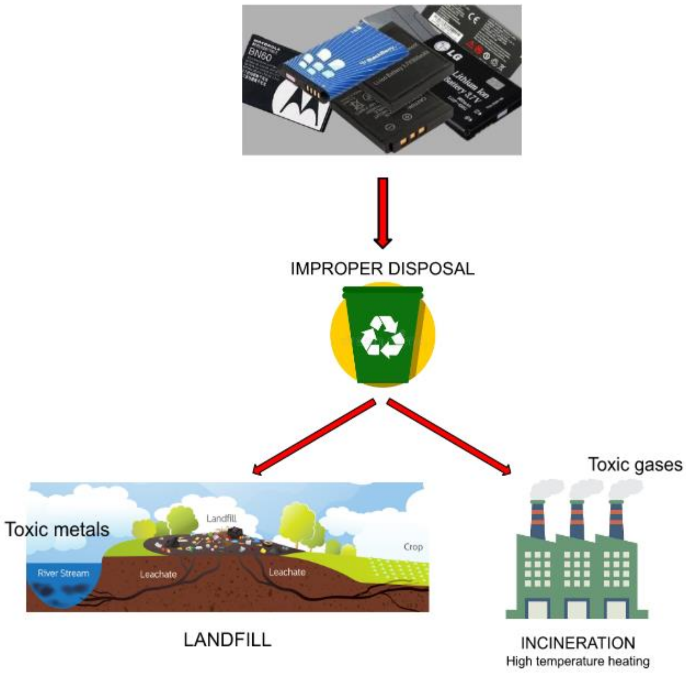


Figure 5. Environmental impacts of improper disposal of LIBs

4.3. Benefits of spent LIBs recycling

The introduction of spent LIBs recycling techniques will allow the recovery of selected materials as high quality products, could provide important economic benefits, reduce the mineral extraction, including high energy consumption and production of CO2 emission, provides resilience against vulnerable links and supply risks in the LIB supply chain and finally leads to the conservation of 51.3% of the natural resource as compared to landfilling. Because of these, we have to continue studying the recycling method of these types of batteries. [12]

Currently, research is mainly focused on optimizing recycling techniques that are currently used, reducing their complexity and also increasing the efficiency and purity of production.

There are different approaches for spent LIBs recycling but I will focus on researching the most environmentally friendly processes.

One of these methods is the use of organic agents in leaching of lithium and cobalt from spent LIBs. However, there is little information about origin, structure and effect of each organic acid on recovery of lithium and cobalt from spent LIBs. [13]

I set out to study the different parts of the different existing processes, focusing on the leaching process which is the one I will take part in the laboratory experiments.

4.4. Recycling methods

To recycle spent LIBs, there have been various approaches including **pyrometallurgy**, **hydrometallurgy** and **bio-hydrometallurgy**.

4.4.1. Pyrometallurgy

A good definition of Pyrometallurgy could be the thermal treatment of minerals at high temperature that causes chemical and physical transformations in the materials in order to recover valuable metals or intermediate compounds for further refinement. This high temperature is used to process waste with the aim of recovering valuable metals. During thermal treatment of battery waste various reactions such as reduction, decomposition of compounds and evaporation of compounds or metals can take place.

In this treatment the organic electrolyte and binders are burnt off and then the metals are dissolved using two furnaces.

Electrolyte and plastic containers are eliminated in the first furnace, and molten metals and alloys are formed in the second furnace. By melting the scrapes, cobalt, nickel and copper would effectively be recovered while other components such as lithium will be lost in the form of slag and gas. Though this method is feasible, it needs high temperatures (500–1000 °C), does not recover organic compounds, consumes lots of energy, emits large amounts of toxic gasses, results in production of non-pure alloys and requires additional refinements. [14]

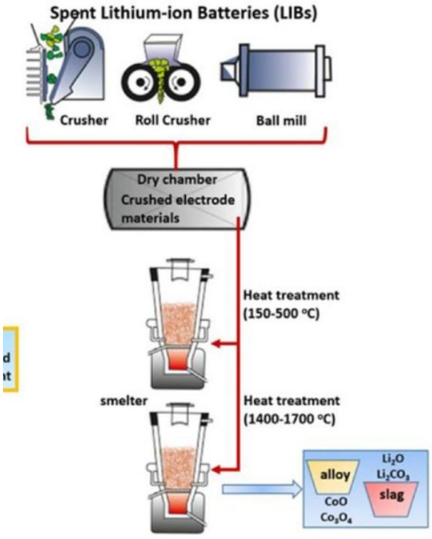


Figure 6. Pyrometallurgical process

4.4.2. Hydrometallurgy

In hydrometallurgy approach, different processes are involved to dissolve, separate and concentrate valuable metals in an aqueous medium. Some examples of these processes are: chemical precipitation, solvent extraction, acid leaching and electrochemical methods.

Hydrometallurgical treatments involve the use of aqueous solutions to leach the desired metals from cathode material. By far the most common combination of reagents reported is H_2SO_4/H_2O_2.

Once leached, the metals may be recovered through a number of precipitation reactions controlled by manipulating the pH of the solution.

Although shredding is a fast and efficient method of rendering the battery materials safe, mixing the anode and cathode materials at the start of the recycling process complicates downstream processing.

It is clear that the current design of cells makes recycling extremely complex and neither hydro-nor pyrometallurgy currently provides routes that lead to pure streams of material that can easily be fed into a closed-loop system for batteries. [15]

Hydrometallurgical recovery processes can recover around 70% of the cathode value.

Figure 7. Hydrometallurgy recovery of spent LIBs

4.4.3. Bio-hydrometallurgy

Finally, the last approach I need to mention is bio-hydrometallurgy, which requires less industrial requirements and is used in recovery of metals from solid waste.

Is a field that encompasses the overlapping areas of biology and hydrometallurgy. The variety of biological reactions and their relationships with metals in mineral and dissolved forms has resulted in the use of microorganisms in a wide range of metal extraction, metal recovery and water treatment applications. [16]

4.4.4. Comparison of recycling methods

Hydrometallurgical and pyrometallurgical methods are the most used in the recycling processes of spent LIBs. However, they come with inherent limitations.
Pyrometallurgical processes are fast due to the non-importance of the physical form of the scrap as required in chemical treatments. Although this method is fast, efficient, relatively simple and also does not require battery disassembly, it generates polluting emissions of dust and hazardous gasses such as SO_2 gas, dioxins and toxic furans. For this reason, it is a method that requires dust collection cleaning systems, which entails a high cost.

In addition, since the temperature of pyrometallurgical processes is very high, they are very energy intensive.
On the other hand, the main drawback of this process that should be taken into account is that in the pyrometallurgy recycling method, the recovery of lithium cannot be achieved.

Compared to pyrometallurgical processes, hydrometallurgical ones are more environmentally friendly, they consume less energy, are more economically sustainable, obtain a high purity of the final metal products and the recovery of leachates is possible.

The main disadvantage is that they need a pretreatment of the waste LIBs which is time-consuming and not environmentally friendly due to the use of substantial amounts of strong acids and chemical reagents.

In comparison with pyrometallurgy and hydrometallurgy methods, bio-hydrometallurgy ones are interesting alternative methods because they have higher efficiency, are relatively simple, have a negligible effect on the environment, are easy to manage and have lower energy consumption. In addition, these processes could be more selective towards metals due to the sensitivity of microorganisms towards high concentrations of various metal ions leading to selective recovery of metals. However, their main drawback is that they have slow kinetics in their processes.

Which means a longer run time is needed to get reasonable yields compared to traditional methods. [17]

However, having compared the three methods, it is clear that further research is needed to improve metal recovery and recycling of spent LIBs.

In my Thesis I will focus on Hydrometallurgy methods which are the friendliest towards the environment, consume less energy, are flexible methods, have acceptable rate of reaction and provide purer valuable metals. Furthermore, I focus on these methods since they are the ones being researched in my department's research group at NTNU.

5. Recycling process

Once the most general part of the Bachelor Thesis has been explained, including explanations about the general operation of batteries up to the different existing types, I will study the entire hydrometallurgy process of recycling lithium-ion batteries (LIB) focusing on the lithium recovery through leaching process and precipitation method.

In the figure 8 is shown a flowchart of a typical hydrometallurgical process.

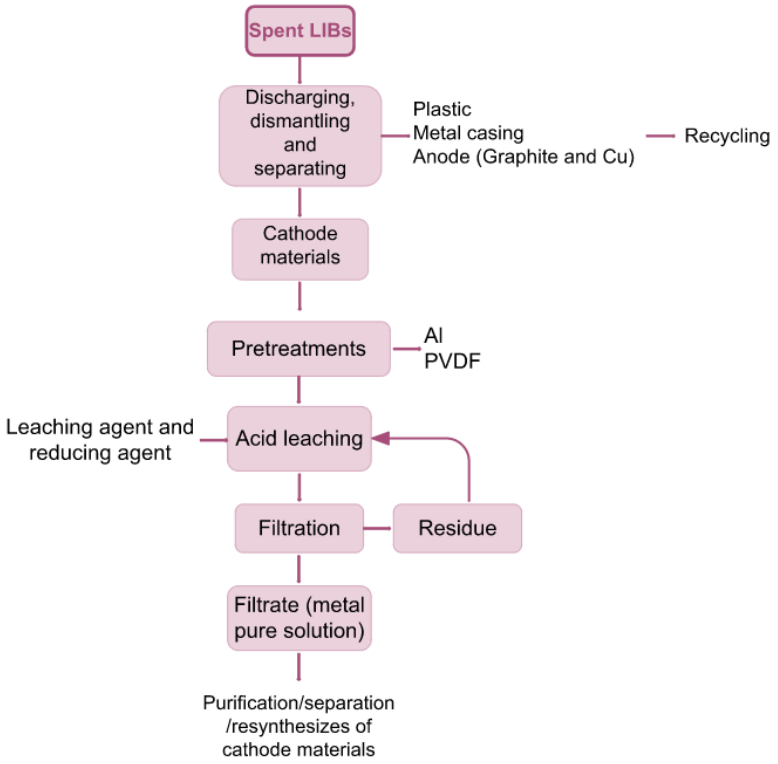


Figure 8. Flowchart of a typical hydrometallurgical process

Pretreatment (physical and chemical), dissolution of valuable metals (chemical), and treatment of metal from leaching solution (chemical) are the main stages in the recycling of spent LIBs by using the hydrometallurgy method.

5.1. Pretreatments

The composition of spent LIBs is very complicated, so once LIBs have been designated for recycling, a pretreatment is necessary to separate their different components and obtain the cathode active materials to be used for the subsequent processes.

Typically, the pretreatment process includes the following steps: discharging, dismantling and separating and the separation of the cathode active materials. All this includes mechanical, thermal and dissolution processes which are associated with benefits such as decreasing the acid consumption, increasing the leaching efficiency, decreasing the impurities in further steps and eventually decreasing the number of purification steps which results in fewer operation costs. [18]

5.1.1. Discharging

Spent LIBs have a small amount of charge and therefore can be detonated during the recycling process for this reason they must be discharged first to discard their remaining capacity to avoid potential self-ignition and short circuit hazards. In other words, the discharging process is performed for security reasons.

The time for complete discharge is dependent on the solubility of the salt and hence the conductivity of the solution; increasing the temperature will also shorten the discharge time.

Once discharge is complete, the cell components can be separated into different materials streams for further processing. [19]

5.1.2. Dismantling and separating

After the discharging process, the spent LIBs were usually dismantled and manually separated into different parts: anodes, cathodes, organic separators and steel or plastic cases. For most remanufacture and recycling processes, battery packs must be disassembled to module level at least. The disassembly part consists in pack removal, pack disassembly, module removal and cell separation. [20]

First, the cases were disassembled and removed to obtain the cell nucleus. And then, the anode and cathode plates were uncurled and separated. [21]

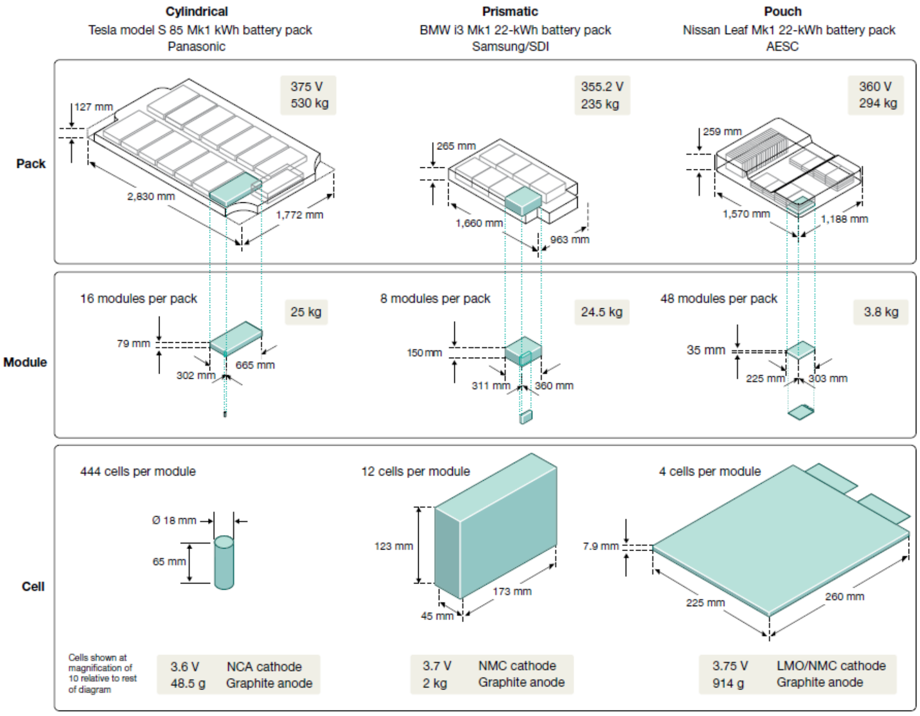


Figure 9. Examples of three different battery packs and modules (cylindrical, prismatic and pouch cells) in use in current electric vehicles.

5.1.3. Separation of cathode active materials

In spent LIBs, the active electrode materials are adhered to the current collectors with binders.

The main different pre-treatments that are carried out involved in the separation of cathode active materials are the following: mechanical method, solvent dissolution method, ultrasonic separation method and thermal method.

5.1.3.1. Mechanical method

The function of the mechanical method is to separate materials according to different properties such as magnetism, density, conductivity, etc.

Generally, a mechanical process involves grinding, sieving, magnetic separation and classification, which were carried out to obtain the particles rich in cathode active materials.

Its function is to treat the outer cases and shells and to concentrate the metallic fraction which will result in a hydrometallurgical or pyrometallurgical recycling process.

The mechanical separation is advantageous as it reduces the volume of waste and separates and enriches the components of batteries.

This separation process also has some drawbacks. For example, in the complicated LIB structure, various metals, inorganic and organic substances interpenetrate each other; moreover, their small volume and complicated structure make components difficult to completely separate. [22]

5.1.3.2. Solvent dissolution method

After the classification and the separation process some released active materials are still attached to the current collectors while other separated active materials are held together by the binders. Therefore, the dissolution of binders or aluminium foils is often performed with appropriate solvents. [20]

The dissolution process is a simple and efficient method to separate the cathode active metals from aluminium foil cathodic current collectors. A common binder used in LIBs is polyvinylidene fluoride (PVDF).

5.1.3.3. Ultrasonic separation method

Ultrasonic separation can be a suitable segregation technique, as long as the micro particles of the lithium ion battery respond predictably to a sound field. LIBs cathodes contain hydrophobic carbon. Due to the incompressibility of a solid, the thin gaseous layer that surrounds these hydrophobic particles must oscillate asymmetrically when subjected to ultrasound. Consequently, the harmonic content of the ultrasound signal radiated by hydrophobic micro particles must be higher than that of hydrophilic micro particles with the same size. [23]

The mechanism of separation was attributed to the dissolution of polyvinylidene fluoride (PVDF) and the cavitation caused by ultrasound. Based on this mechanism, the key parameters affecting the removal efficiency of aluminium foil cathodic materials were identified as solvent nature, temperature, ultrasonic time and ultrasonic power. [24]

5.1.3.4. Thermal method

Thermal treatment is another method widely used to eliminate the carbon and polyvinylidene fluoride (PVDF) binders in the cathode and separate cathode active metals from aluminium foils. Is generally associated with the production of steel, iron alloys or other metal alloys.

This process involves first grinding the cathode and then placing it in a furnace to burn off the carbon and organic compounds at high temperature. The heat treatment process is simple, convenient and suitable for large-scale operations. However, smoke emissions and high toxic gasses from the combustion of carbon and organic binders used up in the process are necessary and, therefore, additional purification equipment is required.

A form of thermal treatment is vacuum pyrolysis, which is also used for the separation of active materials from cathode. In the pyrolysis process the organic materials of the cathode are decomposed or evaporated into low molecular weight products, so the adhesion between the active materials of the cathode and the aluminium foil may be weakened, and the active materials may separate easily. [25]

5.2. Leaching process

Leaching is the process to extract a solid material substance, after having been in contact with a liquid (water). Is a naturally occurring process which scientists have adapted for a variety of methods. [26] One of which, applied to the recycling process of spent LIBs.

This process is done through oxidation, where the oxygen molecules in the water react chemically with the substances causing them to be mobilized in the moving water. The water with the dissolved substances then separates from the parent substance, also known as the solid matrix, and usually moves to areas of lower elevation. [27]

5.3. Acid leaching

Different acids have been studied for leaching of metals from spent LIBs. But they have major environmental disadvantages such as water soil pollution and the emission of various toxic gasses.

Inorganic acids are very strong and their application may result in consumption of a large amount of water, spoiling of non-metallic components, corrosion of the equipment, and leaving a lot of secondary pollutants.

By using organic acids as green and efficient leaching agents, no secondary pollution would be left, they have less potential danger to the operators, the corrosion of the equipment would be delayed, and they are also capable of selective leaching of the metals.

There is a clear relationship between the concentration of the different acids and the efficiency of the leaching. [28]

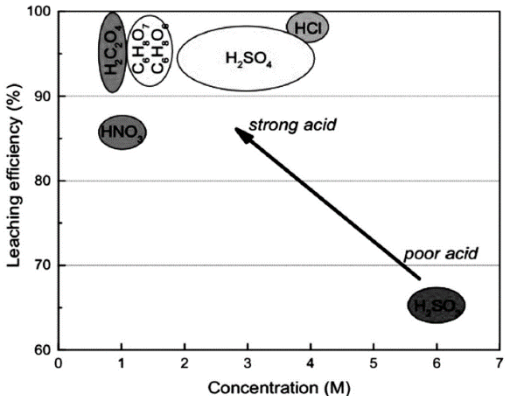


Figure 10. Effect of the concentration of different acids and leaching efficiency

In Figure 10 we can see that when the concentration of the reducing agent increases, the leaching efficiency also increases, and reaction rate will first increase and then reach a plateau (stable level), where leaching efficiency and reaction rate will not be markedly changed.

5.3.1. Inorganic acids

Several inorganic acids such as hydrochloric (HCl), sulfuric (H_2SO_4) and nitric (HNO_3) acids are the most commonly used leaching agents for the leaching of cathode active materials from spent LIBs. Among all the inorganic acids, the hydrochloric acid has the highest leaching efficiency. [20]

Acid	Molecular formula
Hydrochloric acid	HCl
Nitric acid	HNO_3
Sulfuric acid	H_2SO_4
Carbonic acid	H_2CO_3
Phosphoric acid	H_3PO_4
Sulfurous acid	H_2SO_3
Boric acid	H_3BO_4
Hydroiodic acid	HI
Hydrobromic acid	HBr

Table 2. Common inorganic acids and their molecular formula

The use of inorganic acids in the leaching process can cause significant secondary pollution, such as toxic gas emission. And this is why organic acids have been investigated in order to eliminate this secondary pollution without sacrificing leaching efficiencies. [28]

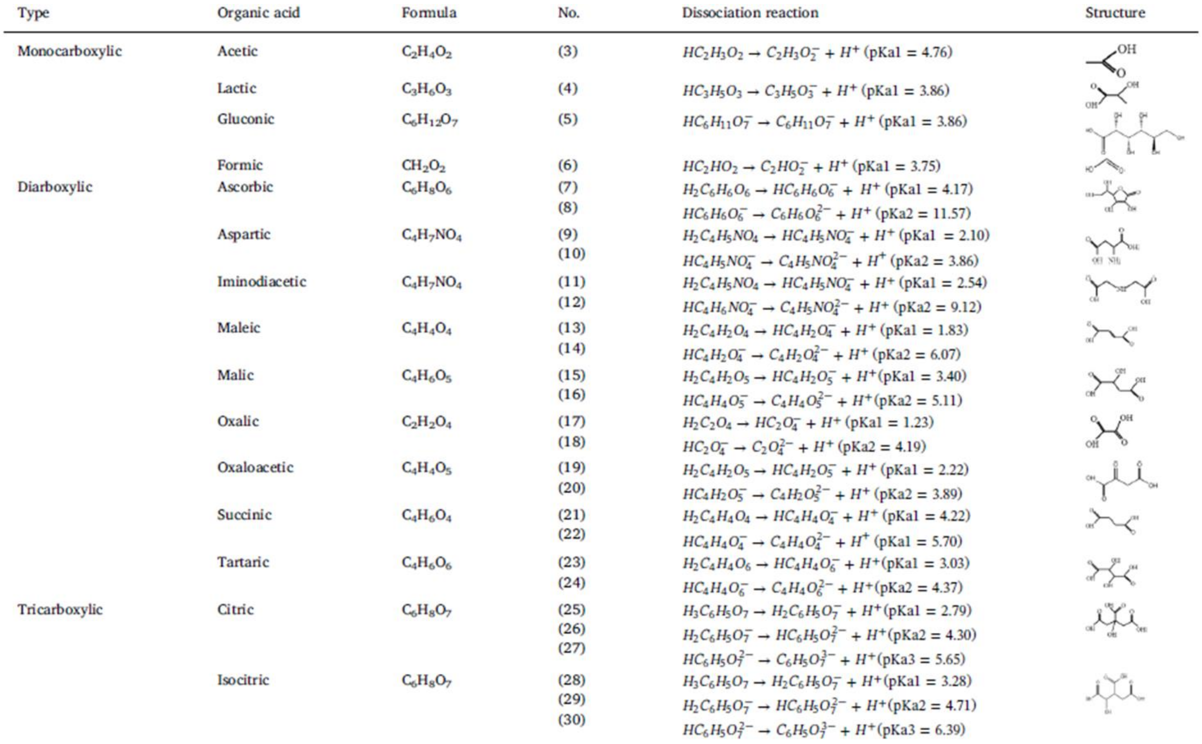
5.3.2. Organic acids

Organic acids are considered as promising agents for leaching of valuable metals from spent LIBs.

Organic acids are playing a key role in recovery of cobalt and lithium from spent LIBs as environmentally friendly and effective leaching agents.

Are mostly produced by microorganisms present in the environment and their acidity depends on their functional group.

Considering these acids are not equal in number of carboxylic groups, hydroxyl groups, and carbon-carbon double bonds in their molecules, they are classified according to their typical carbon chain, saturation, substitution, and their functional groups. [9]



Type	Organic acid	Formula	No.	Dissociation reaction	Structure
Monocarboxylic	Acetic	$C_2H_4O_2$	(3)	$HC_2H_3O_2 \rightarrow C_2H_3O_2^- + H^+$ (pKa1 = 4.76)	
	Lactic	$C_3H_6O_3$	(4)	$HC_3H_5O_3 \rightarrow C_3H_5O_3^- + H^+$ (pKa1 = 3.86)	
	Gluconic	$C_6H_{12}O_7$	(5)	$HC_6H_{11}O_7^- \rightarrow C_6H_{11}O_7^- + H^+$ (pKa1 = 3.86)	
	Formic	CH_2O_2	(6)	$HC_2HO_2 \rightarrow C_2HO_2^- + H^+$ (pKa1 = 3.75)	
Diarboxylic	Ascorbic	$C_6H_8O_6$	(7)	$H_2C_6H_6O_6 \rightarrow HC_6H_6O_6^- + H^+$ (pKa1 = 4.17)	
			(8)	$HC_6H_6O_6^- \rightarrow C_6H_6O_6^{2-} + H^+$ (pKa2 = 11.57)	
	Aspartic	$C_4H_7NO_4$	(9)	$H_2C_4H_5NO_4 \rightarrow HC_4H_5NO_4^- + H^+$ (pKa1 = 2.10)	
			(10)	$HC_4H_5NO_4^- \rightarrow C_4H_5NO_4^{2-} + H^+$ (pKa2 = 3.86)	
	Iminodiacetic	$C_4H_7NO_4$	(11)	$H_2C_4H_5NO_4 \rightarrow HC_4H_5NO_4^- + H^+$ (pKa1 = 2.54)	
			(12)	$HC_4H_6NO_4^- \rightarrow C_4H_5NO_4^{2-} + H^+$ (pKa2 = 9.12)	
	Maleic	$C_4H_4O_4$	(13)	$H_2C_4H_2O_4 \rightarrow HC_4H_2O_4^- + H^+$ (pKa1 = 1.83)	
			(14)	$HC_4H_2O_4^- \rightarrow C_4H_2O_4^{2-} + H^+$ (pKa2 = 6.07)	
	Malic	$C_4H_6O_5$	(15)	$H_2C_4H_2O_5 \rightarrow HC_4H_2O_5^- + H^+$(pKa1 = 3.40)	
			(16)	$HC_4H_4O_5^- \rightarrow C_4H_4O_5^{2-} + H^+$(pKa2 = 5.11)	
	Oxalic	$C_2H_2O_4$	(17)	$H_2C_2O_4 \rightarrow HC_2O_4^- + H^+$ (pKa1 = 1.23)	
			(18)	$HC_2O_4^- \rightarrow C_2O_4^{2-} + H^+$ (pKa2 = 4.19)	
	Oxaloacetic	$C_4H_4O_5$	(19)	$H_2C_4H_2O_5 \rightarrow HC_4H_2O_5^- + H^+$ (pKa1 = 2.22)	
			(20)	$HC_4H_2O_5^- \rightarrow C_4H_2O_5^{2-} + H^+$ (pKa2 = 3.89)	
	Succinic	$C_4H_6O_4$	(21)	$H_2C_4H_4O_4 \rightarrow HC_4H_4O_4^- + H^+$ (pKa1 = 4.22)	
			(22)	$HC_4H_4O_4^- \rightarrow C_4H_4O_4^{2-} + H^+$ (pKa1 = 5.70)	
	Tartaric	$C_4H_6O_6$	(23)	$H_2C_4H_4O_6 \rightarrow HC_4H_4O_6^- + H^+$(pKa1 = 3.03)	
			(24)	$HC_4H_4O_6^- \rightarrow C_4H_4O_6^{2-} + H^+$(pKa2 = 4.37)	
Tricarboxylic	Citric	$C_6H_8O_7$	(25)	$H_3C_6H_5O_7 \rightarrow H_2C_6H_5O_7^- + H^+$(pKa1 = 2.79)	
			(26)	$H_2C_6H_5O_7^- \rightarrow HC_6H_5O_7^{2-} + H^+$(pKa2 = 4.30)	
			(27)	$HC_6H_5O_7^{2-} \rightarrow C_6H_5O_7^{3-} + H^+$(pKa3 = 5.65)	
	Isocitric	$C_6H_8O_7$	(28)	$H_3C_6H_5O_7 \rightarrow H_2C_6H_5O_7^- + H^+$(pKa1 = 3.28)	
			(29)	$H_2C_6H_5O_7^- \rightarrow HC_6H_5O_7^{2-} + H^+$(pKa2 = 4.71)	
			(30)	$HC_6H_5O_7^{2-} \rightarrow C_6H_5O_7^{3-} + H^+$(pKa3 = 6.39)	

Figure 11. Main groups of organic acids, their formula, dissociation reactions and corresponding pKa and structure

One of the notable characteristics of aforementioned agents is their extreme solubility in water which make them appropriate agents for leaching processes.

The organic acids are much more stable than H2O2; therefore, they can be employed in a more effective way if a reducing agent is required.

Strength of organic acids is generally based on several factors including relative stability of the conjugate base of the acid and other groups including, −OH, −OS, enol, alcohol, thiol and phenol groups which is determined by corresponding pKa (the pH in which acid and anion concentrations are equal, the lower the pKa, the more strength acid).

Leaching of lithium depends only on the concentration of H+ in the leaching solution, while cobalt leaching depends on both H+ concentration and the type of anion acid selected.

The hydrogen ion concentration and the ability to release hydrogen ions by using acidic agents during leaching can expressively affect the speed of leaching.

The mineral acids can dissolve all metals with high efficiency. In other words, leaching with organic acids is selective because the presence of the aluminium ion complicates the purification and separation steps.

In addition to reducing agents and acid type, other factors such as **temperature**, **time**, and **solid-liquid ratio** are among the factors that influence cathodic material leaching. [29]

With increasing temperature, due to the better ionic dissociation of the acid and consequently the presence of greater amounts of hydrogen ions in the medium, the leaching rate is increased.
On the other hand, because the acid dissociation reaction is endothermic, at high temperatures, the reaction kinetics rate will increase. But when the temperature rises (> 70°C), the leaching rate of metals decreases. Reduction in the leaching rate of metals at high temperatures can be attributed to the accelerated decomposition of hydrogen peroxide at high temperatures.

With increasing contact time between solid and liquid, the solid dissolution rate increases, so as a result, with increasing time, the leaching efficiency will also increase. [30]

Finally, comment that in the experimental laboratory part of the thesis I will carry out the leaching processes using an organic acid such as Oxalic acid.

5.3.3. Organic acids vs inorganic acids

Organic acids are produced by microorganisms so they are not considered as potential contamination for the environment.

Although many organic acids are more expensive than the inorganic ones, their application is still cost-effective because they don't lead to most of the forthcoming environmental or economic problems associated with inorganic acids.

Although organic acids are weaker and also more expensive than inorganic acids, most of them are thermally stable, they have less environmental effects and are capable of forming strong chelates. These are the main reasons why their application is still cost-effective.

Despite the fact that organic acids are weaker than inorganic ones, most of them are thermally stable, leave a smaller environmental footprint, and are able to form strong chelates. [28]

5.4. Steps after the leaching process (Li recovery processes)

Some elements can be obtained directly from pretreatment, such as Aluminium and Copper. But Cobalt, Nickel, Lithium, Manganese… enter the leaching solution in metallic ions form.

The leaching solution obtained from the leaching process contains different metal ions. Therefore, various techniques such as solvent extraction, precipitation, electrochemical and ion exchange resin are used to recover and obtain the valuable metals.

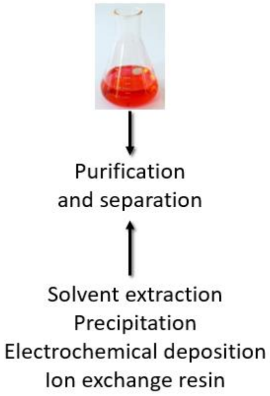


Figure 12. Steps after the leaching process

5.4.1. Solvent extraction

After leaching the electrodes, solvent extraction is the most appropriate method for efficient purification. This process is usually done along with precipitation to produce high purity metal salts.

Has an excellent effect on element separation, mild experimental conditions and simple operation.

Also has excellent adjustability, which can control the composition of the target products and obtain relatively pure materials.

5.4.1.1. The method

The extraction reaction occurs at the interface of two phases of aqueous and organic phase when mixing the organic solvent and aqueous.

It uses organic agents that are immiscible with aqueous to selectively extract target components from aqueous solutions.

The target components in the aqueous interacts with the molecules of organic agent to form complexes and transfers from aqueous to organic phase.

In solvent extraction, metal ions will be separated due to their different relative affinity to the compounds in the organic phase.

The targeted metal ions in the aqueous phase will be transferred to the organic phase, and then the two phases will be separated due to the difference in their density.

Solvent extraction contains three main steps which are extraction, scrubbing and stripping.

In the extraction step, leachate that contains the metal ions will be contacted with an organic solvent that is immiscible with the leachate. At the end of the extraction, the organic phase will be separated from the aqueous part due to its density.

Once the extraction is done, the organic part is brought into contact with a scrubbing solution (aqueous solution which helps to eliminate the impurities). This step can be done by an alkali salt or an acid solution. This step can certify the production of high purity metal.

After that, the scrubbed solution (without impurities) will be contacted with an aqueous solution called strip solution, where the metal ion in the organic part will be transferred to the aqueous phase. [20]

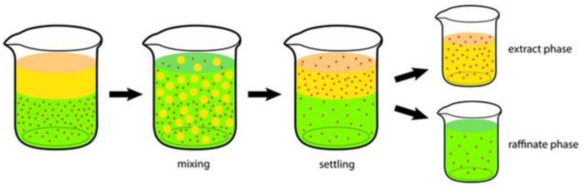


Figure 13. Solvent extraction procedure

5.4.2. Chemical precipitation

Among the various techniques used to recover and obtain the valuable metals from the leachate solution, chemical precipitation is commonly employed as it can be noted as economical, safe and has a high efficiency.

In the precipitation methods, reagents that contains ions such as hydroxide (OH^-), oxalate ($C_2O_4^-$) and carbonate ion ($(CO_3)^{2-}$) are added into a leaching solution, the valuable metals (metal ions) present in the leachate solution will be reacted to these reagents and form precipitates. [12] [32]

The metal salt recovered from the precipitation process can be a mixed metal oxide such as $LiCoO_2$, or a compound containing a single metal salt such as Li_2CO_3. However, it is not easy to control the target products to be recovered from this process because the operating conditions of these precipitation processes are determined by trial and error, without considering the behaviour of the solid-liquid equilibrium phase that governs the chemical precipitation process. Without considering the phase behaviour of these systems, a different compound than the target compound can be recovered from this process. It can also happen that the target compound co-precipitates with other metal salts, resulting in reduced purity of the compound recovered from the process. In order to further separate the mixed metal compounds a more complicated process would be needed. [20]

Due to this process of chemical precipitation, it is possible to separate the valuable metals thanks to the difference of solubility products of the precipitates.

In addition, in order to decrease the precipitation steps, co-precipitation is often employed to precipitate two or more metals together. [12]

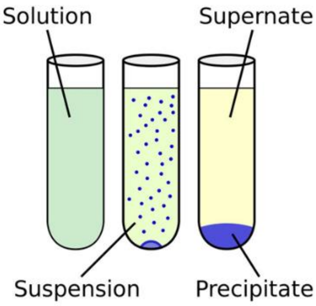


Figure 14. Schematic diagram showing the chemical precipitation

It should be noted that in the experimental part I will carry out the precipitation process in order to recover the lithium previously extracted with the leaching process.

5.4.3. Electrochemical deposition

The aim of the electrochemical deposition process is to provide appropriate conditions for the recovery of the favourable chemical reaction metal using an electrical source.

Is an effective method to selectively separate metals from a solution due to their different electrochemical potential. Despite the high production of pure metals in electrochemical techniques, it is not widely used in metal recovery from spent LIBs. [20] This fact lies in that aluminium and lithium cannot be electrodeposited in a solution because H_2O will be electrolyzed before the electrolysis of the metals due to their very negative electrode potentials. Therefore, this method is not suitable for the complicated spent LIBs leaching solution.

Metal	Eº (Volts)
Lithium (Li+)	-3.05
Aluminium (Al^{3+})	-1.67

Table 3. Electrochemical potential of Lithium and Aluminium

In addition, it has been studied that some other parameters such as current density, metal ions concentration and pH value will also influence the electrodeposition process, which make this method very complicated and not easy to control. [18]

5.4.4. Ion exchange resin

The use of ion-exchange techniques in the recovery of ions from brines is more common than the recovery of ions from the leaching solution of spent LIBs. [20]

5.4.5. Regeneration of cathode materials

Conventional extraction and separation processes such as chemical precipitation, solvent extraction and ion exchange resins are not economically feasible and also have some disadvantages like the high consumption of chemicals, the process complexity and the generation of waste. A short and efficient process to recycle spent LIBs is necessary, so some studies have been carried out on materials synthesis methods. These methods make it possible to shorten the recycling process, reduce secondary pollution and prevent separation problems. [12]

6. Experimental

After having explained the whole recycling process theoretically, in the next section I intend to explain some of the lithium extraction experiments carried out in the laboratory, with all the chemical products used and all the laboratory instruments used in the set up, and the respective results obtained. Associated risk assessment for all experimental work is outlined and can be found in NTNUs risk register (ID: 51104).

6.1. Organic acid leaching

I have carried out a lithium extraction process from carrying out a leaching process with organic acid, specifically, from the use of Oxalic acid ($H_2C_2O_4$). I used this acid to selectively dilute the lithium from the black mass.

The main goal of this experiment has been to see the lithium concentration, applying certain factors such as temperature (ºC) and solid-liquid ratio (g/L).

In Table 4 you can appreciate the different parameters that I used to carry out the experiment.

Temperature [ºC]	Solid-liquid ratio [g/L]	Oxalic acid concentration [M]	Time [hour]
80	30	1	1

Table 4. Factors used in the first experiment

6.1.1. Experimental steps

The first step of the experiment has been to calculate how many grams of Oxalic acid were necessary to carry out the dilution. I used the oxalic acid concentration (1 M) and also the volume of the volumetric flask (500mL) and I obtained that to prepare the dilution I needed 45,015 g of Oxalic acid. I weighed this amount of Oxalic acid (approximately) on the balance and I prepared the solution.

After adding the amount of Oxalic acid to the volumetric flask of 500mL I used a magnetic stirrer which provided agitation and I kept adding purified water (MQ water) until the required volume. In order to help the dilution process, I used a heater.

Figure 15. Dilution of Oxalic acid, showing (a) recently started the dilution, (b) the end of dilution

Next, I calculated how much black mass I needed, starting from using 100mL of Oxalic acid and the solid-liquid ratio marked at the beginning of the experiment. The result of the calculation was 6 grams of black mass and I weighed it on the scale taking all the necessary precautions due to the danger of this component.

The next step was to prepare the set up to carry out the leaching process. In order to regulate the temperature during the experiment an external heating circulator connected to the reactor was used. A condenser was attached to minimize the loss from evaporation, a thermometer was used in order to measure the actual temperature of the reactor and I also used a magnetic stirrer which provided agitation in the whole process.

First, I poured 100mL of Oxalic acid into the reactor and I waited until the thermometer read 80ºC (temperature set at the beginning of the experiment).

Figure 16. (a) Set up of the experiment, (b) Black mass weighed, (c) Graduated cylinder used to pour 100mL of Oxalic acid, (d) Heating circulator which I connected to the reactor

When the thermometer marked 80ºC I added to the reactor the 6 grams of black mass weighed earlier. After that, I waited for 1 hour at a stirring rate of 550 rpm.

Figure 17. (a) Leaching process, showing (a) oxalic acid dilution heating to 80ºC, (b) after pouring into the reactor the amount of black mass

After leaching, I proceeded to do the filtering process. In Figure 18 you can appreciate the two set up of the filtering process in which I used a vacuum flask, a funnel and 2 filter papers to ensure that the filtering was done correctly, also you can see what I obtained due to the process (the precipitate).

Figure 18. (a) Set up A of the filtering process, (b) set up B of the filtering process (c) precipitate obtained in the filtering process

I have replicated the leaching experiment 9 times with the aim of being able to compare results varying the solid liquid ratio and the temperature and maintaining the Oxalic acid concentration and the leaching time.

It is shown in Table 5 the different conditions set by the different experiments carried out in the laboratory.

Nº experiment	**Temperature [ºC]**	**Solid-liquid ratio [g/L]**	**Oxalic acid concentration [M]**	**Time [hour]**
1	80	60	1	1
2	80	110	1	1
3	80	30	1	1
4	52,5	60	1	1
5	52,5	110	1	1
6	52,5	30	1	1
7	25	60	1	1
8	25	110	1	1
9	25	30	1	1

Table 5. Fixed conditions in the 9 experiments

Below I attach photos of all the filters that I have obtained where you can appreciate the variety of colours. This variety in the colour tone is due to the different parameters used in the experiments.

Figure 19. Filtrates from the 9 leaching experiments

Among all the colours of the filtrates, the filtrate from experiment 8 stands out in particular, in which right after filtering I got a rosy/reddish colour and the next day (after 24 hours) the colour changed completely and was bluish/green. I only experienced this phenomenon in this experiment in which I used a temperature of 25ºC and a solid/liquid ratio of 110 g/L. In the rest of the experiments, it can be seen that most colours of the filtrates are yellowish/brownish.

The colour change in experiment 8 could be due to the oxidation of metals. I was able to draw this conclusion by doing research on the internet in which I found the following information.

When metallic compounds are in solution, they can create coloured solutions. Some of this light is transformed and some is transmitted.

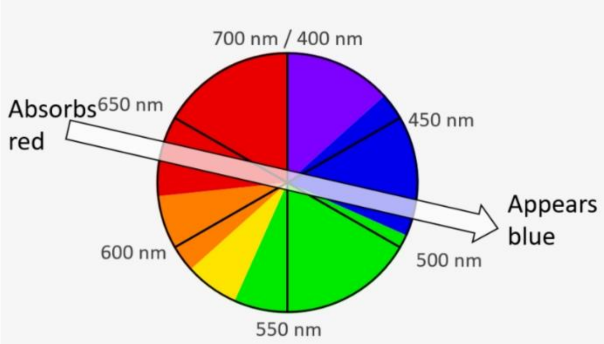


Figure 20. Ring colour wheel wavelength

In Figure 20, we can see that the energy of the absorbed light will be transmitted to the opposite wavelength. Metal compounds are well known to display a variety of vibrant colours.

The light absorbed by a metal can excite electrons. This gives rise to the colours displayed by the metal complexes. The amount of energy by which an electron is excited corresponds to a wavelength of light and that is why I was able to appreciate a change in the colour of the filter. [31]

6.1.2. Results

Use of MP-AES

To analyse the filtrates, I obtained in the leaching experiments I used the Microwave plasma atomic emission spectroscopy (MP-AES) which is a machine used to determine the elemental composition of samples by examining the electromagnetic spectrum of atoms.

Figure 21. MP-AES instrument

The basic operation of this machine is as follows, first a liquid sample is introduced in the MP-AES. In my case I introduced the samples which I prepared before with the leachates diluted x10, x100 and x1000 with Nitric acid 2%. The MP-AES creates an aerosol, from these liquids samples, using a nebulizer and a spray chamber. After that, the aerosol is introduced into the hot plasma. The aerosol dries, decomposes, and is then atomized. The atoms then continue to get excited and emit light at wavelengths characteristic for each element as they return to lower energy states. In my case, I was only interested in knowing the percentage of Lithium so I calibrated the software to just get the amount of Lithium. After emitting atomic wavelengths, these are directed into a scanning monochromator and CCD detector. And finally, the machine quantifies the concentration of the element (Lithium in my case) by comparing it to a standard of known concentration which I prepared before starting the machine.

In Figure 22 it is shown a schematic diagram of the operation of the MP-AES.

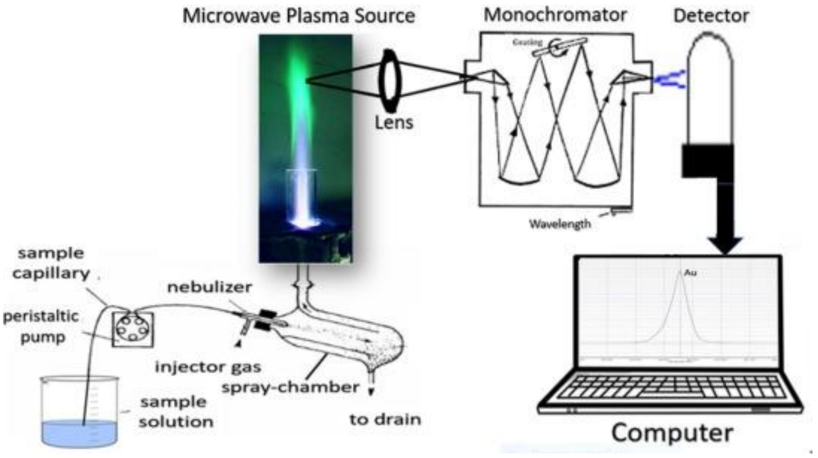


Figure 22. Schematic diagram of Atomic Emission Spectroscopy process

I analysed the 27 samples (3 for each experiment, x10, x100 and x1000) with MP-AES.

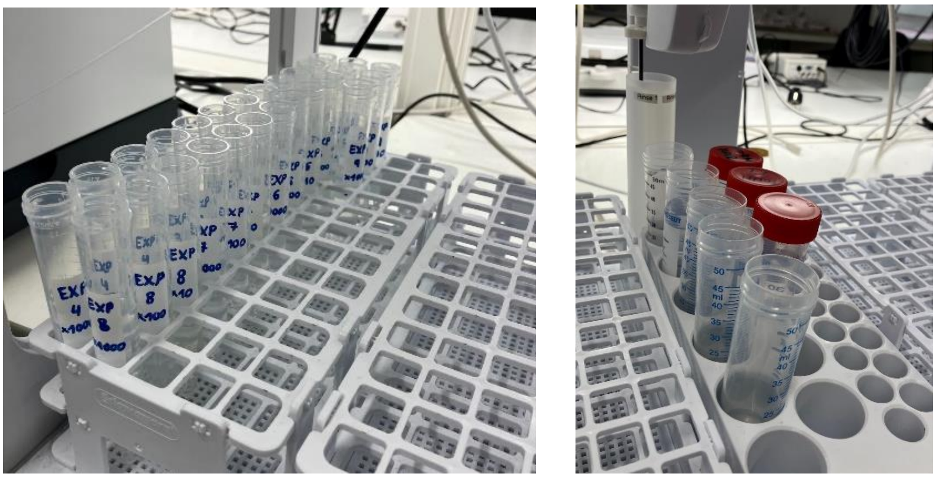


Figure 23. (a) The 27 samples placed in MP-AES, (b) the blanket and 4 standards placed in MP-AES

The results I am going to use are the data of the leachates diluted x1000 (highlighted in orange in the table below) which are the ones inside the range calibration I did which means that are the ones with less error. In Table 6 you can appreciate the results I obtained with MP-AES for the different temperatures and solid/liquid ratios.

Temperature [ºC]	Solid/liquid ratio [g/L]	Solution Label	Lithium concentration [mg/L]
80	60	Experiment 1x10	2292,70
		Experiment 1x100	2130,47
		Experiment 1x1000	1885,56
	110	Experiment 2x10	-
		Experiment 2x100	4544,73
		Experiment 2x1000	3751,47
	30	Experiment 3x10	1141,85
		Experiment 3x100	1022,12
		Experiment 3x1000	975,25
52,5	60	Experiment 4x10	2416,48
		Experiment 4x100	2138,20
		Experiment 4x1000	1876,97
	110	Experiment 5x10	4260,04
		Experiment 5x100	4076,35
		Experiment 5x1000	3580,51
	30	Experiment 6x10	1118,54
		Experiment 6x100	986,21
		Experiment 6x1000	918,17
		Experiment 7x10	1758,07

25	60	Experiment 7x100	1592,23
		Experiment 7x1000	1417,82
	110	Experiment 8x10	3232,60
		Experiment 8x100	3131,26
		Experiment 8x1000	2648,43
	30	Experiment 9x10	855,21
		Experiment 9x100	789,61
		Experiment 9x1000	684,63

Table 6. Results obtained with MP-AES

After performing all the analysis of the 27 samples I am going to compare the different results obtained. For a better understanding and analysis of the results, I have made two graphs.

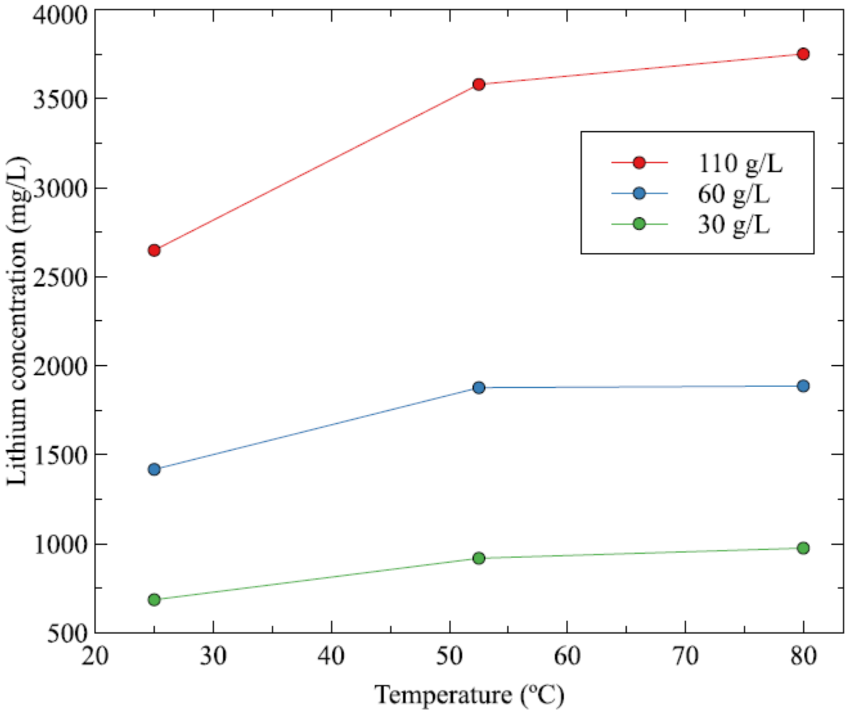


Figure 24. Lithium concentration (mg/L) for different temperatures (ºC)

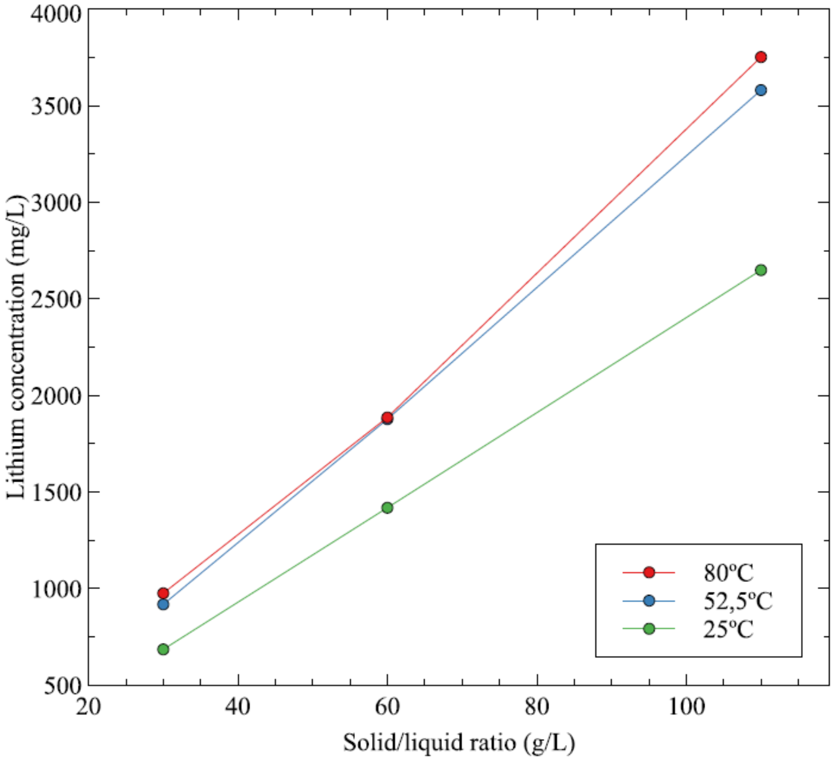


Figure 25. Lithium concentration (mg/L) for different solid/liquid ratios (g/L)

In Figure 24, the graph that shows the concentration of lithium for the different temperatures I used, we can see that the higher the temperature, the higher the lithium concentration. We can also appreciate that the highest lithium concentration obtained has been 3751,47 mg/L and it was produced in the leaching process at 80ºC and with a solid/liquid ratio of 110g/L. On the other hand, the lowest concentration of lithium obtained has been 684,63 mg/L and it was produced in the leaching process at 25ºC and with a solid/liquid ratio of 30g/L.

Analysing the shape of the functions we can see that when the temperature increases from 25ºC to 52,5ºC, the lithium concentration increases significantly and especially as the solid/liquid ratio increases. But on the other hand, when the temperature goes from 52,5ºC to 80ºC the concentration of lithium does not vary significantly and remains fairly constant.

In Figure 25, the graph that shows the concentration of lithium for the different solid/liquid ratios I used, we can see that the shape of the three functions is very similar and in addition the functions of the processes at 52,5ºC and 80ºC overlap in a good part of the range of the graph. We can also appreciate that the higher the solid/liquid ratio, the higher the lithium concentration.

Finally, having analysed the two graphs, the conclusion is that the temperature is more significant than the solid/liquid ratio since this last parameter we have seen that the functions have flat trend. But even so, both parameters significantly affect the concentration of Lithium.

After all, I also measured the pH of the 9 experiments obtaining the results I show below in Table 7 and Figure 26.

Experiment number	pH
1	1,203
2	6,894
3	1,086
4	1,315
5	5,219
6	1,006
7	1,119
8	2,170
9	1,491

Table 7. Values of the pH for the leaching experiments

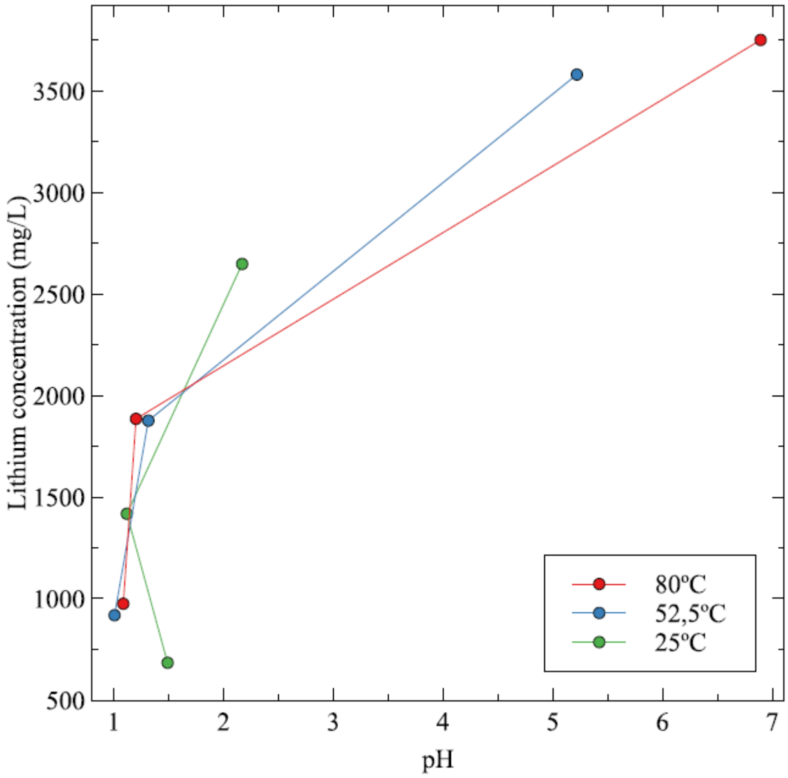


Figure 26. Lithium concentration (mg/L) for different pH

We can see that the highest pH obtained was 6,894 obtained in the experiment 2 with the conditions of 80ºC of temperature and a solid/liquid ratio of 110 g/L.

In Figure 26 you can see how in the functions of the experiments at 80 and 52,5 degrees they follow more or less the same trajectory, the only thing that varies more is in the last point of the functions, that is, with the experiments in which the solid/liquid ratio is 110 g/L.

On the other hand, it can be seen how in the experiments at 25ºC the pH obtained is not very high, the highest has been 2,170 with the solid/liquid ratio of 110 g/L.

6.2. After the leaching process

After having carried out and analysed the leachates I started the next step of the process with the aim to recover lithium. This step was taken to better understand the entire process of the lithium recovery from the battery recycling stream. More specifically, in order to explain in an experimental way, the process that takes place once the lithium is extracted, that is to say, the recovery process.

6.2.1. Up-scale Experiment

The first step to be able to carry out the precipitation process was to choose the best conditions to carry out a final leaching process but in a larger reactor to obtain more volume of leachate.

First of all, having analysed the results obtained from the leaching experiments, it can be observed how I obtained the highest concentration of lithium in experiment number 2, which I performed with the conditions of 80ºC of temperature and with a solid/liquid ratio of 110 g/L.

Knowing the experiment in which I obtained more concentration of lithium, I replicated it but varying the volume of Oxalic acid which was 800mL instead of 100mL and also the black mass was 88g instead of 11g, because I also used the same solid/liquid ratio (110 g/L).

Finally, the temperature I used was not 80ºC, I reduced it to 52ºC in order to reduce the pressure in the reactor and be able to have greater control of the experiment. I also reduced the revolutions per minute of the stirring to 250 rpm for the same reason as with the temperature. The leaching process took place for 1 hour as in the previous experiments.

In Table 8 are shown the factors I used in this up-scale experiment.

Temperature [ºC]	**Solid-liquid ratio [g/L]**	**Oxalic acid concentration [M]**	**Time [hour]**
52	110	1	1

Table 8. Factors used in the up-scale experiment

After knowing the conditions, I started preparing the Oxalic acid dilution as I also prepared in the other experiments but this time I used the oxalic acid concentration (1 M) but the volume of the volumetric flask was 1L instead of 500mL so I calculated the amount of Oxalic acid and I obtained that to prepare the dilution I needed 90,03g of Oxalic acid.

Figure 27. Dilution of Oxalic acid 1M, showing (a) recently started the dilution, (b) the end of dilution

After having the dilution of Oxalic acid I started preparing the set up for the leaching up-scale experiment. As you can see in Figure 28, the reactor was completely different to the one I used for the other experiments, the main difference is its volume since the operation is the same as in the other reactor previously used.

Figure 28. (a) Set up of the experiment at the beginning, (b) set up of the experiment after pouring the black mass

After 1 hour of experiment, I did the filtering which took quite a while of work due to the large amount of volume to filter.

Finally, in Figure 29, you can see the leachate obtained with a greenish colour.

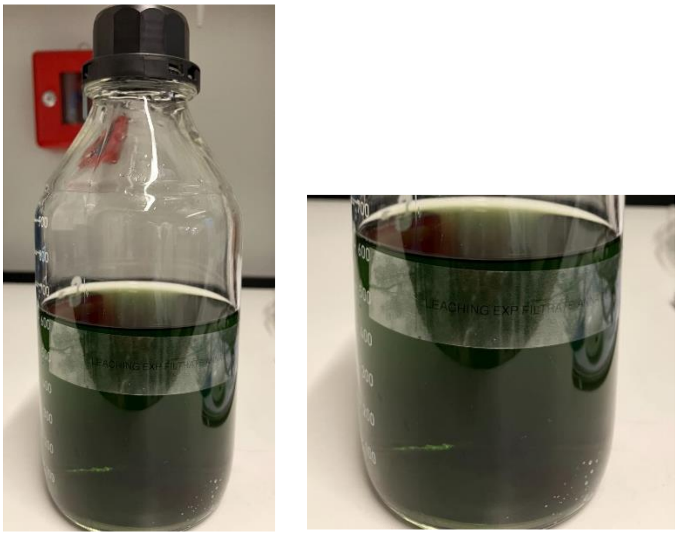


Figure 29. (a) Leachate obtained with the up-scale experiment, (b) appreciation of the greenish colour obtained

Then I proceeded to analyse the concentration of lithium and other metals with MP-AES in which I obtained the Table 9 concentrations (I prepared 3 samples just to make sure about the results and also to have less error).

Samples	**Elements concentration [mg/L]**						
	Fe	**Cu**	**Ni**	**Co**	**Li**	**Mn**	**Al**
1	305,13	350,01	323,08	251,29	3078,26	278,21	17,95
2	290,84	339,32	323,16	242,37	3150,82	282,77	16,16
3	292,20	350,64	340,90	253,24	3214,17	292,20	19,48
Average	296,06	346,65	329,05	248,96	**3147,75**	284,39	17,86

Table 9. Elements concentration in the up-scale experiment

The row highlighted with the orange colour is the concentration average of the 3 samples analysed. As you can see with the red colour marked it is shown the amount of lithium concentration obtained which is the important value I was focused on. I also analysed the concentration of the other elements just to know the residual amount in the leachate of other elements than lithium.

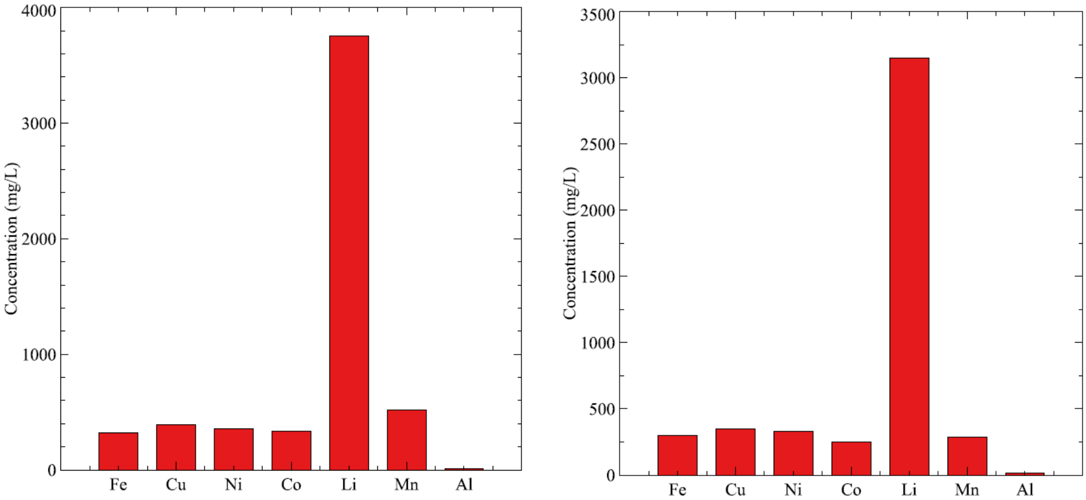


Figure 30. (a) Graph of the concentration of the Experiment 2, (b) Graph of the concentration of the Up-scale experiment

After this analysis, I can see that the concentration of lithium obtained in the up-scale experiment is similar to the one I obtained in experiment 2 (what I expected before the experiment).

Experiment	**Lithium concentration [mg/L]**
Experiment 2 (80ºC, 110g/L, 100mL oxalic acid)	3751,47
xUp-scale experiment (52ºC, 110g/L, 800mL oxalic acid)	3147,75

Table 10. Comparison of the lithium concentration between the two experiments

On the other hand, I measured the pH obtaining a value of 5.894

6.2.2. Removing the impurities from the leachate using a sulfide

After obtaining and analysing the leachate I proceeded to do the next step which was remove the metals still existing in the solution (such as Nickel, Cobalt, Iron…) from the use of $(NH_4)_2S$ (ammonium sulfide). Explained in another way, the purpose of this step was to remove the impurities from the leachate using a sulfide.

The reaction produced was:

$$Metals\ (Fe + Cu + Ni + Co + Li + Mn + Al) + (NH_4)_2S \rightarrow MetalSulfide\ (precipitate) + Li + NH_4$$

The reaction occurs between the metals in the solution and the sulfide, thus creating metal sulfide which precipitates. But the aim of the use of ammonium sulfide is because lithium doesn't react with the sulfide at all. Therefore, I can remove the metal impurities without removing lithium.
To do this, I used the same set-up as the one I used in the leaching experiments but without the use of the condenser. I also used a magnetic stirrer which provided agitation in the whole process with a stirring speed of 400 rpm.

First, I prepared the set-up and I added in the reactor 50mL of the leachate of the up-scale experiment done before. With the water heater I increased the temperature until 25ºC and when I had the constant temperature, which I could control thanks to the thermometer, I added to the reactor bit by bit the amount of ammonium sulfide suitable in each experiment. I performed six identical experiments but varying the amount of ammonium sulfide just to study the effect of this compound in the process to remove the metals.

Figure 31. (a) Ammonium sulfide (NH4)2S, (b) Powerpette plus I used for adding the 50mL of the leachate to the reactor

In Table 11 you can see the different amounts of ammonium sulfide used with the different ratios.

Ratio	**Amount of $(NH_4)_2S$ [mL]**
1:0.5	9,20
1:0.7	12,9
1:0.9	16,6
1:1	18
1:1.2	22
1:1.5	28

Table 11. Amount of ammonium sulfide used in the different experiments with the different ratios

After adding the corresponding amount of ammonium sulfide I waited for 1 hour in order for the experiment to be carried out. After 1 hour I proceeded to do the filtering process in which I kept both, the filtrate and the precipitate, to later analyse the concentrations in them.

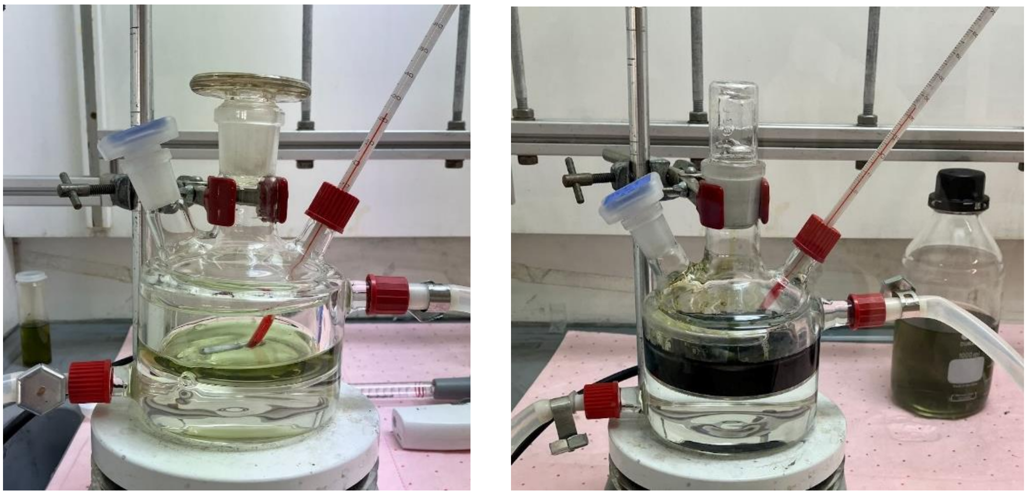


Figure 32. (a) Set-up just having added the leachate, (b) Set-up after adding the ammonium sulfide

After having filtered and obtained the 6 solutions from the respective experiments, I prepared 6 samples which I diluted x100 with nitric acid and analysed them with MP-AES. The results obtained are shown in the following table.

Samples	Elements concentration [mg/L]						
	Fe	Cu	Ni	Co	Li	Mn	Al
Exp1_1:0.5	6,59	10,35	9,41	2,82	3348,39	6,59	0,94
Exp2_1:0.7	0,91	13,67	8,20	0,00	3326,52	1,82	0,91
Exp3_1:0.9	0,00	13,97	8,38	0,00	2823,34	1,86	0,93
Exp4_1:1	5,54	7,38	5,54	0,92	3009,46	1,85	3,69
Exp5_1:1.2	0,94	9,36	4,68	0,94	2846,77	1,87	2,81
Exp6_1:1.5	0,95	11,46	3,82	0,95	2803,85	1,91	2,86

Table 12. Elements concentration in the experiment to remove impurities.

Figure 33. Solutions obtained in the 6 experiments.

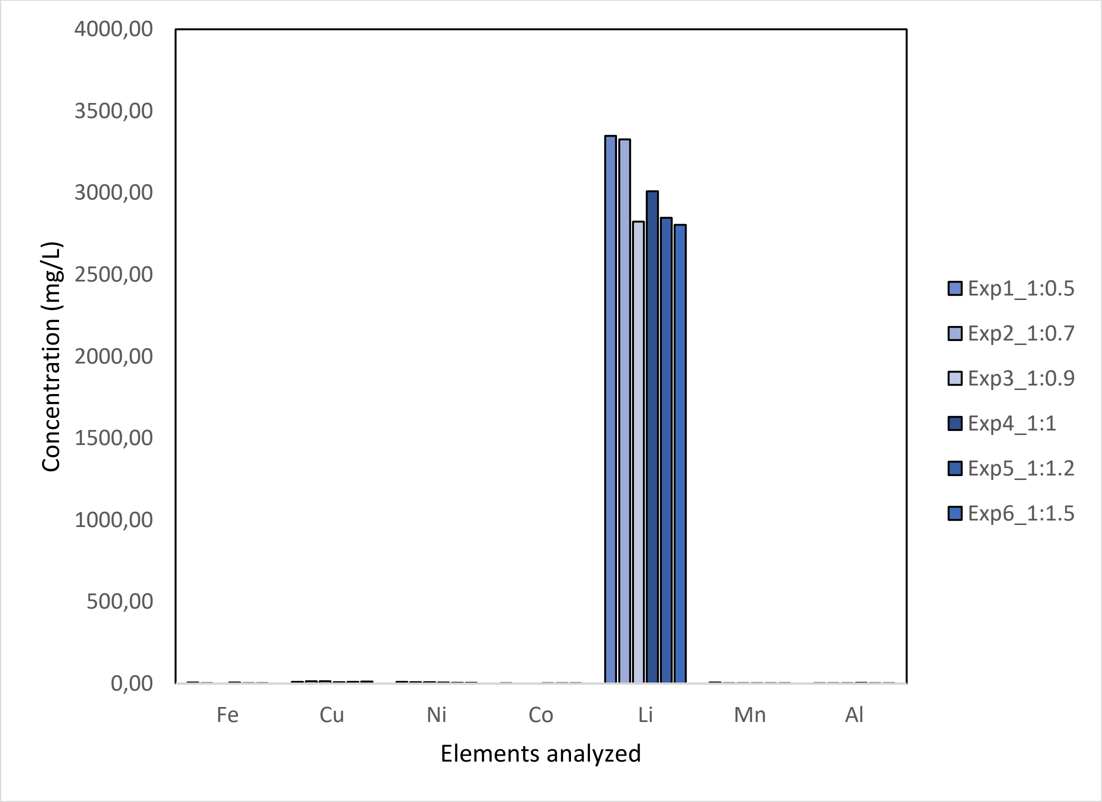


Figure 34. Graph of the concentrations of the experiment to remove impurities

In Figure 34, you can appreciate the concentrations of the different elements analysed in the 6 experiments carried out. As expected, the amount of impurities (Fe, Cu, Ni, Co, Mn and Al) has decreased significantly compared to the Figure 30 (b), a graph that shows the concentrations of these impurities just after the up-scale experiment was carried out, that is to say, before I had performed the last experiment where I used ammonium sulfide.

This means that thanks to the sulfide, I have been able to remove most of the impurities and therefore, in the current solutions, the large concentration is focused only on lithium.

On the other hand, comparing the 6 experiments with each other, that is, the different ratios of ammonium sulfide used (1:0.5, 1:0.7, 1:0.9, 1:1, 1:1.2, 1:1.5), it can be seen how the differences in the results are minimal, therefore, the amount of ammonium sulfide used is not a determining factor when removing impurities.
If we have to base it on which experiments I achieved the highest concentration of lithium, it can be seen in the graph that it was in experiments 1 and 2, with an ammonium sulfide ratio of 1:0.5 and 1:0.7 respectively. But also in the first 2 experiments I obtained a highest concentration of Lithium than in the up-scale experiment which makes no sense. Seeing these results it is clear that having replicated the experiments I would have been able to see the cause of the error or at least have more results to compare.

6.2.3. Final up-scale experiments

After analysing the experiments with different ratios to remove the impurities, I decided to do 2 leaching experiments again with the largest reactor to have a large amount of volume to then remove the impurities and finally proceed to do the precipitation. All these steps using the best conditions obtained in the experiments done previously.

First of all, I did the 2 leaching experiments with the large reactor using the same set-up as the one I explained in the section 6.2.1. and with the conditions shown in the following table.

Temperature [ºC]	Solid-liquid ratio [g/L]	Stirring speed [rpm]	Time [hour]
52	110	300	1

Table 13. Conditions used for the 2 up-scale experiments

Figure 35. (a) Oxalic acid dilution, (b) Black mass weighted in the balance, (c) The reactor with the oxalic acid solution before adding the black mass, (d) The reactor after adding the black mass

Figure 36. Solutions obtained in both experiments

I analysed the concentrations of the 2 leachates obtained and I saw that they were very similar so I put the two solutions together and re-analysed the mixture. In the following table I show the results obtained with MP-AES.

Samples	**Elements concentration [mg/L]**						
	Fe	**Cu**	**Ni**	**Co**	**Li**	**Mn**	**Al**
1	340,66	268,60	137,57	117,92	3367,27	203,08	72,06
2	301,43	339,79	394,60	274,03	3578,80	284,99	43,84
Mixture (1 and 2)	339,03	332,11	283,68	200,65	3473,35	249,08	55,35

Table 14. Elements concentration in the 2 up-scale experiments and in the mixture of both

It can be seen that with this final mixture of the 2 experiments I obtained a lithium concentration more similar to the one of experiment 2.

Experiment	Lithium concentration [mg/L]
Experiment 2 (80ºC, 110g/L, 100mL oxalic acid)	3751,47
Up-scale experiment (52ºC, 110g/L, (800mL+800mL oxalic acid)	3473,35

Table 15. Comparison of the lithium concentration

6.2.4. Final experiment to remove the impurities

After obtaining the leachate I proceeded again to do the experiment with ammonium sulfide to remove the impurities but this time I did the experiment with 400mL of the leachate (using the large reactor) and I used the conditions shown in the next table.

Ratio	Amount of (NH4)2S [mL]	Temperature [ºC]	Stirrer speed [rpm]	Time [hour]
1:0.5	73,6	25	300	1

Table 16. Conditions used to remove the impurities

Figure 37. (a) Reactor before adding the ammonium sulfide, (b) Reactor after adding ammonium sulfide

After analysing the sample with MP-AES previously diluted x100 I obtained the following results.

Elements concentration [mg/L]						
Fe	**Cu**	**Ni**	**Co**	**Li**	**Mn**	**Al**
6,96	6,96	18,90	0,00	3177,62	183,99	3,98

Table 17. Elements concentration in the experiment

It can be seen that I removed most of the amount of impurities, however, the amount of Manganese in the solution is still quite high compared to when I did the small scale experiments. Due to this fact, I proceeded to carry out an experiment focused on removing Manganese from the solution.

6.2.5. Experiment focusing on remove Manganese (reducing agent)

I performed this experiment focusing on removing the Manganese from the solution. I used Hydrogen peroxide, as an oxidation agent, to selectively react with Manganese and create Manganese dioxide. Below I show the reaction that takes place in the experiment.

$$H_2O_2 + Mn^{2+} \rightarrow MnO_2 + 2H^+$$

I performed the same process using 4 different percentages of Hydrogen peroxide to see which was the most effective in removing Manganese. In Table 18 it is shown for the different percentages of the amount of Hydrogen peroxide added.

Percentage	Amount of H_2O_2 [mL]
For 1%	1,67
For 0.5%	0,84
For 0.25%	0,42
For 0.125%	0,21

Table 18. Amount of Hydrogen peroxide added for the different percentages

To carry out the experiment, I used four 100mL flasks in which I added the first 50mL of the PLS and then I added the corresponding amount of Hydrogen peroxide for the different percentages.

Figure 38. (a) Flasks with 50mL of PLS, (b) Flasks after adding and mixing the Hydrogen peroxide

After adding the H_2O_2 I started timing and syringed out 1mL from each flask after 0.5, 1, 1.5, 2, 3, 4, 5 and 6 hours. Each time I extracted 1mL of the solution with the syringe I filtered it and stored it in small jars (previously labelled) for later analysis.

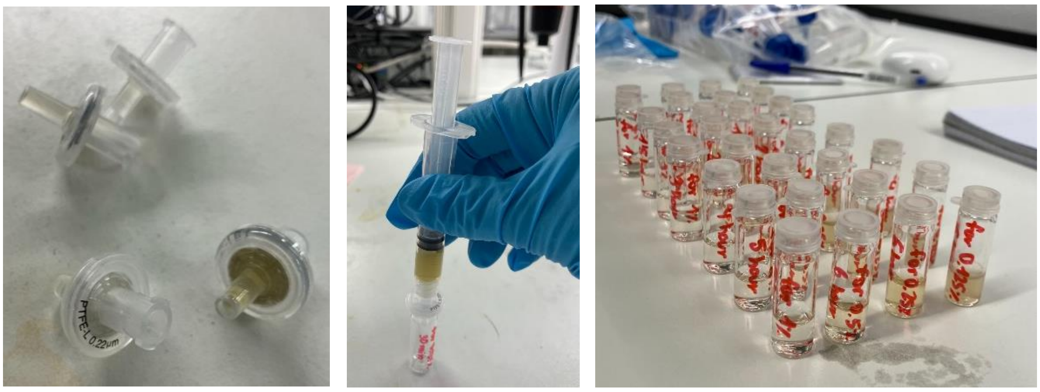


Figure 39. (a) Mechanism for filtering the solution, (b) Filtering process, (c) Small labelled jars with the solutions

After the process I prepared the samples diluting them x100 and then I analysed them with MP-AES focusing only on the concentration of Lithium and Manganese. In the following table I show the results obtained.

	Elements concentration [mg/L]							
Time of the experiment [hours]	**1%**		**0.5%**		**0.25%**		**0.125%**	
	Li	Mn	Li	Mn	Li	Mn	Li	Mn
0.5	3291,19	210,28	3394,60	213,92	3408,16	212,59	3401,26	217,41
1	3308,42	211,38	3389,56	213,61	3412,85	212,88	3400,64	217,37
1.5	3284,94	209,88	3411,94	215,02	3394,69	211,74	3419,89	218,61
2	3332,72	212,93	3366,43	212,15	3375,44	210,54	3646,24	233,07

3	3315,96	211,86	3442,20	216,92	3366,93	210,01	3387,63	216,54
4	3296,19	210,60	3382,40	213,16	3431,75	214,06	3242,42	207,26
5	3340,50	213,43	3348,92	211,05	3415,82	213,06	3362,27	214,92
6	3336,72	213,19	3393,42	213,85	3423,58	213,55	3390,06	216,70

Table 19. Concentrations of Li and Mn for the different times of the experiment

Looking at the results in Table 19, I can clearly see that I have not removed Manganese from the solution despite adding Hydrogen peroxide. On the other hand, I have also appreciated that the amount of H_2O_2 has not been significant since comparing the results for the different percentages they do not vary significantly.

After seeing that I could not remove the Manganese with these experiments I proceeded to perform the last step of the experimental part of my work.

6.2.6. Precipitation and Anti-solvent crystallization

Precipitation and Anti-solvent crystallization were the last experiments carried out in the course of my work.

To do these two experiments, the main compound used was the Ammonium carbonate $(NH_4)_2CO_3$ to selectively react with Lithium producing the following reaction:

$$2Li^{+} + (NH_4)_2CO_3 \rightarrow Li_2CO_3 + 2NH_4^{+}$$

First of all, I prepared a dilution of Ammonium carbonate in a 250mL volumetric flask.

Figure 40. (a) (b) Ammonium carbonate, Dilution of Ammonium carbonate, showing (c) recently started the dilution, (d) the end of dilution

After having prepared the dilution I proceeded to prepare the precipitation experiment in which I used the small reactor in which I added 50mL of the PLS, I used a water heater to perform the experiment at 25ºC controlled by a thermometer, a magnetic stirrer with 500 rpm of speed and the main different thing I used compared to all the other experiments done before was the pump, which helped me to add to the reactor consecutively and at a constant rate the necessary amount of Ammonium carbonate. The rate at which the pump was dropping drops was 0.233 mL/min. I was withdrawing with a syringe 1mL from the reactor at different minutes of the reaction from the moment when the first drop fell inside the reactor. The minutes in which I extracted 1 mL from the reactor were previously calculated based on the different fixed ratios and the drop speed of the pump drops.

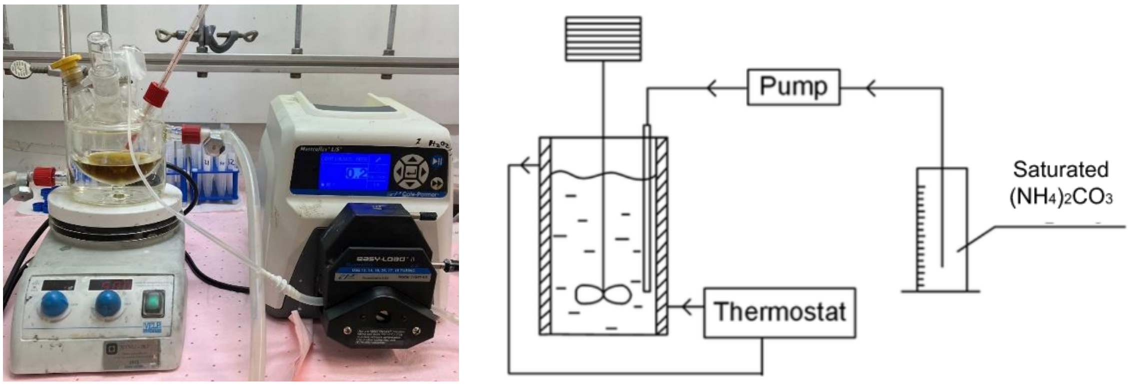


Figure 41. (a) Set-up for the precipitation experiment, (b) Graphical representation

In Table 20 it can be seen for the different ratios used, the amount of Ammonium carbonate added in the reactor and also the minutes of the reaction when I extracted with the syringe 1mL of solution.

Ratio	**Amount of $(NH_4)_2CO_3$ [mL]**	**Time [min]**
2:0.3	2,581	11
2:0.5	4,302	19
2:0.7	6,023	26
2:0.9	7,744	33
2:1	8,604	37
2:1.1	9,464	41
2:1.3	11,185	48
2:1.5	12,906	55

Table 20. Amount of Ammonium carbonate added in the reactor for the different ratios and times of the Precipitation experiment

Figure 42. Solutions extracted from the reactor

After this experiment I proceeded to do the Anti-solvent crystallization which is basically a replica of the precipitation experiment explained above. The main difference is that I initially added 25mL of the PLS inside the reactor instead of 50mL and I also added 25mL of Ethanol. The rate at which the pump was dropping drops was 0.233 mL/min, the same as in the precipitation experiment. The temperature of the experiment and the speed of the magnetic stirrer were the same as those mentioned above (25ºC and 500 rpm respectively).

In Table 21 it can be seen for the different ratios used, the amount of Ammonium carbonate added in the reactor and also the minutes of the reaction when I extracted with the syringe 1mL of solution.

Ratio	Amount of $(NH_4)_2CO_3$ [mL]	Time [min]
2:0.3	1,291	6
2:0.5	2,151	9
2:0.7	3,011	13
2:0.9	3,872	17
2:1	4,302	19
2:1.1	4,732	20
2:1.3	5,593	24
2:1.5	6,453	28

Table 21. Amount of Ammonium carbonate added in the reactor for the different ratios and times of the Anti-solvent crystallization experiment

Figure 43. (a) Ethanol, (b) Solutions extracted from the reactor

After having all the solutions of both experiments (Precipitation and Anti-solvent crystallization) I proceeded to do the analysis with MP-AES of the samples previously diluted x100. When preparing the samples, I added 50L of Indium standard to have less error with MP-AES. Below I attach two tables with the results obtained from the two experiments in which I analysed the concentration of Lithium, Manganese and also Indium.

	Elements concentration [mg/L]		
Ratio	**In**	**Li**	**Mn**
2:0.3	419,28	2693,05	146,36
2:0.5	419,13	2692,04	146,31
2:0.7	419,89	2696,94	146,57
2:0.9	419,35	2693,47	146,38
2:1	415,09	2666,12	144,90
2:1.1	421,74	2708,87	147,22
2:1.3	417,02	2678,54	145,57
2:1.5	418,04	2685,06	145,93

Table 22. Elements concentration for the Precipitation experiment

	Elements concentration [mg/L]		
Ratio	**In**	**Li**	**Mn**
2:0.3	510,26	1232,24	31,22
2:0.5	516,34	1246,93	31,59
2:0.7	513,96	1241,16	31,45
2:0.9	510,13	1231,92	31,21
2:1	479,64	1158,28	29,35
2:1.1	512,63	1237,95	31,37
2:1.3	509,06	1229,35	31,15
2:1.5	494,57	1194,34	30,26

Table 23. Elements concentration for the Anti-solvent crystallization experiment

Evaluating the results, it can be seen how in the precipitation I managed to reduce the amount of Manganese a little but not significantly while in the anti-solvent crystallization experiment I managed to remove a large part of the amount of Manganese. As a counterpart in this last experiment, the amount of Lithium has also been significantly reduced.

Regarding the comparison of the different ratios, it can be clearly seen how this factor is not significant since the results are very similar to each other regardless of the ratio used.

7. Conclusions

After having done the both main parts of the thesis, the theoretical and the experimental one, I can extract some conclusions about it all.

First of all, the theoretical part has been worth it for me to better understand all the recycling process since a Lithium-ion battery is in its end of life until the recovery of the Lithium is done. Doing theoretical research made me able to compare my future results and know If I was inside a normal range of concentration values of Lithium or not. In addition, I was able to learn the procedure that I subsequently carried out experimentally.

Regarding all the experiments I have done I can conclude that it is not that easy as I thought at the beginning to obtain a high amount of Lithium at the end of the whole process. The vast majority of the values obtained were in a range that I supposed before doing the experiments (I compared the values with previous research work). Regarding to the leaching experiments I can conclude that the higher the temperature, the higher the lithium concentration and the higher the solid/liquid ratio, the higher the lithium concentration.

In the final experiment to remove the impurities I didn't remove at all the Manganese and this wasn't expected before the experiment. Also in the experiment to selectively remove Manganese I didn't obtain the results expected, which it means that the Hydrogen peroxide was not effective. These are some examples that explain that chemistry is not an exact science and a lot of factors can influence such as the human factor and also the temperature, lost by evaporation, remains in the containers…

On the other hand, thanks to having experienced the whole process experimentally, I have been able to see that it is a difficult process to apply on a large scale, industrially, since the result can vary greatly depending on the composition of the battery itself, and as I said earlier, also depending on other factors. In my work it can be seen that in the up-scale experiments (replicability of the experiments in a large reactor) I didn't obtain the exact results between the different experiments.

As for the economic part, I think it is an expensive process due to the fact that it cannot be automated in addition to the machinery and the compounds that have to be used.

To conclude with, in this work I have learned that unless you sometimes don't obtain the results expected, that is not a bad thing, because I obtained data and this is the main value that I can obtain.

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