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Effect of Pregnant leach solution on Synergistic Solvent Extraction

Graduate thesis in MSc Sustainable Chemical and Bio-chemical engineering
Supervisor: Sulalit Bandyopadhyay
Co-supervisor: Erik Prasetyo
July 2023

Graduate thesis

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Abstract

Battery recycling is gaining increased traction in today's world for myriad reasons, with the chief ones being the dwindling availability of raw materials and heightened ecological consciousness. While there exist certain established methods for recycling batteries at their end-of-life, the efficacy of these methods remains uncertain and they do not recover all battery components evenly. Modern batteries predominantly consist of lithium, nickel, manganese, and cobalt. Interestingly, while over half of the NMC material is recuperated at a global level, the recovery rate for lithium is a meagre 1%. This can primarily be attributed to the lack of commercially viable techniques for extracting lithium from battery black mass. Consequently, bridging this disparity by augmenting lithium recovery from spent batteries is of critical importance. A method that has often proven to be the most economically viable for extraction is solvent extraction. This method, referred to as synergistic solvent extraction (SSX), boosts extraction efficacy by simultaneously utilizing two or three extractants. Thus, in the present master's thesis, SSX will be deployed to selectively extract lithium from the leach solution of spent battery waste, employing a combination of the cationic extractant HTTA (2-thenoyl trifluoro acetone) and neutral extractant TOPO (trioctylyphosphine oxide), with kerosene serving as the diluent.

The PLS used in this study was obtained as a result of another researcher's work which needed to separate lithium from it. The study focused on lithium extraction from a synthetic Pregnant Leach Solution (PLS) by manipulating pH, Aqueous to Organic ratios (A/O ratios), sulfuric acid concentration, and the ratio between the lithium-loaded organic phase and stripping liquor (O/A ratio). It was found that an increase in pH led to a decrease in lithium concentration due to higher ammonium levels, whereas a pH of 9.5 resulted in a significant improvement in lithium extraction, achieving about 83% efficiency. The addition of toluene helped in improving phase separation while TBP did the opposite. Increasing sulfuric acid concentration up to 0.5M improved the stripping efficiency, but anything beyond led to an efficiency drop due to higher ammonium co-stripping. Increasing the O/A ratio resulted in a more concentrated lithium strip liquor and maintained high stripping efficiency, reaching a lithium concentration of around 22 g/l with less than 2 g/l of co-stripped ammonium. However, the presence of ammonium in higher concentrations led to more co-stripping, indicating a need to strike a balance between the ammonium concentration and lithium extraction efficiency. Despite certain anomalies, the final strip solution contained approximately 22 g/l of lithium and only 0.5 g/l of ammonium, which is promising.

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Chapter 1

Introduction

Due to the widespread usage of fossil fuels today, transportation is the main cause of greenhouse gases. The electrification of automobiles has accelerated in the last ten years to cut emissions and ameliorate the effects of such already released greenhouse gases.

Battery-powered cars have piqued the public's interest as a viable alternative to conventional ignition engines because of their high efficiency and environmentally friendly benefits. According to the International Energy Agency (IEA), sales and inventories of electric cars would rise exponentially, reaching 145 million units in 2030 (excluding two- and three-wheelers) and constituting 7% of the whole fleet of road vehicles [1]. Because of their high energy density, low discharge rate, lack of memory effect, lightweight, and relatively long life cycle, lithium-ion batteries (LIB) have become more and more common in electric vehicles (EV)[2].

By the end of 2020, there were more than 10 million electric vehicles on the road and roughly 3 million had been sold worldwide. Sales of electric vehicles are increasing quickly in Europe, according to Bloomberg New Energy Finance 2021, and an increasing number of governments have set goals for gradually phasing out sales of new internal combustion vehicles. According to BloombergNewEnergyFinance, at this rate, more than 200,000MT of LIBs will have reached their end of life (EOL) in the EU alone by 2030 [3]. Most of them, if not all of them, will wind up in open landfills if they are not handled carefully, which will add to land pollution. Furthermore, the handling of these EOL batteries needs to change right away due to the rising concern over the availability of raw materials used in the production of LIBs.
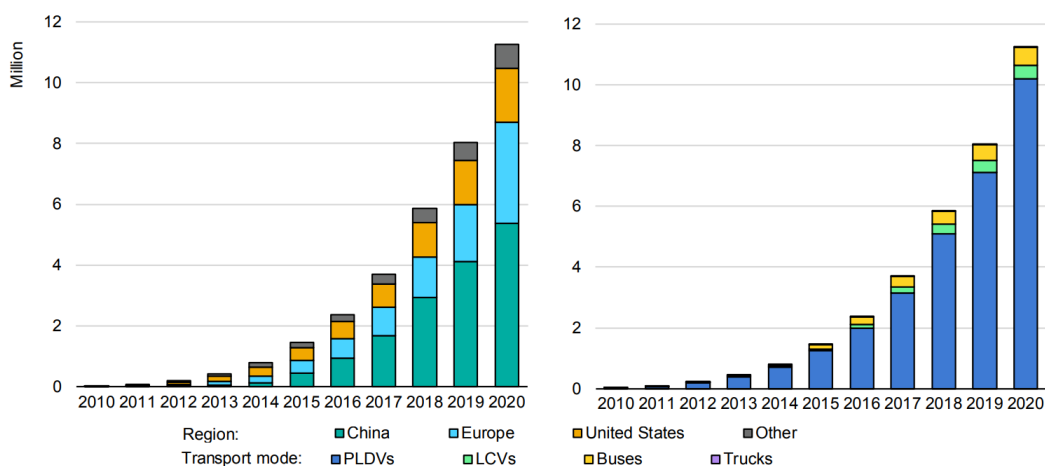

Figure 1.1: Global electric vehicle stock by region (left) and transport mode (right), 2010-2020 [3]

1.1 Lithium Ion Battery

Sony released the first lithium-ion battery in 1991. Anode, cathode, electrolyte, separator, binder, current collectors, and the outer shell that encloses everything make up a standard LIB [4, 5].

Depending on the components they are made of, numerous cathode chemistries exist, including lithium manganese cobalt oxide (NMC), lithium cobalt oxide (LCO), lithium iron phosphate (LFP), lithium nickel aluminium oxide (NCA), and lithium manganese oxide (LMO). [6, 7]. A binder, commonly polyvinylidene fluoride (PVDF), is used to mix all the various metal oxides in the cathode. Because of their higher energy density, increased number of cycles, improved safety, and longer battery life, NMC-type cathodes are the most widely employed in the present EV industry. The anode is typically comprised of graphite, however, because silicon has a theoretically higher gravimetric capacity ($4200\,\mathrm{mAh}^{-1}$) than graphite ($372\,\mathrm{mAh}^{-1}$), it could potentially be used in batteries of more recent generations. Together, the cathode and anode are submerged in an electrolyte solution made of salts like $LiClo_4$, $LiBF_4$, and $LiPF_6$ dissolved in ethylene carbonate (EC) and dimethyl carbonate (DMC), respectively [8]. Better Li ion mobility back and forth between the anode and cathode is facilitated by the electrolyte.

Both the anode and cathode are separated by a physical barrier to prevent them from coming into contact and short-circuiting. The separators are often made of materials like polyethene or polypropylene and should be able to pass Li ions [9]. The current collectors, which are typically made of rigid metals with good conductivity and allow the flow of electrons through the external circuit, are connected to the cathode and anode [10, 11, 12]. PVDF is used as a binder to affix the electrodes to the current collectors. An exterior shell constructed of stainless steel encases all of the functional parts [13].

1.2 The Need to Recycle LIB's

In this section, why recycling the current state-of-the-art Lithium-ion batteries is of absolute importance rather than switching to newer battery materials or even re-purposing the existing end-of-life LIBs is elaborated.

A study claims that the manufacture of battery cells from their raw materials alone is responsible for 60% of the emissions that contribute to global warming. The anode and cathode are produced using materials that have high embodied energies. Nickel (Ni), for instance, has $159 - 175\ MJ/kg$ and primary Cobalt (Co), has 270-300 MJ/kg. Furthermore, the mining operations required to separate these raw materials from their respective ores require a lot of energy and discharge a variety of hazardous wastes into the atmosphere, including Sox and Nox [14]. By recovering valuable elements from the used EOL batteries, it is possible to stop the additional energy and waste produced by mining new raw materials.

Current state-of-the-art Li-ion batteries mostly use NMC 111 cathode chemistry and are gradually transitioning to NMC 811 and, eventually, LNO or LFP. This will reduce their cobalt concentration, and nickel-rich cathodes are projected to perform better in terms of energy density and capacity. Furthermore, the desire to reduce cobalt gained momentum when the free world realized that the majority of cobalt in the West is imported from countries such as the Democratic Republic of the Congo (DRC), where governments are unstable and mining operations are typically conducted in unethical ways [15]. This increases the risk to the environment while also infringing fundamental basic human rights [16].

The scarcity of natural resources has sparked interest in the development of new battery chemistries such as LFPs, LNOs, and even chemistries that replace lithium with sodium. It should be emphasized, however, that the main constituents in LFP and LNO batteries are phosphorous and nickel, respectively. Because phosphorus is essential in the production of fertilizers, which has a direct impact on global food production, experts continue to debate whether it is acceptable to use phosphorus in the production of batteries [17]. Nickel is presently commonly employed in the manufacturing of stainless steel, which is more recyclable and has a longer lifetime than LIBs [18],

making the transition to newer battery chemistry challenging. And, even if for some fortunate reasons, the scientific community can switch towards cobalt-free battery chemistry, lithium is still the most essential component of batteries and its demand will only increase.

Lithium makes up less than 0.007% of the earth's crust and is the 33rd most abundant element in nature [19]. Natural lithium resources exist mostly as ores and salt lake brine [20]. Mining lithium from ore is an extremely energy-intensive and environmentally damaging process. However, it takes nearly 2 years to up-concentrate lithium from salt lake brines by solar evaporation, after which the concentrate can be used for further processing [21, 22]. Because of global scarcity and resource security due to geographical and geopolitical issues, the EU placed lithium on the essential raw material (CRM) list in 2020 [23].

Because of this severe scarcity and necessity of lithium in modern energy, electronics and transportation industries, attention should be taken to collect lithium from waste, particularly spent EV Li-ion batteries, which can be entitled as high-quality lithium ore. The existing waste management system in the EU for recycling EV batteries is governed by the directive 2006/66/EC [24]. This directive mandates that 50% of the materials housed by batteries be recycled, and comparable directions and legislation exist worldwide. However, only less than 1% of lithium is recycled from batteries globally, whereas more than 50% of nickel and cobalt are recovered. The reason for the imbalance is that, while the regulation requires the recycling of 50% of the components included in a battery, it does not require the recycling of any specific substance. Because the market value of cobalt (33 EUR/kg) and nickel (9 EUR/kg) is higher than Li_2CO_3 (6 EUR/kg) [25], and no specific guidelines for the type of material to be extracted are provided, industries have prioritized recycling the materials with the highest monetary value. This is why no specialized technique exists to economically recover lithium from batteries. According to the new EU legislation, at least 35% of lithium must be recovered from LIBs by 2025 and 70% by 2030, and recovery rates for the remaining elements must be near 95% by 2030 [26]. Furthermore, current geopolitical events around the world have increased demand and thus the market price of lithium. Thus, an interest in targeting lithium from spent batteries has been created in the minds of industrialists, and a plethora of studies are currently underway to develop a quick method to recover lithium from spent batteries.

1.2.1 Challenges in the current recycling technologies

Another reason lithium is not recycled as much as other elements is that in most current processes, lithium is the last metal recovered and the system is contaminated with artificial impurities while recovering other materials, making the effort to recover lithium economically unappealing. This section discusses these problems in depth, as well as the current state-of-the-art approach employed in recycling LIBs.

Currently, pyro-metallurgical treatment is the most widely used technology for recovering value from spent EV batteries. This uses extremely high temperatures ($> 600°C$) to successfully convert cobalt, copper, iron, and nickel in old batteries into high-purity alloys. This approach is popular since it involves little to no sorting/dismantling because the battery cells can be put straight into the process. Because Li, Mn, and Al are oxidized and recovered as slag in pyro-metallurgical operations, lithium is not the primary focus of these processes. If lithium is to be recovered, the slag must be subjected to further hydrometallurgical processes, which makes the entire process uneconomical, and the slag is thus sold to the construction industry without any further treatment.

Furthermore, due to the high temperatures in the furnaces, pyrometallurgical operations, in general, are very energy-demanding, but they also pose the risk of *sox* and *nox*, polluting the air[27]. Because pyrometallurgical operations produce metal alloys, additional treatment is required. Thus, another emerging technology for recycling LIBs is direct recycling [27], which focuses on the direct re-synthesis of cathode materials from spent LIBs, thereby eliminating many purification stages. However, unlike pyro-metallurgical operations, direct recycling necessitates extensive sorting and pretreatment to remove other impurities such as casing, binders, current collectors, and so on. This technique is ideal for simple and low-cost battery chemistry; but, more sophisticated cathode chemistry, like as NMCs, will not work with this kind of recycling.

Hydrometallurgical processes for recycling LIBs are currently believed to be the future of EV battery recycling due to their ability to handle heterogeneous feedstocks and robustness to operate in any manner desired. Also, if properly designed, the process can be tailored to recover individual elements or resynthesize the cathode active material as needed. This process is performed at much lower temperatures compared to pyrometallurgical processes, resulting in less cross-contamination and higher recovery rates, making it more efficient [27]. The battery modules are first dismantled to remove the casings and then discharged using a weak base before further deconstruction. Following that, they are heated to produce black mass, which serves as the starting point for hydrometallurgical operations. The valuables are then recovered via hydrometallurgical unit operations such as leaching, precipitation, solvent extraction, ion exchange, and so on. However, hydrometallurgical processes can have a complex flowsheet with many stages, making them less appealing.

A typical hydrometallurgical process used currently involves leaching out the valuables from the black mass using a strong acid and a reducing agent (H_2SO_4 and H_2O2), this process is called leaching. From the leached liquor, first Al, Fe, and Cu are removed by precipitation by adding NaOH at low pH. Then the NMC material is precipitated by increasing the pH by adding more NaOH, and finally, lithium is recovered as lithium carbonate [28, 29]. This is one such example, there are a variety of routes followed which utilizes the addition of various impurities in the process of extracting valuable. If noticed in this process, lithium is the last component to be recovered and recovering this from a mixture containing sodium ions (from the addition of NaOH to increase the pH) as an impurity, is quite difficult as Li and Na have quite similar properties. Hence in most cases, it's economically unattractive to add, impurities intentionally and then try to separate them.

If the early separation of lithium using a suitable method followed by the precipitation process through the addition of NaOH is executed, the resultant solution will solely comprise concentrated Na^+ ions. Alternatively, the utilization of an effective and efficient approach to separate Li and Na could significantly enhance the economic and sustainable aspects of this process. A proficient technique for the effective segregation of lithium and sodium can also be employed for the retrieval of lithium from salt brine rather than awaiting nearly two years for the elevation of lithium concentration employing evaporation. Upon examining these considerations, it is evident that solvent extraction presents itself as a highly suitable substitute for precipitation for retrieving lithium. Moreover, solvent extraction is a conventional hydrometallurgical technique that may be readily expanded to any scale through the manipulation of appropriate parameters. Limited progress has been made concerning the recycling of batteries utilizing solvent extraction.

The present study aims to concentrate on the deliberate recovery of lithium from exhausted battery waste through synergistic solvent extraction, utilizing an extractant system of HTTA-TOPO-kerosene. This particular system has been demonstrated as a favourable option for lithium extraction. Additional information pertaining to SSX techniques can be found in chapter 2. During the specialization project, the candidate used the same extraction system to selectively extract Lithium from a PLS consisting of Lithium with trace aluminium impurities. Currently, as a part of their master thesis, the candidate has attempted to selectively extract lithium from a solution containing an enormous amount of Ammonium impurity ions in comparison to the lithium ions present in the solution as a result of a previous purification process carried out by another researcher in the group. In this more effort has been poured into tuning the parameter of the PLS and verifying how its impacts the extraction capability and selectivity of the extraction system. The parameters include pH of the PLS, A/O (Aqueous to Organic ratio), the addition of a modifier, loading capacity and reusability of the extractant, selectivity of the extractant to various cations and finally stripping of the extracted species to produce an up-concentrated solution lithium which can be later precipitated. More details on the specialization project and the current PLS are discussed at the end of Section 2.6.

Chapter 2

Theory and literature review

As previously indicated in the introductory section, solvent extraction has emerged as a promising technique for the recovery of lithium in the foreseeable future. This section aims to elucidate the fundamentals of solvent extraction, alongside requisite theoretical underpinnings for the present study and prior research work in this area, culminating in the concept of synergistic solvent extraction. The present section briefly introduces leaching, as it is a requisite step for beginning the solvent extraction process, which requires the use of a Pregnant Leach Solution (PLS).

2.1 Leaching

Leaching is a critical stage in the recycling of batteries using hydrometallurgical techniques. It facilitates the recovery of valuable constituents from the solid black mass into a liquid suitable for subsequent processing steps, such as precipitation, solvent extraction, and others, for the purpose of separating precious metals. The leaching procedure entails the application of a liquid medium, which may comprise a potent acidic or alkaline agent, alternatively, ordinary water, contingent upon the specific purposes of the process. The leaching process can be influenced by a multitude of parameters, including but not limited to the concentration of acid, surface area, particle size, the pore size of the solid matrix, homogeneity of solids, temperature, agitation, solid-to-liquid ratio (representing the ratio of the mass of the black substance to the volume of leaching solution), pH, and reaction time [30]. The aforementioned factors, namely solid-to-liquid ratio, reaction time, pH, and type of leaching liquor, occupy a noteworthy position in the context under consideration. The nature and constitution of the black mass are significant determining factors for the kinetics of the leaching process. A reduction in the solid-to-liquid (S/L) ratio produces a greater proportion of leaching liquor relative to the black mass, consequently resulting in an expansion of the surface area available for reaction. This ultimately leads to a boost in the leaching efficiency. However, it is not uncommon for a high solid-to-liquid (S/L) ratio to be utilized to achieve a concentrated leaching solution. Elevating the acid concentration leads to a commensurate enhancement in the efficacy of leaching. The thermal effect on leaching kinetics is a widely observed phenomenon, whereby an elevated temperature accelerates the solute's dissolution from the solid matrix. It is generally recognized that the rate of leaching increases as the temperature is raised, thus indicating a positive correlation between temperature and the kinetics of leaching. Nonetheless, the intricate mechanisms underlying the thermal effect on leaching kinetics remain an active research area. The correlation between temperature and leaching rate is contingent upon the nature of the leaching process. The process of leaching can be classified into two mechanisms, namely diffusion-controlled or reaction-controlled leaching.

Typically, a highly concentrated inorganic acid is employed with a reducing agent to reclaim the majority of the worth contained within the black mass. The function of a reducing agent is to transform the cathode's active substances from a trivalent to a divalent state. The decrease in charge of the metal ions leads to the facilitation of the leaching process, as reported in a study by

Yao et al. in 2018 [2]. A recently published master thesis (Saleem, 2022 [31]) asserts that lithium extraction from black mass containing minimal aluminium impurities can be achieved through selective leaching utilizing water leaching under optimized conditions. The study indicates that a selectively optimized leaching condition has been identified, whereby at a temperature of 80°C, a pH of 10, a duration of 30 minutes, a rotational speed of 400 revolutions per minute (RPM), and a solid-to-liquid ratio of 20 grams per litre, approximately 66.5% of lithium from the black mass can be successfully leached out. Given the objective of the present investigation concerning targeted lithium extraction, the current study employs a leaching technique to extract lithium selectively from the black mass, followed by employing SSX to segregate lithium from aluminium impurities. The residual black mass can be then purged through a highly acidic solution to isolate and recover all residual, valuable components, including but not limited to nickel, manganese, cobalt, iron, and other such elements. The separation of these entities may be achieved through precipitation techniques, as expounded upon within the introductory segment. The present study is focused solely on evaluating the feasibility of segregating lithium from aluminium contaminants in the pregnant leach solution (PLS) procured through the aqueous leaching of black mass. Nonetheless, the examination of the aforementioned topic lies outside the scope of the current investigation.

2.2 Solvent extraction

The hydrometallurgical process of solvent extraction has gained significant attention within various industrial sectors, however, its potential applications within the realm of battery recycling have not been extensively researched. Solvent extraction is a technique utilized to separate components based on their relative affinity towards organic compounds present in the given phase. The metal ions that are the subject of interest present in the aqueous phase will be subsequently relocated to the organic phase, following which the two phases may be segregated owing to their respective difference in density. Solvent extraction essentially consists of 4 stages [32]:

1. Extraction of the targeted species

2. Scrubbing of the extracted organic phase to remove unwanted impurities extracted

3. Stripping of the extracted target species from the organic phase

4. regeneration of the solvent for reuse

The extraction stage represents a critical operation within the process of solvent extraction, as the parameters employed during this step exert a significant influence on both the efficacy and selectivity of the technique. The PLS, comprising of target metal ions and other ions, is subjected to contact with a solvent that is immiscible with it. Upon mixing, there is a point of contact between entities, at which juncture the extraction process occurs. Subsequently, the solution is subjected to stand still, promoting the segregation of the organic and aqueous phases based on their differing densities. The selection of the solvent used in the leaching process effectively dictates the particular metal that will be extracted from the leach solution, as stated by Mukherjee, 2019 [32]. Subsequently, the organic solution that has been extracted is exposed to a scrubbing solution, which typically comprises a diluted acid or base. The process of scrubbing is undertaken to eliminate any impurities that co-extract alongside the targeted metal ions. This process serves to guarantee that the resulting product is of a high degree of purity. Upon the successful elimination of impurities present within the solvent, the desired metal is effectively stripped out of the organic solvent. Accordingly, the process of stripping accounts for the reversal of the prior extraction process. The stripping solution employed in the extraction process typically consists of a potent acid or a heavily diluted solution of the metal sought after, which is then brought into contact with the solution containing the desired metal. After the removal of the organic phase, the solvent's regeneration is achieved by utilizing an acid or alkali solution, contingent on the strip liquor.

For laboratory-scale procedures, the preferable method of extraction is single-stage extraction. Consequently, there is a requisite for a high distribution coefficient, exceptional selectivity, and significant separation factor. In a large-scale industrial process, the extraction is carried out via a
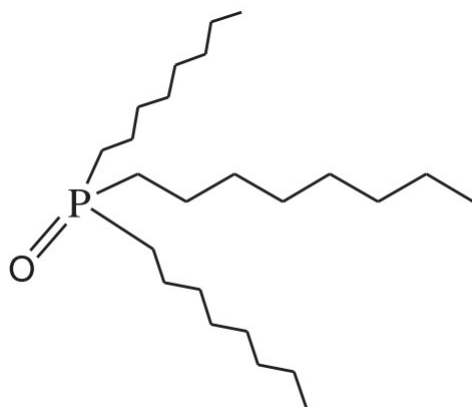
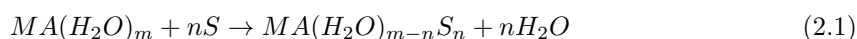Figure 2.1: Structure of Trioctylphosphine oxide (TOPO)[33]

multi-stage and counter-current approach, thus a relatively low separation factor and distribution factor can be regarded as acceptable. The significance of the extraction and stripping rate varies depending on the scale of the process. While it may not bear much significance on a laboratory scale, it plays a pivotal role in industrial-scale operations because of its potential impact on the economics involved [32].

2.3 Type of extractants

In order to achieve selective extraction of metals into the organic phase, it is essential for the solvent component to possess a viable mechanism for attracting the desired metal ion. This is particularly important given that many organic solvents are immiscible with the aqueous phase in which these target ions are suspended. The extractants are categorized based on their extraction mechanism.

2.3.1 Solvating extractant

These compounds are commonly referred to as neutral extractants, owing to their ability to promote metal ion extraction by displacing water molecules in the leaching solution that are bound to the ion in question, thus forming a neutral complex through ion association. Alcohols, ethers, ketones, and alkyl phosphates, containing an oxygen atom as an electron donor, exhibit the properties of a solvating extractant. Tributylphosphate (TBP) is a widely recognized neutral extractive agent. The chemical reaction occurring in the presence of a solvating extractant is depicted by Equation 2.1.

$$MA(H_2O)_m + nS \rightarrow MA(H_2O)_{m-n}S_n + nH_2O \tag{2.1}$$

One of the extractants used in this study is a neutral extractant called TOPO (trioctylphosphine oxide), shown in Figure 2.1.

2.3.2 Anionic extractant

Anionic extractants function as anion exchangers, whereby they selectively remove one of their anions and replace it with the target metals during the extraction process. These substances are alternatively referred to as basic extractants. It is imperative that a metal ion possesses the ability to form an anionic complex with the extractant compound; however, this capability is limited to only a small subset of metals and is contingent upon specific conditions being met. This

phenomenon results in a significant elevation of selectivity for an anionic extractant. Long-chain alkylamines are commonly acknowledged for their efficiency as an anionic extractant. A standard reaction that involves an anionic extractant is presented as follows:

$$(R_3N)_{org} + H^+ + A^- \rightarrow (R_3NH^+A^-)_{org} \tag{2.2}$$

$$n(R_3NH^+A^-)_{org} + MX^{n-} \rightarrow (R_3NH^+)_n MX^{n-}_{org} + nA^- \tag{2.3}$$
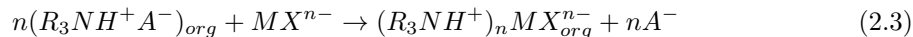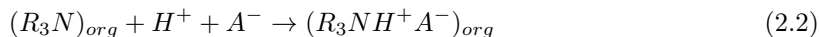
The preceding equations illustrate that the utilization of an anionic extractant is facilitated in an acidic medium and hindered in a basic medium.

2.3.3 Cationic extractant

The cationic extractant is the most extensively employed type of extractant due to its ability to substitute a proton (H^+ ion) in the extractant with a positively charged target metal ion, thus giving rise to its name. This substance is commonly referred to as an acidic extractant. Two methods for implementing cation exchange processes are chelate formation and acid extraction. In the process of chelation, metal ion transfer results from the formation of an electrically neutral 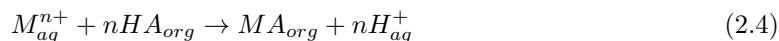coordination compound, known as a metal chelate, facilitated by the chelating agent. The chelating agent must fulfil the requisite valence and coordination number of the associated metal ions. The following presents an illustration of a chelation-induced extraction.

$$M^{n+}_{aq} + nHA_{org} \rightarrow MA_{org} + nH^+_{aq} \tag{2.4}$$

The present phenomenon elucidates that the process of cation exchange leads to an elevation in the concentration of hydrogen ions present in the aqueous phase. Accordingly, adhering to the principles of le Chatlier, a higher concentration of H^+ ions triggers a reversal of the reaction, thereby hindering the extraction process. Consequently, it is imperative to maintain proper command over the acid concentration when employing a chelating extractant.

In contrast to chelating extraction, acid extraction is a more intricate process that is significantly influenced by the intrinsic properties of the solvent. The formation of polymer dimers between organophosphorus and carboxylic acids in the organic phase results in a significant impact on their extractive properties. Alkyl carboxylic, phosphoric, and sulfonic acids are considered acid extractants in chemical processes. The chemical process of extracting a substance can be denoted by the ensuing chemical equation:

$$M^{n+} + \frac{m}{2}(H_2A_2)_{org} \rightarrow [MA_n.(m-n)HA]_{org} + nH^+_{aq} \tag{2.5}$$
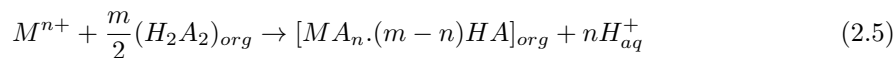
Additionally, it is evident that the efficacy of the extraction process will be enhanced in alkaline conditions whereby the aqueous phase contains a limited number of hydrogen ions. The present study notes that the efficacy of extractants is intricately linked to the process of cation exchange. Specifically, it is observed that metal ions possessing higher charges demonstrate greater extractability. Furthermore, when metal ions exhibit similar charges, their extractability was found to vary inversely with their respective ionic radii [32].

The substance known as HTTA (2-thenoyl trifluoro acetone), which was utilized as an extractant in this thesis, is classified as a cationic extractant and operates via a chelation-based mechanism. The substance known as HTTA Figure 2.2) is classified as a *beta*-diketone and functions as a chelator with acidic properties. A *beta*-diketone is a type of diketone characterized by the presence of two ketone functional groups separated by a solitary carbon atom. This structure imparts unique chemical properties to *beta*-diketones, which have a variety of potential applications in both industrial and scientific settings. Diketones are a class of organic compounds characterized by their molecular structure, which comprises two carbonyl (C=O) bonds. The ketone, on the
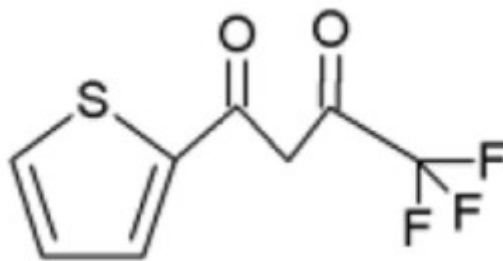
Figure 2.2: Structure of 2-Thenoyl trifluoro acetone (HTTA) [34]

other hand, is a functional group denoted by the structural formula $R_2C = O$, whereby R can represent diverse carbon-containing substituents.

Previous studies have indicated that the di-ketone group of HTTA is prone to undergo Keto-enol tautomerization. Under alkaline conditions, the hydrogen atom associated with the enolic part of the extractant can be substituted by a metal ion. This substitution results in the formation of a chelate ring, which prompts the keto-enol equilibrium to favour the enol form. Consequently, a high pH value of the aqueous phase is necessary for this process [35, 34, 36].

2.3.4   Synergistic extractants

Occasionally, when 2 different extractants from 2 different groups are mixed, the extraction efficiency surpasses the combined outcome of the individual extractants, thus engendering a synergistic effect. Occasionally, despite its prior incapacity to extract a particular metal, an extractant can commence an impressive extraction rate upon the combination with a specific extractant due to the high affinity between the resulting complex and the metal. One notable illustration is that D2EHPA has the capability to extract uranium from sulfuric acid media, while TBP lacks this ability. Adding TBP to D2EHPA results in a substantial enhancement in the efficiency of D2EHPA-mediated extraction. As per Mukherjee, 2019[32], it can be posited that TBP functions as a synergistic constituent. An additional illustrative instance pertains to a system comprising a *beta*-diketone (i.e., HTTA) in combination with a neural extractant, namely TOPO, which exhibits an inability to extract lithium ions from an aqueous feed. The addition of TOPO to HTTA introduces the ability to extract... The extraction efficiencies of Lithium are anticipated to increase due to the heightened stability of the Li noticeably.HTTA.TOPO chemical complex within the organic phase.

2.4   Modifiers

The organic component includes various additives, for example, diluents and modifiers, along with the extractant [32]. The extractant is the principal active ingredient in the organic phase. It can selectively bond with the substance that is targeted for extraction from the aqueous phase. The extractant selection is highly dependent on the specific extraction requirements, such as the type of metal ions being extracted.

The role of diluents in this context is to dilute the extractant and adjust its physical properties, making the solution more manageable and efficient for the extraction process. For instance, by altering the viscosity and density, the diluent can improve the rate at which the two phases (organic and aqueous) separate after mixing. Despite not participating directly in the extraction of the desired substance, the diluent can indirectly affect extraction efficiency. Commonly, diluents are hydrocarbons, such as kerosene, and can be either aromatic or aliphatic. Aromatic hydrocarbons contain a ring structure and may introduce unwanted interactions, while aliphatic hydrocarbons have a straight or branched chain structure and are less reactive.
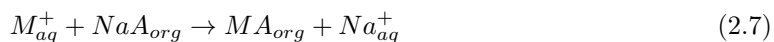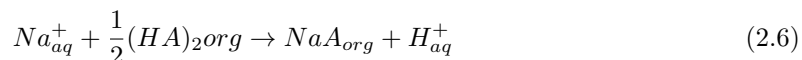
Modifiers, like diluents, don't directly participate in the extraction but have an important role in

the overall process. They are introduced to the organic phase to enhance their performance. One of their primary roles is to inhibit the formation of a third phase, which can be an undesirable byproduct of the extraction process and cause efficiency loss. They also assist in the formation of metal complexes, helping to increase the extraction rate and capacity and even enhance the separation of the organic and the aqueous phase. Typical modifiers can be long-chain alkyl alcohols or neutral extractants, such as Tributyl phosphate (TBP). The choice of a specific modifier depends on the extraction system's requirements and has to be made very thoughtfully, considering its potential impact on extraction efficiency.

So, to summarise, in an organic phase used for extraction processes, extractants, diluents, and modifiers each play crucial roles that work together to optimize the extraction's efficiency and effectiveness. In this study, kerosene is used as the diluent. TBP and Toluene are used as modifiers to enhance the separation time of the extractant and the aqueous phase after extraction.

2.5   Saponification

Sodium hydroxide or ammonium hydroxide can be utilized to neutralize acidic extractants such as D2EHPA, Cyanex 272 and HTTA (in this study). This process is called saponification. This neutralization replaces the hydrogen cations in the extractant with sodium or ammonium ions, which has a lower affinity to the extractant complex compared to hydrogen. Thus they can be replaced with the target metal ion during extraction compared to when H^+ is present. Saponification of the acidic extractant by bases also increases the pH of the system and thereby enhancing the performance of the cationic extractants. The neutralization process and the extraction process followed by neutralization, when sodium hydroxide is used, is illustrated by the reaction given below:

$$Na_{aq}^+ + \frac{1}{2}(HA)_2org \rightarrow NaA_{org} + H_{aq}^+ \qquad (2.6)$$

$$M_{aq}^+ + NaA_{org} \rightarrow MA_{org} + Na_{aq}^+ \qquad (2.7)$$

2.6   Literature review

Solvent extraction is one of the most widely used industrial processes and has gained a lot of attention to be considered as an option to recover valuables from spent battery wastes because of its various advantages as seen in chapter 1. An abundant number of studies have been carried out so far to selectively recover various valuable metals from the leached solutions of black mass by the use of one or more extractants (synergistic). However, this section will only focus on those studies that selectively focus on recovering lithium from synthetic solutions, brines and spent battery wastes using synergistic extractants.

The term "synergism" was originally introduced by researchers Blake et al. to describe a phenomenon in which there is an increase in the extraction of divalent metals from an aqueous solution when a mixture of an acidic dialkyl phosphate and a neutral donor extractant is used as the extraction system, as opposed to using either extractant alone [37]. This synergistic effect was also observed when extracting trivalent rare earth elements using a β-diketone, 2-thenoyl trifluoracetone (HTTA), as the acidic extractant[35]. The synergistic effect of solvent extraction has been observed in several other contexts as well. For example, a mixture of trialkylamine and trialkylphosphine oxide was found to exhibit synergism when extracting p-aminophenol [38]. Overall, the synergistic effect of solvent extraction has been demonstrated to enhance the efficiency of the extraction process by creating more favourable extraction conditions. Therefore a lot of attention has been given to using synergistic solvents to extract valuables or impurities from various systems.

A study by Y. Pranolo et al. (2015) delved into the process of extracting lithium and separating it

from sodium in chloride solutions using a combined solvent extraction system composed of LIX 54 and Cyanex 923. The study found this system to be better than the former HTTA–TOPO system as it offered a higher degree of lithium over sodium separation [21]. The research methods included carrying out shake-out tests in a regulated setup, where the researchers analyzed both extraction and strip distribution isotherms at various A/O (aqueous to organic) ratios under specific pH and temperature conditions. The kinetics of extraction and strip were also studied, followed by a chemical analysis using ICP-AES (Inductively Coupled Plasma Atomic Emission Spectrometry).

The results showed that at a pH level of 11.2, the combined solvent system could extract 97% lithium from a solution containing 23 g/L sodium, with only 0.1–2.6% sodium co-extraction. This led to a maximum lithium over sodium separation factor of 1560. Furthermore, the researchers evaluated the impact of using different types of diluents on the extraction and separation processes. They found ShellSol D70, which is wholly aliphatic, to deliver the best results in terms of lithium extraction and separation factor. The temperature was found to exert a minimal effect on the extraction of lithium and its separation from sodium. The research showed that at 23 °C, lithium extraction and its separation factor over sodium were 95.9% and 1213, respectively, which increased to 97.3% and 1563, respectively, at 40 °C. The study also concluded that the organic system's maximum extraction capacity was around 2 g/L of lithium. As the A/O ratio increased, the separation factor of lithium over sodium decreased due to an increase in lithium concentration in the raffinate or a decrease in lithium extraction.

When it came to stripping, it was observed that the use of 0.17 M HCl significantly boosted lithium stripping efficiency. The researchers also found that the loaded strip liquor could be reused to further strip the solution and achieve a high lithium concentration in the end product. The lithium extraction process involved LIX 54 acting as an extractant and Cyanex 923 as a synergist. For every mole of lithium extracted, one mole of each was required. Under the tested conditions, $Li(A)(Cyanex923)$ was the prevalent species. To summarize, the research demonstrated that the combined solvent extraction system of LIX 54 and Cyanex 923 was successful in extracting lithium and separating it from sodium in chloride solutions. This approach was found to be more efficient than the previously used HTTA–TOPO system, paving the way for more effective lithium recovery from chloride solutions in the future.

In 2018 L. Zhang et al., discussed an experimental investigation into the process of extracting lithium from alkaline brine using a mixer-settler unit, a common piece of equipment in hydrometallurgy [33]. This process was tested on a 7-stage mixer-settler for over 30 hours. The aqueous phase in the experiment was real brine from the lithium carbonation process, while the organic phase consisted of different volumes of HBTA and co-extractants in diluents. The concentrations of metal ions in both phases were determined using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). The mixer-settler used was made of PTFE with an active mixer volume of 0.5 L and a settler volume of 2 L. It was fitted with a feed system containing a peristaltic pump and an injection pump. The device has the advantage of being hydrodynamically independent, allowing for flexibility in adjusting the number of stages based on experiment results.

The experiment also investigated the effect of a synergistic reagent on lithium extraction. When using a single extractant HBTA, lithium extraction was unsatisfactory, so different types of neutral donors were examined for their synergistic effects on lithium extraction. It was found that a neutral phosphine synergic reagent with an alkyl group - TOPO (Tri-octyl phosphine oxide) showed a better synergistic effect compared to that with an alkoxy group - DIMP(di-iso-octyl methyl phosphonate). Anomalies in the data were observed with TBP (Tri Butyl phosphate) and TOP (Tri octyl phosphate), likely due to steric hindrance in lithium extraction with HBTA. The extraction of lithium was enhanced with the addition of a synergic reagent. The effect of diluents on lithium extraction was also examined. Seven diluents with different polarities were tested. Changes in diluents were found to potentially affect keto-enol equilibrium, thereby affecting the extraction ability of β-diketone. It was observed that lithium extraction was significantly lower in chloroform and isoamylol due to the inhibitory effect of hydrogen bonding functional groups on enolization. Green kerosene (18A) was found to perform well in lithium extraction and was chosen for further investigation.

The influence of extractant concentration on lithium extraction was also studied. The results

showed a strong synergistic effect between HBTA and TOPO, with lithium extraction increasing from 60% with 0.4 M HBTA alone to 88% with 0.3 M addition of TOPO. The pH value of the aqueous phase was found to decrease after extraction, suggesting that H^+ was exchanged by metal ions, causing a decrease in pH value. The effect of the volume ratio of organic and aqueous phase (O/A) on lithium extraction was examined. McCabe Thiele method was used to determine theoretical extraction stages, with the overall lithium extraction set as 95%. The study also involved a scrubbing process to reduce the sodium ion in the organic phase with minimal loss of lithium. Different concentrations of HCl were used as scrubbing liquor. The stripping condition was optimized using hydrochloric acid as the stripping agent, with 3 mol/L HCl found to be suitable considering erosion and acidity of the stripping product. The regeneration condition was investigated by using a 2 mol/L $NaOH$ solution as a regeneration agent. The regeneration ratio R should be kept between 70% and 90%. The investigation found that the HBTA-TOPO extraction system is an effective method to recover lithium from alkaline brine with a high Na/Li molar ratio.

Later in 2019, L. Zhang et al. aimed to develop practical extraction systems for recovering lithium from ammoniacal solutions [36]. The organic phase comprised HTTA and neutral ligands mixed with diluents, while the aqueous phase consisted of an NH3-NH4Cl buffer solution with varying Li^+ concentrations. Extraction experiments were conducted at a temperature of 293 K, except for determining thermodynamic parameters where the temperature ranged from 293 K to 333 K. The extraction efficiency was calculated based on the metal amount extracted into the organic phase relative to the total metal in both phases. The pH value of the aqueous phase played a crucial role. After comparing the extraction results, they identified the HTTA(thenoyl trifluoracetone)-TOPO(tri-n-octylphosphine oxide) and kerosene system as the most suitable for recovering lithium. As the pH increased, lithium extraction efficiency continuously improved until reaching a maximum at an equilibrium pH of 8.08. To maintain an alkaline condition, an NH3-NH4Cl buffer solution with a pH of 9.80-9.90 was selected as the aqueous phase.

Solely using HTTA proved ineffective for lithium extraction, necessitating the addition of a synergistic reagent. Among the tested compounds, neutral phosphine synergistic reagents with alkyl groups demonstrated better effectiveness compared to those with alkoxy groups. The inclusion of a synergistic reagent enhanced lithium extraction to varying degrees. The impact of diluents with different polarities on lithium extraction was also examined. N-dodecane exhibited excellent performance, facilitating superior phase separation compared to other diluents. Based on the experiments, combining HTTA with donor extractants significantly improved lithium extraction compared to using each extractant separately. Further investigations explored the synergistic effects of HTTA and TOPO, revealing peak enhancement when both extractants were at a concentration of 0.15 mol/L.

The study also assessed the selectivity of the HTTA-TOPO system for lithium over other alkali and alkali earth metal ions. The system exhibited a preference for alkali earth metal ions, particularly magnesium, which has a similar radius to lithium. The extraction mechanism involved the formation of a complex comprising lithium, HTTA, and TOPO. Thermodynamic analysis indicated that the extraction process was spontaneous and driven by entropy. Stripping and regeneration experiments demonstrated the potential for reusing the organic phase for lithium extraction. Overall, the HTTA-TOPO-kerosene extraction system displayed promise for the recovery of lithium from ammoniacal solutions.

Another study in 2019 by J. Wang et al. was set to determine the compositions of adduct complexes formed between an extractant and a synergist with lithium [39]. This information was believed to serve as a fundamental basis for predicting and designing a lithium extraction process. The findings indicated that the extraction percentage of lithium reached 95.3% within 2 minutes and gradually increased to 96.57% after 10 minutes of extraction. When using PHPD (primary hydroxyoxime extractant) alone as an extractant, the extraction percentage of lithium reached 96.95% at an initial aqueous pH of 13.06, which was slightly lower than the value of 97.83% for the extraction system containing PHPD and Cyanex923 (synergist). The co-extraction percentage of sodium increased from 0.85% to 12.75% as the PHPD/Cyanex923 mol ratio increased from 0 to 4, and then decreased to 10.17% at a PHPD/Cyanex923 mol ratio of 5. At an initial aqueous pH of 13.06, using an extraction system consisting of 0.4 mol/L PHPD and 0.2 mol/L Cyanex923 in kerosene at

an A/O (aqueous-to-organic) ratio of 1:1 and 293.15 K, the lithium extraction percentage was over 97%. The separation factor of lithium over sodium was 1560, indicating a very good separation. The overall recovery of lithium was higher than 98%, and the Mg/Li molar ratio changed from 94.8 in the salt lake brine to 0.03 in the stripping solution.

In conclusion, the study demonstrated the extraction and separation of lithium from a system containing lithium, sodium, chloride, carbonate, and water, using an extraction system consisting of PHPD and Cyanex923. The aqueous pH had a significant impact on the separation process. At an initial aqueous pH of 13.06, the extraction system mentioned above achieved a lithium extraction percentage of over 97%. The separation factor of lithium over sodium was 495.06 at high sodium concentration, indicating a solid separation ability from sodium. The McCabe–Thiele results suggested that two theoretical extraction stages were required at an A/O ratio of 1.8. Through a combination of experimental techniques known as slope analysis and characterizations using EMI-MS spectra, it was discovered that lithium forms adduct complexes with components such as deprotonated PHPD (E) and Cyanex923 (S). These adduct complexes were identified as LiE, LiE(H2O), LiES, and LiES.

L. Zhang et al. in 2020 carried out a detailed study focusing on recovering lithium from spent Lithium-ion Batteries (LIBs [20]. The researchers for the first time used a recyclable effluent from a lithium battery recycling factory for their experiments, which had already been treated for recovery of valuable metals like cobalt and nickel. The authors conducted their experiments by simulating an extraction, scrubbing, and stripping process in a separatory funnel. Atomic Absorption Spectrometer was used to measure the metal ion concentration in the aqueous phase. One critical aspect of the research was understanding the effect of saponification degree on lithium extraction. They found that the pH of the aqueous phase is important for lithium extraction due to the keto-enol tautomerization of the extractants. The extraction effect was unsatisfactory when the solution pH was less than 5, while it showed good extraction for solutions with a pH value higher than 6. The effect of the composition of the organic phase on lithium extraction was also investigated. By varying the proportion of two extractants, HBTA and TOPO, they found that the best result was obtained when the concentration of both HBTA and TOPO was each 0.4 mol/L.

The extraction time effect on lithium and sodium extraction was studied next. They found that 2 minutes was enough to reach near equilibrium in lithium extraction with about 80% efficiency. Furthermore, after 2 minutes, 75% of sodium in the organic phase was replaced by lithium. The impact of the initial lithium concentration was tested by changing the concentration from 0.029 mol/L to 0.720 mol/L. They found that a higher lithium concentration accelerates the chelate of lithium with the extractants, suggesting that the HBTA-TOPO system is suitable for a wide range of lithium concentrations. The phase ratio's effect was studied as well. It was concluded that a phase ratio of 1:15 (organic: aqueous) was ideal, resulting in a lithium extraction rate of 97%.

A metal eluting study was conducted using hydrochloric acid and lithium chloride solution. They found that HCl was better at removing sodium, while lithium chloride improved the lithium concentration in the organic phase. In the metal stripping study, the organic phase was stripped using a HCl solution, leading to a higher concentration of lithium in the solution obtained from the stripping process. Next, the authors precipitated lithium carbonate by adding sodium carbonate to a lithium-rich solution. The precipitated product was confirmed to be lithium carbonate through Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD) results. After the completion of the extraction, elution, and precipitation process, more than 96% of lithium was recovered, with an overall yield of approximately 90%. In a thermodynamic parameter study, the authors determined that the enthalpy change of the extraction system was -5.73 $kJmol^{-1}$, implying that lower temperatures are more beneficial for lithium extraction. However, considering the poor fluidity of the organic phase at low temperatures and difficulties in phase separation, room temperature was recommended. The researchers concluded this, a promising method for lithium recovery from spent LIBs using a novel extraction system of HBTA-TOPO. The process involved a series of extraction, elution, and precipitation steps, resulting in a high lithium recovery rate. The recovered lithium can be further utilized to produce lithium carbonate or lithium chloride based on market demand.

A. Masmoudi et al. (2021) explored extraction using a system of 3-benzoyl-1,1,1-trifluoroacetone

(HBTA) in ionic liquids (ILs). HBTA and Tri-n-octylphosphine oxide (TOPO) were dissolved in 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[C_2mim][Tf_2N]$) to create a solution [40]. Lithium extraction was carried out using this solution in a specific mole ratio of HBTA to TOPO, which was optimized to achieve an acceptable distribution ratio for lithium. The extraction of Li(I) was executed using a concentration of 0.1 M HBTA and 0.025 M TOPO, in the mentioned ionic liquid.

The experiment made use of a higher mole ratio of HBTA to TOPO to achieve an optimal distribution ratio for lithium. In these specific conditions, the equilibrium concentrations of Li(I) in the aqueous phase were quantitatively determined using the Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) technique. It was hypothesized that Tf_2N^- anions present in the aqueous phase would increase the presence of Tf_2N^- in the coordination sphere of Li(I), resulting in a decrease in interactions between HBTA and Li(I). The study concluded that this lithium-ion extraction technique using HBTA in ionic liquids could potentially serve as an alternate method for the separation of lithium ions, particularly from brines. This new system is both environmentally and economically beneficial due to the use of non-toxic solvents and the lack of need for a synergistic agent.

By the end of 2021, L. Zhang et al. investigated the use of deep eutectic solvents (DES), an eco-friendly, diluent-free and effective type of solvent, to extract lithium from alkaline solutions [41]. The DES used in the research was made from benzoyl trifluoroacetate, acting as a hydrogen donor, and different compounds serving as hydrogen acceptors. It highlighted other modern extractant systems, like organic phosphate, ionic liquids, /beta-diketones, and crown ethers, noting their effectiveness in separating alkali metal ions, although their use is typically limited to lithium isotope separation due to high costs and complex synthesis. Ionic liquid-based extraction systems have garnered interest, but their broader use in lithium extraction is hindered by challenges such as water absorption, high viscosity, and difficult preparation.

The researchers indicated that the new DES showcased an impressive ability to handle more lithium than traditional extraction systems. A unique mix of hexafluoroacetylacetone (HBTA) and trialkyl phosphine oxide (TRPO) with a 1:1 molar ratio was identified for its superior lithium extraction and separation from sodium. This success was attributed to phosphine oxide's strong electron donation capability and the hydrophobic nature of long carbon chains. The study was the first to generate a single crystal from a lithium and diketone complex. From this, they discovered that the ratio of components in the complex formed by the alkali metal and HBTA/TRPO-DES was 1:1:1, as confirmed by single-crystal X-ray diffraction.

The researchers then applied the newly created HBTA/TRPO-DES to recover lithium from a lithium carbonate by-product, a complex solution with a high sodium to lithium ratio. They achieved a lithium extraction rate of 90% under specific conditions (O/A = 1/3), and a lithium to sodium separation factor of 335. Importantly, they found that the DES maintained its extraction capability even after being reused for multiple cycles. The researchers suggested that DES could be a sustainable and efficient alternative for extracting lithium from alkaline solutions.

Another study using hydrophobic deep eutectic solvents (HDESs) to recover lithium was carried out by H. Luo et al.(2023) [42]. The study aimed to create a more efficient, environmentally friendly method for recovering lithium from the waste material of lithium carbonate (Li_2CO_3), offering deeper insights into the specific extraction of lithium ions. The HDESs studied showed significantly lower viscosity compared to other HDESs made with quaternary ammonium salts and decanoic acid, as well as usual hydrophobic ionic liquids. This property allowed these HDESs to be used directly in the extraction process as organic phases, eliminating the need for traditional organic diluents used in standard liquid–liquid extraction systems. The HDESs also showed good phase separation from water, attributed to their high hydrophobic nature and substantial density difference with water, indicating their potential for metal ion extraction from aqueous solutions. The researchers developed a range of HDESs, combining beta-diketones and neutral extractants. These novel solvents displayed low viscosity and high hydrophobicity, along with an exceptional extraction capacity and selectivity for lithium ions. The performance of the extraction could be fine-tuned by adjusting the HDESs composition. Two specific systems, those using thenoyltrifluoroacetone-tributyl phosphate (HTTA-TBP) and thenoyl trifluoroacetone-trioctylphosphine (HTTA-TOPO),

were especially effective.

The research leveraged molecular dynamics simulation for the first time to understand the selective extraction mechanism. Lithium ions were mainly drawn into the HDES phase through intense electrostatic interaction with deprotonated HTTA, while TBP coordinated with lithium ions. The extracted complex followed a 1:1:1 stoichiometry, taking the form of $Li^+ \cdot TTA^- \cdot TBP$. The cooperative action of HTTA and TBP in HDES prevented water molecules from participating in the formation of the extracted complex, thereby circumventing emulsification during extraction. The study demonstrated that lithium ions formed stronger bonds with TTA^- and TBP than with sodium and potassium ions, highlighting the high selectivity of HDES towards lithium ions. Both HTTA-TBP and HTTA-TOPO HDESs successfully recovered lithium ions from lithium carbonate waste, achieving over 80% recovery rates using a single-stage extraction, scrubbing, and stripping process. Importantly, these stripped HDESs could be directly reused for subsequent extraction cycles without needing regeneration, demonstrating stable extraction performance.

J. Zhang et al. (2023) pursued a process for producing battery-grade lithium carbonate from salt lake brines [43]. This process involves the use of a new synergistic extraction system consisting of LIX 54, TRPO, and surfactant ADD-1 for efficient lithium extraction from the brine and subsequent separation of impurities. Carbon dioxide gas was used for the effective stripping of lithium, leading to the production of a high-purity lithium bicarbonate solution. In this process, lithium carbonate solid was produced from the loaded strip solution through thermal decomposition. The yield of lithium was impressively high, exceeding 95%, and the quality of the lithium carbonate product met the battery chemical grade standard.

The specific extraction system used in this process consisted of 0.25 mol/L LIX 54, 0.25 mol/L TRPO, and 0.25 mol/L ADD-1, and was used to extract lithium from the Baqiancuo Salt Lake brine. To strip lithium from the loaded organic phase, carbon dioxide gas was employed, resulting in a high-purity LiHCO3 solution. After simple treatment, a battery-grade Li2CO3 product was obtained. The process's stability was validated through a long-term continuous experiment, and it demonstrated a comprehensive recovery efficiency of lithium exceeding 95%.

Prior research has indicated that the combination of HTTA-TOPO in kerosene as a diluent system exhibits significant attraction to extract lithium from brine solutions, which frequently contain impurities such as sodium and other alkali ions. Nevertheless, limited research exists on the potential for lithium recovery from pregnant leach solutions obtained from black mass of spent electric vehicle batteries through synergistic solvent extraction, which involves the utilization of the synergists HTTA and TOPO. Keeping this in mind, the candidate, as a part of their specialization project, assessed the feasibility of the targeted separation of lithium ions by employing a synergistic solvent extraction method on the pregnant leach solution (PLS), which has been generated by subjecting a specific black mass sourced from an industrial collaborator to water leaching [44]. The optimization of leaching parameters has been previously conducted as evidenced by Saleem, 2022 [31]. The PLS comprised of lithium along with some aluminium impurities. The specialization project was solely concerned with evaluating the feasibility and enhancing the efficacy of the extraction procedure. A comprehensive analysis of the process of stripping lithium from the extracted organic phase was concurrently undertaken. During the extraction process, various factors were considered, including the concentration, extractant ratio, aqueous to organic ratio, mixing effects, and initial lithium concentration in the aqueous phase. It is pertinent to note that all parameters were carried out using the pregnant leach solution (PLS) except for one investigating initial lithium concentration for which a synthetic solution closely resembling the PLS was utilized. The stripping study investigated the impact of acid type and concentration and the ratio of organic material to stripping liquor on the stripping process.

The project demonstrated that lithium could be successfully separated from a solution with aluminium impurities, with a minimal amount of aluminium being co-extracted. The tests were conducted at the natural pH of the primary leach solution (PLS) of 10.2. It was determined that the highest lithium extraction rate (55.79%) and the lowest aluminium co-extraction (4.6%) from the PLS were achieved with an extractant concentration of 0.2 M HTTA/TOPO. Economical scalability of the extraction process was suggested by the A/O ratio study. It was discovered that a minimum lithium concentration of around 0.1 g/l in the PLS was necessary, and theoretically, a

50% extraction of lithium from a PLS containing 0.23 g/l lithium could be achieved in two stages of cross-current extraction. However, an A/O ratio above 8 increased aluminium co-extraction. The reciprocal shaker and magnetic stirrer comparison revealed no significant difference in extraction, suggesting the possibility of using mixer settlers. The impact of lithium concentration in the aqueous phase was tested using synthetic LiOH solutions rather than PLS. Despite promising results, an unexpected observation was made. With the same initial lithium concentration (0.23 g/l), only around 55% extraction was achieved from PLS, while more than 80% extraction was achieved from a synthetic solution with a similar lithium concentration (0.146 - 0.290 g/l). It was proposed that this discrepancy could be due to different pH levels in the PLS and synthetic $LiOH$ solution, as the HTTA-TOPO system is known to perform best in alkaline conditions. Further research is needed to confirm this hypothesis. In addition, stripping studies were conducted on the organic phase loaded with synthetic $LiOH$. These showed that 91.41% of lithium could be stripped from a loaded organic phase containing around 1.2 g/l lithium using 0.8 M acetic acid, whereas 0.5 M sulphuric acid could completely strip the lithium. Moreover, O/A tests suggested that sulphuric acid was a better choice if the goal was to concentrate the lithium. It was able to yield almost a tenfold concentration increase in the strip liquor at an O/A ratio of 10.

Although the study showed promising results, it also left many questions to answer such as why there is a difference in extraction efficiencies when there is a pH difference. is it solely because of the pH or could there be a possibility of different species of Li^+? The working mechanism of cationic extractants suggests that a high pH is required for the best working of this extractant system. The previous studies indicated that this holds true but it can be seen that the value of the pH does not hold to be a constant in different studies. From this, one conclusion can be drawn, which is the nature of the solution plays an important role. Thus keeping this in mind and with a goal to develop a process which can be easily scaled up with ease and works similarly on different types of PLS and hence different battery chemistry, the master thesis was started.

The PLS used in this study was estimated to have 1.7 g/l of Li^+ as either $LiOH$ or $LiSO_4$ and 1 M of NH_4 as $(NH_4)_2SO_4$. All the other components available in the black mass were separated by various hydrometallurgical studies carried out by a post-doctoral researcher in the group (Figure 2.3). This PLS was achieved by acid leaching of the black mass provided by an industrial partner. The leachate was then subjected to solvent extraction which separated the impurities such as copper, iron and aluminium leaving out the valuables such as lithium, Nickel, manganese and cobalt in the leachate. On further precipitation using a suitable base to precipitate the nickel, manganese and Cobalt at various pH, while leaving the final solution with lithium and ammonium sulphate at a pH of 9. This solution is the PLS used in the current study. More specific details on the previous hydrometallurgical operations cannot be given at the current time as they were a part of another study. More details on it will be revealed later while considering a collective publication.
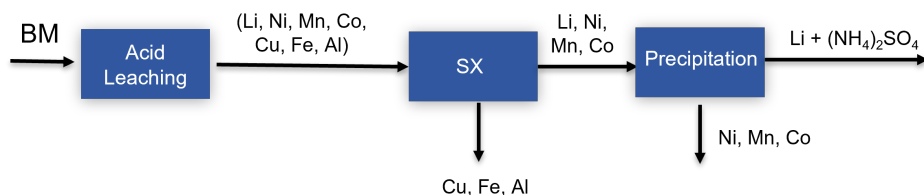

Figure 2.3: Hydrometallugical operations involved in obtaining the PLS

The specialization project only focused on analyzing the aqueous phase and correlating with the organic phase, however many of the unanswered questions from this study could only be answered if a thorough analysis of the organic phase is done, which was a good suggestion for future work. Hence, during the master thesis, this was planned to be done using FTIR (Fourier-transform infrared) spectroscopy. However, due to the presence of kerosene (potentially can be carcinogenic) in the extractant system and the inability of having a proper ventilation setup in the FTIR equipment available in both the chemical engineering and material sciences departments, This was given up. Also, it was evident that an increase in pH increases the extraction capacity of the HTTA/TOPO system. Hence pH studies are mainly focused on this master's thesis. The pH was set to increase

by either adding a base or by saponification of the extractant system before extraction studies. Another suggestion is to use different black masses and different leaching conditions to produce different types of PLS with varying impurities, in that way, this process can be optimized efficiently for a variety of feedstock.

Chapter 3

Materials and Methods

This chapter offers a comprehensive summary of the chemicals, equipment, and procedures employed in this study. The selection of chemicals was informed by previous scholarly works, and the choice of equipment was guided by both existing literature and the practicality of using such tools in the available laboratory setting. The equipment utilized is further elaborated on under the corresponding experimental methods discussed in this chapter.

1. Preparation of synthetic Pregnant leach solution

    (a) 98% reagent grade Lithium Hydroxide from Sigma Aldrich

    (b) Analysis grade Ammonium Sulphate from Sigma Aldrich

    (c) 98% H_2SO_4 and 25% NH_4OH from Sigma Aldrich for pH adjustments

    (d) MQ water

2. Synergistic Solvent extraction

    (a) HTTA (2-Thenoyltrifluoroacetone) from Sigma Aldrich

    (b) 90% TOPO (Trioctylphosphine oxide) from Sigma Aldrich

    (c) Reagent grade kerosene from Sigma Aldrich

    (d) Analysis grade Tributyl Phosphate and Toluene from Sigma Aldrich to use as modifiers for diluents

3. Synthetic PLS for cation selectivity tests

    (a) 98% reagent grade Lithium Hydroxide from Sigma Aldrich

    (b) 25% NH_4OH from Sigma Aldrich

    (c) Analysis grade $NaOH$ from VWR chemicals

    (d) 85% KOH from Sigma Aldrich

    (e) 98% H_2SO_4 from Sigma Aldrich for pH adjustments

    (f) MQ water is used to make all solutions

4. Stripping reaction

    (a) 98% H_2SO_4

    (b) MQ water is used to make all acid solutions

5. ICP multi-element standard solution IV from Sigma Aldrich for standards preparation while performing MP-AES

It is to be noted that all the experiments were carried out at room temperature.
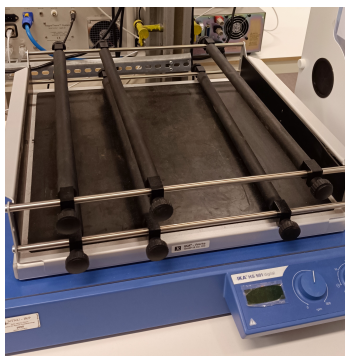
(a) Reciprocal shaker

(b) Magnetic stirrer

Figure 3.1: SSX Apparatus

3.1 Preparation of pregnant leach solution

To carry out the experiments by solvent extraction, a pregnant leach solution (PLS) with loaded lithium was needed. This can be done by either preparing a synthetic solution of lithium or selectively leaching out lithium from the black mass of a spent EV battery. It can be seen in chapter 2, that the current PLS involves a lot of pre-steps to make it. Hence, to save time, it was decided to proceed with a synthetic solution resembling the components of the PLS. $LiOH$ and $(NH_4)_2SO_4$ was used to induce the necessary Li^+ and NH_4^+ ions in the PLS. As for other required compositions, 1.7 g/l LiOH was needed to produce 1.7 g/l of Li^+ ions in the PLS and 0.5M of ammonium sulphate is required to produce 1M of NH_4^+ ions in the PLS. The required calculations can be found in Section A.1. The synthetic PLS containing 1.7 g/l of Li and 1M of NH_4 had a pH of 9.56, which was later decreased to 9 (pH of the original PLS) or increased to 10 by using either 98% H_2SO_4 or 25% NH_4OH respectively. The pH was measured by a Mettler Toledo Seven Excellence pH meter.

3.2 Preparation of stock solution of extractants for SSX studies

HTTA and TOPO, which exhibit solid characteristics at room temperature, necessitate the introduction of kerosene as a diluent to assist in dissolution and lower viscosity, thereby promoting efficient mass transfer. Hence, it's critical to liquefy these substances before blending them with kerosene to produce standardised stock solutions. Throughout this study, mainly 0.5 M (with occasional use of 1 M) stock solutions of HTTA and TOPO were prepared individually.

To prepare 0.5 M stock solutions of HTTA and TOPO separately, the precise weights of 5.55 g and 10.74 g respectively of the substances were measured and moved to individual beakers. To aid in their melting, the contents of each beaker were heated to 50 °C. Following this, kerosene was used to dilute both solutions to a final volume of 50 ml in a volumetric flask. These prepared stock solutions were then combined with kerosene to reach the desired concentration of the extractants. An example calculation for the creation of 0.5 M HTTA and TOPO stock solutions is provided in Section A.2.

3.3 SSX studies

All the synergistic solvent extraction (SSX) investigations were performed utilizing 50 ml centrifuge tubes located in a reciprocal shaker. Unless specified otherwise, the total volume for these experiments was kept at 20 ml. Prior to the studies, stock solutions of HTTA and TOPO in kerosene were prepared. To achieve the desired HTTA/TOPO ratios, specific volumes of HTTA-kerosene

solution, TOPO-kerosene solution, and kerosene were added to the centrifuge tubes. To attain the intended aqueous/organic (A/O) ratio, the necessary quantity of the HTTA/TOPO solution was then introduced into a certain volume of PLS, ensuring that the total volume remained at 20 ml.

Certain experiments (preparation of the loaded organics for stripping studies) were conducted using a magnetic stirrer. This was chosen as the results during the specialization project proved that there were no significant changes in extraction between the reciprocal shaker and the magnetic stirrer [44]. These specific trials performed using the magnetic stirrer, were executed with a total volume of 200 ml (100 ml organics + 100 ml aqueous). Except for these particular cases, the total volume was limited to 20 ml for all other experiments.

The reciprocal shaker was operated at a rotational speed of 250 RPM, and the extraction process was conducted for 10 minutes. For the experiments involving the magnetic stirrer, the rotational speed was set at 300 RPM, as this stirring method achieved a similar level of mixing at a lower speed. This speed was optimized during the specialization project. Following the completion of the extraction process, the samples were centrifuged at 4000 RPM for 5 minutes. This step ensured a complete separation of the organic and aqueous phases. The separated phases were then transferred using micropipettes into glass storage containers with screw caps. The aqueous phase was subsequently analyzed for composition using MP-AES and TOC-TN analyzer.
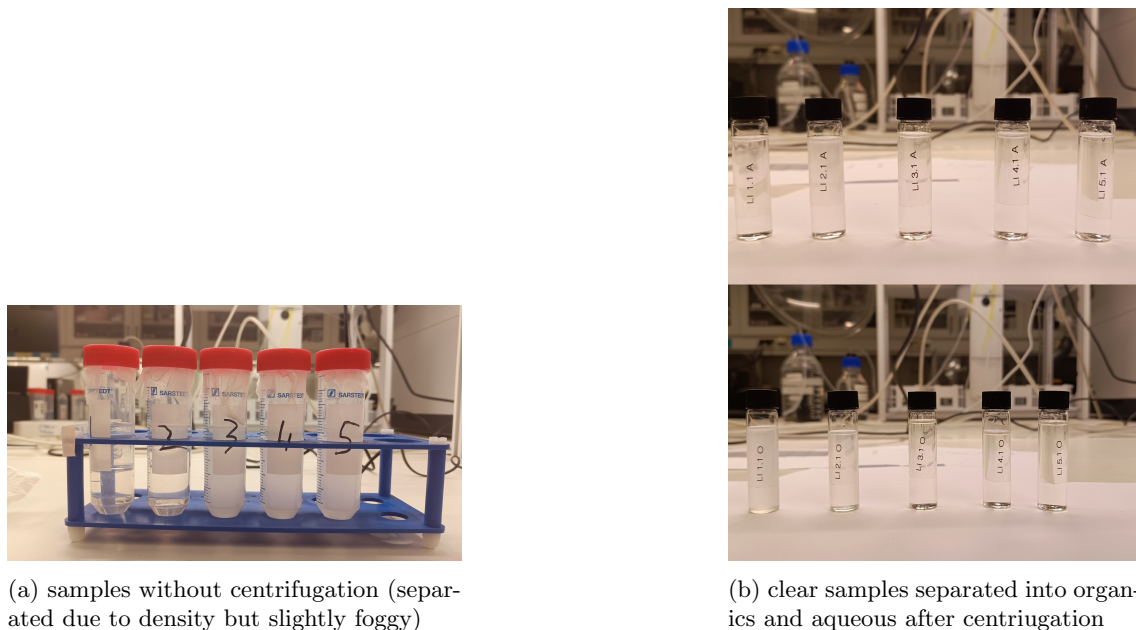
(a) samples without centrifugation (separated due to density but slightly foggy)

(b) clear samples separated into organics and aqueous after centriugation

Figure 3.2: Samples after SSX

In the initial stages of preparing samples for SSX extraction, volume calculations were performed by weighing the samples and utilising density calculations to estimate volume (more details are discussed in chapter 4). The parameters investigated in the SSX studies included the pH and the A/O ratio, the effect of modifiers, the effect of different cations in the PLS and the maximum loading capacity of the extractant system. Unless stated otherwise, all experiments were conducted twice and the results were reported as mean and standard deviation values.

3.4   Stripping studies

Once lithium has been drawn from the Pregnant Leach Solution (PLS) into the organic phase (which constitutes the HTTA-TOPO-kerosene system), it's necessary to extract it back into an aqueous phase. This stripping stage is crucial in obtaining lithium in a more concentrated form, which can be sold or employed in battery production. Given the volume of organics necessary for these experiments, 100 ml of "loaded" organics were prepared using a synthetic PLS. An A/O

ratio of 1 was maintained during this preparation, performed in a magnetic stirrer under the same optimal conditions reported during the SSX study. after 2 cycles of extraction, It was found that the loaded organic with an HTTA/TOPO concentration could hold around 2.6 g/l of lithium on average. This loaded organic system was employed in stripping studies.

Stripping studies on the loaded organics were conducted with sulfuric acid, due to their ability to form lithium sulfate which is a potential raw material in the production of lithium-ion batteries. Also, during the specialization project sulphuric acid performed better than acetic acid [44]. The loaded organics were mixed with the stripping solutions in a predetermined ratio, culminating in a total volume of 20 ml within 50 ml centrifuge tubes.

Stripping was performed by placing these tubes in a reciprocal shaker set at 250 RPM for 10 minutes. Following the stripping, the tubes were centrifuged at 4000 RPM for 5 minutes to ensure complete phase separation. The stripped organic phase and the aqueous phase were carefully pipetted into separate containers and stored for subsequent analysis. The parameters examined during the stripping phase include the type and concentration of the acid used, as well as the organic-to-aqueous (O/A) ratio. Unless otherwise specified, all experiments were performed twice for validation purposes.

3.5   Characterization technique

The prepared PLS, aqueous part after SSX and stripping was analyzed using MP-AES (Microwave Plasma Atomic Emission Spectroscopy) and TOC-TN analyzer to measure the lithium and ammonium concentration respectively. UV-VIS spectrometer (Agilent Cary 60 UV-VIS) was used in certain cases where there was a need to measure the turbidity and sulphate concentrations in certain solutions for some validation (explained in chapter 4).

MP-AES

Agilent 4210 MP-AES (Figure 3.3) is used to measure the lithium concentration in aqueous solutions in this study. In MP-AES, the equipment automatically measures the standard solutions and compares them with sample solutions. The foundation of this theoretical framework is rooted in the principles of atomic emission, a phenomenon whereby the constituent atoms of a particular material emit radiation upon excitation. This process can be elucidated as the release of photons by atoms in an excited state. When an element becomes excited, it releases light that is characterized by a distinct wavelength as it reverts to its original ground state. The plasma produced by Microwave Plasma Atomic Emission Spectroscopy (MP-AES) has the capacity to attain high temperatures of up to approximately 5000K, leading to significant atomic emissions. The instrument utilizes a magnetron as an energy source for generating microwaves. The nitrogen plasma is generated through the compression of air utilizing an in-house nitrogen source. A nebulizer and spray chamber facilitates the conversion of a sample into an aerosol state, subsequently enabling its utilization in diverse analytical methods. The gaseous state of matter known as plasma is the target of direction. Upon contact with the heated plasma, the aerosol undergoes decomposition. Essentially, undergoing the process of atomization. Per contemporary scientific understanding, it can be asserted that atoms which are presently stimulated experience a discharge of light exhibiting particular frequencies. As electromagnetic radiation interacts with matter, it can be absorbed at specific wavelengths, causing transitions of electrons from higher to lower energy states. The beam of light is directed towards the monochromator. The process involves the utilization of an apparatus that conducts a scan based on a predetermined wavelength and subsequently compares the spectra and background. Concurrently providing precise outcomes in terms of concentration.

The Microwave Plasma-Atomic Emission Spectroscopy (MP-AES) possesses the capability to effectively analyze and detect elements that emit light within a wavelength range of 180-780 nm and the allowable limit for total dissolved solids not exceeding 3% are key parameters to be adhered to in this study.

The standard solutions were prepared in the order of 50, 25, 12.5, 6.25, 3.125 and 1.5625 mg/l Using a multi-element ICP standard. All the samples were diluted to a factor of 10, 50, 100, 500 or 1000 (depending on the anticipated value) to fit inside the calibration curve.

Figure 3.3: Agilent 4210 MP-AES

3.5.1 TOC-TN analyzer

The analytical instrument used to calculate the ammonium concentration by quantifying the total nitrogen present in the system is known as Shimadzu TOC-L. It utilizes the combustion catalytic oxidation method at a temperature of 680 °C to effectively measure total organic carbon concentrations. These analyzers offer a broad range of sensitivity spanning from 4 μg/L to 30,000 mg/L, while simultaneously achieving a precision limit of 4 μg/L. This impressive precision is attained through the integration of NDIR (Non-Dispersive Infrared) technology. The combustion catalytic oxidation method offers the utmost degree of detection sensitivity attainable. Furthermore, the process of combustion catalytic oxidation provides an efficient means of oxidizing both low-molecular-weight organic compounds that are readily decomposed as well as insoluble and macromolecular organic compounds that are difficult to decompose. Moreover, the supplement of the TN analyzer extends its measurement capability within the range of 20 μg/L to 10,000 mg/L. It employs catalytic thermal decomposition/chemiluminescence techniques at a temperature of 720 °C to discern the presence of nitrogen in the sample.

The process of calibrating carbon is conducted using sodium bicarbonate. The calibration curves have been segmented into three distinct parts. The three respective ranges of concentration levels under consideration, namely 0-25 ppm, 25-150 ppm, and 150-500 ppm, warrant examination in an academic context. Each of the aforementioned calibration standards represents a reduction in the concentration of a pre-existing standard with a concentration of 1000 ppm. The total nitrogen measurement protocol encompasses two distinct calibration curves, spanning the ranges of 0-150 parts per million (ppm) and 150 ppm, respectively. The calibration standard employed in this study comprises MEA diluted in MQ Water. The calibration standards employed across the board are based on a measure of 1000 ppm of nitrogen. The calibration of the used equipment is given in Section A.4.

The TN analyzer only measures the total nitrogen concentration of the solution, using which the ammonium concentration can be estimated. sample calculations are appended in Section A.4

3.5.2 UV-VIS

The Agilent Cary 60 UV-VIS is the spectrometer used in this study to measure the turbidity of the extracted phases and specific time intervals and thereby establishing the separation properties of the extractant and the aqueous phase. It was also used to measure the sulphur concentration in the stripped solution to validate the sulphate ion concentration in some instances. Agilent Cary 60

Figure 3.4: Shimadzu TOC-L

UV-VIS is a reputable UV-Vis spectrophotometer, known for its ability to measure light absorbance across the ultraviolet and visible regions of the electromagnetic spectrum. This instrument is particularly distinguished by its outstanding scan speed, consistent performance, and broad application range from routine testing to advanced research scenarios, demonstrating its significant versatility. Underlying the operation of the Agilent Cary 60 UV-VIS spectrophotometer are the principles of photometry. When a light beam is directed through a sample, the sample absorbs a proportion of the light, allowing the rest to transmit. This light absorption provides valuable insight into the sample, facilitating assessments of its concentration, purity, and reaction kinetics.

The instrument's light source, a xenon flash lamp, generates a beam that is subsequently dispersed into its component wavelengths by a monochromator. This light, which spans wavelengths from 190 to 1100 nm, is then transmitted through the sample held in a cuvette. A special feature of this spectrophotometer is its 18-cell temperature-controlled cuvette holder, providing enhanced experimental conditions. Upon light-sample interaction, some light gets absorbed while the remainder is detected by the spectrophotometer. The device then compares the intensity of the incident light (pre-sample) with that of the transmitted light (post-sample). The device, with a spectral bandwidth of 1.5 nm and a maximum scanning speed of 24,000 nm/min, records the amount of light absorbed at each wavelength to generate an absorbance spectrum. Since different compounds absorb light at unique wavelengths, the absorbance spectrum analysis allows the identification and quantification of specific substances in the sample. This feature, coupled with its impressive specifications, underscores the Agilent Cary 60 UV-VIS's ability to deliver precise and comprehensive results.
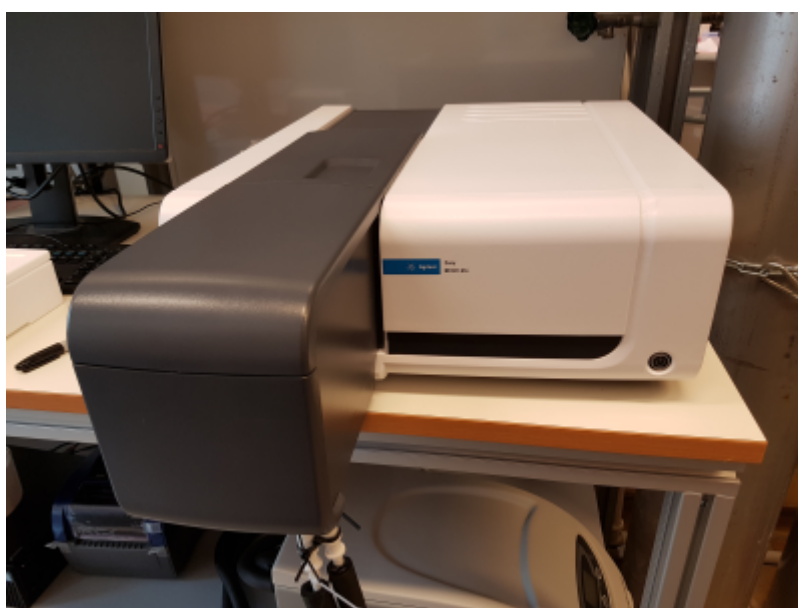
Figure 3.5: Agilent Cary 60 UV-VIS spectrometer

Chapter 4

Results and Discussion

4.1   Synthetic PLS

The synthetic PLS is set to have a Li concentration of 1.7 g/l and NH_4 concentration of 1M. However, adding either 98% H_2SO_4 or 25% NH_4OH changes the initial concentration of ions especially in the ones where the PLS pH is increased to 10 by adding ammonium hydroxide. Since the pK_a value of 25%, NH_4OH is very low (4.75) and thus a big quantity of it is needed to increase the pH and thereby, drastically increase the initial ammonium concentration at a pH of 10. In the case of pH reduction by sulphuric acid, very less acid is needed to get the job done and thereby the initial concentration is not affected significantly.

Table 4.1: Average initial concentration of PLS at different pH

pH	Li con. (g/l)	NH4 con. (g/l)
9	1.643	17.012
9.5	1.685	18.436
10	1.537	24.642

Table 4.1 shows the average initial concentrations of the synthetic PLS and various pH used in the study reported with a standard deviation of less than 6%. As can be seen, the measured lithium and ammonium concentrations using MP-AES and TOC-TN analyzer are very similar to each other and close to the values of the original PLS (1M NH_4 18 g/l NH_4). However, at pH 10 the ammonium concentration seems to be highly elevated to around 24 g/l and Li concentration has dropped to around 1.54 g/l. This is because of a large amount of ammonium hydroxide being used to increase the pH. Since at pH 10, the ammonium concentration is almost increased to 1.5 times it may be expected that the extraction drops but it is also to be noted that from previous literature, an increase in pH seemed to increase the extraction. However, in most of the previous studies, the pH was increased by using NaOH and the competing ion was sodium but in this case its ammonium. Thus only further tests will reveal the answer to this question, keeping this in mind, the effect of pH of the extraction and extraction of lithium and ammonium is studied in the next section.

4.2   Effect of pH and A/O ratio

The effect of the A/O ratio and the pH of the PLS are looked into in this section. Table 4.2 shows the constant parameters in which all the extraction experiments are carried out in this thesis. These parameters were optimized in the specialization project carried out by the student [44]. Everything was kept constant while the only variables being the pH and the aqueous to organic ratio.

Table 4.2: Extraction conditions kept constant throughout the study

Condition type	Constant value
Total volume	20 ml
Reciprocal shaker RPM	250
Shaking time	10 min
Centrifugation RPM	4000
Centrifugation time	5 min
HTTA concentration	0.2 M
TOPO concentration	0.2 M

Figure 4.1 shows the effect of AO on different pH of the PLS, the x-axis holds the various A/O ratio (0.2, 0.3, 1, 3 and 5) and the y-axis indicates the % extraction and the subfigure a, b and c denotes the variation in pH. It can be seen that at a pH of 9, the maximum possible Li extraction was close to 40% at a lower A/O ratio and increasing the A/O, not only decreases the Li extraction but also increases the Ammonium co-extraction. It is also worth noting that until an A/O ratio of 1, there was no ammonium co-extraction. Increasing the pH to 9.5 seems to have increased the % extraction of lithium to ≈83% from that of 40% at a pH of 9 and as expected the lithium extraction decreased with increasing A/O ratio. The ammonium co-extraction seemed to be existent at ratios below 1 although the co-extraction of NH_4 seemed to have dropped and stayed below 4% for all the A/O ratios. This confirms the theory that an increase in pH not only increases the lithium extraction capacity but also the selectivity of the HTTA/TOPO system toward lithium. At an A/O ratio of 1 and pH 9.5, about 84% of lithium has been extracted into the organic phase which is around 1.4 g/l(0.2M) of Li, indicating the saturation of the extractant system (0.2M of HTTA and TOPO). This indicates that one molecule of Li forms a complex with 1 molecule of HTTA and TOPO, affirming the previously reported studies [33, 36, 20, 34].

At pH 10, almost all of the lithium was extracted into the extractant at lower A/O ratios (0.2 and 0.3) and around 80% of Li extraction was noted at A/O ratio 1. An anomaly was noted at the lower A/O ratios, more ammonium was co-extracted into the organic phase and while visually observing the system after extraction, one was able to notice some solids in the aqueous phase even after centrifugation. At first, it was presumed to be a precipitate of Li but was later confirmed to be soap (as an effect of saponification) which is a result of adding a lot of ammonium hydroxide to the PLS to increase the pH. Thereby resulting in an enormous co-extraction of ammonium which is not good.

If looked carefully at Figure 4.1, it can be noted that for A/O ratios 0.2, 0.3 and 1, increasing the increases to Li extraction until pH 9.5 and after that, it either starts to plateau(A/O ratio 0.2 and 0.3) or decrease (A/O ratio 1). However, for ratios above 1 pH does not seem to have much effect on the Li extraction. When it comes to ammonium co-extraction for lower A/O ratios increase in pH seems to drastically increase NH_4 co-extraction and at higher A/O ratios pH does not seem to have much effect on the co-extraction. For easy interpretation of the above-explained phenomena, check Figure A.2 in Section A.8.

Although, higher pH seemed to extract all of the lithium, the high ammonium co-extraction and formation of a third phase will be not economical in the later stages (the third phase affects the separation of organic and the aqueous phase and high ammonium co-extraction require the introduction of a scrubbing step to improve the purity). Thus keeping this in mind future experiments are decided to be carried out at pH 9.5 and at an A/O ratio of 1 which extracted around 84% of lithium while only co-extracting less than 3% of ammonium.
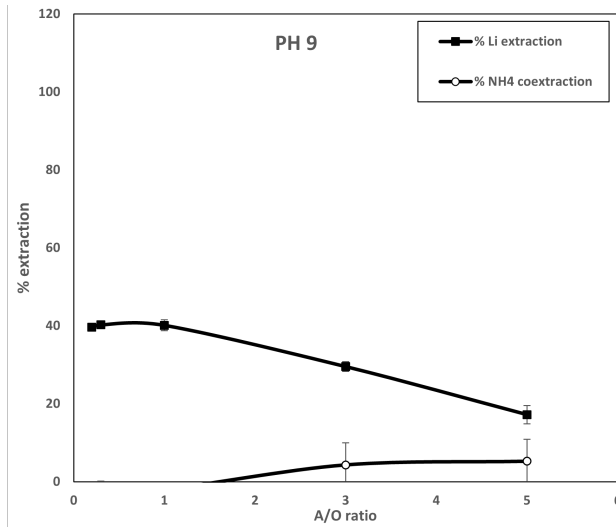
(a) pH = 9
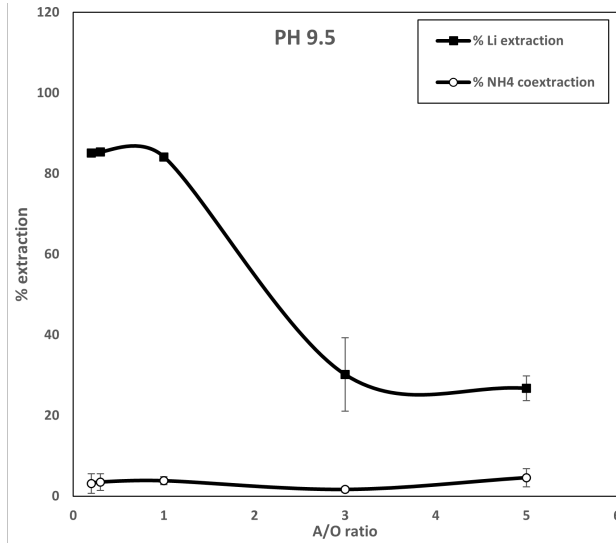
(b) pH = 9.5
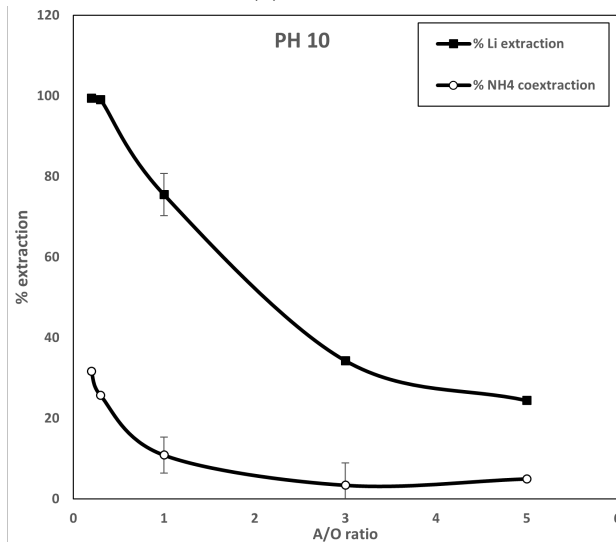
(c) pH = 10

Figure 4.1: Effect of AO ratio on different pH

4.3 Effect of modifiers

In the previous section, pH 9.5 and A/O ratio seemed to show the optimal lithium extraction and ammonium co-extraction. However, it was noted that when the pH was increased from 9 to 9.5, the separation of the organic phase and aqueous took a little longer and the system remained cloudy thus requiring a definite centrifugation to appear clear. Although centrifugation was done on all the samples to achieve uniformity, the industries would not prefer centrifugation. Therefore to enhance the separation of the organic and aqueous phases without affecting the extraction, it was decided to use modifiers. The ones used in this study were TBP and Toluene and their composition in the organic phase was increased from 0 - 20 %.

(a) % Extraction
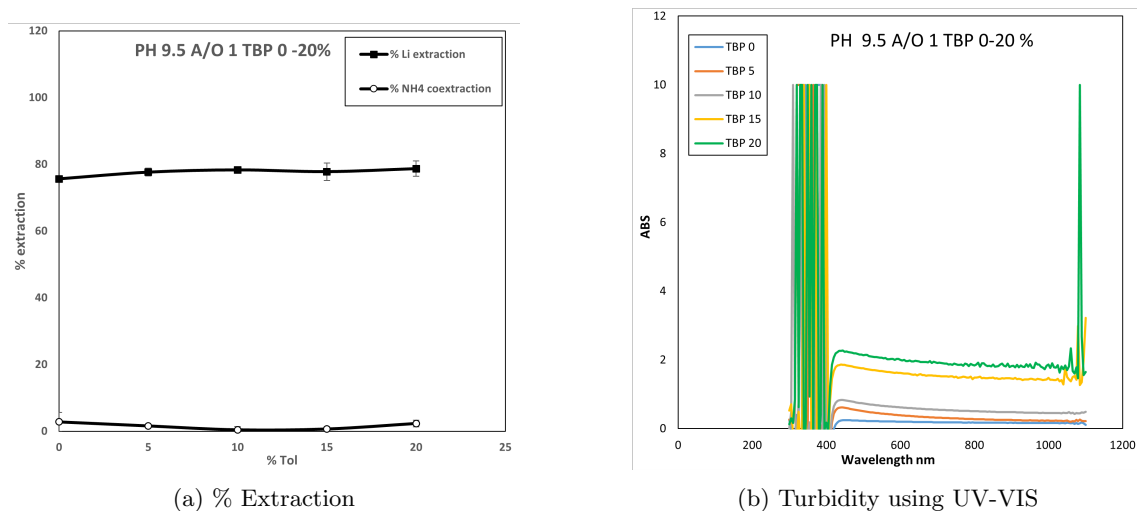
(b) Turbidity using UV-VIS

Figure 4.2: Effect of TBP (0-20%) at pH 9.5

Figure 4.2 and Figure 4.3 show the effect of adding TBP and Toluene to the extractant phase. Subfigures (a) indicate the extraction and co-extraction of lithium and ammonium respectively while subfigures (b) indicate the absorbance measured in UV-VIS spectroscopy. These absorbances directly correlate to the turbidity of the organic phase at the given point in time (being constant 10 s after extraction). A higher value of turbidity can correspond to the lower rate of separation of the extractant phase from the aqueous phase. This data was also backed by physical observation of the separation of 2 phases after extraction. Initially with the use of any modifiers, it was noted that the phase separation took around 1 minute and 15 seconds at pH 9.5. On increasing the amount of TBP in the extractant system from 0 to 20 %, the separation time became longer to around 5 minutes and this was clearly backed by the data from UV-VIS (Figure 4.2). It can be seen that increasing the concentration of TBP seemed to have increased the turbidity. Moreover, from the %extraction graph, it can be seen that there was no significant change in the extraction and co-extraction of lithium and ammonium respectively.

When toluene was used as a modifier, the rate of phase separation increased with increasing concentration of toluene. At 20% toluene, it was noted that both the organic and aqueous phase was completely separated within 20 seconds which is quite good considering the high % Li extracted with low ammonium being co-extracted (less than 8%) as seen in Figure 4.3. The absorbance data also backs the visual observation of faster separation with the decrease in absorbance with increasing concentration of toluene in the extractant system. Another observation from the extraction graphs in Figure 4.2 and Figure 4.3 will indicate that slightly more ammonium is being co-extracted when Toluene was used as a modifier. This may be because of the increase in mass transfer coefficient with adding toluene or may just plain human error but more studies are needed to affirm that, which unfortunately are not performed due to lack of time.

The effect of adding a modifier was also studied at pH 10, the results of which are appended in the Section A.9. They showed similar trends as at pH 9.5, hence it can be concluded that the addition of toluene as a modifier enhances the phase separation and when all the diluent is replaced with kerosene the phase separation is maximum with no significant changes in the extraction.

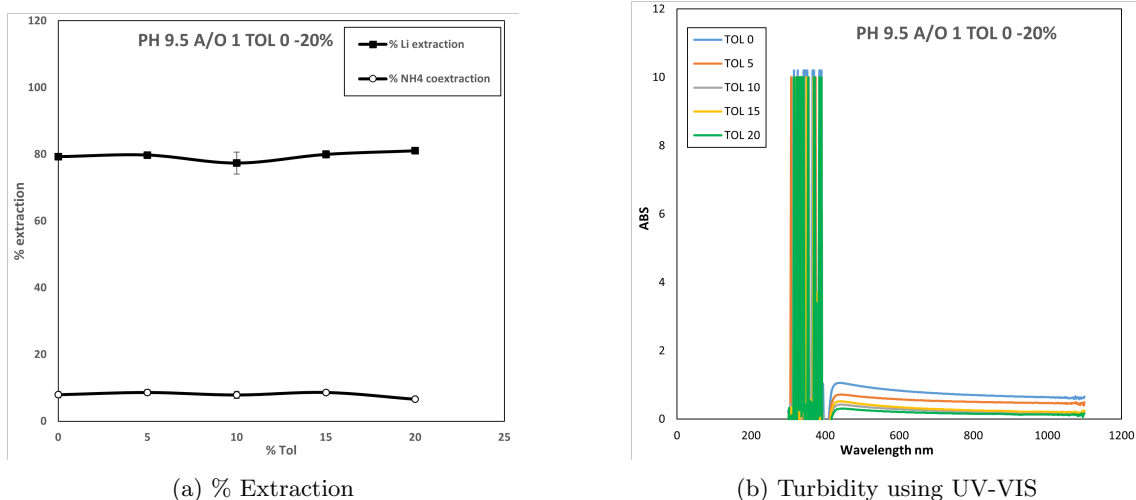(a) % Extraction

(b) Turbidity using UV-VIS

Figure 4.3: Effect of Toluene (0-20%) at pH 9.5

This set of experiments indicates that the addition of TBP Does not improve the phase separation but rather worsens it in the case of this system. This may be attributed to the fact that the density of TBP (0.979 g/ml) is much closer to the density of the PLS used (1.02 g/ml) making the phase separation difficult. however, the density of toluene (0.87 g/ml) is slightly far from the density of the PLS, which may be the cause for enhanced phase separation. Thus further studies are set to be carried out using 20% toluene as a modifier which replaces all of the kerosene in the system.

4.4   Maximum loading capacity of the organic phase

For any solvent extractant system scalability and reusability of the extractant is very crucial to be utilized in the industry. As explained in the specialization project [44] and at the beginning of this thesis in chapter 1, scaling up is the prime focus of this study. In the specialization project, the maximum loading capacity of the 0.2M HTTA/TOPO system was theoretically found to be around 1.2 g/l using Mccabe Thiele's method. Thus this set of experiments is carried to out to verify them experimentally and study what happens if the extracted phase was re-used. 0.2M HTTA/TOPO with 20% toluene is used as the extractant phase, and the PLS at pH 9.5 is selected as the aqueous phase (Figure 4.4). The extractant system was reused 5 times without regeneration with a freshly prepared PLS each time and the aqueous phase from each cycle was collected for analysis.

It can be seen from the Figure 4.4, in the first cycle almost 80% of lithium has been extracted while around 10% of ammonium has been co-extracted. In the second cycle and afterwards, the lithium extraction drops to 0% indicating that the extractant is saturated in just one cycle, however, extraction (less than 5%) of ammonium continued to be seen in all 5 cycles. From Table 4.3, it can be seen that in the first cycle, almost 1.26 g/l of lithium has been moved into the organic phase and almost 0 in the second cycle. 1.26 g/l of lithium corresponds to 0.18M of lithium, indicating the saturation of 0.2M HTTA/TOPO system, this value is also close to the theoretically determined value during the specialization project.

Table 4.3: Amount of Li entering the organic phase each cycle using 0.2M HHTA/TOPO

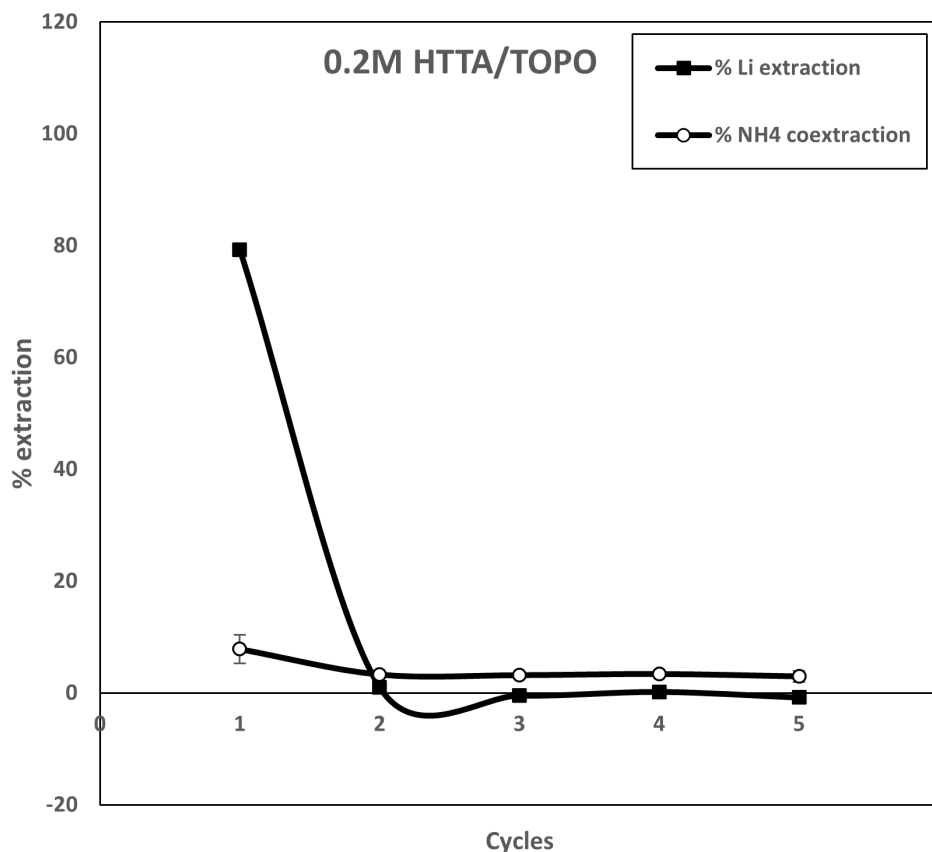| Cycle	Li moved to organic phase (g/l)	NH4 moved to organic phase (g/l)
1	1.26	1.4
2	0.017	0.58
TOTAL	**1.28**	**1.98**

Figure 4.4: Li loading experiments 0.2M HTTA/TOPO

On input from the supervision team, a 0.4M HTTA/TOPO system was utilized to see if that enhances the number of cycles the extractant system can be used by increasing the capacity of the extractant system. As expected the results were promising. Figure 4.5 shows the %extraction and %co-extraction of lithium and ammonium respectively with the increasing number of cycles. It can be clearly seen that the Li extraction only drops to 0 after the second cycle, thereby indicating that this system can be used to extract lithium from 2 different cycles without regeneration. However, there is a small drop in Li recovery in the second cycle as the system attains saturation (2.65 g/l Li $\approx$ 0.375M Li), as it can be seen in Table 4.4. After 2 cycles the system was able to extract 2.65 g/l of lithium from the PLS while only co-extracting 2.04 g/l of ammonium. On further carrying on with cycles 3, 4 and 5, no more lithium was extracted while the NH_4 co-extraction continued. 0.6M HTTA/TOPO was not tested as that would make the system more vicious [44]

Table 4.4: Amount of Li entering the organic phase each cycle using 0.4M HHTA/TOPO

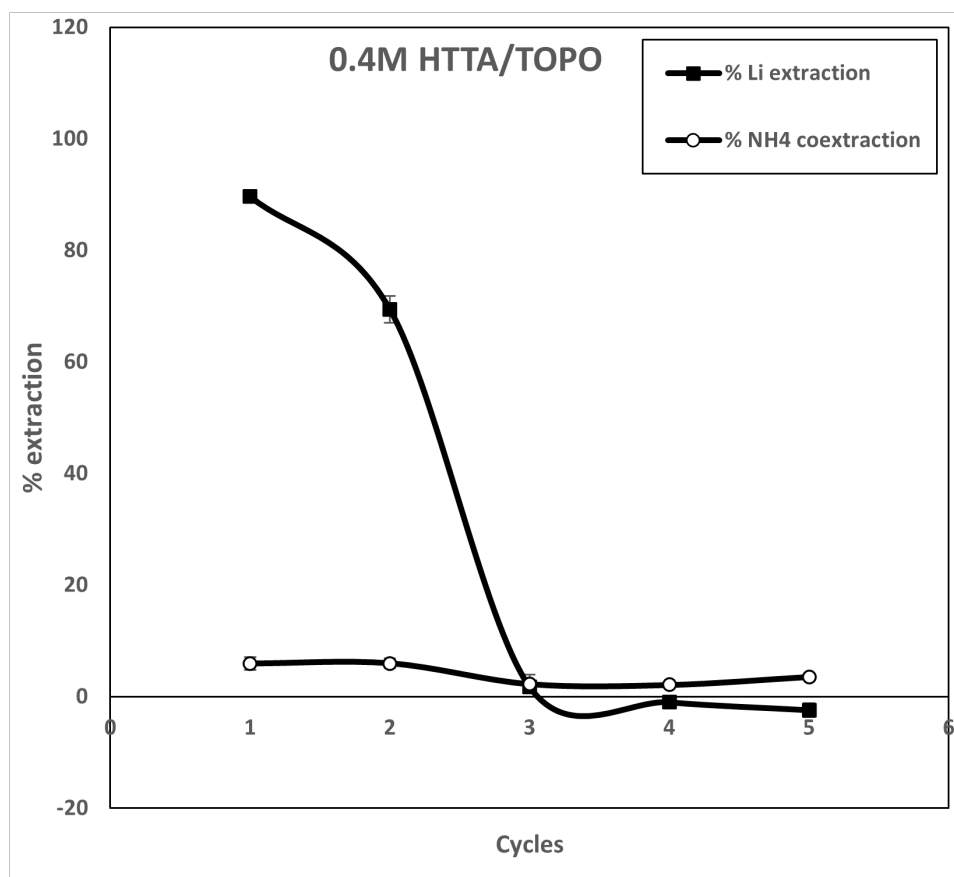| Cycle	Li moved to organic phase (g/l)	NH4 moved to organic phase (g/l)
1	1.49	1.02
2	1.16	1.02
TOTAL	**2.65**	**2.04**

Figure 4.5: Li loading experiments 0.4M HTTA/TOPO

4.5 Effect of different cations in the PLS

The problem with current extraction systems in battery recycling is that a large variety of battery chemistries available, give out a variety of impurities along with the targeted material. Hence to combat that and to understand the selectivity of the HTTA/TOPO system towards various alkali metals (which are usually present in lithium brines or after extensive extraction of other valuables from spent battery wastes), this test was carried out. The cations selected for this controlled study are sodium, potassium and ammonium produced from their respective hydroxides.

The PLS used in this thesis has 1.7 g/l of lithium ions which closes translates to 0.25M. Thus individual solutions of LiOH, NaOH, KOH and NH_4OH are prepared with a concentration of 0.25 M (before extraction the pH of all solutions has been adjusted to 9.5 using sulphuric acid)and 0.2M HTTA/TOPO with 20% toluene is used to extract the respective ions from the respective solutions, the results of which are shown in Figure 4.6. It can be seen that when the same amount of different ions are used, the HTTA/TOPO system showed more preference for the extraction of lithium and the least preference for the extraction of ammonium. The extraction is in the order of $Li^+ > Na^+ > K^+ > NH_4$. This is because of the size of the cations themselves for the alkali elements ($Li^+ < Na^+ < K^+$). The smaller the size the more the intensity of forming bonds with counter ions and this could be the reason for the decrease in extraction efficiency with increasing atomic radii. However, the size of ammonium ions is smaller than that of sodium but still ammonium is the one which is least extracted. This could be because the ammonium ion is a compound whereas the others are an element and thus have a lower affinity toward counterions.

Another set of tests was done to see the selectivity of the extractant system towards these cations when all of them are present together (which would be an extremely realistic case). 2 solutions were prepared to contain all four cations each of concentrations 0.25M and 0.0625M in a single solution. The same extractant system (0.2M HTTO/TOPO) was used (shown in Figure 4.7). It
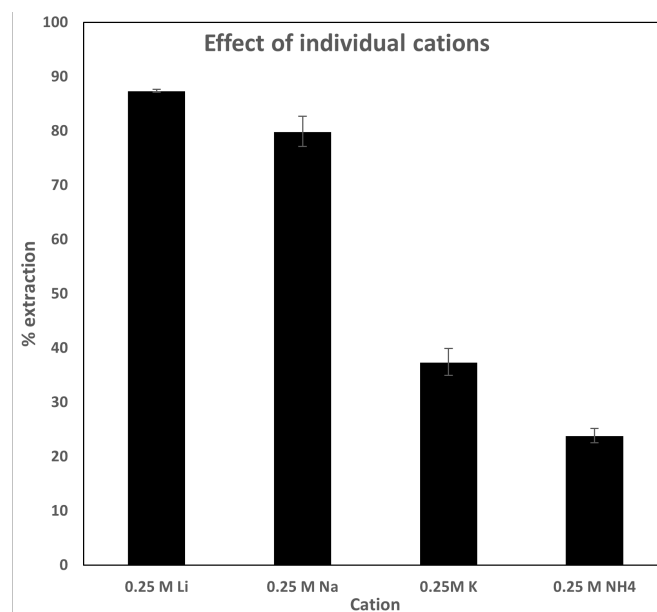
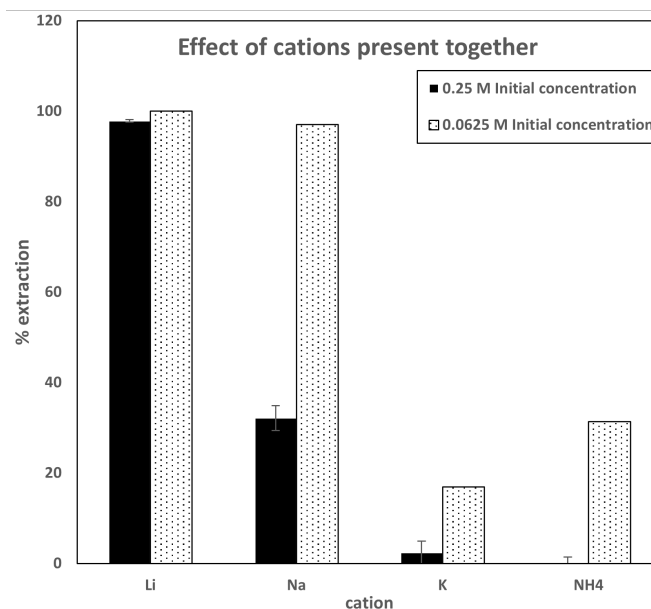Figure 4.6: Extraction from individual solutions of 0.25M

Figure 4.7: Extraction from solutions containing all 4 counter ions

can be seen that for both the initial concentrations, the Li extraction reaches near 100%, this could be because in the presence of other bases like NaOH, KOH and NH_4OH, saponification may happen and later these cations can easily be replaced by lithium as explained in chapter 2. At an initial concentration of 0.25M the order of preference of the extractant system remains the same as with the individual solutions. For almost 100% of lithium extraction only less than 30% and 2% of sodium and potassium have been co-extracted. On decreasing the initial concentrations, the co-extraction of sodium increases to 100% and the co-extraction of potassium and ammonium also increases. This is because when the initial concentration of the ions in the solution decreases, the extractant is not saturated by only extracting lithium and there is more room for the other cations to also be co-extracted. However, from these tests, it can be concluded that the system of HTTA/TOPO is highly selective toward lithium and least selective towards ammonium which corresponds to the previous studies carried out in this thesis where in almost all the extraction studies the ammonium co-extraction remained less than 10%.

Table 4.5: Stripping study with sulphuric acid

S/N	Sample name	Initial Li in Organic (g/l)	Li in stripped aqueous solution (g/l)	Final Li in Organic (g/l)	% Li Stripped
1	S H2SO4 1M - A	2.597	2.082	0.515	80.17
2	S H2SO4 0.8M - A	2.597	2.384	0.213	91.82
3	S H2SO4 0.5M - A	2.597	2.587	0.010	99.62
4	S H2SO4 0.3M - A	2.597	1.708	0.889	65.77
		Initial NH4 in Organic (g/l)	NH4 in stripped aqueous solution (g/l)	Final NH4 in Organic (g/l)	% NH4 CO-stripped
1	S H2SO4 1M - A	1.665	1.268	0.397	76.15
2	S H2SO4 0.8M - A	1.665	0.867	0.798	52.07
3	S H2SO4 0.5M - A	1.665	0.555	1.110	33.34
4	S H2SO4 0.3M - A	1.665	0.378	1.287	22.71

4.6 Stripping studies

Upon successful extraction of lithium into the organic phase, it is crucial to return it back to an aqueous environment as a saleable salt form. The importance of having a relatively high lithium concentration in the reclaimed aqueous phase cannot be understated, as this makes the subsequent recovery stages of the lithium salt more cost-effective. As such, this part of the study evaluates the feasibility of reclaiming lithium in the form of lithium sulphate utilizing sulphuric acid. The concentration of the acid up to 1 Molar (M) is taken into consideration as it could potentially impact the stripping process. Subsequently, this section also includes an analysis of the organic-to-aqueous (O/A) ratio, an essential aspect in determining the potential for enhancing the lithium salt concentration in the stripped aqueous phase. This examination serves as a foundational step towards the goal of scaling up the recovery process.

4.6.1 Effect of acid concentration

For stripping studies the loaded organic solution is prepared by 2-cycle loading as done in Section 4.4 using 0.4M HTTA/TOPO with 20% Toluene. The loaded solution seemed to have around 2.6 g/l of Li and 1.8 g/l of $NH4$ on average. These loaded organics were prepared using magnetic stirrers in 100 ml batches. Once the loaded organics has been prepared, the stripping studies were carried out in 50 ml centrifuge tubes in batches of 20 ml. Figure 4.8, shows the effect of sulphuric acid concentration on stripping and co-stripping of lithium and ammonium respectively. It can be evidently seen that an increase in the sulphuric acid concentration increases the stripping efficiency until 0.5M acid concentration after which the efficiency starts to slowly fall down, a similar trend was also noticed in the specialization project [44]. In the specialization project ammonium was not present in the loaded organic, increasing the acid concentration beyond 0.5M, not only decreases the stripping efficiency of lithium but also increases the co-stripping of ammonium which is undesirable. This can be attributed to the fact that high H_2SO_4 concentration facilitates the complete removal of the contents of that solution thus inducing the require meant of a middle scrubbing stage. At a H_2SO_4 concentration of 0.5M, the stripped solution had 2.58 g/l of lithium and 0.555 g/l of ammonium (Table 4.5) which is quite optimal for further operations. Thus keeping this in mind the further O/A ratio test for upscaling the concentration of lithium in the strip liquor is carried out with 0.5M sulphuric acid.
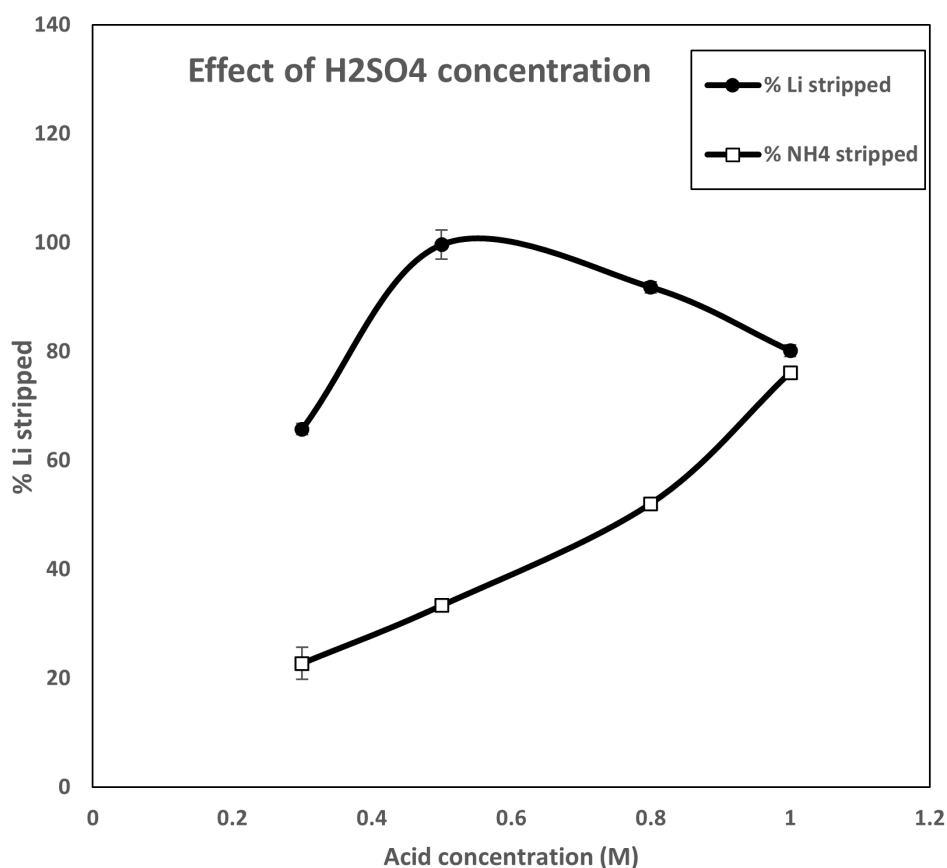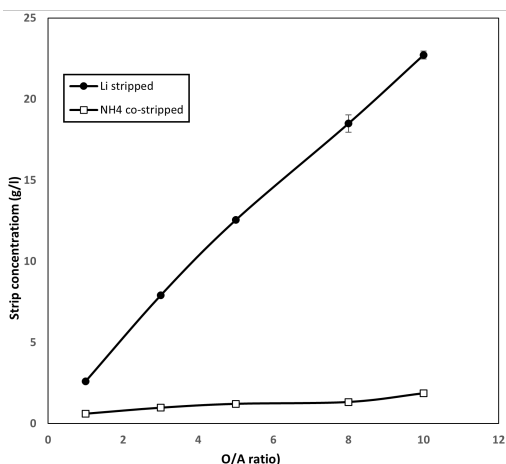
Figure 4.8: Effect of acid concentration on stripping
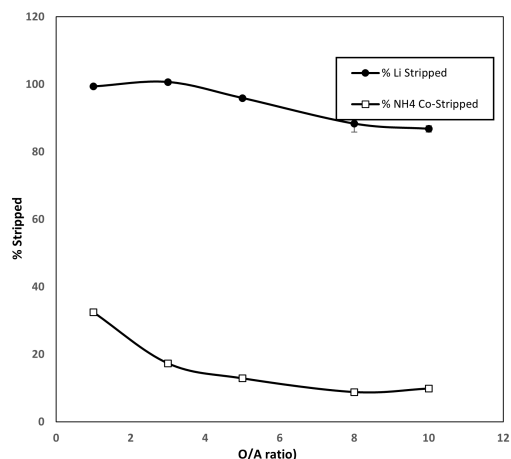
4.6.2 Effect of O/A ratio

This research was conducted by augmenting the ratio between the organic phase containing lithium and the stripping liquor. A heightened ratio implies a decreased necessity for acid to remove lithium from the organically extracted phase. This approach leads to the production of a highly concentrated lithium strip liquor, a product suitable for immediate subsequent processing. Such a strategy negates the need for increasing the concentration further, which could result in both improved cost-effectiveness and sustainability of the entire operation.

The procedures were performed twice to validate the data, with average values being presented. The standard deviation for all experiments was consistently less than 3.3%, confirming the reliability of the results. The starting concentration of lithium in the organic phase was known, and together with the final lithium concentration in the aqueous phase, the volume of both organic and aqueous phases (refer to Table in Table A.3), it is possible to calculate the ending lithium concentration in the organic phase and the percentage of lithium stripped. The computed figures are elaborated in the Table titled Table 4.6. Figure 4.9 shows the stripping efficiency and the concentration of the stripped solution. It can be seen that at O/A ratios of 1 and 3, the stripping efficiency remains 100%, further increasing the O/A ratio only slightly decreases the stripping efficiency to 86% at the O/A ratio of 10 which is quite good. On seeing the graph with stripped solution concentration and Table 4.6, it is evident that it is possible to get a final stripped solution of approximately 22 g/l of Li while only co-stripping less than 2 g/l of ammonium which is very good.

An anomaly which is noted is that even though 22 g/l of lithium has been extracted, it is to be noted only 0.5 M sulphuric acid has been used for stripping which can theoretically only strip 6.94 g.l of lithium into the strip solution (0.5M sulphuric acid has 1M H^+ ions which can only replace 1M Li^+ ions which roughly approximates to 6.94 g/l). However, this is not the case. Thus the

(a) Stripped solution concentration

(b) Stripping efficiency

Figure 4.9: Effect of O/A ratio on stripping using 0.5M H_2SO_4

Table 4.6: O/A ratio study with 0.5M sulphuric acid

S/N	O/A ratio	Initial Li in Organic (g/l)	Li in stripped aqueous solution (g/l)	Final Li in Organic (g/l)	% Li Stripped
1	10	2.62	22.72	0.345	86.83
2	8	2.62	18.50	0.304	88.37
3	5	2.62	12.55	0.106	95.94
4	3	2.62	7.90	-0.018	100.67
5	1	2.62	2.60	0.017	99.35
		Initial NH4 in Organic (g/l)	NH4 in stripped aqueous solution (g/l)	Final NH4 in Organic (g/l)	% NH4 CO-stripped
1	10	1.89	1.87	1.71	9.85
2	8	1.89	1.33	1.73	8.81
3	5	1.89	1.22	1.65	12.88
4	3	1.89	0.98	1.56	17.34
5	1	1.89	0.62	1.28	32.51

stripping experiment with the O/A ratio has been repeated 2 more times to see if there are any changes but there were not any leaving more questions than answers. One another anomaly which was noted is that after stripping on opening the centrifuge tube an extreme odour of ammonia was noticed and a higher O/A ratio. Thus the candidate came up with a hypothesis that ammonium that was coextracted in the organic phase may give up one hydrogen ion to form ammonia gas and that the released hydrogen ion may further strip out more lithium. However, this was only a hypothesis.

Hence on discussion with the supervision team, a controlled study was proposed to prove this hypothesis. As it was presumed the presence of ammonium in the extracted organic phase enhanced stripping efficiency, a controlled study with more ammonium and no ammonium in the loaded organic phase would prove this hypothesis. So 2 loaded organics with were prepared with 0.4M HTTA/TOPO:

1. one with the PLS having an initial Li concentration of 1.7 g/l and 0M NH4 concentration

2. and the other with the pls having an initial Li concentration of 1.7 g/l and 2M NH4 concentration

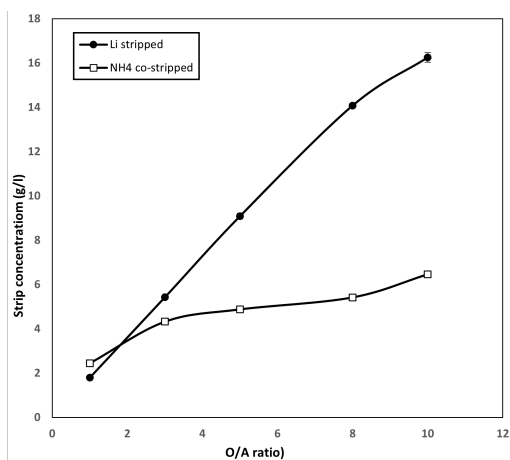The loaded organic of the first PLS with no ammonium had a lithium concentration of 2.7 g/l
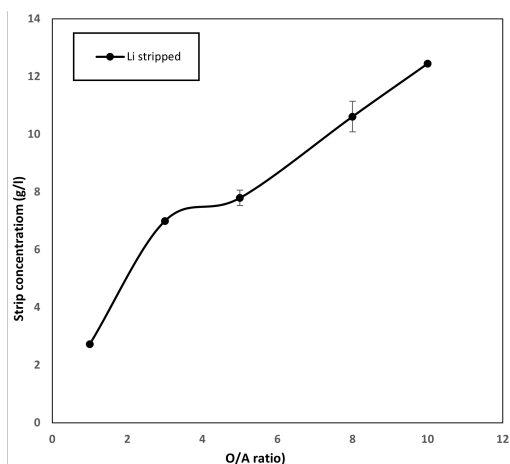
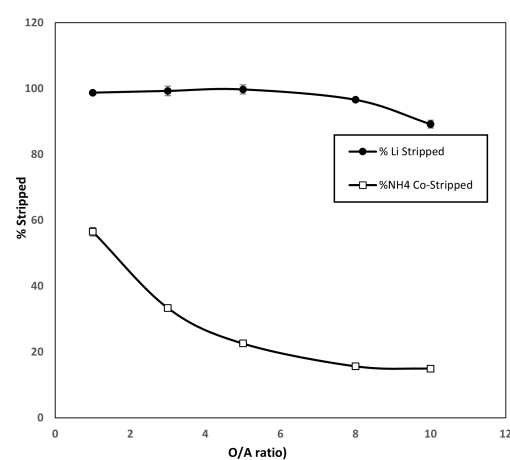(a) Stripped solution concentration
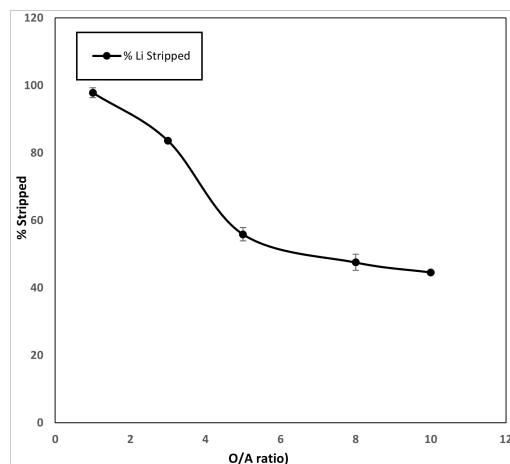
(b) Stripping efficiency

Figure 4.10: Effect of O/A ratio on stripping using 0.5M H_2SO_4 (0M NH_4)

(a) Stripped solution concentration

(b) Stripping efficiency

Figure 4.11: Effect of O/A ratio on stripping using 0.5M H_2SO_4 (2M NH_4)

lithium and the loaded organic with PLS containing 2M ammonium had 1.8 g/l lithium and 4.3 g/l ammonium. The high concentration of ammonium in the initial pls (2M) seemed to have co-extracted more ammonium into the organic phase. The effect of the O/A ratio on stripping with there was no ammonium and 2M ammonium in the initial PLS is shown in Figure 4.10 andFigure 4.11 respectively and the stripping study with a PLS of initial ammonium concentration of 1M was already seen in Figure 4.9. It can be seen from the Figure 4.10 andFigure 4.11, that when there is no loaded ammonium in the organic phase the stripping efficiency starts to decline after O/A ratio of 1 and increasing the ratio to 10 only concentrates the solution upto 12 g/l which is almost half as that of seen before when the loaded organic has ammonium loaded from 1M ammonium concentration PLS. Also seeing the stripping data of organic loaded with 2M ammonium concentration PLS, % of lithium stripped almost remained at 100% until the O/A ratio of 10 and it was able to achieve a strip solution of 16 g/l which is quite more than when no ammonium was present. However in this case more ammonium was co-stripped, this may be because of the very high content of ammonium. This proves the hypothesis put forward to be true.

Thus it was concluded that NH_4^+ releases an H+ ion (which strips out more lithium in addition to the H+ ions from sulphuric acid) to become ammonia gas, the ammonia gas later reacts with the water molecules in the strip solution to form NH_4^+ and OH^- ions. These NH_4^+ ions can further release H+ ions which will further act as a stripping agent. This could be the reason why very less ammonium is co-stripped most of it escapes as ammonia gas giving more hydrogen to be replaced

with lithium. Also, the formation of the OH^- in the strip solution due to the reaction of ammonia with water molecules can be confirmed by measuring the pH of the final strip solution. It can be seen from Figure 4.12, that increasing the O/A ratio increases the pH of the extracted acid strip liquor to 6.5, the increase in OH ions should increase the pH more than 7 but may be due to the buffering effect of Ammonium hydroxide, the pH may remain not increased. Even though these hypotheses were attributed to the control studies, more concrete studies are needed to prove them. However, it is fortunate to come to the conclusion that it is possible to concentrate the strip solution with around 22 g/l of lithium and only 0.5 g/l of ammonium, which can be later precipitated out.
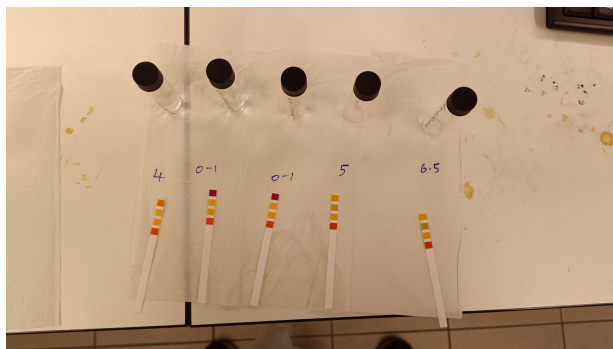

Figure 4.12: pH of the strip solution with increasing O/A ratio

Chapter 5

Conclusion

The whole study starts with the specialization project which was started with a main goal of developing a process that can be easily scaled up. However, the results from the project indicated that more studies are required to understand the principle. Thus this master's thesis is started with the hope of developing a process which would uniformly on most PLS chemistries. The study investigates the extraction of lithium (Li) from a synthetic Pregnant Leach Solution (PLS) with various pH levels and Aqueous to Organic ratios (A/O ratios). Initial observations show that when pH is increased to 10 by adding ammonium hydroxide, the ammonium concentration rises due to the large quantity needed to achieve this pH level, resulting in a drop in Li concentration. Conversely, when pH is reduced by adding sulfuric acid, the initial concentrations of Li and NH4 are less impacted. When analyzing the effects of different pH levels and A/O ratios on extraction, it's discovered that at a pH of 9.5, Li extraction significantly increases to approximately 83% from 40% at pH 9. At the same time, NH4 co-extraction decreases and stays below 4% for all A/O ratios, showing an increase in the selectivity of the HTTA/TOPO system toward Li. However, at pH 10, while most Li is extracted at lower A/O ratios, there is an unintended co-extraction of NH4.

The research finds that adding toluene as a modifier enhances the separation of the extractant phase from the aqueous phase. However, the addition of TBP worsens the phase separation. The maximum loading capacity of the organic phase was also studied, indicating that a 0.4M HTTA/TOPO system can extract Li from two cycles without regeneration. Further investigations to understand the selectivity of the HTTA/TOPO system towards various alkali metals are also discussed.

The research conducted investigated two primary factors affecting the efficiency of lithium extraction: the concentration of sulfuric acid used and the ratio between the lithium-loaded organic phase and the stripping liquor (O/A ratio). For the stripping studies, the loaded organic solution was prepared with approximately 2.6 g/l of lithium and 1.8 g/l of ammonium. When observing the influence of sulfuric acid concentration on the process, an increase in concentration enhanced the stripping efficiency up to 0.5M. Beyond this point, efficiency started to decline and undesirable co-stripping of ammonium increased. The optimal sulfuric acid concentration was determined to be 0.5M, resulting in a stripped solution with 2.58 g/l of lithium and 0.555 g/l of ammonium, deemed suitable for further processing. The second aspect of the study involved altering the O/A ratio. A higher ratio led to the production of highly concentrated lithium strip liquor, a process outcome that enhanced both the economic feasibility and sustainability of the process. It was noted that even when the O/A ratio was increased to 10, the stripping efficiency was still high, at 86%. Remarkably, a lithium concentration of approximately 22 g/l was achieved in the stripped solution, with only minor co-stripping of ammonium (<2 g/l).

However, some intriguing anomalies were observed. Despite the extraction of 22 g/l of lithium, only 0.5 M sulfuric acid, theoretically capable of stripping 6.94 g/l of lithium, was used. Repeated experiments did not resolve this anomaly. A hypothesis was developed that co-extracted ammonium in the organic phase might be contributing to this efficiency by releasing a hydrogen ion that could

strip out more lithium. A controlled study was conducted to test this idea. Two loaded organics were prepared; one with an initial lithium concentration of 1.7 g/l and no ammonium, and another with the same lithium concentration but a 2M ammonium concentration. The study showed that the presence of ammonium in the loaded organic phase significantly increased the stripping efficiency and the final lithium concentration in the stripped solution, thus supporting the initial hypothesis. However, the study also revealed that more ammonium was co-stripped when it was present in high concentrations, suggesting a balance must be struck between ammonium concentration and lithium extraction efficiency. Furthermore, the pH of the final strip solution also increased with the O/A ratio, possibly due to the formation of OH- ions when ammonia reacted with water molecules.

In conclusion, while the study offered promising results, further research is needed to fully understand the underlying mechanisms and to optimize the process. It's nevertheless encouraging that the strip solution can concentrate approximately 22 g/l of lithium and only 0.5 g/l of ammonium, an outcome beneficial for subsequent processing stages.

This thesis was strictly centred on examining the water-based phase and establishing connections with the organic phase. Nonetheless, a comprehensive investigation of the organic phase is essential for answering many of the remaining questions from this study, which can be a promising avenue for future research. Another proposal for advancing the work could involve the utilization of diverse black masses and varied leaching conditions. This can result in the creation of several kinds of PLS, each with unique impurity levels, thereby paving the way for efficient optimization of this process to meet future needs. also, another suggestion is to look more into the stripping phenomenon, why more lithium is being stripped out in comparison with the hydrogen ion concentration from sulphuric acid.

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Appendix A

Additional calculations and data

A.1 Preparing synthetic PLS

1. 1000 ml 1.7 g/l Li^+ solution:
   1.7 g of LiOH in 1000 ml of water

2. 1000 ml 1M NH_4^+ solution:
   0.5M $(NH_4)_2SO_4$ has 1M NH_4^+ ions
   The molecular weight of $(NH_4)_2SO_4$ = 132.14 g/mol
   Therefore,
   $$0.5\frac{mol}{l} * 132.14\frac{g}{l} = 66.07\frac{g}{l}$$

   66.07 g of $(NH_4)_2SO_4$ in 1000 ml of water

1 litre of the PLS can be made by adding 1.7 g of LiOH and 66.07 g of $(NH_4)_2SO_4$ and making up the solution to 1 litre by adding MQ water. Afterwards, Sulphuric acid or ammonium hydroxide solutions are used to alter the pH.

A.2 Preparing stock solutions of HTTA and TOPO

1. 50 ml 0.5 M HTTA solution:
   The molecular weight of HTTA = 222.18 g/mol
   Therefore,
   $$\frac{x}{222.18} = 0.5M * 0.05l$$
   $$x = 5.555g$$

2. 50 ml 0.5 M TOPO solution:
   The molecular weight of TOPO = 386.63 g/mol
   Therefore,
   $$\frac{x}{386.63} = 0.5M * 0.05l$$
   $$x = 9.67g$$

   However, the TOPO used in this study is 90% concentrated. Therefore,

   $$\frac{9.67}{0.9} = 10.74g$$

3. 10 ml solution of 0.2 M HTTA and 0.2 M TOPO from 0.5 M stock solutions
   For HTTA, to achieve $0.5M \rightarrow 0.2M$, the dilution factor is

$$DF = \frac{.05}{0.2} = 2.5$$

To get 10 ml of 0.2 M HTTA,

$$x = \frac{10}{2.5} = 4ml$$

Similarly, for TOPO the dilution factor to achieve a 0.2 M solution from 0.5 M is 2.5. Therefore, to get 10 ml of 0.2 M TOPO,

$$x = \frac{10}{2.5} = 4ml$$

Finally, to achieve an extractant concentration of 0.2 M HTTA and 0.2 M TOPO in a 10 ml solution, 4 ml of 0.5 M HTTA stock solution should be mixed with 0.5 M TOPO stock solution and the remaining 2 ml can be filled with kerosene. In the experiments where the modifiers such as TBP and Toluene are used, the kerosene is simply replaced by them.

A.3 MP-AES dilutions

Let's take a sample to be diluted to a factor of 10, and a 10 ml diluted solution is desired. In this case, 1 ml of the sample is diluted with 9 ml of MQ water to get a total volume of 10 ml.

First, 9 ml of MQ water is added to a centrifuge tube while weighing and let's say it weighs 8.959 g. then 1 ml of sample is added while weighing and let's say the 1 ml sample weighs .994 g. Now using the mass-density relation the exact volume of the dilutions. $\rho_{MQwater}$ (measured experimentally) is 1.0091 g/ml and ρ_{PLS} is .986 g/ml. The densities can be found in Table A.1.

$$\rho = \frac{mass}{volume} \tag{A.1}$$

From Equation A.1, the exact volume of MQ water and sample used is found 8.878 and 1.008 respectively giving a total volume of 9.886.

$$Dilution factor = \frac{Total volume}{Volume of sample} \tag{A.2}$$

From Equation A.2, we can see that the actual dilution factor is 9.806 and not 10. This could lead to huge differences when the dilution factors are high which is more likely in this study.

A.4 Calibration curve for TOC-TN analyzer

No new calibration was made for the TN analyzer as the equipment itself had inbuilt calibration, unlike the MP-AES. The calibration curve is given in Figure A.1

The total ammonium concentration can be interpreted from the total nitrogen concentration as follows: If,
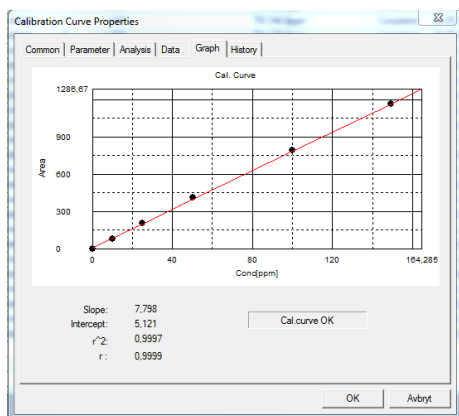Total estimated N = 12.759 g/l
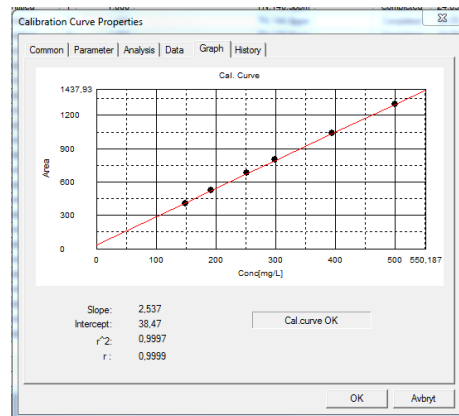MW NH_4 = 18.04 g/mol
MW N = 14 g/mol
Therefore the total ammonium concentration can be estimated by

$$12.759\frac{g}{l} * \frac{18.04\frac{g}{mol}}{14\frac{g}{mol}} = 16.44\frac{g}{l}$$

(a) Calibration curve 0 - 150 ppm

(b) Calibration curve 150 - 500 ppm

Figure A.1: TOC-TN analyzer total nitrogen calibration curve

A.5   Density calculations

The density of all the components used in this study is given in the Table A.1. All the densities are measured manually in the replicates of 3 and the average value is noted down. These densities are used for finding the mass of extractant when the volume is known and finding the exact volume when mass is measured while diluting the samples for MP-AES measurement using the Equation A.1.

Table A.1: Densities of various components used in the study

Solution	Density (g/ml)
PLS	1.02
Kerosene	0.778
0.5 M HTTA	0.852
0.5 M TOPO	0.8307
MQ water	1.0091
0.3 M H2SO4	1.02
0.5 M H2SO4	1.03
0.8-1 M H2SO4	1.05
Toluene	0.87
TBP	0.979
25% NH_4OH	0.88

A.6   SSX study

1. % Recovery:

$$\%Recovery = (\frac{InitialConcentrationofAqueousphase - FinalConcentrationofAqueousphase}{InitialConcentrationofAqueousphase})*100$$

(A.3)

2. Calculating the mass of stock solutions added to attain the desired concentration:
Let's take an example where the A/O ratio is 1, in this case the volume of organics is 10 ml and the PLS is also 10 ml. To prepare an 10 ml organic solution with 0.2 M HTTA and 0.2 M TOPO from 0.5 M stock solutions, 4 ml of 0.5 M HTTA, 4 ml of 0.5 M TOPO and 2 ml of kerosene is needed (Section A.2). The required mass can be found by Equation A.1.

(a) Mass of 4 ml 0.5 M HTTA

$$Mass = 4ml * 0.852g/ml$$
$$Mass = 3.41g$$

(b) Mass of 4 ml 0.5 M TOPO

$$Mass = 4ml * 0.808g/ml$$
$$Mass = 3.23g$$

(c) Mass of 2 ml kersene

$$Mass = 2ml * 0.778g/ml$$
$$Mass = 1.56g$$

(d) Mass of 10 ml PLS

$$Mass = 10ml * 1.02g/ml$$
$$Mass = 10.20g$$

When these masses are known, it was made sure that while adding the required volume of extractant or PLS, slightly more or less amount was added to the system making sure that this mass is constant and thus reducing the room for error. And when a modifier is used, it is also taken into account making very less room for error and thereby enhancing the repeatability.

A.7 Volumes of Organics and aqueous phase used in A/O SSX study

Table A.2: Volumes of organic and aqueous used in A/O study

A/O ratio	Volume of organic phase (ml)	Volume of aqueous phase (ml)
0.2	16.7	3.33
0.3	15	5
1	10	10
3	5	15
5	3.33	16.67

A.8 Effect of pH
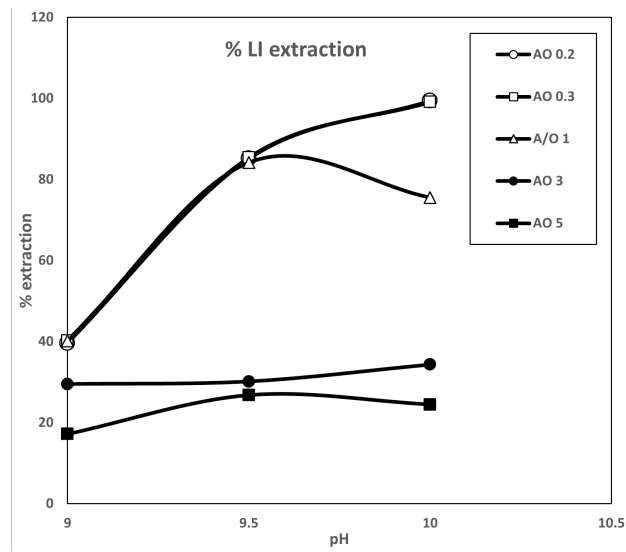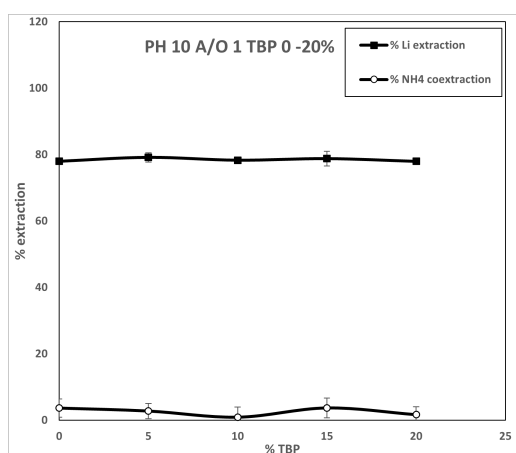

(a) %Li extraction
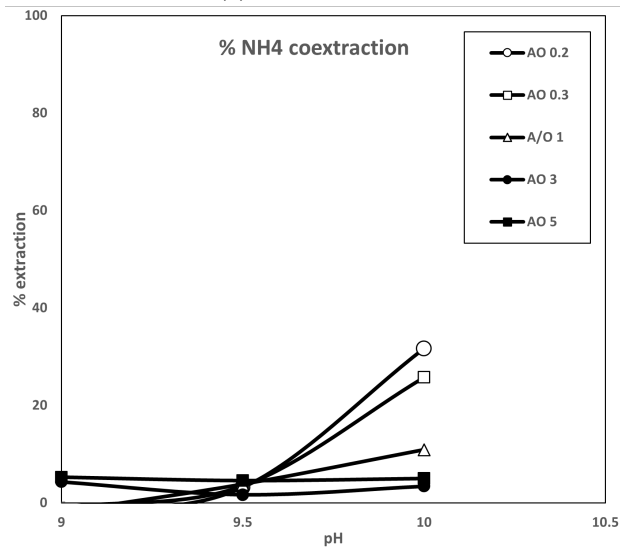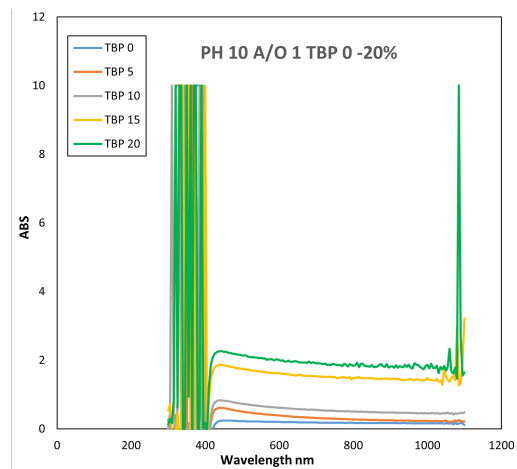

(b) % NH_4 co-extraction

Figure A.2: Effect of pH on different A/O ratio

A.9   Effect of modifier

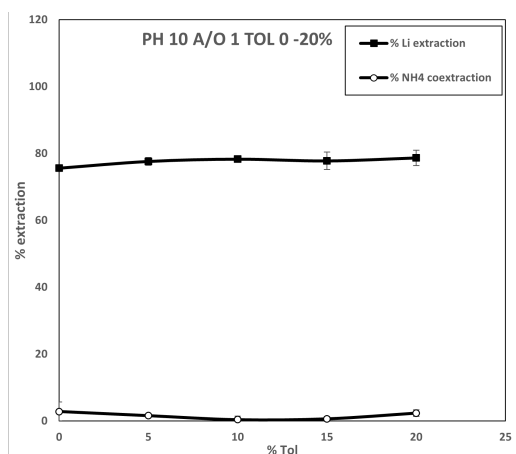The effect of modifiers at a pH of 10 is shown here
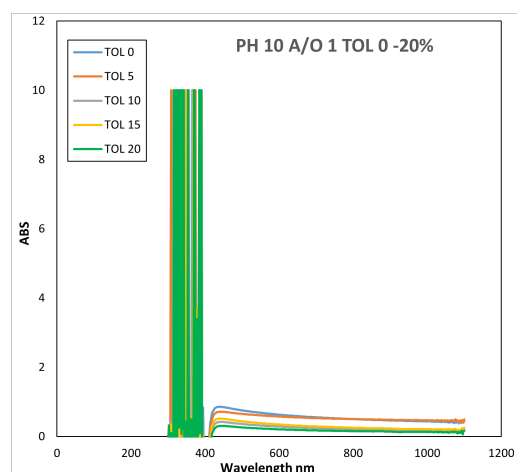

(a) % Extraction

(b) Turbidity using UV-VIS

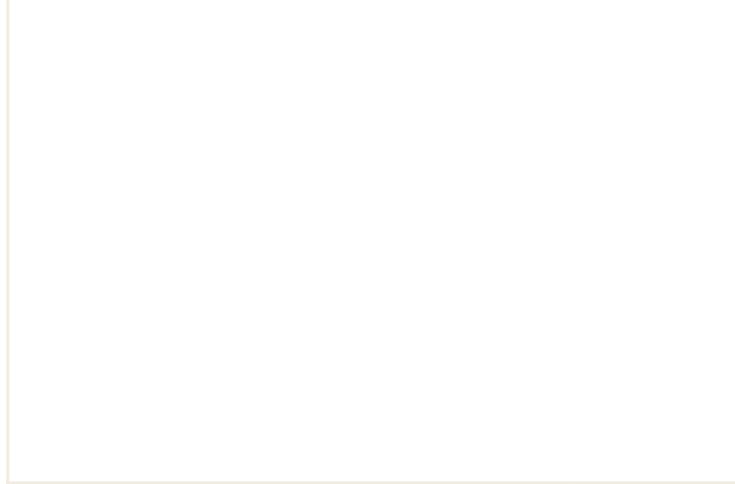Figure A.3: Effect of TBP (0-20%) at pH 10
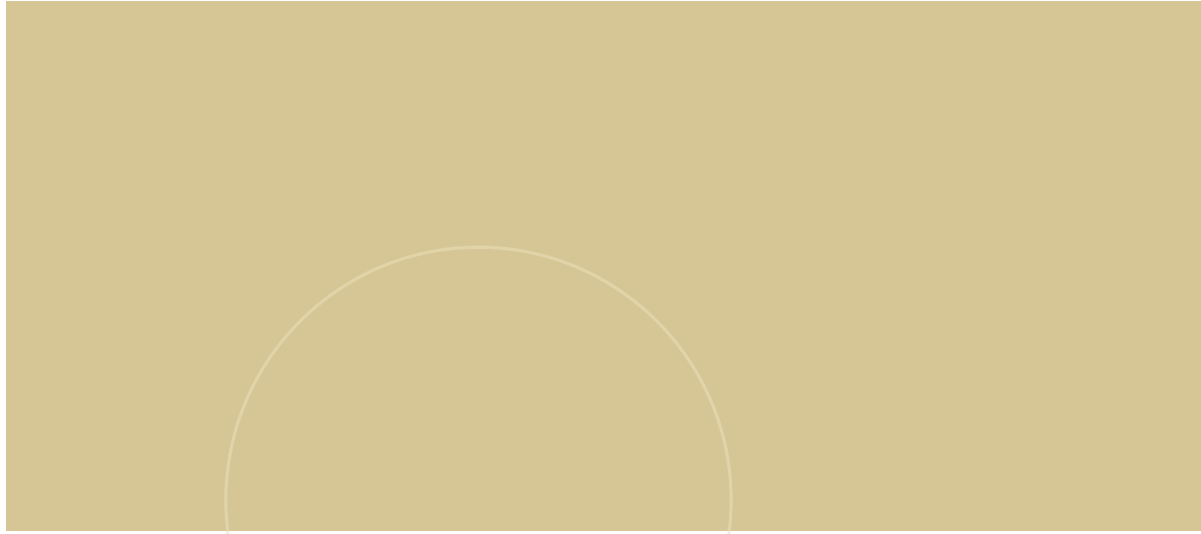

(a) % Extraction

(b) Turbidity using UV-VIS

Figure A.4: Effect of Toluene (0-20%) at pH 10

A.10 Volume of aqueous and organics used in O/A stripping study

Table A.3: volume of organic and aqueous used in O/A stripping study

O/A ratio	Volume of organic phase (ml)	Volume of aqueous phase (ml)
10	18.18	1.82
8	17.78	2.22
5	16.67	3.33
3	15.00	5.00
1	10.00	10.00