Lithium and Cobalt Extraction from Waste Lithium Ion Batteries for Resources Recovery and Reuse

BY

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LIST OF ACRONYMS

LIBs	Lithium Ion Batteries
ICP-OES	Induced Coupled Plasma Optical Emission Spectroscopy
Wt	Weight
M	Morality
ITU	International Telecommunications Union
PTA	Pakistan Telecommunication Authority
EV	Electric Vehicle
XRD	X-ray Diffraction
RPM	Revolutions Per Minute
WEEE	Waste Electrical and Electronic Equipment
EDS	Energy Dispersive Spectroscopy
S/L	Solid to Liquid Ratio
LCO	Lithium Cobalt Oxide

ABSTRACT

Lithium ion batteries (LIBs) are being used in communication and transportation vehicles for last 30 years. LIBs has become an essential alternative resource for its high contents of worthwhile components like lithium and cobalt. After use, batteries are getting accumulated at dumping sites globally, causing fires at dump sites, pollution in soil and water streams. In this research, a hybrid process was developed with citric acid as leaching agent and hydrogen peroxide (H_2O_2) as a reductant for recovery of lithium and cobalt element from waste mobile phone LIBs. Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), X-Ray Diffraction (XRD) and Energy Dispersive Spectroscopy (EDS) were used to analyze the elemental contents. The results exhibited 90.20% of cobalt and 93.46% of lithium leaching efficiency under optimized conditions with concentrations of 1 molar Citric acid, H_2O_2 content of 3 vol.%, solid to liquid ratio of 20 g L^{-1}, leaching temperature of 80 °C and reaction time of 2 h. Leached cobalt and lithium ions were converted into cobalt oxalate and lithium carbonate using oxalic acid and sodium carbonate with a recovery efficiency of 95% and 91% with sample purity of 99.72% and 98.77%, respectively. Recovered products have high market value of cobalt oxalate worth Rs 12,000/kg and lithium carbonate worth Rs 10,000/kg in the Pakistani chemicals market. Cobalt oxalate is used in the synthesis of cobalt powder, desiccants, additives, ceramics, pigments, foam, stabilizers, catalysts, in cobalt oxide preparation and for the production of cathode active material. Lithium carbonate is used as a catalyst, lithium salt, ceramic material, dental material, swelling joint therapy material and in the reduction of critical psychological disorders. The developed hybrid process was found efficient, low cost, easy to handle and environmentally safe.

Chapter 1

INTRODUCTION

1.1 Background

Lithium ion batteries (LIBs) have vast applications in communications, portable electronic devices, electrochemical power sources and electric vehicles due to high energy density, long storage life, low self-discharge rate, high cell voltage and wide working temperature. The working load on electronic products has increased over the years due to the origination of latest software's, which is the reason for short life span of LIBs and generation in large quantities. Millions of waste lithium ion batteries (LIBs) have been abandoned worldwide, including Pakistan, which causes harm to the environment and a waste of resource (Jha et al., 2013).

Conventionally, batteries are discarded along with municipal waste but LIBs market is abruptly growing and they become a severe environmental issue until firm actions are taken regarding recycling of LIBs (Li et al., 2010a). Lithium ion batteries recycling is now being center of attention because of the presence of hazardous and highly flammable elements that causes contamination of soil, water and air (Zhu et al., 2012). There are also economic benefits which these waste LIBs have, that can be attained through the recovery of cobalt and lithium (Li et al., 2013).Europe and USA utilized around 8 billion units of lithium ion batteries per year (Nayaka et al., 2015). There are 161 Million cellular phones in pakistan which are running on LIBs. Mobile phone LIBs average working life vary from 1- 2 years, after used these batteries are going to dump sites.

Batteries are now essential source of lithium, cobalt and other useful elements, at least portable LIBs cell contain one third of their production cost. It is compulsory to recycle for environmental sustainability and safety purpose (Chagnes & Pospiech, 2013). LIBs waste have capability to emit hazardous metals to underground water resource if thrown on the land

in an unrestricted way. It was reported that disposal of LIBs into dump sites/landfill sites resulting in deterioration of ground resources. The possibility of LIBs to pollute the groundwater resources depends on soil properties, landfill design and water table distance from ground level (Song et al., 2013). When batteries burned with municipal waste in dump sites an immense amount of toxic gases specially hydrogen fluoride (HF) produced, contaminating the aerosphere. These batteries are also showing adverse impacts on environment and human health (Yang et al., 2006).

The number of elements in spent LIBs electrode scraps are enough to recycle, they become an essential secondary source to cope with the limitation of natural resources. For better utilization of natural resources recycling need to be execute and it also aid to decrease the production cost of battery. Sometimes concentrations of useful elements present in the lithium ion batteries are more than ores (Jha et al., 2013). The market price of cobalt and lithium has elevated exceptionally in last few years, making recycling of metal an achievable task (Li et al., 2013). Cobalt and lithium are very valuable, expensive and are strategic metals used in various industry for chemical production. Recycling of integral metals from LIBs become essential for the development of green technologies and to attain economical benefits.

1.2 Problem Statement

Dependence on lithium ion batteries increases day by day in term of smart phones, electric vehicles and electronic equipment's. These batteries contain lithium which can be burst and catch fire if pressed, punctured or provided high temperature. One of the major reason of landfill site fire is LIBs, which is very difficult to extinguish. To deal with enormous amount of waste LIBs going to dump site, it is a need of time to propose a process to recover potential useful elements. Those recovered elements will help to decrease toxicity and give economic benefits.

1.3 Objectives of the Study

1. To identify lithium and cobalt as recoverable elements from mobile phone lithium ion batteries (LIBs) using organic acid (citric acid) as leaching agent.

2. To optimize leaching process performance by evaluating parameters such as:

   - Temperature

   - Acid concentration

   - Reductant concentration

3. Purification of recoverable cobalt as cobalt oxalate and lithium as lithium carbonate.

1.4 Relevance to National Needs

The recovered and recycled products from LIBs are useful in industries and helpful in gaining economic growth.

1.5 Advantages

- Discourage the amount of waste LIBs going to dump site.

- Waste LIBs converted into useful industrial products.

- Decreases the adverse effects such as fire and soil pollution in dumping site.

- Recoverable products have high market value .

1.6 Uses of End Products

Cobalt oxalate is used in the synthesis of cobalt powder, desiccant, additives, ceramic, pigments, foam, stabilizer, catalysts and cobalt oxide. It can also be used for the manufacturing of parent cathode active material (Habashi, 1997).Lithium carbonate utilize in the medical field such as manufacturing of dental materials, therapy of swelling joints material and critical psychological disorders medicine, also used in the manufacturing of ceramic, catalyst and most importantly parent lithium cobalt oxide ($LiCoO_2$).

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Chapter 2

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LITERATURE REVIEW

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2.1 History of Lithium Ion Batteries (LIBs)

In 1990s commercialized lithium ion batteries (LIBs) were developed, which are used as energy storage unit in portable electronic devices, mobile communications and electrochemical power sources**.** Their modest size, light weight, electrochemical properties and wide working temperature make them exceptional from other battery types, LIBs represent 37% of the rechargeable battery sector globally (Zu & Li, 2011).

2.2 Sources of Lithium Ion Batteries (LIBs)

Batteries become indispensable module for mobile phones, cameras, laptops, hand tools and hybrid electric vehicles. An ocean of batteries is produced and utilize every day, the number of LIBs can surpass 25 billion in 2020 and weight of 500 thousand tons in china only (Zeng X, Li J, Singh N 2013).

 As per population of world there is equivalent number of mobile phones which is around 7.6 Billion (ITU), all are running on LIBs. Pakistan has 161 Million mobile phone operating (July-2019 PTA) with LIBs as a core segment. The average life of LIBs is 1-2 years, this tremendous amount of waste mobile phone batteries is going to dump sites. LIBs developing their application in electric vehicles generating high demand which will be the major contributor of waste stream in near future (Winslow et al., 2018). It is appraised that the inflow of electric vehicle and hybrid electric vehicle (HEV) will be 20% of total vehicles till 2020 (Swain, 2016). It is expected that Electric vehicle (EV) which are running on battery elevated from 5 million in 2015 to around 190 million in 2045 (Li et al., 2017). Average working life of 4-8 years of EV LIBs was observed, waste of over 200 million tons generated in 2017 and in 2020 it will be about 400 million tons (Gu et al., 2017).

For the diminishing of waste pile up necessary steps are need of time. Lithium prices become tripled in last 10 years (Guo et al., 2016). The ubiquitous use of these batteries show elevated lithium ion batteries waste generation and properly recycling of waste become global issue (Provazi et al., 2011).

2.3 Lithium Ion Batteries (LIBs) Components

LIBs comprise of a cathode, electrolyte/separator, an anode and an outer shell. The cathode composed of metal oxide with a coating layer of aluminum foil, in most of cases active cathode material consisting 90% of metal oxide, 7-8% acetylene and 2-3% organic binder, the anode portion consist of copper foil with a layer of powdered graphite carbon or activated carbon, anode with 91% graphite, 4-5% acetylene and 3-4% organic matter. Electrolyte made up of dissolved organic solvent that allow restricted transfer of lithium ions between cathode and anode during charging and discharging cycle (Amarakoon et al., 2013). An outer cover make up of steel, aluminium or plastic separate the inside portion from the external environment (Kushnir, 2015). The cathode and anode thickness is 0.18-0.20 mm, divided by a 10μm electrolyte (Li et al., 2013; Weng et al., 2013). The general weight constitution of lithium ion batteries is 5–21% Co, 15% organics, 4–9% Ni, 5–7% Li, and 7% plastics, variations of components depend on the manufacturer (Bertuol et al., 2016). Components of lithium ion battery shown in figure 2.1 (Chen et al., 2015).

Figure 2.1. Components of lithium ion batteries

Type of LIBs depends on the metal oxides used as a cathode active material, usually it includes $LiCoO_2$, $LiMn_2O_4$, $LiFePO_4$ and $LiNiMnCoO_2$. Cathode chemistry is a vital factor that dictate cost effectiveness for recycling. From the above mention cathode materials $LiCoO_2$ covered 94% of the market share in 2015. $LiCoO_2$ is the first commercialized battery material and has been extensively used in consumer electronic devices because of its character of high density, specific energy and durability (Nayaka et al., 2015). Lithium cobalt oxide has a largest discard amount, lithium and cobalt consumption has increased abruptly as there is an exponential rise in the growth of electronic equipment with rechargeable batteries (He et al., 2016). The average recycling worth for lithium ion batteries fluctuate from $860 per ton for $LiMn_2O_4$ to $8900 per ton for $LiCoO_2$ cathode material (Wang et al., 2014). The lithium cobalt oxide (LCO) has highest recycling worth among the batteries chemistries, because of high market cost of cobalt and lithium (Amarakoon et al., 2013).

2.4 Disposal of Waste Lithium Ion Batteries (LIBs)

Disposal of waste batteries in dumping sites or incinerators causes air and groundwater pollution due to presence of hazardous metals (Guo et al., 2016). Waste LIBs become center of attention due to possibility of extracting worthwhile elements like cobalt, lithium, nickel and aluminum, recycling of batteries also reduce the potential of environmental contamination from these electrolyte and toxic substances (Gao et al., 2017; Li et al., 2015b). Elevated LIB disposal without recycling can badly impact human health because of noxious matters significantly polluting the environment. Cobalt is considered as hazardous metal and surplus deposition of cobalt in the nervous system cause metallosis (Dhar & Bhatnagar, 2009; Mao et al., 2011). Specialized landfill sites capacities are insufficient and rising disposal cost intensify the issue. To encounter the industrial requirement, energy issues, carbon footprint elevation and future need, recovering of various elements from waste cell is a realistic approach for economy growth and prevent environmental pollution (Lieder & Rashid, 2016).

Recycling of fundamental components of LIBs such as Li, Co is very appealing instead of new production (Wang et al., 2016).

Recycling of LIBs and extraction of valuable metals is multi favourable as it pile up all the toxic elements in one spot, the metals retrieve are reused, reclaim lithium to manufacturing process, saved the disposal cost of waste batteries, environmentally safe, avoid mining of natural resources and conserves resources for next generations (Dewulf et al., 2010). Recycling of discard batteries aid to compliance with numbers of environmental regulations (Ellis & Mirza, 2014). Literature review regarding lithium recovery is very restricted. In some cases content of worthwhile metals in lithium ion batteries (LIBs) are more than those in natural ores (Nayaka et al., 2015). The most practically remedy is recycling of waste LIBs which is eco friendly and reduce demand for virgin raw materials.

2.5 Lithium Ion Batteries Recovery Technologies

It's the need of time to recover valuable components from waste lithium ion batteries for environmental benefits. A UNEP report on recycling rates reported less than one percent of lithium being recycled (Swain, 2017). Future demand of lithium for LIBs considering the supply could not reach in 2023. This catastrophe can only be averted through 100% LIBs recycling with lithium recovery above 90%. Right now, up to 3% of LIBs are recycled with the priority of essential metal recovery with a minimum focus on lithium recovery (Sonoc et al., 2015). Researchers reported the recovery of cobalt and lithium from the waste lithium ion batteries mostly by applying pyrometallurgy, biohydrometallurgy, hydrometallurgy process and few with the hybrid process (Swain, 2017; Zheng et al., 2017).

2.5.1 Pyrometallurgy Process

In pyrometallurgy process plastic housing, separators, conductive agents, organic electrolytes and binders are burnt for the recovery of worthwhile elements (Nayaka et al., 2015). Pyrometallurgical process are generally used in industrial organization (Inmetco, Umicore and Xstrata) for the recovery worthwhile metals, giving high product efficiency but

there is loss of worthwhile metals (lithium) into the slag (Georgi-Maschler et al., 2012). High capital cost, emission of poisonous gases such as hydrogen fluoride, furan, dioxin, dust and consumption of intensive energy restrict the large scale application of pyrometallurgy process (Joulié et al., 2017). The utmost drawback of this process as it need large amount of energy to treat exhaust pollutant gases (Winslow et al., 2018).

2.5.2   Biohydrometallurgy Process

Biohydrometallurgy is a emerging integrative process that combine chemistry, biology and metallurgy. Bioleaching process use chemo lithotrophic and acidophilic bacteria which dissolve waste LIBs components. Biohydrometallurgy process attract due to low cost, eco-friendly and modest apparatus requirement but lack of adaptability, low efficiency and rigid working conditions subside its applicability (Chen & Zhou, 2014). High metals concentration and incubation of microbes at harsh condition for bioleaching is yet to be up scaled (Sattar et al., 2019).

2.5.3   Hydrometallurgical Process

Hydrometallurgical process include pretreatment of the batteries as discharging, dismantling, spilt into the components, dissolution and leaching (Li et al., 2010a). Hydrometallurgy offers benefits of less energy requirement, limited air emissions, high leaching efficiency and high purity (Li et al., 2010a). Most of work performed on leaching using inorganic acid such as hydrochloric acid, nitric acid and sulfuric acid. These acids are high cost, severe equipment corrosion, wastewater generation and produce secondary air pollutants such as So_x, NO_x and Cl_2 which cause serious threats to the human health and environment (Weng et al., 2013). Some studies have reported on leaching of cathode materials utilizing organic acids such as malic, oxalic, aspartic and succinic acid with the aid of reducing agents. Limitation of hydrometallurgy process is long run time, slow process and low leaching efficiency (Takacova et al., 2016).

2.5.4 Hybrid Process

Hybrid process is the combination of pyrometallurgy, biohydrometallurgy and hydrometallurgy process. It follows discharging, dismantling, crushing, dissolution, calcination, acid leaching, separation, purification and many other process (Dutta et al., 2018; Swain, 2017). It provide maximize leaching efficiency, ease for separation, purification and squeeze the time period for recycling (Nayaka et al., 2015).

To limit secondary pollution without compensating leaching efficiency organic acids such as oxalic , succinic, ascorbic, malic, aspartic and citric acid used as leaching agent with the aid of reducing agent. Organic acids are almost as effective as mineral acids (Li et al., 2013; Li et al., 2015a; Sun & Qiu, 2012).

2.6 Pervious Lithium Ion Batteries Recycling Work

Sattar et al. (2019) worked on the leaching of cathode active material using sulfuric acid for the recovery of valuable metals from waste LIBs, at optimized conditions of 5% solid to liquid ratio, 2 M H_2SO_4, 50 °C temperature, 4 vol% H_2O_2 and leaching time of 30 min the efficiency became 98%. Selective precipitate of Co^{+2} and Li^{+1} into $CoSO_4$ and Na_2CO_3 respectively.

Pinna et al. (2017) reported dissolution by utilizing phosphoric acid as leachant and hydrogen per oxide as reductant, dissolution of almost 99% was observed. The conditions maintain during process were temperature of 363K, H_3PO_4 concentration of 2%v/v, H_2O_2 concentration of 2 vol.% and solid to liquid ratio of 8 g/L. Lithium converted into lithium phosphate (Li_3PO_4) with recovery of 88% , the product revealed a 98.3% purity, cobalt recovered as CoC_2O_4 with 99% efficiency and a purity of 97.8%.

Meshram et al. (2015) purposed optimize conditions as 1 M H_2SO_4, 368K temperature, 50 g/L solid to liquid ratio and 240 min leaching time for leaching of the metals from cathode material, this show recovery of 50.2% Mn, 66.2% Co, 93.4% Li and 96.3% Ni

Gao et al. (2018) purposed the process or the recovery of lithium and cobalt by scrutinizing the parameters of leaching speed and recovery rate of metals. Organic acid leachant can leach out lithium and cobalt, while inorganic acids mostly leach out all metals from cathode with elevated leaching efficiency without reductant. Hydrochloric acid (HCl) show maximum leaching efficiency for leaching out metals in the absence of reductant.

Li et al. (2015a) studied hydrometallurgical method using succinic acid as leaching reactant come up with cobalt leaching efficiency of 100% and lithium efficiency of 96% during optimized conditions of acid concentration of 1.5 mol L^{-1}, temperature of 70 °C, H_2O_2 of 4 vol.%, reaction time of 40 min and solid to liquid ratio of 15 g L^{-1}.

Jha et al. (2013) purposed a process for recovery of lithium and cobalt using sulfuric acid as lixiviant. Under the optimum condition of sulfuric acid of 2 M, temperature of 75 °C, solid to liquid ratio of 100 g/L and H_2O_2 of 5% (v/v) in 60 min reaction time, leaching of 99.1% for Li and 70.0% for Co were observed.

Nayaka et al. (2016) purposed an environmentally benign hydrometallurgical route for the dissolution of cathode material. A composition of tartaric acid (0.04M) and ascorbic acid (0.02M) was initiate to dissolve sample at 80 °C in about 3–4 h and leaching efficiency above 90% achieved for Co and Li. The dissolved solution was subjected for selective precipitation of cobalt as Co-oxalate by the addition of oxalic acid. Maximum dissolution of 95% obtained while using sulfuric acid as leachant, cobalt recovered through precipitation with NaOH (Nayl et al., 2017).

2.7 Hybrid Process for Recycling Lithium Ion Batteries

A green process proposes for the extraction of high worth metals from waste LIBs. Hybrid process was adopted as its environmental friendly, less energy consuming, minimum gases emission, high recovery rate and user friendly working conditions to recover the essential metals (Bertuol et al., 2016). Considering the environmental and economical point of view

hybrid treatment is preferred process for recovery of the metals from LIBs in comparison to hydrometallurgy, pyrometallurgical and biohydrometallurgical processes.

Hybrid recycling consist of pretreatment, which is discharging, dismantling, dissolution, calcination, leaching of cathode material and precipitation of required elements from leach solution. Leaching plays a vital role in recycling process (Joulié et al., 2014). Most of studies have considered mineral acid such as HCl, HNO_3, H_2SO_4 etc. for the leaching of active cathode material (Granata et al., 2012). Using inorganic acid develop remarkable quantity of secondary pollutants such as discharge of Cl_2, SO_x and NO_x. In compare to mild organic acids, the inorganic acid have flaws of high cost, difficult to handle in large scale, complication during separation and purification steps and lastly produced secondary pollutants (Sun & Qiu, 2012). Metal recovery from waste batteries using organic acid as leachant in the presence of reductant which change the metal ions to a better soluble oxidation state.

2.7.1 Citric Acid as Leachant

In this research work citric acid ($C_6H_8O_7 \cdot H_2O$) used as leachant, it's the most economically available acid, easily dissolved in water, mostly utilized as a raw material in the industry and with outstanding leaching performance (Li et al., 2010b). As a natural biodegradable acid, ($C_6H_8O_7$).H_2O it can be used for recovering metals from sewage sludge, it decay smoothly under aerobic and anaerobic conditions so effluent from recycling unit can be treated efficiently (Li et al., 2010b). The motive for selecting the citric acid as leaching agent is due to its weak complex with the metal ions (Smith & Martell, 1989). The log K of Co(II)–citrate is reported to be 6.187 (Lee & Reeder, 2006). This weak complexation is beneficial for the later precipitation of Co (II) ions in oxalate or hydroxide form. It can be than easily went by ion exchange to select metal ions through dissociation process (Ananthan et al., 2003).

2.7.2 Hydrogen Per Oxide as Reductant

Hydrogen peroxide (H_2O_2) used as reductant to facilitate the release of cobalt and lithium from the LCO structure. Hydrogen per oxide (H_2O_2), glucose, sodium hydrogen sulphite ($NaHSO_3$) are used as reducing agent to change the metal ions from high valances (Co^{+3}, Mn^{+4}) to lower valance ions (Co^{+2}, Mn^{+2}) which are more stable/soluble in the solution (Gao et al., 2018). Reductant rise the dissolution of cathode active material as it accelerated the release of cobalt and lithium atom from the LiCoO structure. In one of study addition of H_2O_2 in malic acid the leaching efficiency of cobalt rise from 37% to 93% and lithium from 54% to 99% (Li et al., 2010a), H_2O_2 using as reductant in aspartic acid elevated the leaching from 1% to 60% (Li et al., 2013). In most of studies, 1–6 vol.% of H_2O_2 was used. Finally using H_2O_2 as reducing agent didn't not induce anion or cation into the solution and no altering in pH of leaching system (Gao et al., 2018).

MATERIALS AND METHODS

3.1 Chemicals

The sample of waste mobile phone lithium ion batteries (LIBs) of various brands and models were collected from local mobile market. The chemicals utilized in the study are citric acid, sodium carbonate, oxalic acid and hydrogen peroxide (H_2O_2) with 99% purity and manufactured from "SIGMA-ALDRICH" Pakistan. Aqua regia prepared by the hydrochloric acid (HCl) and nitric acid of 10 molar concentration. All the reagents were of analytical grade and solutions were prepared with deionized water.

3.2 Phases of Research

The research study consists of three phases. In the first phase pretreatment was performed with include operational activities as discharging, dismantling, dissolution and calcination. In second phase leaching of active material with the aid of citric acid performed at various operating conditions. In third phase conversion of Co^{+2} ions into cobalt oxalate by reaction with oxalic acid and Li^{+1} ion into lithium carbonate by reaction with sodium carbonate. Three phases of research shown in figure 3.1
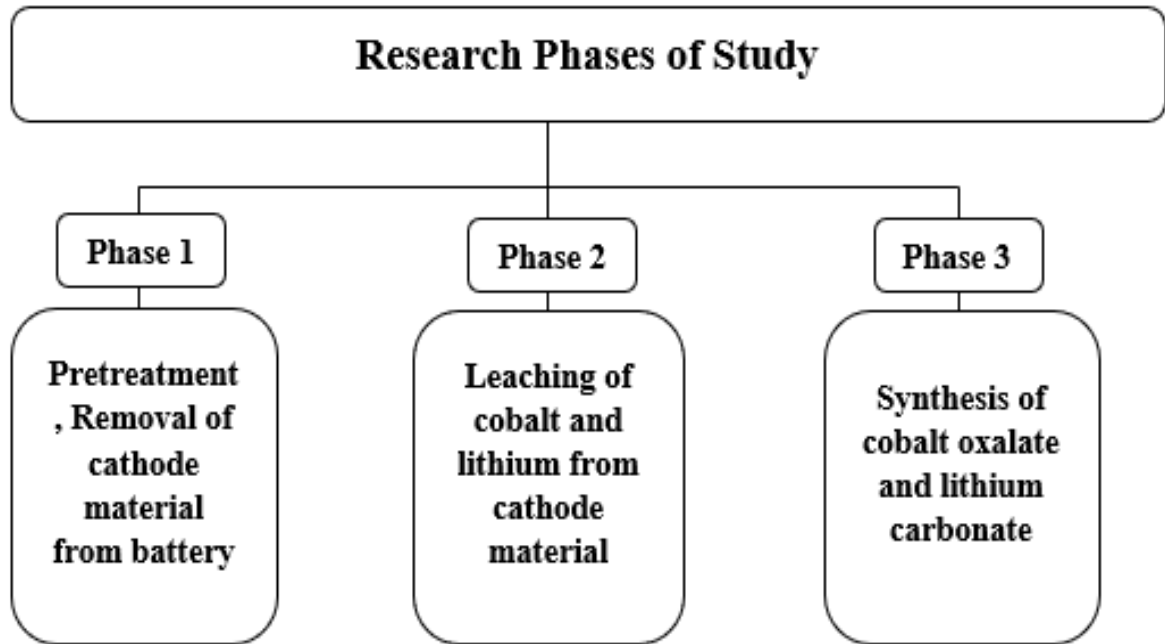
Figure 3.1. Phases of Research

3.3 Pretreatment

Pretreatment of research study consists of four further operational activities. Each will be explained in detail as,

3.3.1 Discharging

Exhausted LIBs contain certain amount of electric charge when disposed of which can cause short-circuit, self-ignition if dismantle without proper discharging. Mobile LIBs were completely discharged by placing in a 5% wt. sodium chloride solution for 5 h at room temperature. Batteries than removed from the sodium chloride solution, washed with distill water and placed for 1 h at 60°C, which help to remove the moisture content. Figure 3.2 shows the submerged batteries in the solution.
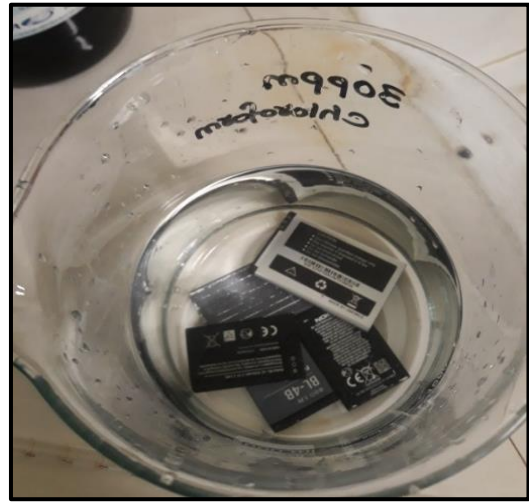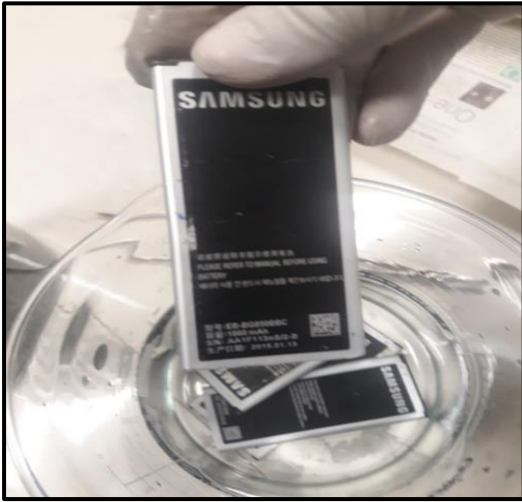
Figure 3.2. LIBs submerge in NaCl solution

3.3.2 Dismantling

In industry special cutters are used to dismantle lithium ion batteries while in laboratory they were manually dismantled with plier cutter tools (Golmohammadzadeh et al., 2017) (figure 3.3). Battery dismantling work was performed in a aerated section of laboratory to diminish exposure to hazardous gases (Larsson et al., 2014). Waste mobile phone lithium ion batteries separated into following major portions; Cathode, anode, plastic/metallic/shells and electrolyte/separators. Metallic shells and aluminum can be recycled directly. After dismantling cathode part was dried at 60 °C for 2 h to remove the moisture content.

Figure 3.3. Dismantling of lithium ion batteries

3.3.3 Dissolution

The cathodes part was cut into parts (about 1 cm × 1 cm) using scissor and submerged in 5% sodium hydroxide solution. Beaker was placed in magnetic stirrer which stirred at 300 RPM for 1 hour at 100°C shown in figure 3.4. This step helps to detach aluminum from cathode material and separated Al foil using 'tong' from the dissolution solution, which in metal form can be used. Cathode material in dissolution was filtered, screened and dried for 2 h at 80°C.

Figure 3.4. Dissolution process to separate aluminum from cathode

3.3.4 Calcination

Calcination was performed with muffle furnace (Ney 525) at 700 °C for 2 h to burn out the volatile carbon content in cathode material. It will aid to elevate the leaching efficiency of lithium cobalt oxalate ($LiCoO_2$). Black residue left after calcination was extracted cathode material shown in figure 3.5 which further used in leaching.

Figure 3.5. Calcination using muffle furnace apparatus

3.4 Leaching of Cathode Material

Leaching experiments were performed using a 250 ml Pyrex 3 neck bottle. The methodology of cathode material leaching shown in figure 3.6. Citric acid and hydrogen peroxide (H_2O_2) were poured into the reactor to make the solution of 100 ml, stirred mechanically by a magnetic stirrer. Fixed amount of extracted cathodic material was added to the solution when it attains the preselected temperature. Operating parameters were studied as concentration of citric acid $(0.25 - 4 \text{ M})$, concentration of hydrogen per oxide $(0 - 5 \text{ Vol \%})$, and temperature $(50 - 100 \text{ °C})$ measured with thermometer , solid to liquid ratio of 40 g/L, leaching time of 2 h and stirring speed of 350 RPM. Equation (3.1) show the leaching of LiCoO and cobalt and lithium citrate.

$$LiCoO_2 + 2H_3Cit + H_2O_2 \rightleftharpoons Co\text{-}Cit + Li\text{-}Cit + 4H_2O \qquad (3.1)$$

As Co^{+3} in $LiCoO_2$ require to be converted to Co^{+2} for this reductant used which change the metals to more soluble oxidation state. It also facilitates the release of cobalt and lithium from the LCO structure and raise dissolution. In our case H_2O_2 use as reducing agent since it didn't insert any positive or negative ions the mixture and without altering the pH of leaching system (Gao et al., 2018). Remaining black carbon residue was filtered with filtration assembly having filter size of 2 micron and 47 mm dia. The leach liquor was draw out to find the concentrations of cobalt and lithium by ICP-OES to find out the leaching efficiency.

Figure 3.6. Leaching Apparatus (leaching setup and filtration assembly)

Leaching efficiency was determined by using following expression,

$X\% = ((m_o / m_a) \times 100$

$X\%$ = Leaching efficiency.

m_o = Metals leach with citric acid in a design condition.

m_a = Metals completely leach with ideal conditions using aqua regia.

3.5 Material Recovery

3.5.1 Synthesis of Cobalt Oxalate

After leaching the leachate solution contains Co in citrate form as $Co_3(Cit)_2$, $Co(HCit)$ and $Co(H_2Cit)_2$ which required to recovered through precipitation, stoichiometric amount of oxalic acid added to leach liquor and reaction started which shown in equation 3.2 – 3.4. The experimental conditions of stirring speed of 350 RPM for one hour at room temperature was provided and precipitate was formed, one hour settling time was given for precipitate to settle which than filter and dried.

$$Co_3(Cit)_{2\ (aq)} + 3H_2C_2O_{4\ (aq)} \rightleftharpoons 3CoC_2O_{4\ (s)} \downarrow + 2H_3Cit_{\ (aq)} \tag{3.2}$$

$$Co(HCit)_{\ (aq)} + H_2C_2O_{4\ (aq)} \rightleftharpoons CoC_2O_{4\ (s)} \downarrow + H_3Cit_{\ (aq)} \tag{3.3}$$

$$Co(H_2Cit)_{2\ (aq)} + H_2C_2O_{4\ (aq)} \rightleftharpoons CoC_2O_{4\ (s)} \downarrow + 2H_3Cit_{\ (aq)} \tag{3.4}$$
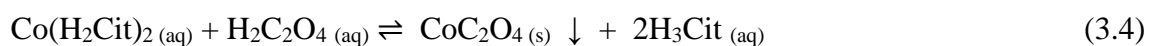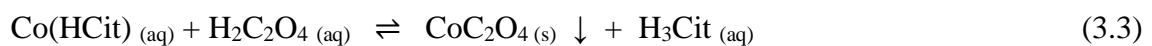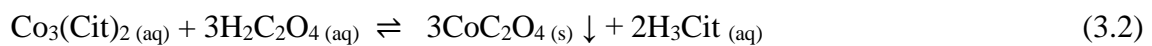
3.5.2 Synthesis of Lithium Carbonate

Lithium carbonate precipitate synthesis only in basic conditions, for this pH above 11 was attained by the addition of 2,3 drop 1 M NaOH solution. Leach liquor filtrate from first step containing Li_3Cit, $Li_2(HCit)$ and $Li(H_2Cit)$ were allowed to be reacted with sodium carbonate considering stoichiometry showing in equation 3.5 to 3.7, stirring speed of 350 RPM provided for 1 hour. Precipitate of lithium carbonate were than allow to settle for one hour, which than were filtered and dried.

$$2Li_3Cit_{(aq)} + \quad 3Na_2CO_{3\,(aq)} \rightleftharpoons 3Li_2CO_{3\,(s)} \downarrow + 2Na_3Cit_{(aq)} \tag{3.5}$$

$$Li_2(HCit)_{(aq)} + \quad Na_2CO_{3\,(aq)} \rightleftharpoons Li_2CO_{3\,(s)} \downarrow + \quad Na_2HCit_{(aq)} \tag{3.6}$$

$$2Li(H_2Cit)_{(aq)} + Na_2CO_{3\,(aq)} \rightleftharpoons Li_2CO_{3\,(s)} \downarrow + \quad 2Na(H_2Cit)_{(aq)} \tag{3.7}$$
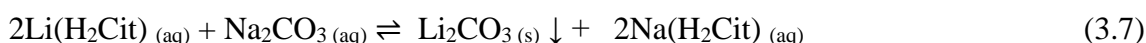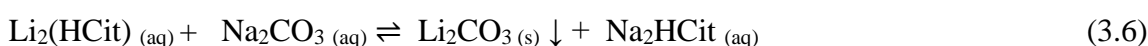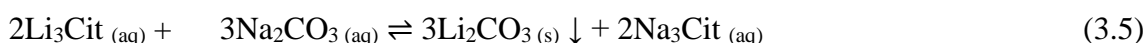
3.6 Theory of Recovery Efficiency
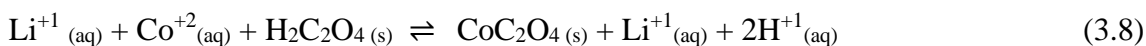
3.6.1 Recovery of Cobalt (Co^{+2}) as Cobalt Oxalate

$$Li^{+1}_{\,(aq)} + Co^{+2}_{\,(aq)} + H_2C_2O_{4\,(s)} \rightleftharpoons CoC_2O_{4\,(s)} + Li^{+1}_{\,(aq)} + 2H^{+1}_{\,(aq)} \tag{3.8}$$

Cobalt conc $= Co^{+2} = 320$ mg/L (ICP-OES),

320 mg/L $Co^{+2} \times$(1 mol Co^{+2}/59g)$\times$(1mol CoC_2O_4/1mol Co^{+2}) = mol CoC_2O_4

CoC_2O_4 from cobalt ion = 0.00546 mole

0.55 g of oxalic acid used

0.55 g $H_2C_2O_4 \times$(1mol $H_2C_2O_4$ / 90g)$\times$ (1mol CoC_2O_4 /1mol $H_2C_2O_4$) = mol CoC_2O_4

CoC_2O_4 from oxalic acid = 0.0061 mole

 0.00546 < 0.0061   (Cobalt ion is limiting reactant)

Mole of CoC_2O_4 produced = 0.00546 mol

Mass of CoC_2O_4 = molecular mass$\times$0.00546 mol

Molecular mass of CoC_2O_4 = 147 g/mol

Mass of CoC_2O_4 = 147 g/mol $\times$ 0.00546 mol

Mass of CoC_2O_4 = 0.803 g, So Theoretical yield is 0.803 g

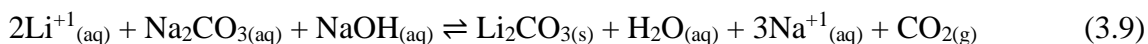Actual average yield at the end of experiment = 0.763 g

% Yield = (Actual Yield / Theoretical Yield)

% Yield = (0.763/0.803)×100

%Yield = 95.02% for cobalt oxalate.

Recovery efficiency for **Cobalt Oxalate is 95.02%**

3.6.2   Recovery of Lithium (Li^{+1}) as Lithium Carbonate

$$2Li^{+1}_{(aq)} + Na_2CO_{3(aq)} + NaOH_{(aq)} \rightleftharpoons Li_2CO_{3(s)} + H_2O_{(aq)} + 3Na^{+1}_{(aq)} + CO_{2(g)} \qquad (3.9)$$

Concentration of Li^{+1} = 76 mg/L (ICP-OES)

0.076 g Li^{+1} × (1mol Li^{+1} / 6.94gLi^{+1}) × (1mol Li_2CO_3/2mol Li) = mole of Li_2CO_3

Li_2CO_3 from lithium ion = 0.0055 mol

Concentration of Na_2CO_3 by stoichiometric = 0.7 g/L

0.7g Na_2CO_3 × (1mol Na_2CO_3 / 106 Na_2CO_3) × (1mol Li_2CO_3/1mol Na_2CO_3) = mol Li_2CO_3

 Li_2CO_3 from sodium carbonate = 0.0066 mol

0.0055 < 0.0066   (Li^{+1} is limiting reactant)

Mass of Li_2CO_3 = (Mol Li_2CO_3) × Molecular mass

Molecular mass of Li_2CO_3 = 74 g/mol

Mass of Li_2CO_3 = (0.0055)×(74)

Mass of Li_2CO_3 = 0.41 g, So Theoretical Yield = 0.41 g

Actual average yield from the experiment = 0.375 g

% Yield = (Actual Yield / Theoretical Yield) × 100

% Yield = (0.375/0.41)×100

% Yield = 91.46%

Recovery efficiency for **Lithium Carbonate is 91.46**

3.7 Analytical Methods

Inductively coupled plasma optical emission spectrometry (ICP-OES, Optima 2100 DV, Perkin Elmer, U.S) was used to find the cobalt and lithium in a leach liquor solution. X-ray

diffraction (XRD Bruker D8 Advance，GER used for the XRD test having diffractometer equipped with Cu Kα radiation (λ=1.5406 Å), employing a scanning rate of 0.02 (°)/s and 2θ ranging from 5° to 80° utilized for the characterization of cobalt oxalate and lithium carbonate. Diffraction patterns were compared with reference data. Energy Dispersive Spectroscopy (EDS) was performed with JSM-IT 500 for the analysis of cathode active material and for the purity of produced compounds.

RESULTS AND DISCUSSION

4.1 Analysis of Waste Mobile Lithium Ion Batteries (LIBs)

Waste mobile lithium ion batteries were manually dismantled with the help of plier cutter tools which consist of four major components as cathode, anode, electrolyte (aluminum, separator) and outer shell (plastic/steel). Hundred mobile batteries were analyzed on the basis of weight percent, composition of batteries is shown in Table 4.1.

Table 4.1. Weight compositions of LIBs

Sr No	Battery Wt (g)	Cathode Wt (g)	Anode Wt (g)	Outer shell Wt (g)	Electrolyte Wt (g)
1	31.73	7.76	14.25	7.38	2.35
2	34.39	9.25	15.53	7.72	1.82
3	31.73	9.93	13.32	6.76	1.72
4	32.20	9.72	13.98	6.56	1.67
5	35.02	10.54	17.04	5.84	1.60
6	28.73	8.53	12.51	6.21	1.47
7	31.20	9.42	13.58	6.51	1.67
8	35.41	10.45	16.59	6.579	1.76
9	35.29	10.56	15.92	7.14	1.67
..	..	..	..	..	..
	..	..	..	..	..
100	36.92	11.96	16.62	6.42	1.88

Standard deviation from mean value for 100 mobile phone batteries was analyzed as shown in the Table 4.2. This depict the portion of various components in LIBs. Figure 4.1 shows the portion of various component and their weight percent in the lithium ion battery.

Table 4.2. Standard deviation of components of LIBs

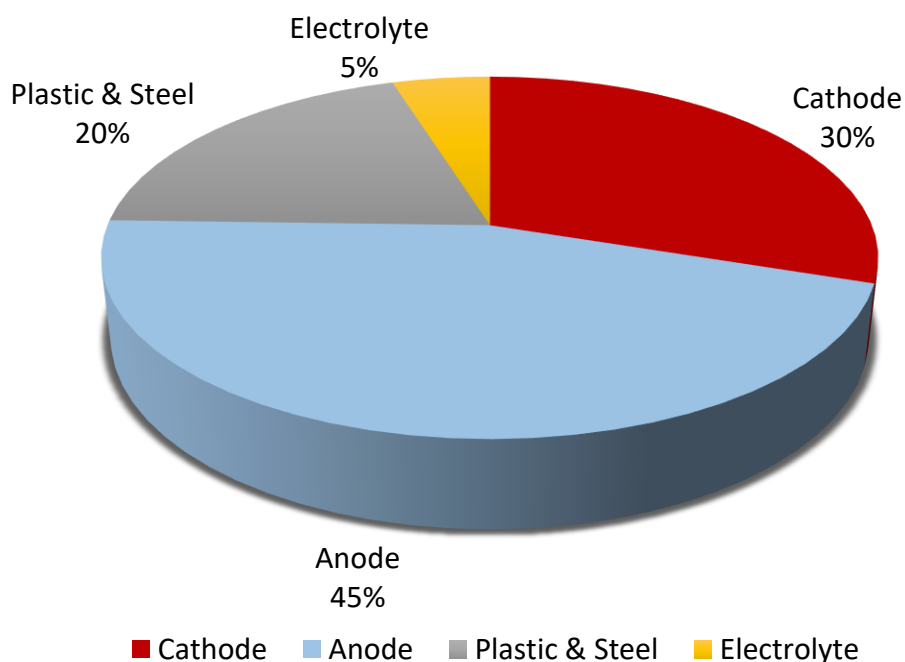| Weight (g)	Cathode (g)	Anode (g)	Outer shell (g)	Separator (g)
32.73 ± 3.34	9.83 ± 1.26	14.83 ± 1.66	6.44 ± 0.82	1.58 ± 0.24

Figure 4.1. Percent components of lithium ion batteries

4.2 Characterization of Powder Cathode Active Material

Powder of cathode active materials ($LiCoO_2$) was used as raw materials for the leaching process, the mass fractions of the extracted cathode material shown in Table 4.3 with the help of Energy Dispersive Spectroscopy (EDS). Cathode active material included Li (6.59%), Co (56.55%), Mn (0.71 %), and Al (0.5%). Aluminum found in analysis due to decaying of cathode material before dismantling, manganese present there help to enhance the capacity of the battery. The EDS results also show presence of carbon and oxygen which termed as "others" that didn't dissolve in acidic solution and remains left as ash layer after

leaching. These left residues separated from leach liquor using filtration process having filter paper size of 2 microns and 47 mm dia.

Table 4.3. Metals in cathode active material ($LiCoO_2$)

Metals	Weight %
Li	**6.59**
Co	**56.55**
Al	0.50
Mn	0.71
Others (C+O)	35.65

4.3 Impact of Temperature on Leaching

Temperature is a crucial factor that influence the chemical reactions on both thermodynamic and kinetic aspects. The impact of temperature was analyzed in the range of 50 – 100 °C with remaining parameters kept constant as 1 M citric acid concentration and reductant dosage of 3 vol.% H_2O_2, 350 RPM stirring speed, 40 g/L solid to liquid ratio and 2 h leaching time. Figure 4.1 and figure 4.2 shows that the leaching efficiencies for cobalt was 20.34 ± 1.84% and lithium 25.76 ± 2.41% at 50 °C, rise in temperature show increase in leaching efficiency. At 80 °C maximum leaching efficiency of 90.57 ± 3.43 % for cobalt and 93.38 ± 4.66% for lithium was observed, after further rise in temperature efficiency show declining trend. Increase in efficiency with the rise in temperature was due to endothermic nature of reaction and after a certain increase of temperature the leaching efficiencies showing a declining trend due to breakdown of H_2O_2 at that extended temperature which shown in equation 4.1 which was possibly due to instability of H_2O_2.

$$H_2O_{2\ (aq)} \rightarrow H_2O_{\ (aq)} + \tfrac{1}{2} O_{2\ (g)} \qquad\qquad\qquad (4.1)$$

Furt her rise in temperature above 80º C was loss of energy and decline in leaching efficiency. For this the optimum temperature was chosen as 80 °C.
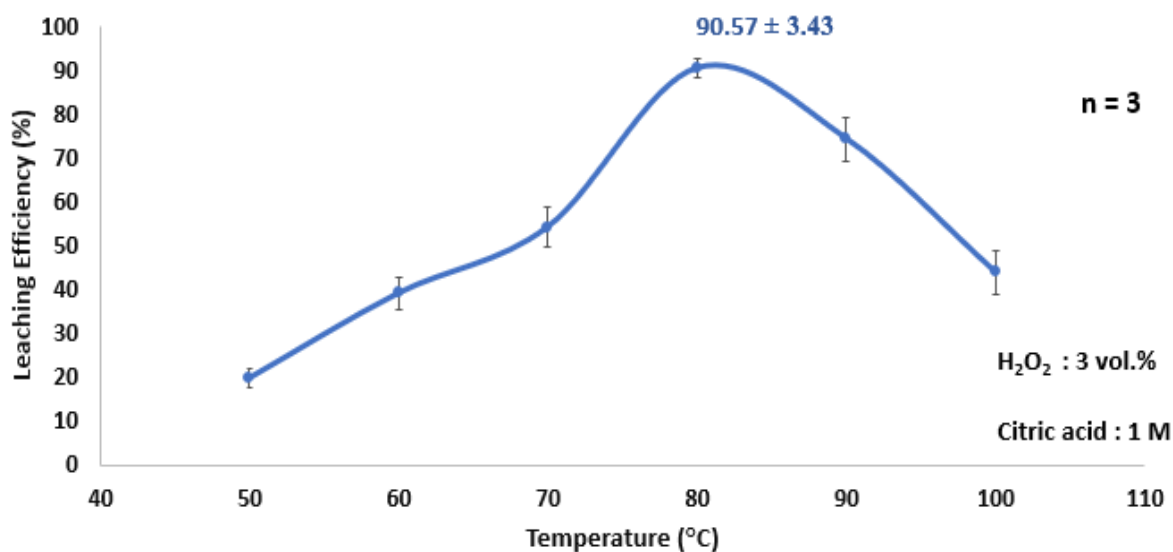

Figure 4.2. Impact of temperature on cobalt leaching efficiency
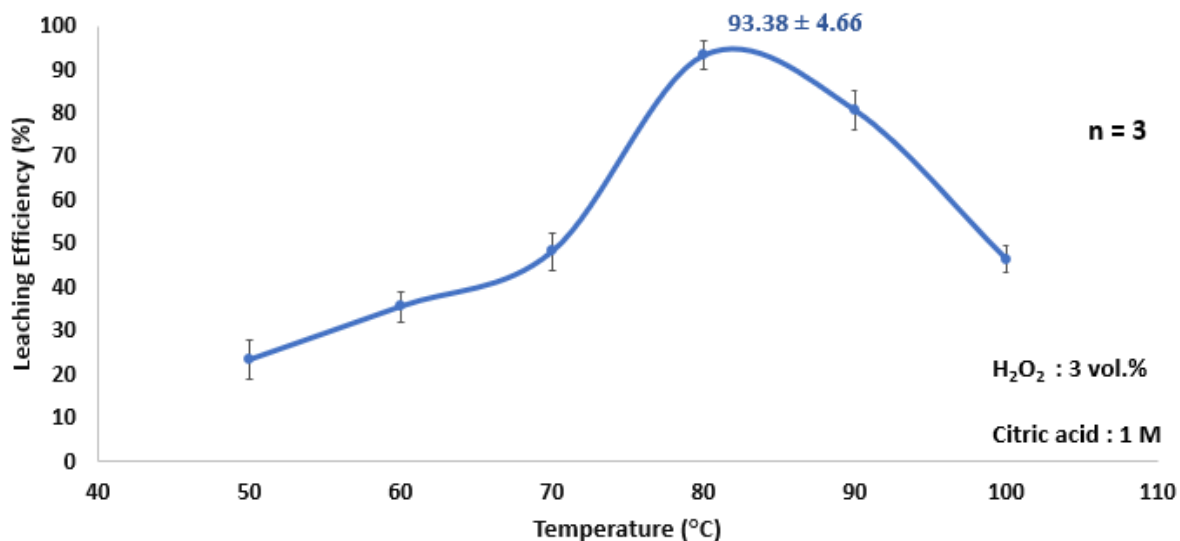
Figure 4.3. Impact of temperature on lithium leaching efficiency

4.4 Impact of Acid Concentration on Leaching

Citric acid concentration varies from 0.25 M to 3 M to analyze the impact on leaching efficiency. The experimental working conditions were kept constant as H_2O_2 concentration of 3 vol.%, temperature of 80°C solid to liquid ratio of 40 g/L, stirring speed of 350 RPM and leaching time of 2 h. Result presented in figure 4.3 shows at 0.25 M acid concentration

cobalt leaching efficiency was 33.12 ± 1.73 and figure 4.4 show lithium efficiency of 28.01 ± 2.39. –Rise in acid concentration gave increase in leaching efficiency, at 1 M citric acid concentration the leaching for Co became $90.63 \pm 3.01\%$ and Li $93.71 \pm 3.68\%$. Further increase of citric acid concentration had no significant increase in leaching efficiency. This can be attributed to the fact increasing the leaching agent concentration gives rise to a larger number of H^+ ions available to react with $LiCoO_2$ and also improves the frequency of collisions between the reactants, thus speeding up the rate of reaction. Insignificant change in the leaching efficiency after 1 M acid concentration. By stoichiometric calculation Li and Co become limiting reagent and which the rise of acid concentration there was no further increase in leaching efficiency.

For this the leaching efficiencies of Co and Li did not show remarkable change with the elevation of acid concentration. In consideration of the cost and efficiency 1 M citric acid concentration was selected as the optimal concentration for leaching.
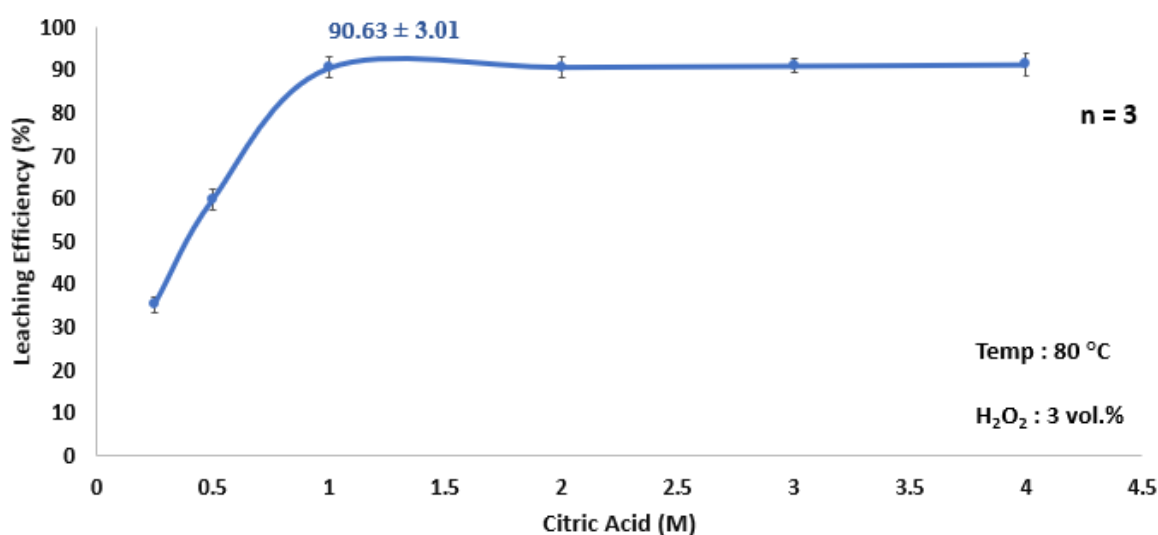

Figure 4.4. Impact of citric acid on cobalt leaching efficiency
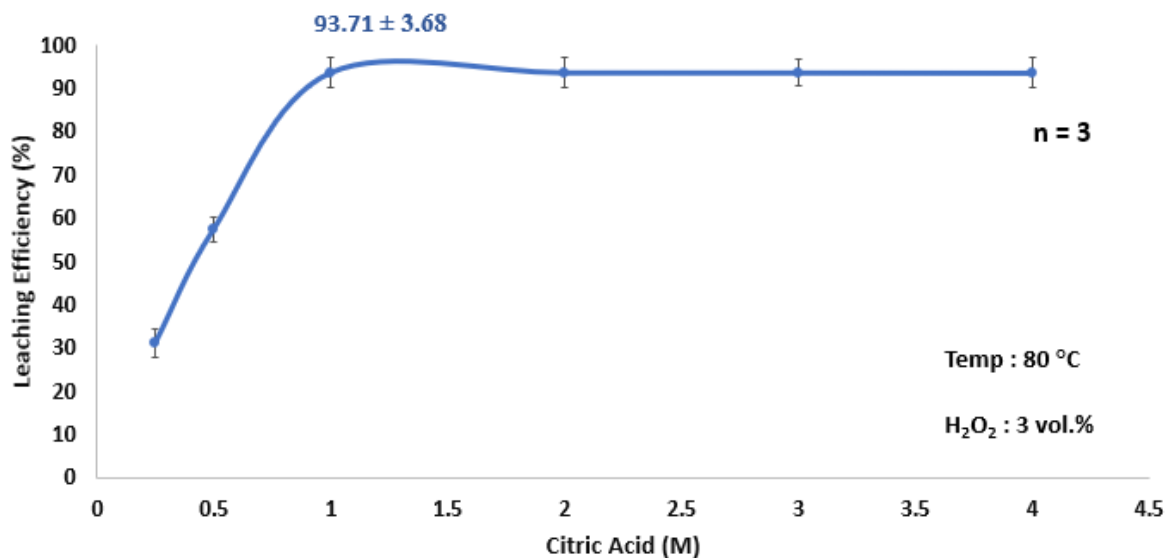
Figure 4.5. Impact of citric acid on lithium leaching efficiency

4.5 Impact of Hydrogen Per Oxide (H_2O_2) Concentration on Leaching

The study of the addition of hydrogen peroxide was carried out between 0 and 5 vol.%, other experimental conditions were kept constant as citric acid concentration of 1 M, temperature of 80 °C, stirring speed of 350 RPM, solid to liquid ratio of 40 g/L and leaching time of 2 hours. Figure 4.5 and figure 4.6 show that in the absence of H_2O_2 the leaching efficiency was only 32 ± 3.92 % for Co and about 46.67 ± 3.02% for Li. When the hydrogen per oxide concentration start increasing the leaching efficiencies increased significantly, at 3% v/v

Figure 4.6. Impact of H_2O_2 on cobalt leaching efficiency

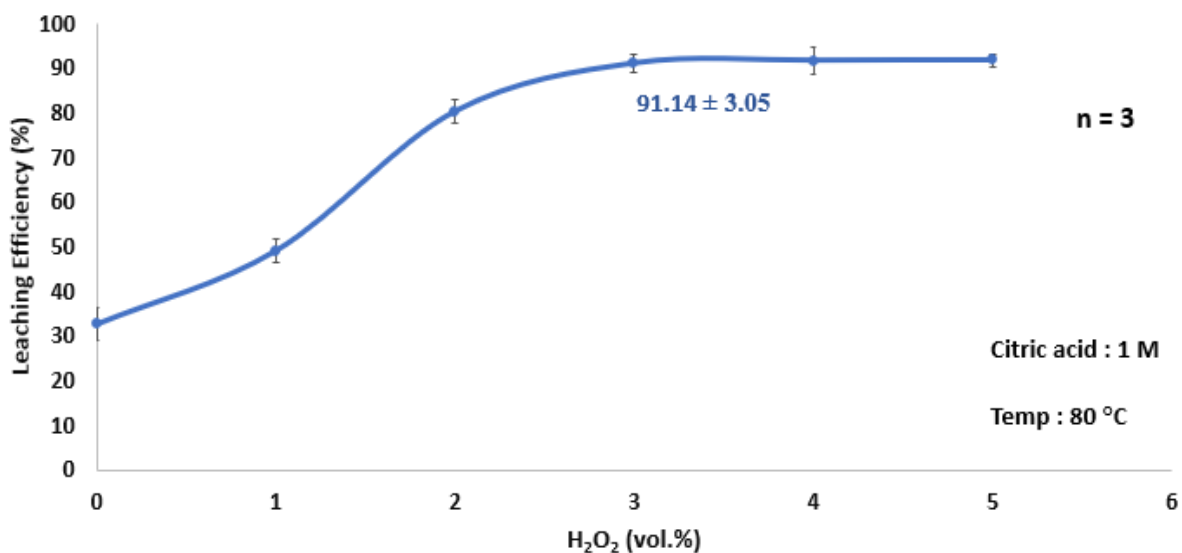H_2O_2, leaching efficiency of Co became $91.14 \pm 3.05\%$ and Li $93.18 \pm 3.83\%$. With a further increase in the H_2O_2 concentration the leaching efficiency show a very minimal rise. After 3 vol.% H_2O_2 concentration it did not cause notable change in leaching efficiency, for this 3 vol.% considered as optimal concentration.
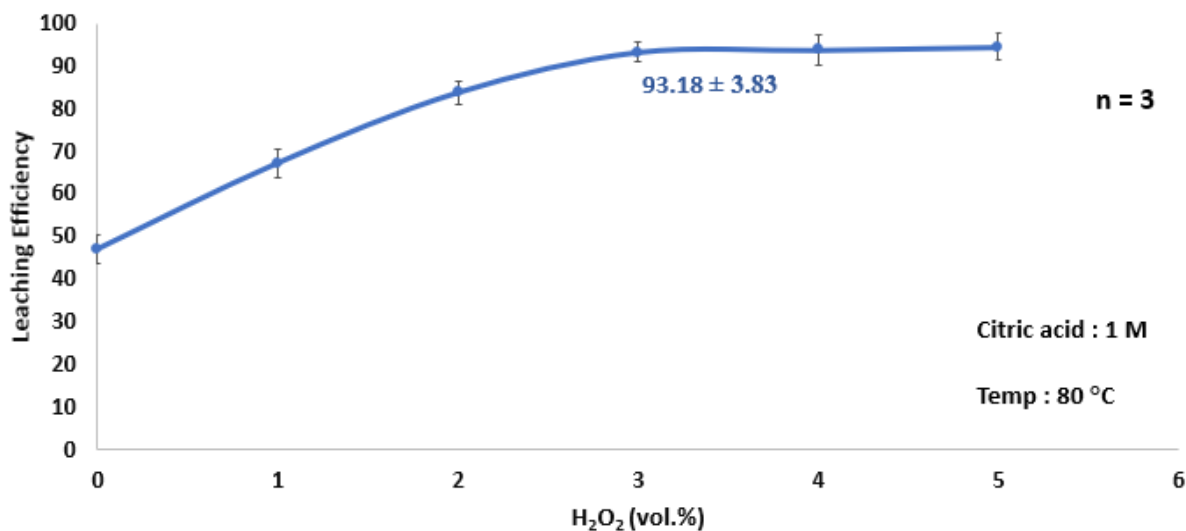
Figure 4.7. Impact of H_2O_2 on lithium leaching efficiency

4.6 Optimized Conditions for Leaching

Series of experiments were repeated under optimized conditions of citric acid concentration of 1 M, H_2O_2 of 3 vol.%, solid to liquid ratio of 40 g L^{-1}, leaching temperature of 80 °C, and reaction time of 2 h, maximum leaching efficiency of Co was $90.20 \pm 3.21\%$ and Li was 93.46 ± 2.85 % shown in figure 4.7. Leaching efficiency of lithium was higher than that of cobalt due to Li^{+1} ion is free between $LiCoO_2$ molecule structure, it can easily be leached out as compare to Co^{+2} which sandwich between the oxygen ions. Also, there is difference in bond lengths and binding energies of lithium and cobalt.
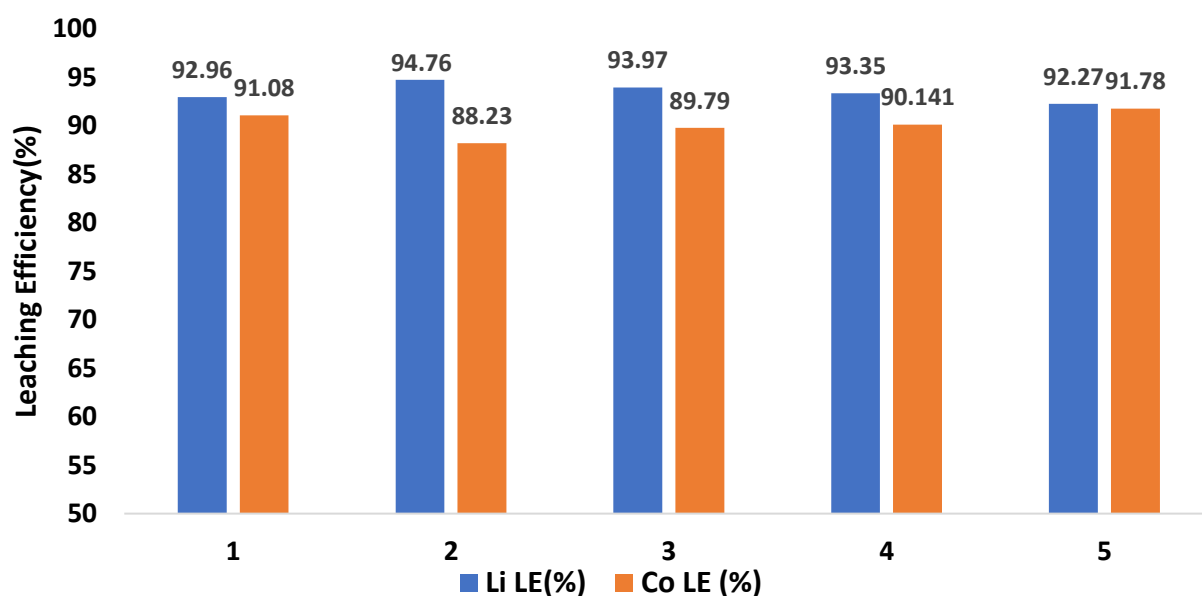
Figure 4.8. Leaching efficiency under optimize conditions

4.7 Synthesis of End Products

4.7.1   Precipitation of Cobalt Oxalate

After filtration of the residue from the leaching solution, filtrate leach liquor allow to reach with stochiometric amount of oxalic acid and control conditions of temperature, stirring speed provided for 1 h. 1 h settling time was given until pink precipitate settle down, which remove from the solution by filtration as shown in Figure 4.8. to precipitate. The precipitating process expressed as;

Figure 4.9. Pink precipitate of cobalt oxalate

4.7.2 Precipitation of Lithium Carbonate

After recovering CoC_2O_4 from the leach liquor, sodium hydroxide was added to rise the PH of solution above 10. Stoichiometric amount of sodium carbonate was added with the control conditions of temperature, stirring speed provided for 1 h and 1 h settling time for precipitate. White lithium carbonate precipitate settled out separate out from the solution using filtration as shown in figure 4.9. The reaction in this formation of lithium carbonate as follows;
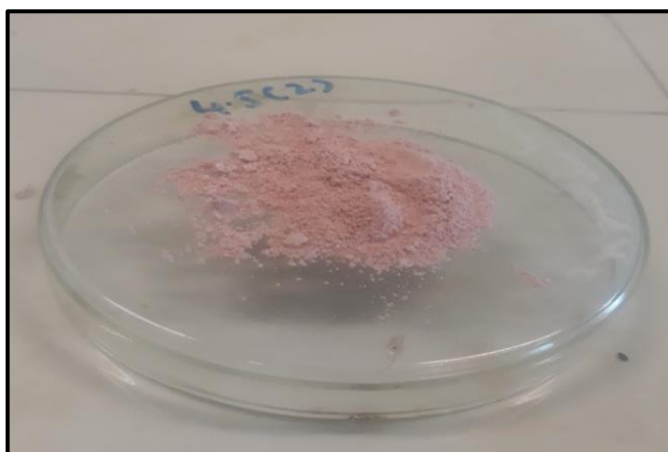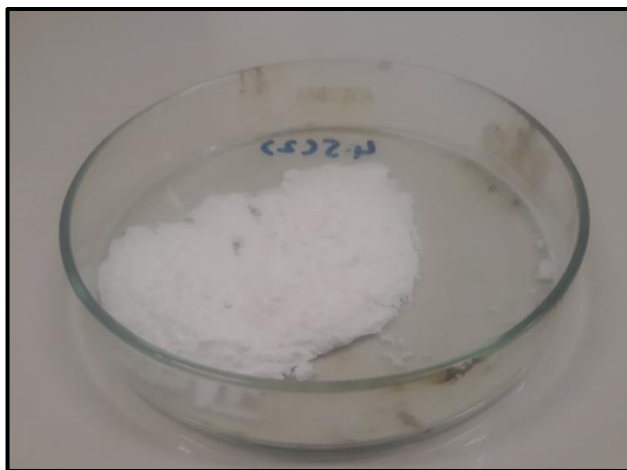

Figure 4.10. White precipitate of lithium carbonate

4.8 Recovery Efficiency

Recovery efficiency was calculated by comparison of theoretical yield and actual yield, theoretical yield of Co^{+2} as cobalt oxalate calculated using equation 4.2 and Li^{+1} as lithium carbonate find by using equation 4.3.

$$Li_2\text{-Cit}_{(aq)} + Co\text{-Cit}_{(aq)} + H_2C_2O_4 \rightleftharpoons CoC_2O_{4(s)} + Li^{+1}_{(aq)} + 2H^{+1}_{(aq)} \qquad (4.2)$$

$$Li_2\text{-Cit}_{(aq)} + Na_2CO_{3\,(aq)} \rightleftharpoons Li_2CO_{3\,(s)} + H_2O_{(aq)} + Na_2\text{-Cit}_{(aq)} + CO_{2\,(g)} \qquad (4.3)$$
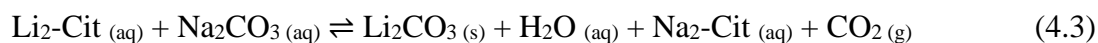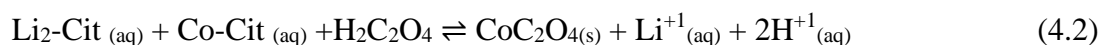
Numbers of times recovery cycle was repeated under optimize conditions and actual yield was note down and compare with theoretical yield to find out recovery efficiency as shown in table 4.4.

Table 4.4. Recovery Efficiency (RE) of synthesis products

Serial No	Cobalt RE (%)	Lithium RE (%)
1	94.52	90.49
2	95.39	92.44
3	96.01	93.17
s4	93.77	89.76
5	97.26	90.24
6	93.15	92.93

Recovery efficiency of lithium as lithium carbonate was 91.5 ± 2.7 and cobalt as cobalt oxalate was 95.02 ± 3.1.

4.9 Analysis of Synthesis Products

4.9.1   Cobalt Oxalate Analysis

An XRD analysis of cobalt oxalate was performed shown in graph in figure 4.9, major peaks are at 15°, 19°, 29.6^o , 31.2^o and 38.3^o that are compare with reference peak using JADE software which conform the presence of cobalt oxalate.
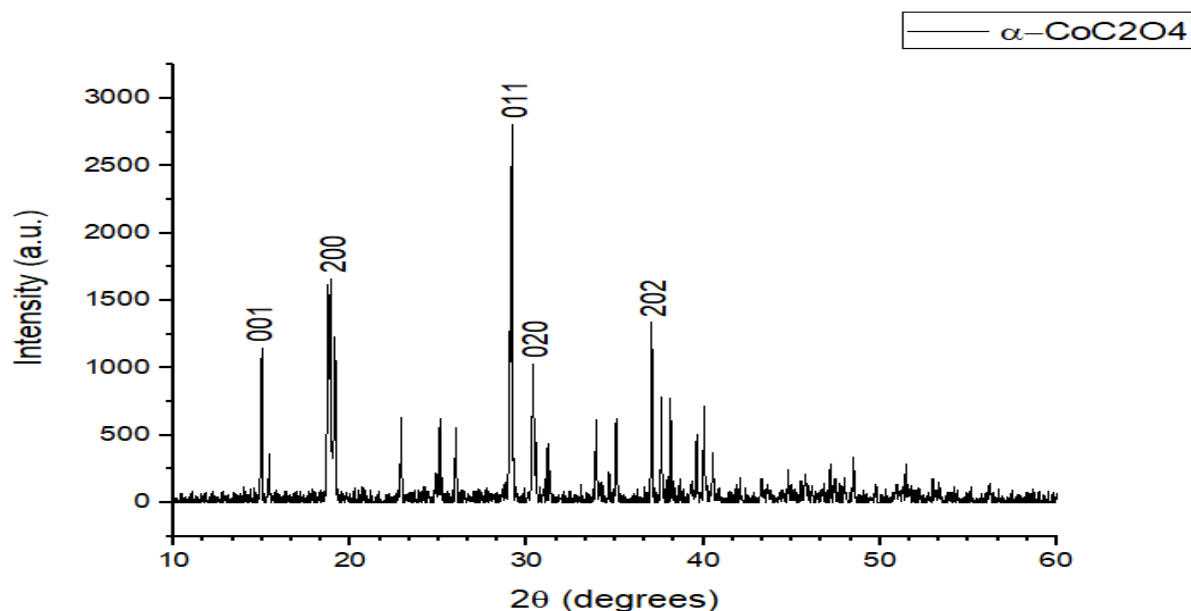
Figure 4.11. XRD of synthesize cobalt oxalate

Purity of synthesis product further confirm by EDS which shows high cobalt oxalate purity of 99.16 in Table 4.5, Small amount of manganese detected as it was present in the original sample of cathode active material.

Table 4.5. EDS of cobalt oxalate produce precipitate

Elements	Weight %
C	18.04
O	62.56
Mn	0.83
Co	18.56
Co_2CO_3	**99.16**

Purity of cobalt oxalate = 99.16 %

4.9.2 Lithium Carbonate Analysis

An XRD analysis of lithium carbonate was performed and graph shown in figure 4.10, major peaks are at 21.25º, 23.35º, 29.31º, 30.48º, 31.68º, 34º,35.92º, 36.81 and 39.48º , compare

with the reference peak with the help of JADE software that confirm the presence of lithium

carbonate.
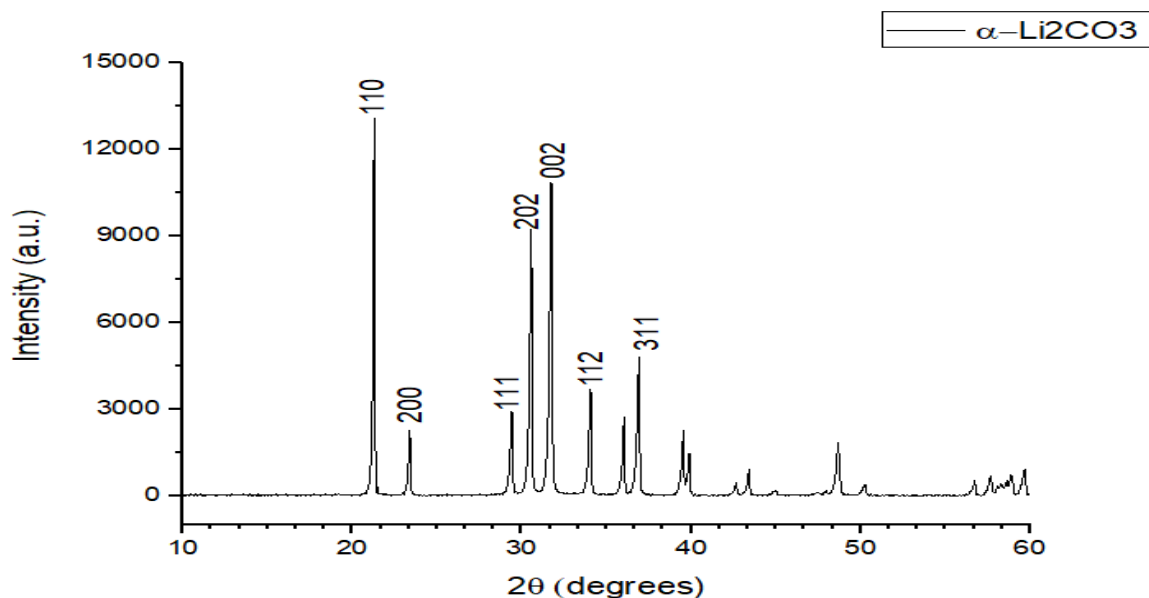
Figure 4.12. XRD graph of precipitated lithium carbonate

The table shows the Energy Dispersive Spectroscopy (EDS) of lithium carbonate with a

high purity of 98.77 in Table 4.6, the minute amount of Mn and Co were detected in the

results as impurity.

Table 4.6. EDS of lithium carbonate produce precipitate

Elements	Weight %
C	19.37
O	59.23
Li	20.17
Mn	0.26
Co	0.97
Li_2CO_3	**98.77**

Purity of Lithium Carbonate = 98.77%

4.10   Comparison of Recovery Rate and Purity of Lithium and Cobalt

Recovery rate calculated with actual yield and theoretical yield while purity of cobalt oxalate and lithium carbonate using EDS (Energy Dispersive Spectroscopy). These two crucial parameters dictate about the worth of recycling lithium ion batteries. Figure 4.10 shows the high purity of about 99% and recovery efficiency above 91% for Li and 95% for Co.
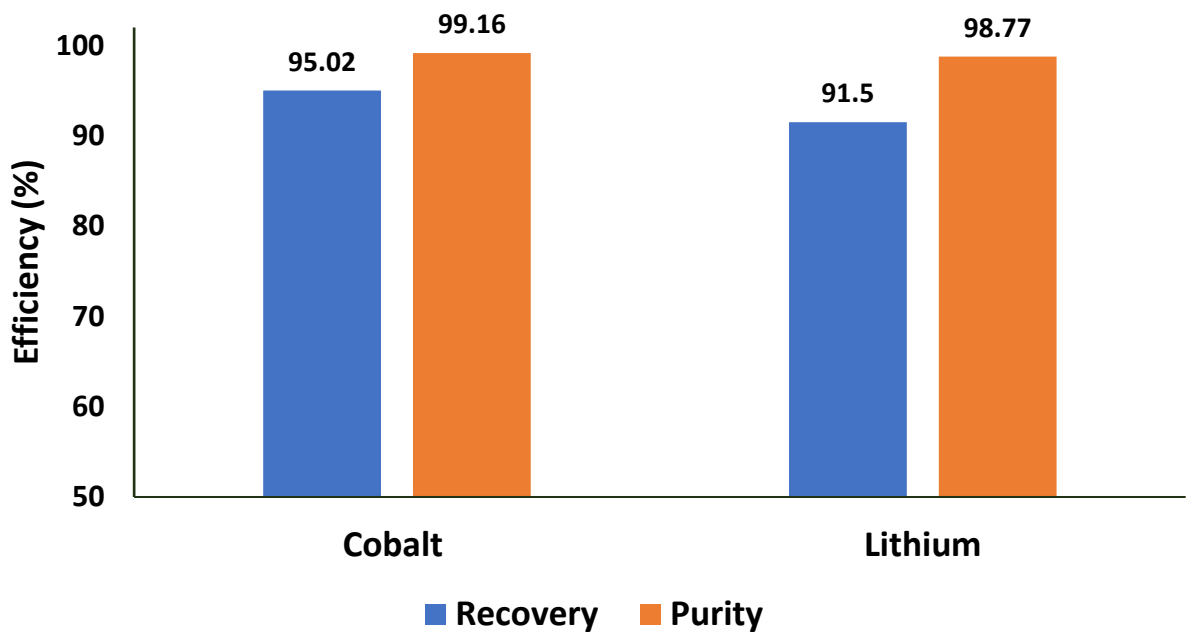
Figure 4.13. Recovery and purity comparison of cobalt and lithium

4.11   Economics of Operations

Lithium ion batteries are converted into useful resources by the synthesis of cobalt oxalate and lithium carbonate. It is economically feasible and both compounds have high market value.

4.11.1   Cobalt Oxalate

Cobalt oxalate = (1kg cathode) × (Co-weight percent) × (Leaching efficiency) × (Dissolution & calcination) × (Recovery efficiency)   (4.4)

Cobalt oxalate = 1 kg cathode ×56% ×90% ×90% ×95.02%

Cobalt oxalate produced using 1 kg cathode material = 0.4536 kg

Market Price of cobalt oxalate = 12,000 Rs/kg

Cobalt oxalate = 12,000 Rs/kg×0.4536 kg

Cobalt oxalate worth = **5,443 Rs**

4.11.2 Lithium Carbonate

Lithium carbonate = (1kg cathode) × (Li-weight percent) × (Leaching efficiency) × (Dissolution & calcination) × (Recovery efficiency)   (4.5)

Lithium carbonate = 1 kg cathode × 6.56% × 90% × 90 × 91.50%

Lithium carbonate = 0.0486 kg = 48.6 g

Market price of lithium carbonate = 10,000 Rs/Kg

Lithium carbonate = 10,000 Rs/kg×0.0486 kg

Lithium carbonate worth = **486 Rs**

4.11.3 Chemical Cost

It's the sum of all the chemicals used during the treatment of one-kilogram cathode material.

4.11.3.1 Citric Acid

1 Kg of cathode treatment required = 1 kg of citric acid

Market price of citric acid = 750 Rs/Kg

Required citric acid = **750** Rs

4.11.3.2 Hydrogen Peroxide

1 Kg of cathode treatment required = 375 ml of H_2O_2

Market price of H_2O_2 = 700 Rs/L

Required H_2O_2 = **262.5** Rs

4.11.3.3 Sodium Hydroxide

1 Kg of cathode treatment required = 200 g of sodium hydroxide

Market price of sodium hydroxide = 1100 Rs/Kg

Required sodium hydroxide = **220** Rs

4.11.3.4 Oxalic Acid

Cobalt ions = (1kg cathode) × (Co-weight percent) × (Leaching efficiency) × (Dissolution & calcination)   (4.6)

Cobalt ions = 1 kg cathode × 56.55% × 90% × 90%

1 Kg of cathode Produce = 453.6 g of Co^{+2}

By Stoichiometry

0.32 g of cobalt ion required = 0.55 g of oxalic acid

453.6 g of Co^{+2} required = (0.55/0.32) × 453.6 g

453.6 g of Co^{+2} required = 779.6 or 0.78Kg of oxalic acid

Market price of oxalic acid = 750 Rs/kg

Required oxalic acid = **585** Rs

4.11.3.5 Sodium Carbonate

Lithium carbonate = (1kg cathode) × (Li-weight percent) × (Leaching efficiency) × (Dissolution & calcination)   (4.7)

Lithium carbonate = 1 kg cathode × 6.56% × 90% × 90%

1 Kg of cathode Produce = 53.1 g of Li^{+1}

By Stoichiometry

0.076 g of lithium ions required = 0.7 g of oxalic acid

53.1 g of Li^{+1} required = (0.7/0.076) × 53.1 g

53.1 g of Li^{+1} required = 489 g or 0.489 Kg of sodium carbonate

Market price of sodium carbonate = 650 Rs/kg

Required sodium carbonate = **318** Rs

4.11.4 Energy Expenditure

Energy requirement for the treatment of one-kilogram cathode material by following steps

4.11.4.1 Leaching Process

By specific heat formula.

$Q = m_{ca} \times Cp_{ca} \times \Delta T$ (4.8)

Heat capacity $= Cp_{ca} = 252.1$ J/mol.K

$\Delta T = 80°C = 353$ K

density $= m_{ca} / vol$

$d = 1.018$ kg/L & Vol $= 25$ L

$m_{ca} = 1.018$ kg/L $\times 25$ L

$m_{ca} = 25.45$ kg $= 25450$ g

molar M $= 192.12$ g

Moles $= 132.5$ mol   Now,

$Q = 132.5$ mol $\times 252.1$ J/mol.K $\times 353$ K

$Q = 11,791,347 =$

$P = 11,791,347$ J $/ 7200$s

$P = 5,637$W $= 5.64$ KW

Cost $= 5.64$ KW $\times 2$ h $\times 17 =$ Rs 192

4.11.4.2 Dissolution Process

$Q = m_{na} \times Cp_{na} \times \Delta T$

Heat capacity $= Cp_{ca} = 28.23$ J/mol.K

$\Delta T = 100°C = 373$ K

density $= m_{ca} / vol$

$d = 2.13$ kg/L & 1 kg $= 25$ L

$m_{ca} = 2.13$ kg/L $\times 25$ L

$m_{ca} = 53.25$ kg $= 53250$ g

Molar mass of sodium hydroxide $= 40$ g

Moles $= 1,331.25$ mol

$Q = 1,331.25$ mol $\times 28.23$ J/mol.K $\times 373$ K

$Q = 14,017,783$ J

P = 14,017,783 J / 3600s

P = 3894 W = 3.9 KW

Cost = 3.9 KW × 1 h × 17 = Rs 2.65 Rs

4.11.4.3 Calcination Process

Muffle furnace energy requirement = 1.5 kW

Run time is 2 h so 3 kW

Commercial unit rate = 17 Rs/kWh

Cost of calcination activity = 51 Rs

Labor Cost

Discharging activity required = 6 h

Dismantling activity require   = 3 h

Dissolution activity require   = 1 h

Calcination activity require   = 2 h

Precipitate activity require   = 4 h

Total time for 1 kg cathode material = 16 h

8 h labor cost = 600 Rs

16 h labor cost = 1200 Rs

Total labor cost for treating 1 kg cathode material = 1200 Rs

4.11.5 Net Profit

Net profit included the economic benefits of products subtracting the chemical cost and energy expenditures and labor cost while ignoring miscellaneous cost.

Net Profit = (Economical benefits of products) - (Chemical Cost + Energy Expenditures + Labor Cost)

Net Profit = (5,443 + 486) - (750 + 262.5 + 220+ 585 +318 + 309 + 1200)

Net Profit = 5,929 – 3,644

Net Profit = **2,285 Rs/kg** cathode material of LIBs treated.

Chapter 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

➢ The sustainable recovery of metals from waste LIBs promise economic and environmental benefits.

➢ This work is mainly focused on a green strategy by using organic acid for the sustainable recovery of metals from spent LIBs.

➢ About **90%** of Co and **93% of Li** were leached under the optimized conditions of, 80 °C temperature, 1.0 M citric acid concentration, 3 vol.% hydrogen peroxide, 2 h leaching time, 40 g/L solid to liquid ratio and 350 RPM stirring speed.

➢ Product recovery efficiency of **95.02 ± 3.1** for cobalt as cobalt oxalate and **91.5 ± 2.7** for lithium as lithium carbonate was obtained.

➢ Purity of cobalt oxalate obtained was **99.16%** and lithium carbonate was **98.77%.**

➢ By treating 1 kg of lithium ion batteries cathode material net profit of **2,285 Rs** can be earn.

5.2 Recommendations

➢ Laptop and electric LIBs can also be used instead of used mobile LIBs for recovery of useful metals.

➢ Future research should be on other component of LIBs such as anode, steel and plastic for the development of new market.

➢ Various organic acid with high leaching efficiency can be used in place of citric acid to leach out lithium and cobalt.

➢ Lab scale setup should be upgraded to pilot scale in IESE NUST for future research.

Chapter 6

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