THE RECOVERY OF NICKEL, MANGANESE, COBALT, AND LITHIUM FROM SPENT LITHIUM-ION BATTERIES BY CHEMICAL PRECIPITATION

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ABSTRACT

Lithium-ion batteries (LIBs) have increased interest due to their high potential for efficient energy storage and environmental sustainability. Recovering valuable metals from spent Li-ion Batteries has significant environmental and economic benefits and has become an urgent area of research worldwide. This study reports on the recovery of valuable metal composites and compounds using a chemical precipitation process for the recovery of Li-ion batteries, which uses lithium-nickel-manganese-cobalt oxide as the cathode material.

First, the cathode material was leached using 2M H_2SO_4 + 6 vol.% H_2O_2, a 45 g/L S/L ratio and conducting leaching for 2h at a temperature of 40°C. After that, the NMC leachate was adjusted at varying pH levels to precipitate the active metal species (Ni, Mn, and Co) as $Ni_{0.5}Co_{0.2}Mn_{0.3}(OH)_2$ composite micro particles by adding NaOH. The overall recovery efficiency for Ni, Mn, and Co was found to be 96.1%, 95.7%, and 97.1%, respectively. After the $Ni_{0.5}Co_{0.2}Mn_{0.3}(OH)_2$ product was collected by filtration, the Li_2CO_3 residues were obtained by adding Na_2CO_3 to the resultant filtrate. 98% of the Ni, Co and Mn were precipitated in hydroxide form with <1 % impurities. 96% of Li can be recovered respectively in the form of Li_2CO_3 with <1 % of contaminants. The metal elemental composition was analyse by ICP-OES, and the phase composition was analysed through XRD Analysis.

Keywords: *Lithium-ion Batteries; Recovery; Valuable Metals; Chemical Precipitation.*

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1 INTRODUCTION

1.1 Background

Environmental issues and the energy crisis have led to the development of renewable energy and environmentally friendly energy storage systems. Batteries are essential energy storage systems because renewable energy sources like wind, water, and solar are intermittent (Kumar and Jaipal 2022). Energy storage devices are in high demand due to their reliability and efficiency. As a result of their high energy and power density, high cell voltage, wide operating temperature range, and long cycle life, lithium-ion batteries (LIBs) have gained much attention in recent years (Ma et al. 2018).

Li-ion batteries have recently gained widespread recognition as the best power source for vehicles that use alternative fuels, including completely electric battery-powered vehicles that might significantly contribute to the fight against anthropogenic climate change. Due to their excellent performance and energy density, they are currently found in portable electronics like laptops and cell phones (Hawley et al., 2019).

The widespread application of lithium-ion batteries has resulted in an increased need for its production and disposal. Lithium-ion batteries' production, use, and disposal can contribute to severe environmental risks primarily due to hazardous components like heavy metals and electrolytes (Jin et al., 2022). Recycling major components from spent Li-ion batteries is a beneficial way to prevent environmental pollution and alleviate resource shortage and depletion. According to Dewulf et al. (2010), Co and Ni from spent LIBs can be recycled and used again, saving 51.3% of natural resources and reducing the need to extract metals from new mineral sources. Lithium-ion batteries contain valuable metals, such as Co, Mn, and Ni, that could negatively affect the environment. The recovery of the battery's cathode material is crucial to recycling and sustainability (Du et al., 2022).

The recovery of lithium-ion batteries can be attained by various physical and chemical processes. These processes can vary depending on the battery type and chemistry (Sommerville et al., 2020). One approach for recovering valuable metals from lithium-ion batteries is the precipitation method. Chemical precipitation is frequently utilized among these recovery methods, primarily because of its energy-intensive characteristics. The metal salt recovered from the precipitation process includes mixed and single metal hydroxides or a compound containing a single metal salt, such as Li_2CO_3 (Cai et al., 2014; Huang et al., 2016; Zhu et al., 2012). It involves the formation of solid metal compounds by chemical reactions, which are then separated and processed to obtain the desired metal-rich materials. It is straightforward and easily adopted in the industrial setting (Chen et al., 2016).

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1.2 Problem statement

The disposal of LIBs pose a serious threat to both human and environmental health therefore it is necessary to recover all constituents of LIBs, to minimize the accrued damage. The present work focuses on the recovery of Ni, Mn, Co and Li. In light of this, this work focuses on recovery of $NMC(OH)_2$ and Li_2CO_3 through pH and chemical-based precipitation of leached metals in NMC 532 leachate to separate the metals effectively.

1.3 Significance of research

Effective recovery of valuable metals from lithium-ion batteries contributes to a more responsible and environmentally friendly approach to the lifecycle of these essential energy storage devices. The recovered metals can be reused in the production of new lithium-ion batteries. Thus, contributing to reduced costs associated with new material extraction.

1.4 Research questions

- How does the choice of precipitation reagents and conditions impact the efficiency of metal recovery from lithium-ion battery materials?
- What is the optimal pH range for precipitation processes in the recovery of metals from lithium-ion batteries, and how does it affect the purity of recovered materials?

1.5 Research Hypothesis

If the temperature is increased, the recovery rate and efficiency of Nickel, Manganese, and Cobalt will also increase.

1.6 Aims and objectives

The aim is to recover $NMC(OH)_2$ and Li_2CO_3 through pH and chemical-based precipitation of leached metals in NMC 532 leachate to separate the metals effectively. In order to achieve the aim, the following objectives are set:

- To leach NMC 532 cathodes using H_2SO_4 and H_2O_2 to recover the valuable metals.
- To precipitate metal hydroxides at different pH and Temp in order to establish optimal levels of each variable that yields high precipitation efficiency.
- To precipitate Li_2CO_3 at different temperature, Carbonate to Lithium ratio, and pH to establish optimal levels of each variable that yields high precipitation efficiency.

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2 LITERATURE REVIEW

Numerous technologies have been developed for recycling used lithium-ion batteries, including mechanical process, thermal treatment, mechano-chemical process, acid (or base) leaching, bioleaching, solvent extraction, chemical precipitation, and electrochemical processes (Zeng et al., 2014). Generally, LIBs exhibit complex chemistry and structural configurations. Therefore, pre-treatment is applied to disintegrate this complex structure, making downstream resource recovery processes more manageable.

Pre-treatment offers several benefits, including enhanced metal recovery rates, reduced energy consumption, decreased environmental risks, and avoidance of safety hazards. The pre-treatment process consists of five stages, namely (1) sorting, (2) stabilisation/discharge, (3) dismantling/disassembly, (4) grinding/crushing, and (5) separation. The pre-treated materials from spent LIBs, primarily cathodic material, are then advanced to the next step of the recycling process to extract valuable metals.

The process recovery of these valuable metals from spent LIBs commonly employs four methods, including direct recycling and three metallurgical-based techniques: pyro-metallurgy, hydrometallurgy, and bio-hydrometallurgy. Among these, pyro-metallurgy and hydrometallurgy are the primary means for recycling Ni, Co, Mn, and Li from spent LIBs. The efficiency of the pyro-metallurgical method depends on various factors, including processing temperature, residence time, flux addition, and types of purge gas (Makuza et al., 2021). However, despite its industrial viability for large-scale recycling of spent LIBs, pyro-metallurgy exhibits poor performance in Li recovery.

In the hydrometallurgical method (aqueous processing), valuable metals within the cathodic materials are dissolved into a liquid at low temperatures. This is followed by separation and purification to recover these valuable metals (Ali et al., 2022). The three critical steps of the hydrometallurgical method include leaching, precipitation, and solvent extraction. The leaching of NMC materials from cathodic material is conventionally carried out in mediums using inorganic acids, such as H_2SO_4, HCl, and HNO_3, as leaching agents, and H_2O_2 is generally added to convert Ni and Co to higher oxidation state for subsequent recovery by electrochemical, precipitation or solvent extraction techniques (Barik et al., 2017; Xiao et al., 2020). Chemical precipitation is frequently utilised among these recovery methods, primarily because of its energy-intensive characteristics (Tawonezvi et al., 2023). The hydrometallurgical method offers more advantages due to reduced greenhouse gas emissions, such as CO_2, and lower energy consumption (Vasconcelos et al., 2023). Furthermore, hydrometallurgical processing yields highly pure-grade Li.

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2.1 Types of Lithium-ion Battery Chemistry

There are several types of lithium-ion battery chemistry, each with its unique characteristics and applications. Understanding Li-ion cells' chemistry is essential for selecting the most suitable one for an application (Warner 2015). Figure 2-1 shows comparisons of Li-ion battery chemistry performance parameters.

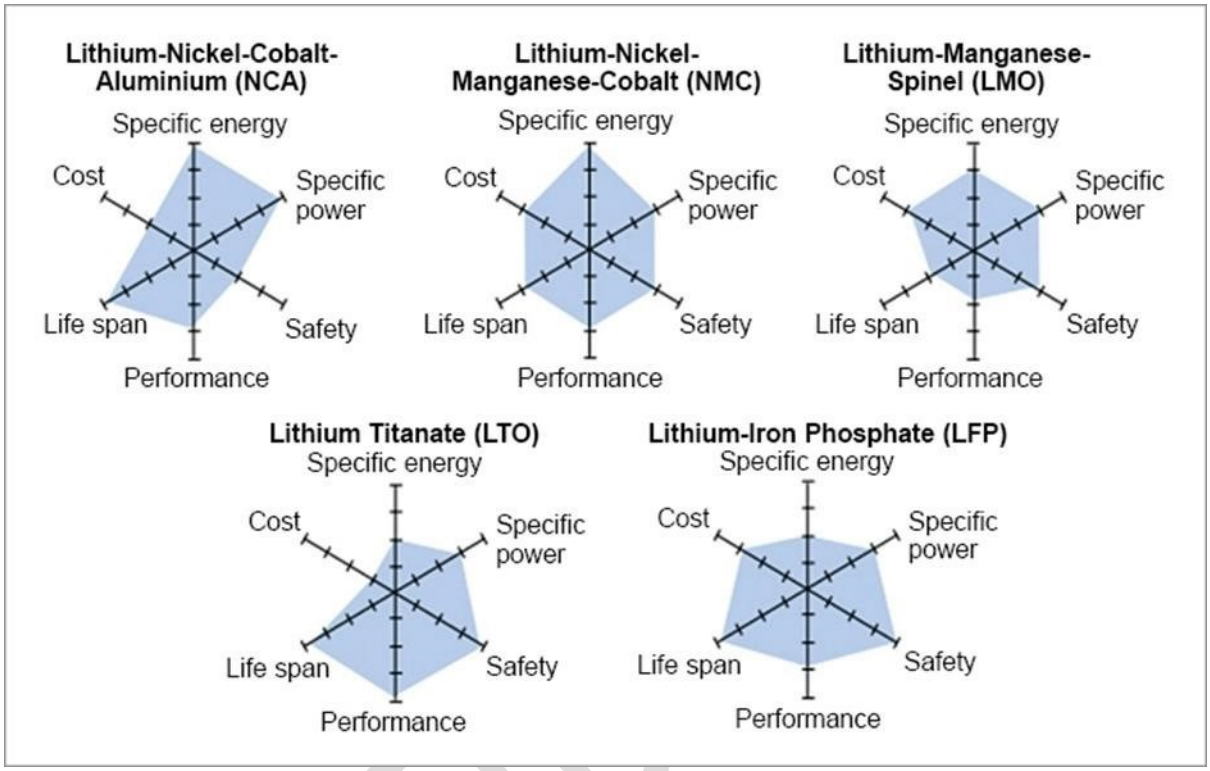

Figure 2-1: Comparisons of LIB chemistry performance parameters (Tsirinomeny et al., 2012).

Each of these lithium-ion battery chemistries has its strengths and weaknesses, and the choice of the most suitable chemistry depends on the application's specific requirements, such as energy density, power capability, cycle life, safety, and cost considerations. As battery technology continues to advance, new chemistries and improvements to existing ones are continuously being explored to meet the demands of various industries and applications (Nitta et al., 2015).

The needs and factors should be contemplated when choosing the appropriate lithium-ion battery chemistry. Important variables such as energy density, power density, safety, cycle life, etc., must be considered when selecting lithium-ion battery chemistry (Rivera-Barrera et al., 2017).

2.2 NMC cathode and its key advantages

NMC cathode is a type of cathode material used in lithium-ion batteries. It is a popular and widely used chemistry due to its balanced combination of performance characteristics. NMC cathodes are used in various applications, including electric vehicles, portable electronics, and grid energy storage systems. It is preferred for lithium-ion batteries due to its balanced combination of several

advantageous properties, making it a versatile and widely used chemistry across various applications (Camargos et al., 2022)

The metal oxides of nickel (Ni), manganese (Mn), and cobalt (Co) are the main components of the NMC cathode. Varying NMC compositions can emerge from varying ratios of these metals, which are commonly written as NMC x: y: z, where x, y, and z stand for the atomic ratios of nickel, manganese, and cobalt, respectively.

The most popular NMC cathode compositions are NMC 111, which contains an equal amount of nickel, manganese, and cobalt; NMC 532, which contains more nickel; and NMC 622, which contains more cobalt. Additionally, variants, such as NMC 811, have a larger nickel content to boost energy density (Jung et al., 2019).

NMC cathodes offer a good balance of energy density and specific capacity, making them suitable for applications where both energy and power requirements are essential. Compared to cathode materials like lithium cobalt oxide ($LiCoO_2$), NMC cathodes generally offer better safety performance, with reduced risk of thermal runaway and other safety-related issues (Peng and Jiang, 2016). The battery can withstand numerous charge-discharge cycles with little to no capacity loss because it gives a relatively extended cycle life. The overall dependability of the lithium-ion battery is increased by the NMC cathodes' excellent chemical and thermal stability while in use. High Rate Capability: NMC cathodes have good high-rate capability, allowing for faster charging and discharging rates, which makes them suited for applications requiring quick power delivery (Das et al., 2023).

While NMC cathodes have many benefits, they are not without limitations. Zhang et al. (2022) state that one of the challenges associated with NMC cathodes is the potential for capacity fade at elevated temperatures or under certain charging conditions. Researchers are continuously working to optimize the composition and improve the performance and safety of NMC cathodes and other lithium-ion battery materials to meet the evolving needs of various applications.

A key component of recycling and sustainability is the recovery of valuable metals from NMC (Nickel Manganese Cobalt) lithium-ion batteries. In order to lessen the demand for raw materials and the environmental effects associated with mining and manufacturing, lithium-ion batteries contain precious minerals such as lithium, cobalt, nickel, and manganese that can be recovered and reused (Chen and Ho 2018).

2.3 Types of Li-ion Battery Recovery Processes

Several types of lithium-ion battery recovery processes aim to recycle and reclaim valuable materials from used batteries. These processes can vary depending on the battery type,

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chemistry, and recycling facility capabilities (Gaines 2018). Some standard LIB recovery processes are shown in Figure 2-2 below.

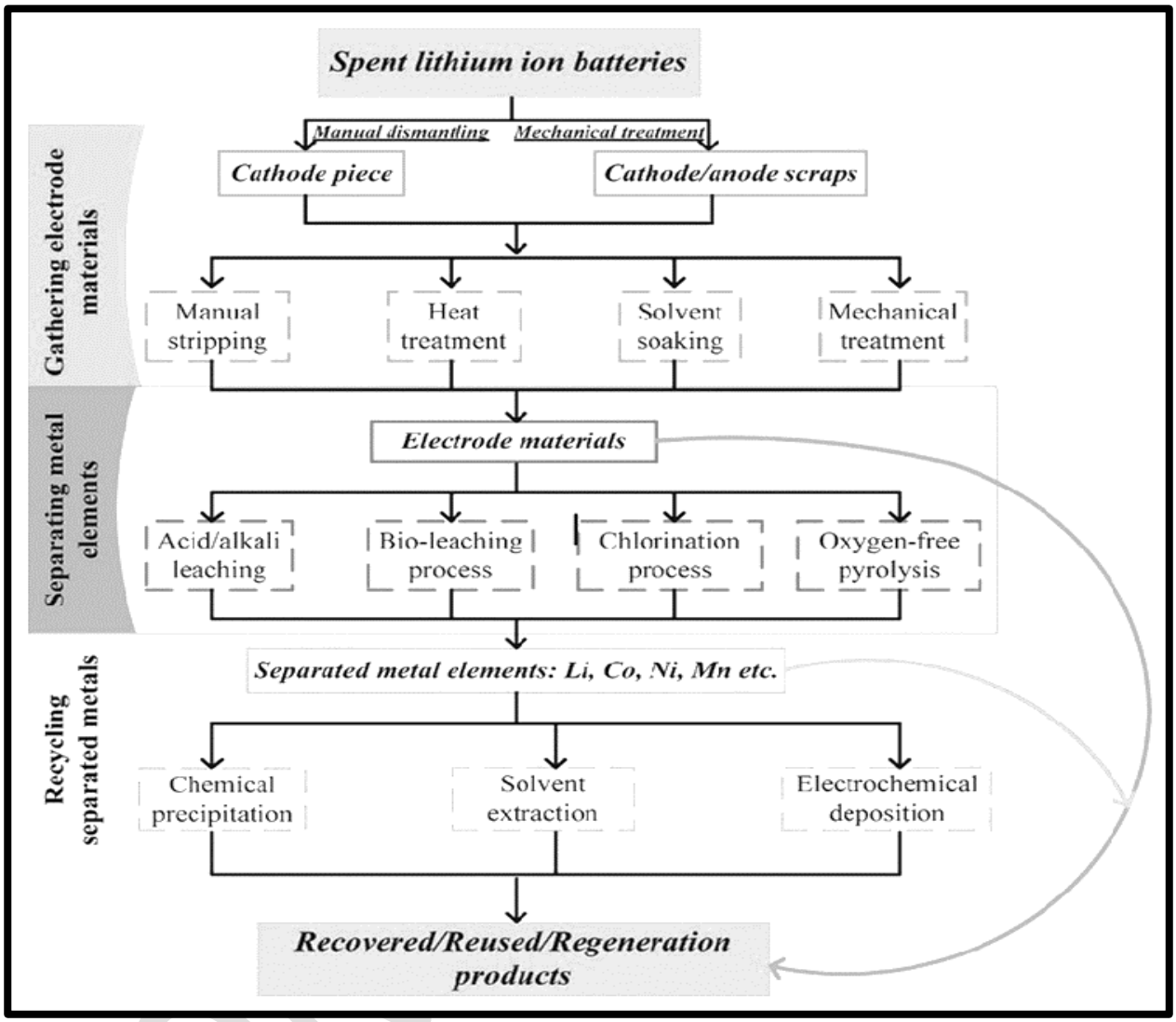

Figure 2-2: Lithium-ion battery recovery processes (Zhao et al., 2021).

According to Neumann et al. (2022), ongoing research and development in battery recycling technologies continue to improve the efficiency and effectiveness of these recovery processes. Proper recycling of lithium-ion batteries is crucial to reduce environmental impact, conserve valuable resources, and promote sustainable practices in the battery industry.

There is no single preferred method for lithium-ion battery recovery that universally applies to all scenarios. The choice of the most suitable method depends on various factors, including the battery chemistry, recycling facility capabilities, local regulations, and the specific materials to be recovered (Samarukha 2022).

2.3.1. Precipitation Process of recovering spent LIB.

At low temperatures, the hydrometallurgical procedure (aqueous processing) dissolves the valuable metals in the cathode materials into a liquid. Separation and purification come next to recover these priceless metals (Biswal and Balasubramanian 2023). The three critical steps of the hydrometallurgical method include leaching, precipitation, and solvent extraction. Inorganic acids like H_2SO_4, HCl, and HNO_3 are typically added to mediums to leach NMC materials from cathodic material, and H_2O_2 is usually added to raise Ni and Co's oxidation state in preparation for recovery using electrochemical, precipitation, or solvent extraction methods later on (Xuang et al., 2021).

The precipitation method is one of the techniques used to recover valuable metals from lithium-ion batteries. It involves the formation of solid metal compounds through chemical reactions, which are then separated and further processed to obtain the desired metal-rich materials. Used lithium-ion batteries are collected and shredded into smaller pieces to increase the surface area and facilitate subsequent chemical reactions. The shredded battery materials undergo a leaching process, where they are treated with acids or other chemical solvents to dissolve and extract valuable metals from the cathode and anode materials. This process generates a leachate containing metal ions. In the precipitation step, a chemical agent or a combination of agents is added to the leachate to induce the formation of solid metal compounds through precipitation. The choice of the precipitating agent depends on the metals to be recovered and their specific properties. After precipitation, the solid metal compounds (Precipitates) are separated from the liquid phase (filtrate) using filtration techniques (Tawonezvi et al., 2023).

The filtrate contains unwanted impurities and can be further treated or processed for environmental compliance. The separated precipitates are then dried to remove excess moisture and obtain solid metal-rich materials suitable for further processing. In some cases, the precipitates may undergo calcination or roasting, where they are heated at controlled temperatures to convert them into more stable metal oxides or other forms, depending on the intended application. The recovered metal-rich materials may undergo additional refining processes to increase their purity and remove any remaining impurities. Depending on the intended application, the recovered metals can be directly reused in the production of new batteries or other products. Alternatively, they may undergo further processing to convert them into the desired form for specific industrial applications.

The precipitation method is just one of several approaches used in lithium-ion battery recycling. The choice of the most suitable method depends on factors such as the specific battery chemistry, recycling facility capabilities, and the desired output materials. As battery recycling technology continues to advance, researchers and industries are continuously exploring and

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optimizing various recovery methods to improve the efficiency and sustainability of the recycling process.

Recovering metals from lithium-ion batteries presents several challenges, which can impact the recycling process's efficiency, cost-effectiveness, and environmental sustainability (Xiao et al., 2019).

Lithium-ion batteries come in various chemistries, sizes, and designs, making it challenging to develop a one-size-fits-all recycling process. Each battery type may require different recovery methods, adding complexity to the recycling process. Lithium-ion batteries can be hazardous if mishandled during the recycling process. They may contain flammable electrolytes or be in a state of charge that increases the risk of thermal runaway or fire. Proper safety protocols and handling are essential to mitigate these risks. The availability of recycling facilities and appropriate technologies may be limited in some regions, making it challenging to scale up the recycling efforts to match the growing volume of used lithium-ion batteries.

Mishra et al., (2022) state that efficiently separating valuable metals from other battery components and impurities is crucial for high-quality recycling. Some recovery processes may require multiple steps and advanced technologies to achieve adequate separation.

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3 MATERIALS AND METHODS

3.1 Materials

The spent Li-ion batteries (NMC 532) cathode material was sourced from our in-house lab (ESIL, South Africa). All reagents used here were analytical grade, and solutions were prepared with deionized water. Sodium hydroxide (98 %, Kimix, South Africa), sulphuric acid (98 % from Alfa Aesar, USA), hydrogen peroxide (50%, Kimix, South Africa) and sodium carbonate (98 %, Sigma Aldrich, USA) were purchased and used without further purification.

3.2 Leaching process

Acid leaching for spent lithium-ion batteries was carried out in a 1000mL beaker using Sulphuric acid and hydrogen peroxide. After adding 52.8g of the NMC powder, as shown in Figure 3-1 below, the mixture was heated at 40˚C fixed at 300rpm for 3h with a liquid/solid mass ratio of 45. After leaching, the solution was then precipitated.

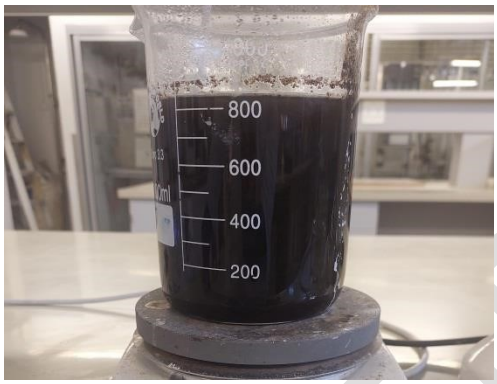

Figure 3-1: Leaching solution.

3.3 Precipitation process

The recovery and separation process of the valuable metals from spent NMC cathode material was achieved by a two-step precipitation method. After filtration, the pH of the leachate solution was adjusted from pH 5.5 to pH 13 using 10 M NaOH solution to precipitate Mn, Co, and Ni. The following operating variables were explored: pH (1, 3, 5, 6, 7, 8, 9, 10, 11, 12, 13 and 14) and temperature (20 and 40°C). During precipitation, aliquots of liquid samples were taken periodically (at every experimental variant) to determine the metal content for elemental analysis. The supernatant liquid was filtered, the residue was hot air dried, and the $Ni_xMn_yCo_z(OH)_2$ composite material was obtained and stored for ICP analysis.

Recovered metals are precipitated and filtered from the leaching solution at varying pH using NaOH solution. Different stages of leachate are illustrated in Figure 3-2 below.

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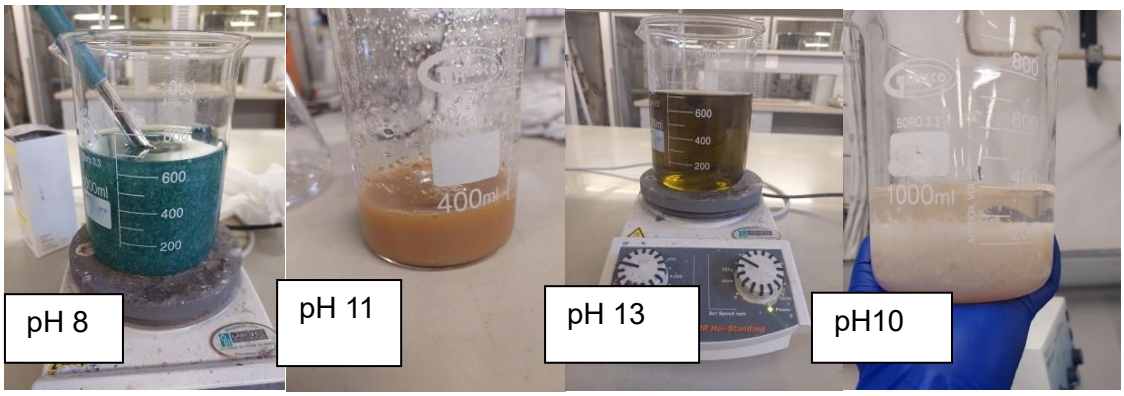

Figure 3-2: Images of leachate at different pH levels.

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4 RESULTS AND DISCUSSION

4.1 Effect of H_2O_2 Concentration and S/L Ratio on the Leaching Recovery Efficiency.

In the first step, the effect of H_2O_2 concentration on the leaching recovery efficiency of the spent cathode active materials was investigated. The spent $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ material was leached with 3 M H_2SO_4 acid solution at an S/L ratio of 50 g/L and a speed of 350 rpm. In addition, the temperature was maintained at 70°C, and the leaching time was 3h during the metal leaching process. The results (Figure 4-1) indicate that the concentration of H_2O_2 increases proportionally with leaching recovery efficiency.

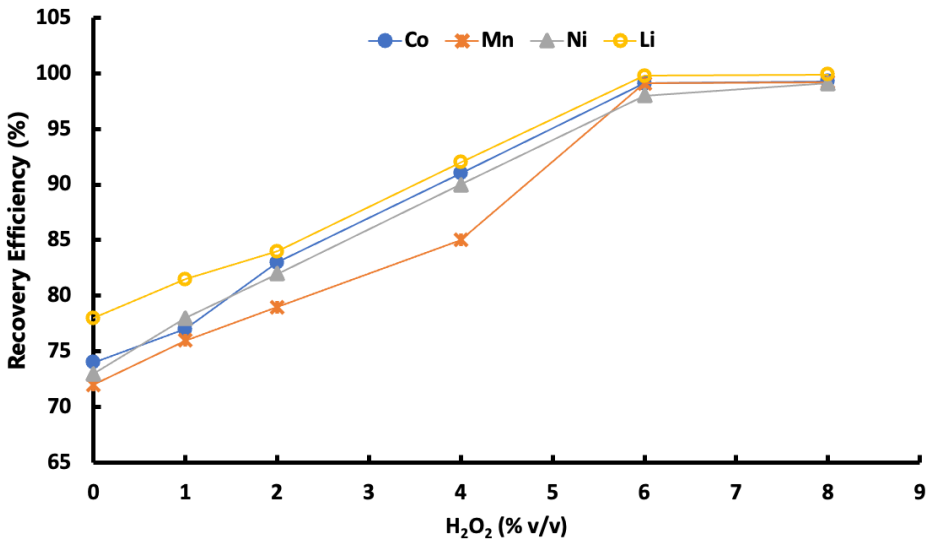

Figure 4-1: Effect of H_2O_2 concentration on leaching recovery efficiency (H_2SO_4 =3M, Time=3h, S/L=25 g/L, T=70 °C, IS=350 rpm).

In the absence of H_2O_2, the leaching efficiency of the spent $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ was 74%, 69%, 71%, and 64% for Li, Co, Ni, and Mn, respectively. This relatively high leaching recovery efficiency can be attributed to the fact that Li^+, Ni^{2+}, and Co^{2+} ions can be readily and effectively leached in the mere contact presence of the H+ protons from the acid leachate through reductive leaching while Ni^{3+}, Ni^{4+}, Co^{3+}, and Mn^{4+} ions require a reductant to convert them to more stable M^{2+} (M=> Co, Li, Mn and Ni) ionic form. The addition of H_2O_2 effectuated an increase in the leaching recovery efficiency, which consequently increased remarkably and reached above 95 % for all (Li, Ni and Co), excluding Mn (91 %) when the H_2O_2 content was 6 vol.%. The leaching efficiency did not exhibit any significant variation when the concentration of H_2O_2 was further increased to 8%. The oxidant H_2O_2 can disintegrate at high temperatures because of its low thermal stability.

A higher solid-to-liquid (S/L) ratio is typically preferred to produce the best leaching results because it increases the leaching process's recovery effectiveness. The solid/liquid ratio (S/L) varied from 30 to 90 g/L, and its respective effect on the leaching recovery efficiency of Co, Ni,

Mn, and Li was studied under experimental conditions of 75°C, 3 M H_2SO_4, 3h leaching reaction time and a speed of 350 rpm. As shown in Figure 4-2, Li, Co, Ni, and Mn leaching recovery efficiencies decrease negligibly as the S/L ratio increases and then drop sharply after the 75 g/L S/L ratio. At an S/L ratio of 75 g/L, more than 97% of the Li, 94% of the Co, 95% of the Ni, and 90% of the Mn was leached.

The leaching recovery efficiency dramatically dropped when the S/L ratio went above 75 g/L. At a low S/L ratio, more acid leachate molecules surround solid molecules during leaching. Therefore, the recovery efficiency will be higher when there is a higher S/L ratio; in this case, the solid becomes the limiting reagent, resulting in reduced recovery efficiency. With time, the increase in leaching recovery efficiency is due to increased collisions between solid material sub-particles and oxidant H^+ ions from the acid leachate. However, a further increase will not affect the leaching reaction kinetics when the solid concentration exceeds the saturation concentration point. The ideal solid/liquid ratio was consequently identified to be 75 g/L after accounting for chemical consumption and leaching recovery efficiency.

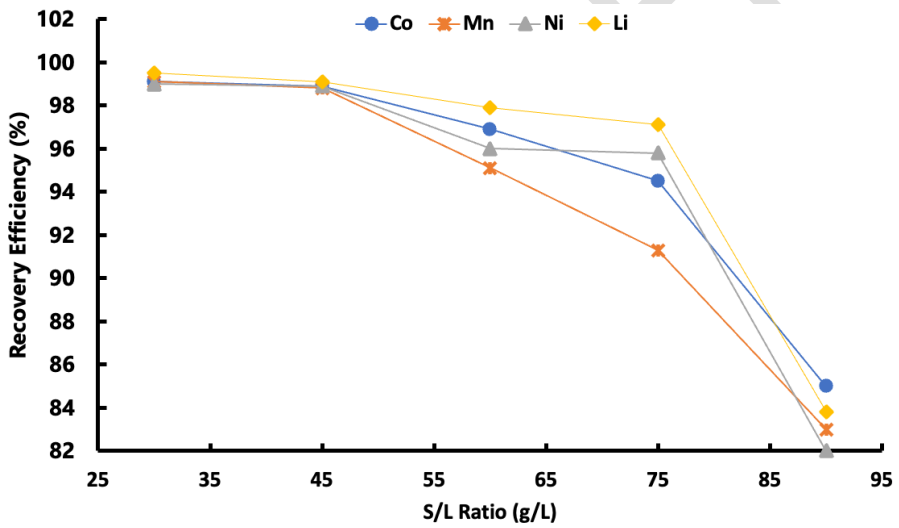

Figure 4-2: Effect of solid-to-liquid ratio on the leaching recovery efficiency (H_2SO_4=3 M, t=3h, T=75°C, IS=350 rpm).

4.2 Effect of H_2SO_4 Acid Concentration on Leaching Recovery Efficiency

The effect of H_2SO_4 acid concentration on the leaching recovery efficiency was studied under the following conditions: S/L ratio of 75 g/L, leaching reaction time of 3h speed of 350 rpm, and reaction temperature of 75°C. As depicted in Figure 4-3 the leaching recovery efficiencies of various metals (Li, Ni, Mn, and Co) demonstrated a positive correlative trend with increasing H_2SO_4 acid concentration from 0.5 M to 2 M. At 2 M H_2SO_4 concentration leaching process achieved satisfactory recovery efficiencies of over 96.8% for lithium, 94.7% for cobalt, 95.8% for

nickel, and 91.3% for manganese. Leaching recovery efficiency increased significantly as the H_2SO_4 acid concentration increased from 0.5 M to 1 M, and then gradually increased 1-2 M. Further increase of the H_2SO_4 acid concentration (at over 2 M) does not effectuate any significant increase in leaching recovery efficiency. The increase in leaching efficiency is due to increased collisions between solid material sub-particles and oxidant H^+ ions from the acid leachate. However, when the oxidant H^+ ions concentration exceeds the saturation concentration point, further increase of the acid concentration will not affect the leaching reaction kinetics. Hence, the optimal H_2SO_4 acid concentration for the leaching process is restrained at 2 M after considering both chemical consumption and leaching recovery efficiency.

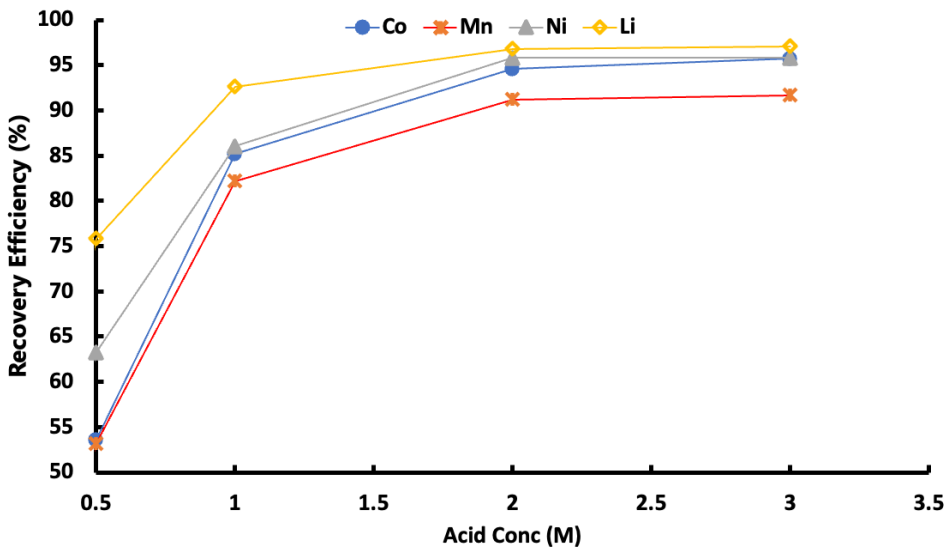

Figure 4-3: Effect of H_2SO_4 acid concentration on leaching recovery efficiency (t=3h, S: L=75 g/L, T=75°C, IS=350 rpm).

4.3 Effect of leaching Reaction time on Leaching Recovery Efficiency

The effect of leaching reaction time (0-3h) on the leaching of Co, Ni, Mn, and Li was examined using specific constant conditions: H_2SO_4 acid concentration of 2 M, solid-to-liquid (S/L) ratio of 75 g/L, reaction temperature of 75°C, and a speed of 350 rpm. As illustrated in Figure 4-4, the leaching reaction time significantly affects the leaching recovery efficiency for all the metals leached. The leaching recovery efficiencies of Co, Li, Ni, and Mn substantially increased by about 41%, 21%, 36%, and 62% when the leaching reaction time was increased from 15 to 180 min. The effect was attributed to the facts that with the increase in the leaching time, a greater and greater surface area of the unreacted particle cores collide and react with the oxidant H^+ ions from the sulphuric acid leachate. The most significant increase in leaching efficiency per unit of time was apparent in the first 30 min. As the reaction proceeded at times more than 30 minutes, the leaching recovery efficiency-time slope became less steep. The leaching recovery efficiency

peaked at 2h, with efficiencies of over 97%, 96%, 96%, and 95 % for Li, Co, Ni, and Mn, respectively. Thereafter, the recovery efficiency remained relatively stable without significant changes. Consequently, a 2h leaching reaction was identified as the optimal leaching time.

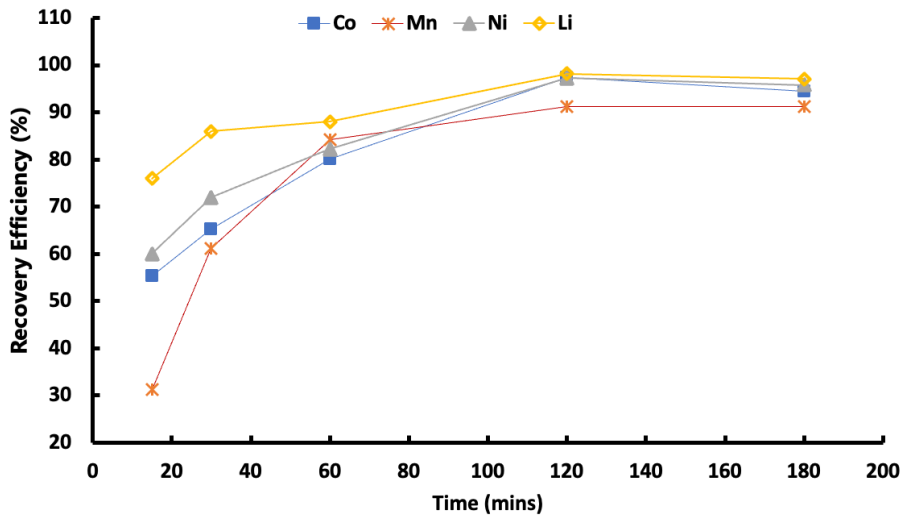

Figure 4-4: Effect of time on leaching recovery efficiency (H2SO4 =2M, S/L=75 g/L, T=70°C, IS=350 rpm).

4.4 Effect of Leaching Temperature on Leaching Recovery Efficiency

The effect of the temperature on the leaching recovery efficiency is illustrated in Figure 4-5. The leaching recovery efficiency increased with the increasing temperature due to the significant kinetic effect temperature has on the metal leaching reaction. The increase in temperature increases the ionic, electronic and molecular movement frequency and leaching chemical reaction rate, thus accelerating the ion migration and diffusion and mass transfer rate in the metal-leaching system and ultimately favouring the metal-leaching kinetic process.

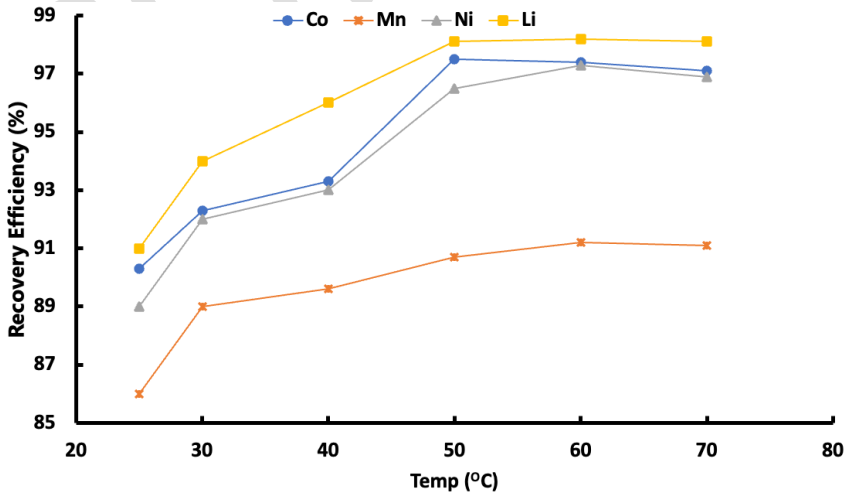

Figure 4-5: Effect of temperature on leaching recovery efficiency (H_2SO_4 =2M, S/L=75 g/L, Time=2h, IS=350 rpm).

In light of the discussion above, the optimal conditions for leaching Co, Ni, Mn, and Li from waste $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ can be determined. Through the utilization of leachate solutions comprising 2M H_2SO_4 + 6 vol.% H_2O_2, and a 75 g/L S/L ratio, and conducting leaching for 2h at a temperature of 60°C, peak leaching recovery efficiency of 98.1% for Li, 97.1% for Co, 96.1% for Ni, and 95.7% for Mn can be attained as shown in Table 4-1. The maximum metal recovery that was attained is $0.595_{total\ metal}/_{cathode}$.

Table 4-1: Leaching yields obtained using a 75 g/L S/L, 2M H_2SO_4 + 6 H_2O_2 v/v% solutions at 60°C for 2h.

Element	**[g/L]**	**Extraction [%]**
Li	4.98	98.9
Ni	19.94	96.9
Co	8.214	97.1
Mn	11.59	95.7

The effects of temperature and pH on the precipitation efficiency of Co, Li, Ni and Mn were investigated. The experiment results illustrated in Figure 4-6 indicate that pH and temperature significantly affect the precipitation process. The recovery rate and efficiency of Ni, Mn and Co decreased with temperature (from 20 to 40ºC). This phenomenon was caused by the correlation between the formation of $Ni_{0.5}Mn_{0.3}Co_{0.2}OH_2$ and its respective solubility with temperature. Since the precipitation of $Ni_{0.5}Mn_{0.3}Co_{0.2}OH_2$ is an exothermic process, the increase in temperature facilitated the reverse reaction of the precipitation of $Ni_{0.5}Mn_{0.3}Co_{0.2}OH_2$, resulting in the decrease in the recovery rate of Co, Mn and Ni. On the other hand, the increase in temperature also increases the solubility of the precipitated metal oxides effectuating a decrease in the metal recovery rate.

When the temperature was low (20 °C), the precipitation was favoured. Therefore, with the increase in temperature from 20°C to 40°C, the recovery efficiency of Co, Li, and Mn decreased from over 99.2% to an approximate value of 84.5% at the pH of 13.5. With further increasing the reaction temperature (to 40 °C), precipitate dissolution eventually becomes the prevailing factor, effectuating the decrease in the recovery rate of Ni, Co and Mn at a higher reaction temperature.

a]

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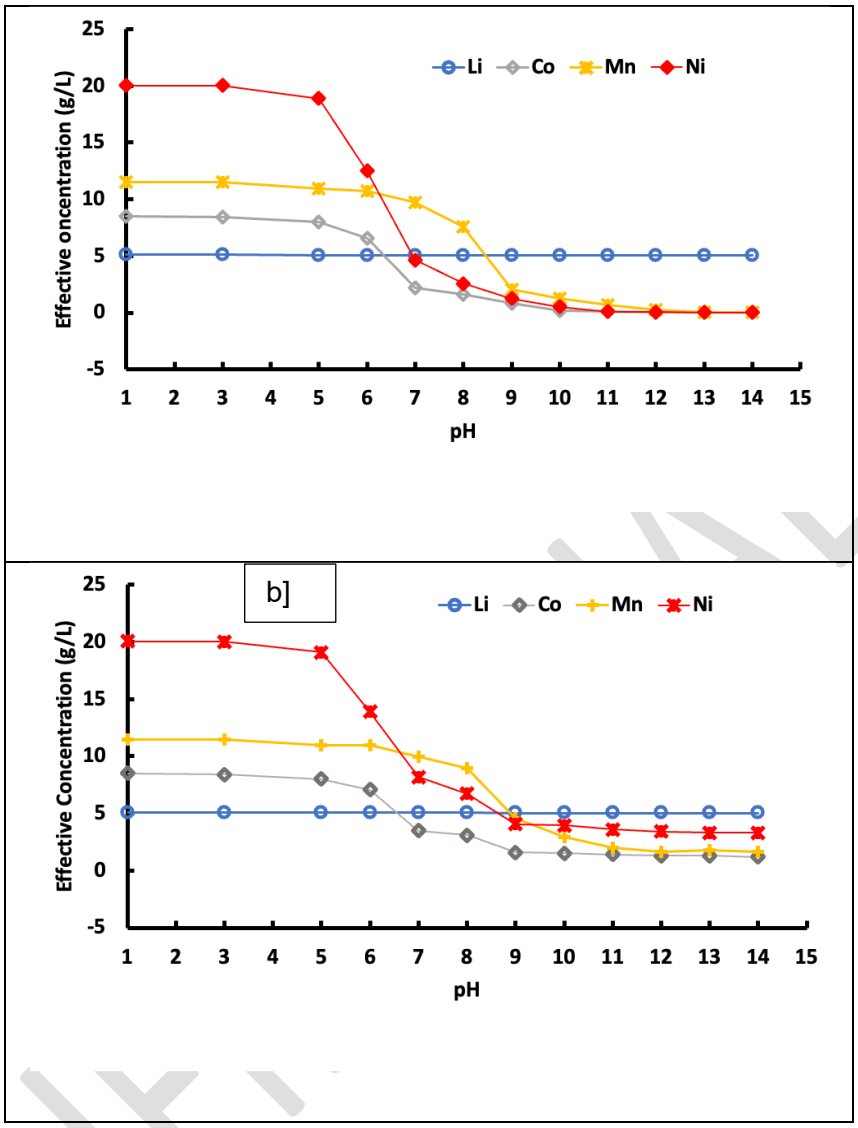

Figure 4-6: Concentration of the NMC metal at different pH levels (a) Temperature=20°C b) Temperature=40°C.

When the pH value was low (less than 4), the increase in equilibrium pH exhibited a negligible effect on the Li, Ni and Mn in the leachate solution, as indicated in Figure 4-6(b). From Figure 4-6(b), the precipitation rate of Ni and Co rapidly increases (from pH=5 to 7) and suddenly, gradually decreases (after 7) with the equilibrium pH. The precipitation of Mn also exhibited a similar trend of rapid initial increase (from pH= 7-10) and then sudden decrease (after pH=10) with the equilibrium pH.

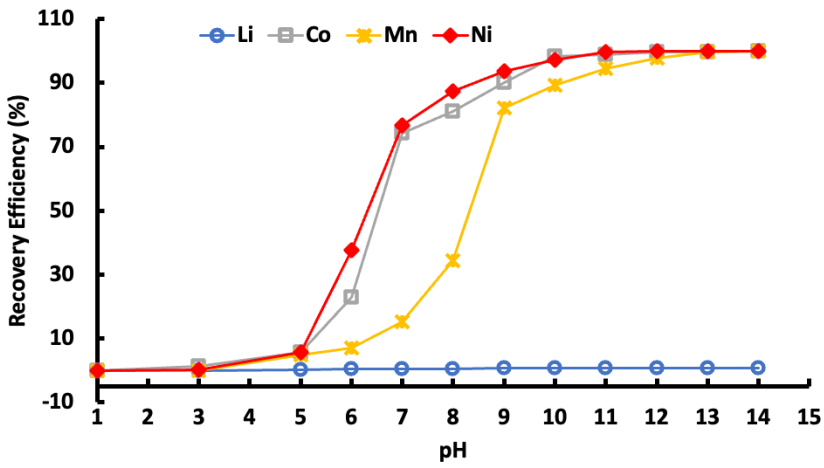

Figure 4-7: Recovery efficiency of the NMC metals at different pH levels (Temp=20°C).

Most metal ion in the typical spent NMC solution can be precipitated by OH^-, while Li cannot. Li(OH) cannot be precipitated due to its respective higher solubility (higher Ksp) at any pH level. Mn, Ni and Li can precipitate at different pH levels because of their separate saturation point, the point at which the concentration of the respective metal ions (Mn^{2+}, Ni^{2+}, or Co^{2+}) and hydroxide ions (OH^-) in the solution reaches a level where the compound starts to precipitate and form a solid phase, can be reached before pH level of 14. It is worth noting that the precipitation behaviour of Li, Ni, Mn and Co depends on their respective solubility products and the pH-dependent formation of hydroxide or other complex ions (Chen et al., 2022; Entwistle et al., 2022; Zhu et al., 2012).

$Mn(OH)_2$ has the highest Ksp value among these three compounds, indicating relatively higher solubility in water. This means that $Mn(OH)_2$ requires a higher concentration of Mn^{2+} and OH^- ions (higher pH) than Ni^{2+} and Co^{2+} in the solution before it reaches its saturation point and begins to precipitate. As shown in Figure 4-7, the precipitation efficiency of Li, Ni and Co metal ions increased with pH, while that of Li did not change. Significant amounts of Ni^{2+} and Co^{2+} ions and small amounts of Mn^{2+} were precipitated as the pH increased from 5.5 to 7, and Mn^{2+} ions were also precipitated completely when the pH rose to 12. The Ni, Mn and Co metal ions were removed effectively (about 99%), and a low-level loss of Li (4%) was obtained when the solution pH value was maintained around 13.5.

The results demonstrate the proposed method as a highly efficient and stable $Ni_{0.5}Mn_{0.3}Co_{0.2}(OH)_2$ precipitation recovery method. Based on the experiment results above, the optimum condition of recovering $Ni_{0.5}Mn_{0.3}Co_{0.2}(OH)_2$ is determined as follows: the optimum

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equilibrium pH is 13.5, temperature is 20°C, reaction time is 60 min, and agitation speed is 300 rpm.

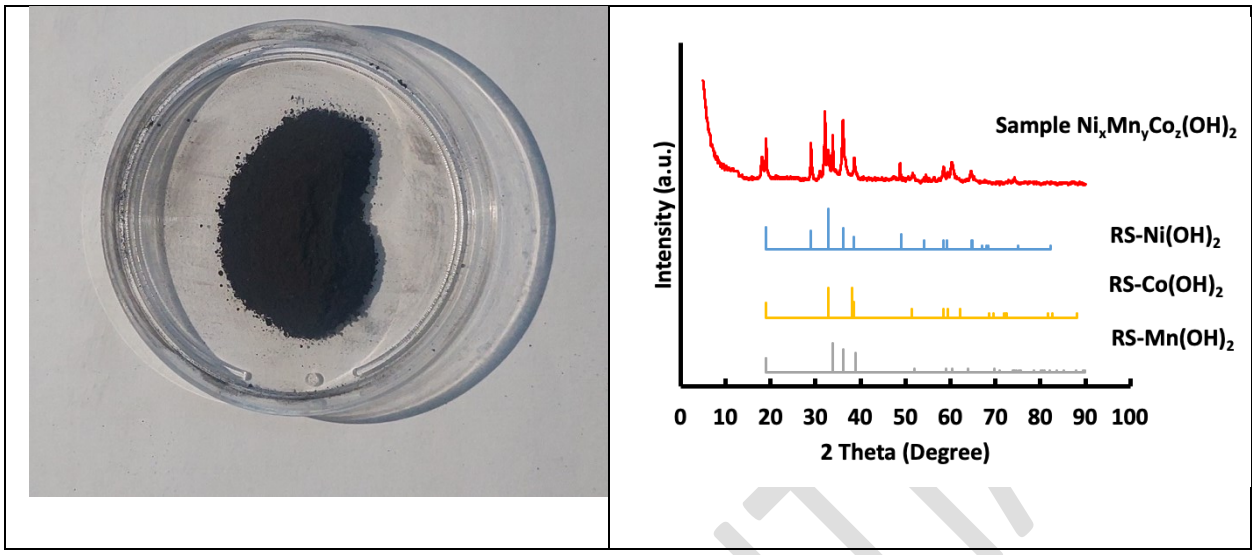

Figure 4-8: Photo (a) and XRD pattern (b) of products of Ni0.5Mn0.3Co0.2OH2 obtained by precipitation.

The XRD pattern of $NMC(OH)_2$ powder phase is shown in Figure 4-8, which confirms the presence of Ni(OH)2, $Mn(OH)_2$ and $Co(OH)_2$ phases in the precipitate. Table 4-2 lists the elemental composition of the product. It is shown that about 99.9 % Ni, Co and Mn were deposited as their respective hydroxides with less than 0.5% impurities. Lithium was not detected in samples.

Table 4-2: Elemental composition analysis of Li, Co, Mn and Ni Hydroxide composites after co-precipitation.

Element	Composition (%) Before Co-PPT	Composition [%] After Co-PPT (pH 13.5)
Li	11.1	0.0
Ni	55.8	63.1
Co	18.4	20.7
Mn	25.9	29.3

4.5 Co-Precipitation of Li_2CO_3

After NMC has been recovered, the precipitate of lithium carbonate was precipitated by adding an excess amount of Na_2CO_3 in the remaining filtrate.

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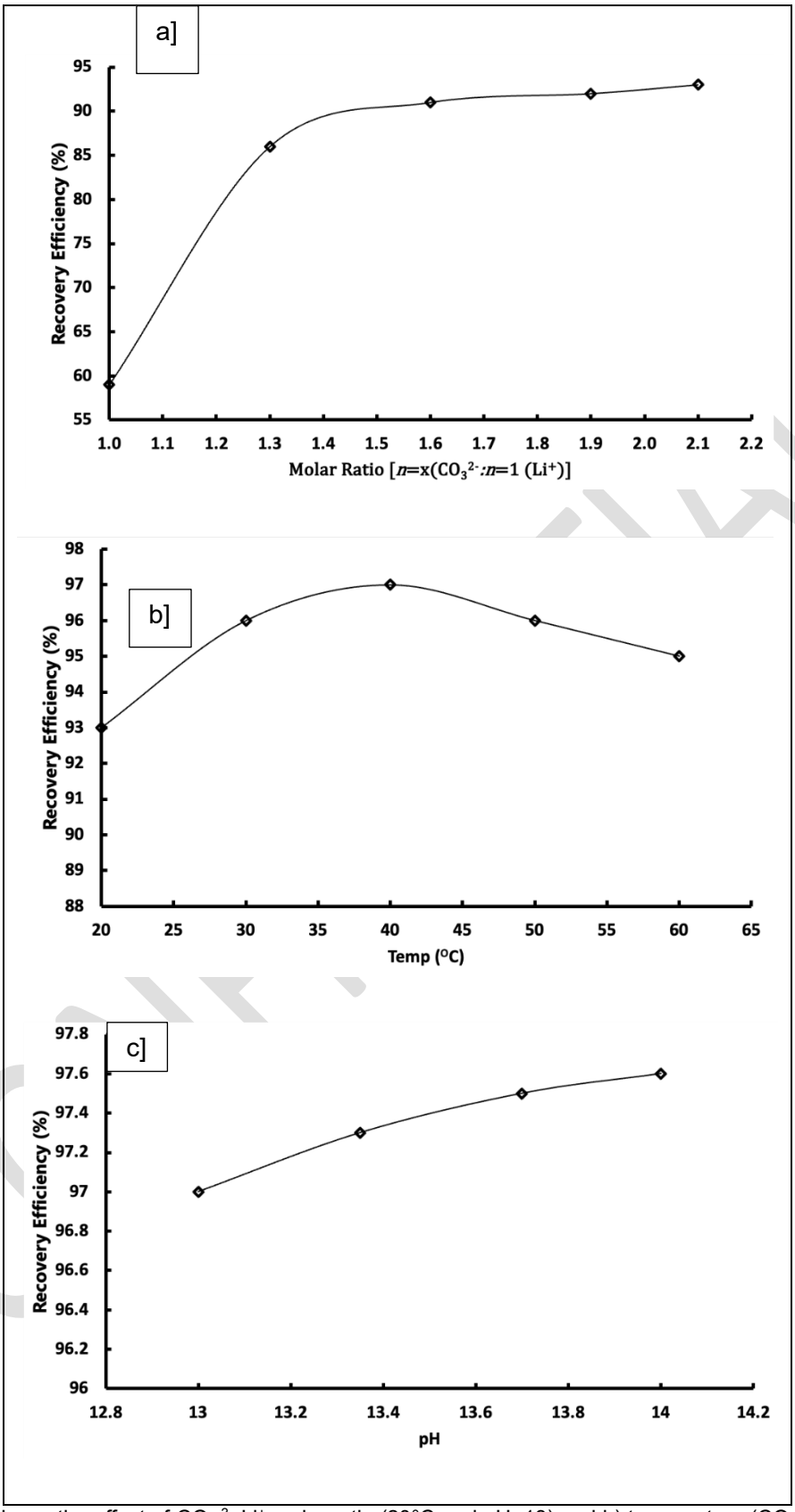

Figure 4-9: (a) shows the effect of CO_2^{-3}: Li^+ molar ratio (20°C and pH=13) and b) temperature (CO_2^{-3}: Li^+ molar ratio of 1.5:1.0 and pH=13) and c) pH on Li+ recovery efficiency (CO_2^{-3}: Li+ molar ratio of 1.5:1.0 and 40°C).

Figure 4-9 (a) shows that the Li-recovery rate increased from 59 % to 85 % with molar ratio of Na_2CO_3 to Li^+ increased from 1.0:1.0 to 1.3:1.0. With a further increase in molar ratio of Na_2CO_3 to Li^+ from 1.3:1.0 to 1.6:1.0, the Li recovery efficiency did not increase markedly. Similar to the formation of NMC532, the precipitation of Li_2CO_3 is also an exothermic reaction; therefore, increasing the temperature is negligibly beneficial to the precipitation of Li_2CO_3 and inadvertently favours the dissolution of precipitated Li_2CO_3 in the solution (Song and Zhao, 2018). Figure 4-9(b) shows that the precipitation of Li_2CO_3 reaction was favoured at the condition of temperature lower than 40°C, resulting in a significant increase in the Li recovery rate with the temperature. When the reaction temperature was raised to 40°C, the dissolution of precipitated Li_2CO_3 turned out to be in equilibrium with the formation of Li_2CO_3, and the recovery rate of Li showed negligible change with the increase in temperature.

Since CO_3^{2-} ions (from Na_2CO_3) can easily combine with H^+ to form HCO_3^-, the reduction of H^+ is beneficial to the precipitation of Li_2CO_3, i.e., the Li^+ recovery rate showed a slight increase with the increase in equilibrium pH (from 13 to 14) since there is little to no H^+ at higher pH values. Meanwhile, increasing Li_2CO_3 precipitated in solution can enhance its dissolution. Therefore, when the equilibrium pH was increased to a certain value (about pH 13.5) in Figure 4-9(c), the precipitation of Li_2CO_3 turned to be in equilibrium with its dissolution. Consequently, the Li^- -recovery rate did not increase significantly with the pH. From the description above, the optimum condition of recovering Li_2CO_3 is as follows: the molar ratio of Na_2CO_3 to Li^+ is 1.6:1.0, equilibrium pH is 13.5, temperature is 40 °C, Li^+ concentration is 4.75 g/L, reaction time is 1 h, and agitation speed is 500 rpm. The crystalline Li_2CO_3 phase is clearly identified by XRD analysis shown in Figure 4-10.

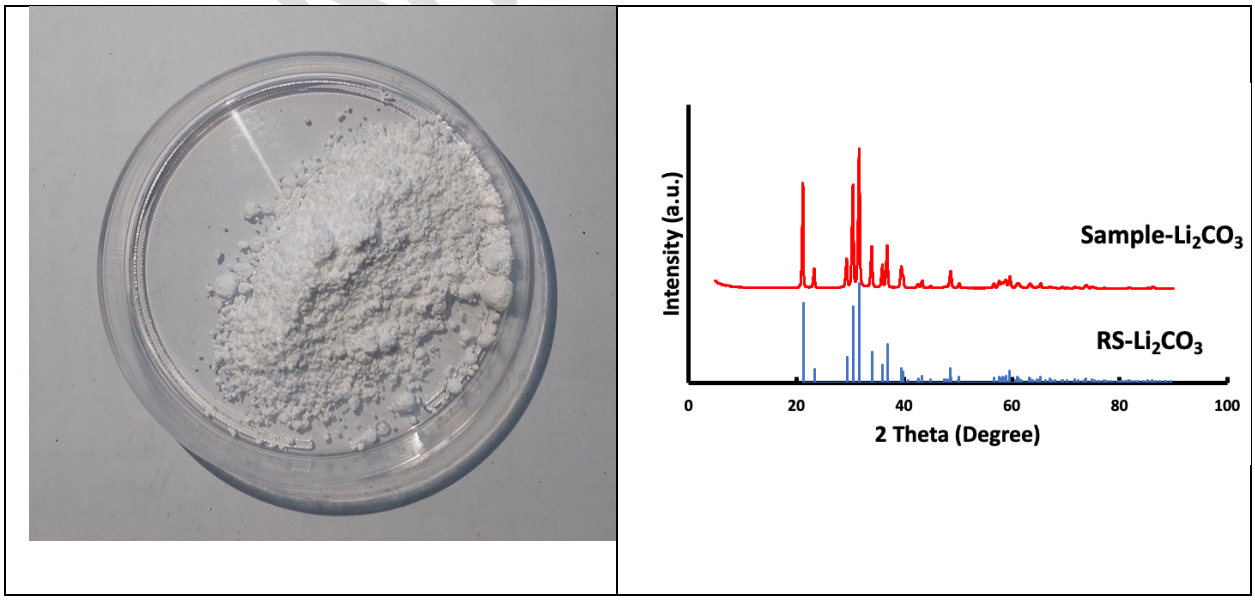

Figure 4-10: a) Photo and (b) XRD pattern of Li_2CO_3 products obtained by precipitation.

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The experimental results showed that around 93% of lithium was precipitated as carbonate with less than 0.5% impurities. Co and Ni were not detected in the obtained samples.

Table 4-3: ICP-OES analysis of the resultant solution after leaching and multistage precipitation.

Element	**[g/L]**	**ppm**	**ppm (disposal limit-EPA)**
Li	0.021	21	-
Ni	0.016	16	100
Co	0.012	12	50
Mn	0.018	18	50
(OH)-	-	10-11.5M	10-12M
Conductivity	-	281 mS/cm	2000 mS/cm

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5 CONCLUSION AND RECOMMENDATION

The experimental results show that leachate concentration, temperature, oxidant dosage and leaching time have a significant influence on the leaching efficiency of Ni, Co, Li and Mn from spent NMC Li-ion batteries cathodes, and the solution temperature, pH value, and the amount of precipitant added significantly affect the precipitation of Co, Ni, Mn and Li from NMC leachates. Through the utilization of leachate solutions comprising 2M H_2SO_4 + 6 vol.% H_2O_2, and a 75 g/L S/L ratio and conducting leaching for 2h at a temperature of 60°C, peak leaching recovery efficiency of 98.1% for Li, 97.1% for Co, 96.1% for Ni, and 95.7% for Mn can be attained.

The dark grey coloured $Ni_{0.5}Mn_{0.3}Co_{0.2}OH_2$ powder is precipitated using NaOH as a precipitating agent at pH of 13, a temperature of 20 °C for 1h. In the chemical precipitation process, more than 99.2% of Co, Ni and Mn elements were recovered from the leach liquor. Following collection of the $Ni_{0.5}Mn_{0.3}Co_{0.2}OH_2$ product by filtration, the Li_2CO_3 precipitates are obtained by addition of Na_2CO_3 in the left filtrate when the molar ratio of Na_2CO_3 to Li^+ is 1.2:1.0, equilibrium pH is 13.5, temperature is 40°C, Li^+ ion concentration is 4.75 g/L, reaction time is 1h, and agitation speed is 500 rpm. Through this precipitation process, 93% of Li can be recovered in the form of Li_2CO_3. The process exhibits great potential for recovery of valuable materials from spent Li-ion batteries.

5.1 RECOMMENDATIONS

Based on the observations and deductions made throughout the process of achieving the aim and objectives of this study, several recommendations can be made that would necessitate further study in order to improve the findings of the present study.

Thus, the recommendations made for future studies are listed below:

- Utilisation of LiOH for precipitation, as it can be recovered as Li_2CO_3.
- Synthesis of low cost precipitation agents that can effectively separate Ni from Co so that the recovered metals can be repurposed.

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