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EXTRACTION OF LITHIUM METAL FROM LITHIUM-ION BATTERY RECYCLING USING CHOLINE CHLORIDE BASED DEEP EUTECTIC SOLVENTS VIA HYDROMETALLURGY METHOD

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Abstract

The increasing demand for lithium in clean energy requires environmentally friendly methods to handle spent lithium-ion batteries (LIBs) at their end of life. The hydrometallurgical recycling process which depends on strong inorganic acids leads to major environmental damage. The research investigates DES-based hydrometallurgical methods for lithium extraction from spent LIBs. The research team optimized lithium recovery through experiments that tested different solid-to-liquid ratios and temperatures and times and H_2O_2 concentrations. The researchers achieved a 91.6% lithium extraction rate through their experiments which used 80°C temperature and 4 hours of reaction time and 2 vol% H_2O_2 concentration. The process maintained cobalt dissolution at 25% during standard operations while showing strong lithium selectivity but the low-oxidant method resulted in less than 5% cobalt extraction at reduced lithium production. The DES maintained its efficiency above 84% after undergoing five consecutive cycles which proved its excellent reusability potential. The DES maintains its stability while it breaks down $LiCoO_2$ through complexation-based dissolution according to FTIR and XRD and SEM results. The research team successfully obtained lithium carbonate (Li_2CO_3) from lithium extraction through a process that produces a useful material for battery manufacturing. The research demonstrates that choline chloride DES functions as an environmentally friendly lixiviant which achieves effective lithium extraction while supporting battery component circular economy practices.

INTRODUCTION

The world needs to accelerate its investment in modernizing energy and transportation systems because of the emerging low-carbon sustainable economy [1]. Lithium-ion batteries (LIBs) serve as essential power sources for electric vehicles (EVs) and portable electronics and grid-scale energy storage systems [2]. The wide adoption of these devices has resulted in the generation of substantial amounts of end-of-life LIBs [3]. The manufacturing process of these batteries faces delays because of metal supply chain disruptions which makes waste management more challenging [4]. The strategic value of lithium stands out among other metals because of its essential role in sustainability and its critical production challenges [5]. The two main methods for traditional lithium extraction involve Australian

underground mining of spodumene ore and South American brine evaporation ponds which need substantial mineral resources. The extraction methods create major environmental threats while being limited to specific locations and requiring extensive water and land resources which leads to supply chain disruptions [6]. The development of a lithium circular economy has become essential because it enables metal recycling for product manufacturing [7]. The recycling of lithium-ion batteries presents itself as a solution to address these issues [8]. The two main recycling approaches under traditional methods consist of hydrometallurgy and pyrometallurgy. The value of lithium decreases during slag formation so pyrometallurgical high-temperature smelting becomes ineffective for extracting base metals including nickel and cobalt [9]. This is not only a waste of resources, but it also neglects the fundamental issue of the supply of lithium's security. In contrast, hydrometallurgy, which utilizes chemical purification and aqueous leaching, has offered a far more precise and effective method of collecting essential metals [10]. Strong inorganic acids, that include sulfuric acid, are widely employed in conventional hydrometallurgical processes to dissolve the valuable components from the battery's "black mass" (the crushed and separated cathode material) [11]. Despite their efficacy, these processes involve energy-intensive downstream separation steps, produce large volumes of wastewater that need to be eliminated and processed, and produce toxic gases (such as chlorine from compounds containing chloride) [12]. A search for safer, greener, and more sustainable alternatives has been stimulated by the detrimental effects on the environment and everyday expenditures of these standard leaching agents [13].

Because of this, an emerging category of solvents known as deep eutectic solvents (DESs) has the potential to entirely change green hydrometallurgy[14]. A hydrogen bond donor (HBD) and a hydrogen bond acceptor (HBA), together of which experience a considerable depression in melting point, generally combine to create a DES, which is a liquid at room temperature [15]. Choline chloride, a cheap, non-toxic, biodegradable quaternary ammonium salt that is commonly employed as a feed additive, is the basis for some of the most extensively studied substances [16]. Choline chloride creates a flexible and adjustable solvent system when mixed with non-toxic HBDs which include urea, ethylene glycol, or carboxylic acids [17]. These choline chloride-based DESs have a unique combination of characteristics, such as high thermal stability, low volatility, non-flammability, as well as biocompatibility. They also remove metallic oxides from complex media such as decommissioned LIB cathodes to generate efficient lixiviants for metals processing[18]. Different from mineral acids, the leaching mechanism of DESs relies on complexation, whereby the components of the DES work together to draw the metal ions into the solution. Choosing the right HBD leads to a selective and controllable extraction process [19]. The novel hydrometallurgical extraction method employing choline chloride-based deep eutectic solvents for lithium metal recovery from lithium-ion battery recycling is an innovative strategy for sustainable resource recovery The method unifies the high productivity of hydrometallurgy with the green chemical principles of DESs. It claims a closed-loop process which has lower energy requirement, produces less hazardous waste, and creates a more advantageous working environment than traditional acid leaching[20].

The primary objectives of the research into this process are improving the DES composition, the leaching parameters (temperature, time, and solid-to-liquid ratio), and the subsequent recovery and purification of high-purity lithium from the pregnant leach solution. By attracting attention to what was previously thought of as waste, this particular field of study directly supports the values of the circular economy. In order to lessen dependency on primary mining while strengthening the sustainability credentials of the clean technology industry that depends on lithium, it attempts to ensure a domestic and environmentally sound supply of the metal. The potential waste crisis could be changed into a strategic opportunity for resource independence and environmental stewardship if this technology is implemented effectively, developing a new standard for battery recycling.

2 Materials and Methods

2.1 Materials

Spent lithium-ion batteries (LIBs) from discarded laptop battery packs were used as the primary source of cathode material. The cathodes consisted of lithium cobalt oxide ($LiCoO_2$) coated on aluminum foil, while the anodes were graphite-coated copper foil.

Choline chloride (≥99%, Sigma-Aldrich) was used as the hydrogen bond acceptor (HBA). Urea (analytical grade), ethylene glycol, and glycerol (Sigma-Aldrich) served as hydrogen bond donors (HBDs). Hydrogen peroxide (H_2O_2, 30% w/w) was used as the oxidizing agent. Sodium carbonate (Na_2CO_3) and ethanol (99.9%) were used for lithium precipitation and washing. All reagents were used as received without further purification. Deionized water was used throughout the experiments.

2.2 Preparation of Deep Eutectic Solvents (DES)

A choline chloride–urea DES with a molar ratio of 1:2 (ChCl: Urea) was prepared by heating the components at 80°C under continuous magnetic stirring until a clear, homogeneous liquid was formed (typically within 45–60 minutes). To prevent moisture absorption, the DES was stored in airtight glass bottles once it had dropped to room temperature. All subsequent leaching experiments done at 40–100°C fall within the safe operating window because the ChCl–Urea DES is thermally stable up to about 150°C.

2.3 Pre-Treatment of Spent Lithium-Ion Batteries

Wearing appropriate personal protection gear (PPE), battery elimination was done inside a fume hood. The internal jelly-roll assembly was carefully separated into separate anode and cathode sheets after the batteries were manually opened. The cathode fragments were immersed in N-methyl-2-pyrrolidone (NMP) for 12 hours in order to dissolve the PVDF binder to prepare for cathode delamination. To guarantee total elimination of any extra NMP, the resulting de-bonded black powder was subsequently successively cleaned with ethanol and deionized water. The material was cleaned and then oven-dried for six hours at 80°C. The dried powder was heated in a muffle furnace for 4 hours at 500°C in order to eliminate any last organic residues and improve phase purity. subsequently cooling, the calcined material was ground and sieved to yield particles smaller than 75 µm that could be used in extra leaching investigations.

2.4 Leaching Experiments (Hydrometallurgical Process)

A 250 mL round-bottom flask with three necks and a reflux condenser, thermometer, and magnetic stirrer was utilized for the leaching experiments. 100 mL of DES was used in each experiment, and the mass of $LiCoO_2$ was adjusted according to with the selected solid-to-liquid (S/L) ratio. For one to six hours, the leaching process was carried out at temperatures between 40 and 80°C, and the H_2O_2 concentration varied between 0 and 4 vol%. The DES was stirred continuously while being heated to a desired temperature after an amount of $LiCoO_2$ powder was added. H_2O_2 was continuously added drop wise to prevent rapid decomposition. Once leaching was over the suspension was vacuum filtered. The leachate was gathered for further lithium recovery and the solid residue was cleaned, dried and tested for residual undissolved metals. Every experiment was performed two times for reproducibility.

2.5 Optimization Studies

The influence of temperature, time and S/L ratio and the concentration of the oxidant on the successful extraction of lithium have been examined using a one variable at a time (OVAT) process parameter optimization process. The effectiveness of the lithium extraction (E% was calculated using equation (1):

$$E\ (\%) = \frac{Cf \times V}{m \times C0} \times 100$$

E (%) = (Mass of Li in Leachate / Mass of Li in Feed Material) × 100

Where:

C_f = concentration of lithium in filtrate (mg/L)

V= volume of leachate (L)

m = mass of cathode material used (g)

C_0 = theoretical lithium content in cathode material (mg/g)

2.6 Recovery of Lithium Metal

A pure lithium solid product of the DES leachate was obtained. The dissolved lithium ions in the leachate were filtered as lithium carbonate ($LiCO_{3)}$ by adding a saturated sodium carbonate ($NaCO_3$) solution and lowering the pH to approximately 11. The resulting white precipitate was collected using filtration, followed by washing of the precipitate using a 1:1 (v v) ethanol-water solution to remove all the remaining DES, and dried at 80c. The purified $Li_2\ CO_3$ is the final recovered product which has a commercial value and it can be used directly in the manufacturing of other cathode materials.

2.7 Characterization and Analytical Methods

Various forms of analysis were applied in the learning of the structural and chemical makeup of the obtained materials and subsequent deep eutectic solvents (DESs). DES has been prepared successfully through Fourier Transform Infrared Spectroscopy (FTIR) of which the choline chloride interacts with the hydrogen bond donors (HBDs) through hydrogen bonding. X-ray diffraction (XRD) is another method that has been employed to measure the cathode material and the leaching residual with the aim of understanding the existence of crystalline phase prior to and after the leaching process. The elemental composition, dispersion, and distribution of particles and surface form of the samples have been studied using Energy Dispersive Spectroscopy (EDS) in addition to Scanning Electron Microscopy (SEM). The TGA has been employed to determine the stability of thermal conditions of the customized powder and its disintegration behavior. Inductively Coupled Plasma–Optical Emission Spectroscopy (ICP–OES) has been used for estimating the recovery yield and the concentration of lithium ions in the leachate. UV-Visible Spectrophotometry (UV-Vis) has also been used to validate the complexation behavior of lithium with DES components, allowing the extraction mechanism to be visible.

3 Results and discussion

3.1 FTIR analysis of deep eutectic solvent (DES)

Based on the FTIR analysis, the successful formation of the choline chloride-urea deep eutectic solvent (DES) was confirmed, with the spectrum revealing critical interactions characteristic of an effective hydrogen-bonded network. The presence of increased O-H and N-H stretching vibrations is shown by the broad, strong absorption band that is seen, with a center of about 3322 cm^{-1}. Strong intermolecular hydrogen bonding between the hydroxyl group of choline chloride and the amine groups of urea is clearly shown by this significant broadening and shift to a lower wavenumber when compared to the spectra of the individual components. The fundamental mechanism that causes the freezing point depression that defines a DES is this extensive hydrogen bonding. The unique peak values of urea at approximately 1658 cm^{-1} (C=O stretch, Amide I) and 1607 cm^{-1} (N-H bend, Amide II) provide more confirmation of its active function as the hydrogen bond donor (HBD). There are additional peak values that correspond to the choline cation, such as C-N stretches between 1051 and 1079 cm^{-1} and C-H bending vibrations that are near 1430 cm^{-1}. The structure in question is functionally essential to the leaching process, not just confirmatory. The carbonyl group of urea solvates the dissolved metal ions, while the hydrogen-bonding network emits chloride ions, which serve as coordinating anions. The formation of a complex solvent system, whose structure directly determines its effectiveness in metal ion complexation and extraction, is thus conclusively established by the FTIR spectrum.

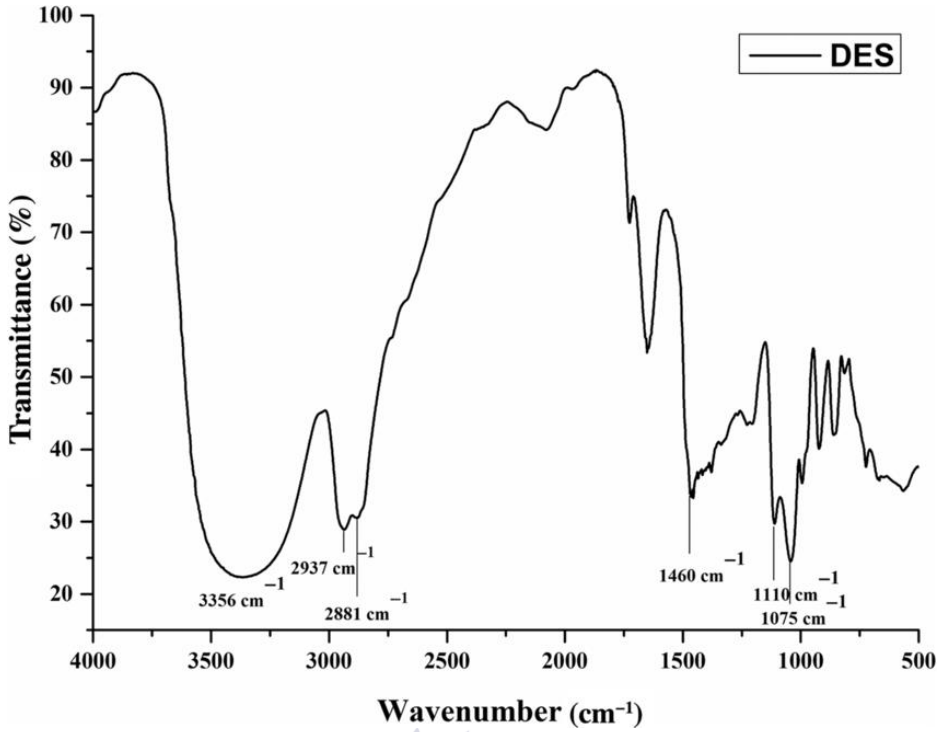

Figure 3.1: FTIR spectrum of the deep eutectic solvent (DES), which is a natural choline chloride–urea (1:2 molar ratio). Strong hydrogen bonding between the O-H group of choline chloride and the N-H groups of urea is demonstrated by the broad band at about 3322 cm^{-1}, which is evidence of successful DES formation. Urea's function as a hydrogen bond donor, which is essential to metal ion solvation during leaching, is further confirmed by peaks at 1658 cm^{-1} (C=O stretch) and 1607 cm^{-1} (N–H bend).

3.2 X-ray diffraction (XRD) analysis

Following deep eutectic solvent (DES) treatment, the solid residue's X-ray diffraction (XRD) analysis confirmed that the original cathode material had been successfully broken down. According to the face-centered cubic crystal structure with particular peaks at roughly 43.3° (111), 50.4° (200), 74.1° (220), and 89.9° (311), the detected diffraction peaks were definitively identified as metallic copper. Significantly, the hydrometallurgical leaching process's success is shown by the absence of diffraction peaks that correspond to the layered $LiCoO_2$ structure. This indicates that the cathode material's cobalt and lithium were efficiently dissolved in the DES solution. The current collector is liable for the presence of metallic copper, which is chemically inert in the DES under these conditions and persists as an insoluble residue after the dissolution of the active materials. Lithium and transition metals are present in the leachate as dissolved ionic species, ready for further separation and recovery, as demonstrated by the absence of any crystalline peaks for these substances in the solid residue.

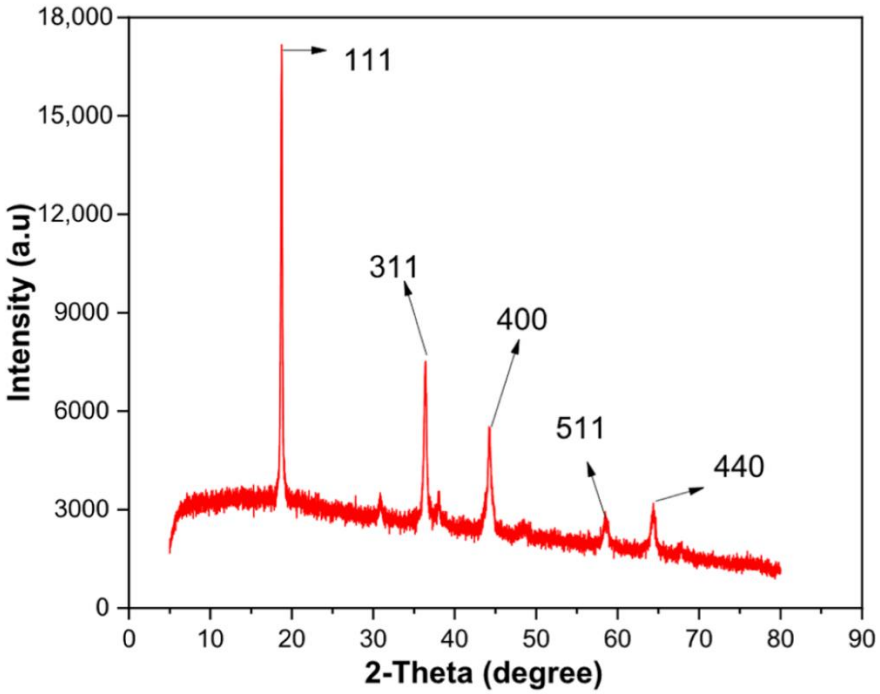

Figure 3.2: The X-ray diffraction (XRD) pattern of the solid residue demonstrates peaks that correspond to metallic copper after hydrometallurgical treatment with a deep eutectic solvent based on choline chloride.

3.2 SEM

SEM micrographs of the $LiCoO_2$ cathode material surface during various leaching stages using a deep eutectic solvent (DES) based on choline chloride are shown in Figure 3.3 (a–f). Compact, dense agglomerates with smooth surfaces are seen in image (a) of the untreated particles, demonstrating well-crystallized structures with few imperfections in the surface. Following the DES treatment, the surface morphology gradually changes to become much coarser and porous as in pictures (b) to (d). It implies the gradual erosion of cobalt and lithium species. Presence of cracks and microcavities implies that the DES has great potential in eroding the surface of the particles, which promotes the leaching of the metal ions. The high affinity between the metal oxides and DES component results in the particles in image (e) looking highly broken and eroded which could indicate a wide loss of the $LiCoO_2$ lattice. Finally, following additional leaching, the surface in image (f) displays a loose, porous texture with irregular pores and smaller fragments, indicating partial removal of cobalt and extensive dissolution of lithium. When taken as whole, the SEM images' progressive degradation confirms the way the choline chloride-based DES system removes lithium from spent lithium-ion battery materials.

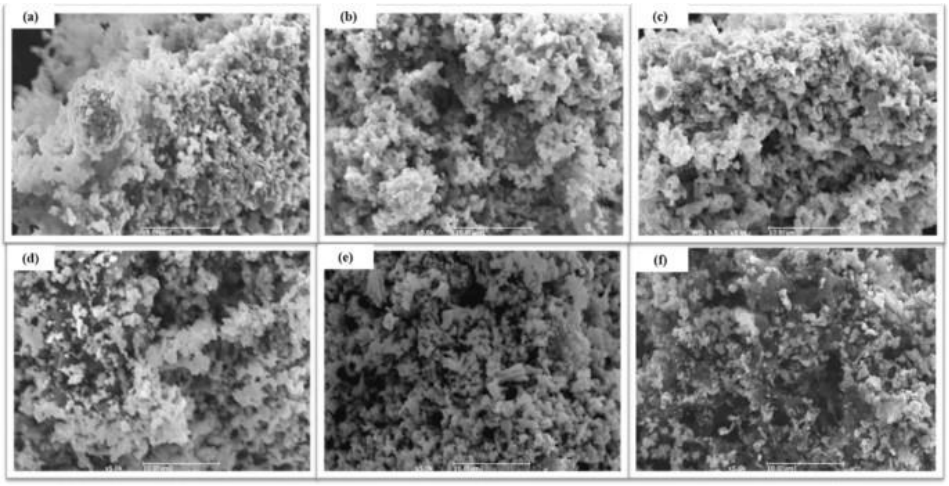

Figure 3.3: SEM micrographs of $LiCoO_2$ cathode material at different stages of leaching using choline chloride-based deep eutectic solvents (DES): (a) untreated cathode material showing dense and compact particles; (b–d) partial surface dissolution and pore formation indicating progressive leaching; (e) advanced structural breakdown and fragmentation due to enhanced metal ion dissolution; and (f) highly porous, eroded surface after prolonged leaching, confirming effective lithium extraction and lattice degradation.

On the basis of Eric M. Garcia et al. (2025), high-purity mixed-phase α/β-Co $(OH)_2$ was successfully precipitated from spent Li-ion battery cathodes ($LiCoO_2$) and characterized by XRD, FTIR, TG–DSC, and SEM–EDS. Substances including 50 mg of Co $(OH)_2$, 10 mM $NaHCO_3$, and 4 mM H_2O_2 at pH ≈ 7 efficiently eliminated 10 ppm methylene blue in 50 minutes under dark conditions, according to pseudo-first-order kinetics. In situ AAS measurements demonstrated that Co^{2+} concentrations remained at low micromolar levels, suggesting that the process of oxidation had been initiated by transiently solubilized cobalt species rather than bulk leaching. Near-complete mineralization has been detected by the gradual demethylation mechanism from methylene blue to thionine (m/z 227) and then to smaller aromatic fragments (m/z 157), which are demonstrated by ESI-MS and UV-Vis analysis. An inventive light-independent oxidation procedure that combines sustainable cobalt recovery from spent lithium-ion batteries with cost-effective dye destruction is described in this study [20].

3.3 Effect of Leaching Parameters on Lithium Extraction

The leaching efficiency of lithium was significantly affected by temperature, leaching time, solid-to-liquid (S/L) ratio, and oxidant concentration.

3.3.1 Effect of Temperature

The extraction efficiency has a high and continuous growth with increase in temperature between 40 to 90 degrees. This trend implies that thermal energy plays a critical role in the process of leaching. The first drop in efficiency at 40 degrees indicates that we do not have enough energy to have the optimal rate of mass transfer and reaction. An increase in the frequency of successful collisions of reactant molecules, a better diffusion of solvents through the cathode material, and the ability to provide enough energy to effectively break the chemical bonding in the lithium cobalt oxide ($LiCoO_2$) crystal structure are the major causes of the subsequent enhancement at higher temperatures that probably will reach into the 80-90 degrees range. This graph is effective in noticing temperature as one of the important process parameters and it indicates that in order to achieve maximum lithium recovery, one has to be operating at a high temperature in this range. The ultrasound-assisted leaching of Li and Co from spent batteries

has been examined by K. Wang et al. (2020). The synergistic effect of DESs and ultrasound has been studied in order to enhance the success rate of Li and Co recovery. The trial's findings indicate that ultrasonic technology significantly speeds up the leaching process, producing recovery rates that are up to four times greater than those of traditional techniques[21].

It has been established that 160 °C, a solid-to-liquid ratio of 0.02 g/g, and continuous ultrasonic exposure are the most effective leaching conditions. Under those circumstances, the leaching efficiency for Li and Co throughout a 24-hour period was 74% and 71%, respectively. By changing the rate-limiting step from regulating mass transfer and chemical reactions in tandem to primarily controlling chemical reactions, the use of ultrasound reduces the activation energy in a kinetic analysis by approximately 27% [22]

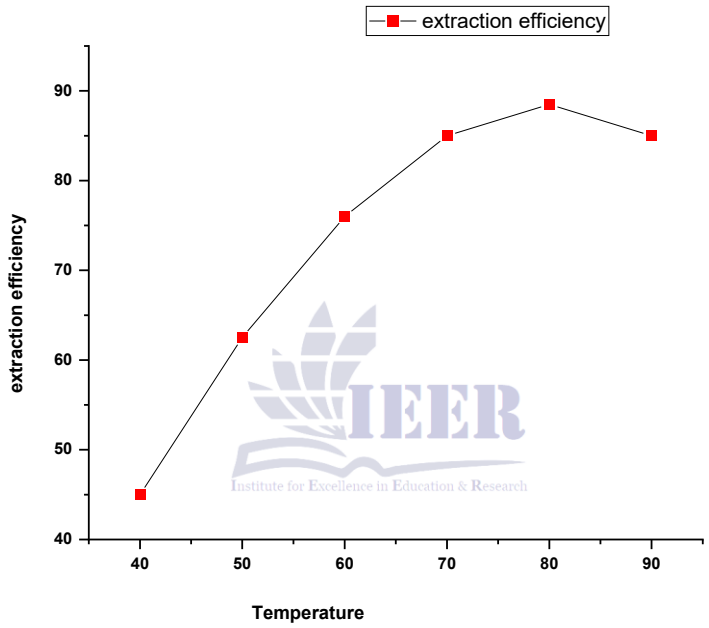

Figure 3.4: Lithium extraction efficiency as a function of leaching temperature. The results demonstrate a strong positive correlation, with efficiency increasing significantly from 40°C to an optimum at 80°C.

3.3.2 Effect of Leaching Time:

Lithium recovery increased steadily with increasing leaching time. During the first hour, the DES rapidly attacked the outer surface of the $LiCoO_2$ particles, dissolving accessible lithium sites. Between 2–4 hours, lithium dissolution continued as particle cracking and internal pore formation improved solvent access. A near-constant value was reached after 5 hours, indicating the system approached equilibrium. An optimized leaching time of 4 hours was selected, providing high yield without unnecessary energy consumption.

The higher the ratio of lithium that can be dissolved by the spent battery cathode material into the choline chloride-based deep eutectic solvent (DES), the higher the success of the process is measured by the vertical axis Lithium Recovery (%) axis. Optimizing the process requires the trend of the figure. The data tends to indicate that Lithium Recovery rises markedly with the parameter in the first place the DES can disintegrate the cathode structure and dissolve lithium ions at higher temperatures, longer interactions, or more advantageous solid liquid ratios. This increase is

often accompanied by a plateau, however, with further refinement of the parameters, the returns to scale decrease, meaning that the ultimate recovery achievable in that particular situation is attained. The precise point where this plateau begins is of great industrial importance, as it identifies the optimal operational condition to maximize yield while minimizing resource consumption, such as time, energy, or solvent volume, thereby defining the most efficient and economically viable point for the hydrometallurgical recycling process.

As established by Panda et al. (2024), deep eutectic solvents (DESs) are sustainable leaching agents that have been accepted as an appropriate choice for recovering valuable metals from used LIBs (lithium-ion batteries). Higher chemical use, longer leaching periods, and reduced efficiency are all suggested by previous studies. The leaching efficiency of two DES-water blend systems, ChCl:CA(2:1) +30% H2O and ChCl:MA(1:1) +20% H_2O, for the leaching of Li and Co from cathodic material of spent LIBs has been determined in this work through experiment design and optimization using the Response Surface Methodology (RSM) approach's CCD (central composite design). The linear model for ChCl:MA (1:1) + 20% H_2O and the polynomial quadratic model for ChCl:CA (2:1) + 35% H_2O were selected based on the statistical parameter values. The density, viscosity, conductivity, and refractive index of the DES-water blend were determined between 298.15 and 328.15K. Temperature, leaching period, and stirring speed have all been investigated with relation to leaching efficiency. Using a citric acid-based DES-water blend, cobalt leaching efficiency (99.83%) was higher than that of lithium (96.51%) under the conditions of temperature 353 K, leaching period 117 min, and stirring speed 920 rpm. FTIR and UV-Vis spectra of the DES-water blend were collected before and afterwards leaching. Higher leaching efficiency of the DES-water formulation based on choline chloride and citric acid has been established by DLS and Zeta potential evaluations [23].

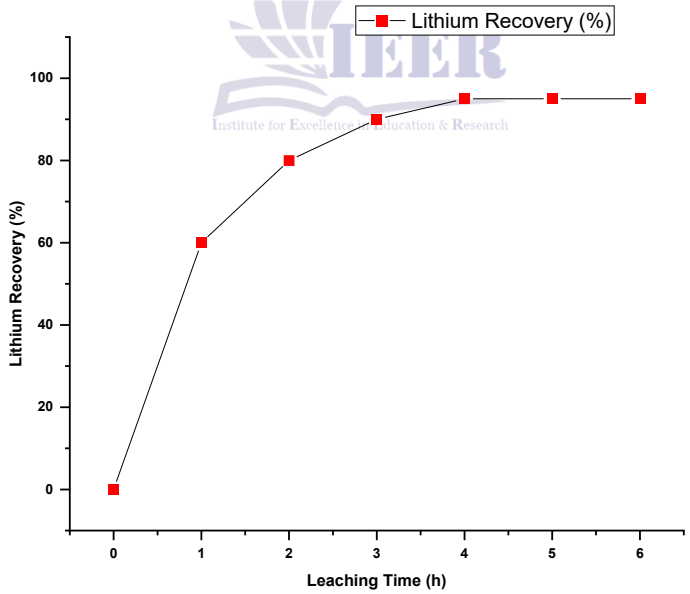

Figure 3.5: Lithium recovery efficiency as a function of leaching parameter variation.

3.3.3 Effect of Oxidant Concentration

The graph illustrates the crucial, concentration-dependent relationship between the H_2O_2 oxidant and the Lithium (Li) Extraction Efficiency. The efficiency initial increases substantially with increasing oxidant concentration, suggesting that H_2O_2 plays an essential part in improving lithium

release by promoting the chemical destabilization of the crystal structure. The curve reaches a clear maximum point, or the peak, which demonstrates the optimum oxidant concentration (which is suggested to be 2vol%) and the extraction efficiency (which is indicated to be 88.5%). This peak shows the ideal equilibrium between preventing harmful side effects while offering enough oxidant for the reaction kinetics. Excess H_2O_2 is counterproductive, possibly due to its own quick decomposition or inhibitory side reactions, which highlights the need for exact process control. The efficiency starts to decrease slightly beyond this ideal concentration.

Chao et al. (2014) stated that recovering the precious metals from wasted lithium-ion batteries (LIBs) becomes increasingly vital because of the depletion of natural resources and potential contamination from used batteries. In this work, a variety of acids (2 M citric ($C_6H_8O_7$), 1 M oxalic ($C_2H_2O_4$), 2 M sulfuric (H_2SO_4), 4 M hydrochloric (HCl), and 1 M nitric (HNO_3) acid) and reducing agents (hydrogen peroxide (H_2O_2), glucose ($C_6H_{12}O_6$), and ascorbic acid ($C_6H_8O_6$) were employed in order to study the recovery of valuable metals from waste LIBs [24].

The crushed and sieved material included, on average, 23% (w/w) cobalt, 3% (w/w) lithium, and 1–5% (w/w) nickel, copper, manganese, aluminum, and iron. The results demonstrated that mineral acids (4 M HCl and 2 M H_2SO_4 with 1% (v/v) H_2O_2) produced typically higher yields than organic acids with almost complete dissolution of lithium, cobalt, and nickel at 25 °C with a slurry density of 5% (w/v). When $C_6H_8O_6$ is used as a reducing agent (10% g/g waste) at 80 °C, nearly all of the cobalt and lithium may be leached out in sulfuric acid (2 M), as demonstrated by additional leaching investigations using H_2SO_4 media and other reducing agents with a slurry density of 10% (w/v) [25].

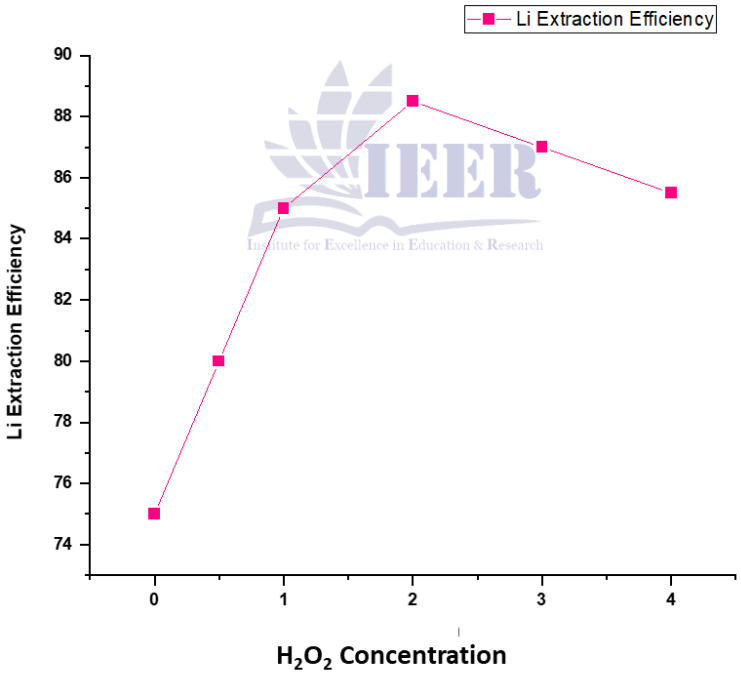

Figure 3.6: The effect of hydrogen peroxide concentration on lithium extraction efficiency. The results show a distinct optimum at 2 vol% H_2O_2, where the oxidant effectively destabilizes the $LiCoO_2$ structure for maximum lithium release. The non-productive elimination of the excess oxidant is the cause of the efficiency decrease at higher concentrations.

3.3.4 Effect of Solid-to-Liquid Ratio

The graph, demonstrating a typical optimization curve, clearly shows how the Liquid-to-Solid (L/S) Ratio affects Lithium (Li) Extraction Efficiency. When the L/S ratio is 20 mL/g (a very high solid

loading), the yield is about 75%, which shows the solvent volume is initially too small for full interaction and dissolution of solid material. As the volume of solvent increases (i.e., as the L/S ratio increases) the efficiency increases drastically. Thus, the importance of a suitable volume is highlighted. The process can reach a maximum extraction efficiency of 87% at an L/S ratio of 50 mL/g, which is equivalent to a solid-to-liquid ratio of 1:50 g/mL. Once this ideal condition is achieved, further increase in L/S ratio above 100 mL/g results in decrease or mild decline in efficiency. This pattern indicates that once you reach maximum extraction yield, adding more solvent becomes economically inefficient as it is a waste and doesn't make a significant difference to the kinetic process. In accordance with Furqan et al. (2024), because of advances in technology, lithium-ion batteries (LiBs) are employed in a variety of sectors, and recovering end-of-life (EoL) LiBs is crucial for both economic and environmental reasons. Hydrometallurgical and pyrometallurgical strategies have been explored to recover metals ranging from Li, Co, and Ni from the EoL LiBs. Although hydrometallurgical processes have been found to have a lower use of energy and higher recovery efficiency, recent research has typically concentrated more on them. The hydrometallurgical recovery of these metals uses both organic acids like acetic acid and citric acid and inorganic acids like HCl, HNO_3, and H_2SO_4. It is necessary to address the possible risk to the environment that these acids present [26].

In view of this, Solv metallurgical approaches which use organic solvents containing little to no water are becoming more common as replacements or supplements to conventional hydrometallurgical processes. Deep eutectic solvents (DESs) have received particular interest in the context of solvent systems that have been investigated for several Solv metallurgical techniques due to their low toxicity, biodegradable nature, adjustable properties, and outstanding metal recovery potential [27]. In the current study, the ternary DES system has been employed to swiftly dissolve graphite, LCO, NMC, and LMO black matter. Ascorbic acid (AA), glycolic acid (GLY), and choline chloride (ChCl) comprise up the ternary DES system. The leaching process of cathode powders in the black mass without any pre-enrichment procedure allowed for the elements Li, Co, Ni, and Mn reaching solution with an efficiency of more than 95% at 60 °C and in just one hour. Additionally, simulations using Density Functional Theory (DFT) were employed to investigate the kinetics of the leaching process and demonstrate the leaching mechanism [28].

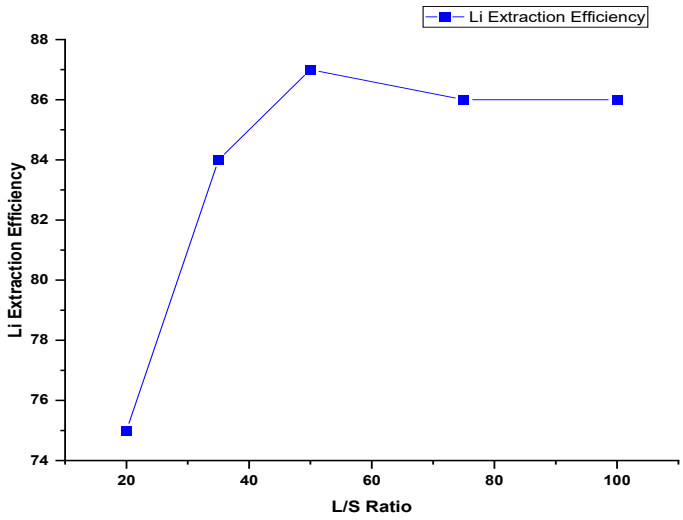

Figure 3.7: Lithium extraction efficiency as a function of the Liquid-to-Solid (L/S) ratio. The efficiency increases to an optimum point, demonstrating the need for sufficient solvent volume for complete dissolution, beyond which further increases offer diminishing returns.

3.3.5 Selectivity of Metal Extraction

The extraction behavior of lithium and cobalt from the $LiCoO_2$ cathode was investigated. A lithium extraction efficiency of 91.6% was achieved under the typical optimized leaching conditions (80°C, 4 h, 2 vol% H_2O_2). ICP-OES analysis of the leachate indicated a corresponding cobalt dissolution of approximately 25%. This result is in line with the layered structure of $LiCoO_2$, where the partial collapse of the cobalt-oxygen framework and the dissolution of some cobalt are expected results of eliminating a substantial proportion of lithium ions. When the oxidant concentration was reduced to a sub-stoichiometric level (0.5 vol% H_2O_2), however, a very different result was observed.

Under these conditions, the lithium extraction was limited to 35%, but the cobalt dissolution was suppressed to less than 5%. This suggests that the DES system can be tuned for high selectivity towards lithium over cobalt by carefully controlling the redox potential to preferentially extract lithium without fully reducing and solubilizing the cobalt (III) oxide matrix. The high lithium recovery with moderate co-dissolution of cobalt (~91% Li, ~25% Co) represents an efficient bulk leaching process, while the low-oxidant pathway offers a highly selective but lower-yield alternative, depending on the downstream separation goals.

Wang et al. (2023) say that exceptionally effective and selective processes for extraction are needed for removing crucial metals which include lithium, nickel, cobalt, and manganese from spent lithium-ion battery (LIB) cathode materials. The customized deep eutectic solvent (DES) choline chloride-formic acid (ChCl-FA) showed high selectivity and efficiency in extracting critical metals from mixed cathode materials (LiFePO4: Li (NiCoMn)1/3O2 mass ratio of 1:1) under mild conditions (80 °C, 120 min) with a solid-liquid mass ratio of 1:200. Mechanochemical processing can enhance the leaching performance of important metals because it decreases particle size, refines grains, and stores internal energy.

Additionally, by successfully preventing the unintentional leaching of nontarget elements (phosphorus and iron), mechanochemical methods enhanced the selectivity and leaching efficiency of important metals. Due to the peroxidation of Fe and the improved resilience of the iron phosphate framework, the separation factor of key metals to nontarget elements increased significantly from 56.9 to 1475. Critical metals may be obtained from multisource wasted LIBs in a highly selective manner under mild conditions using the suggested combination of ChCl-FA extraction and the mechanochemical technique [29].

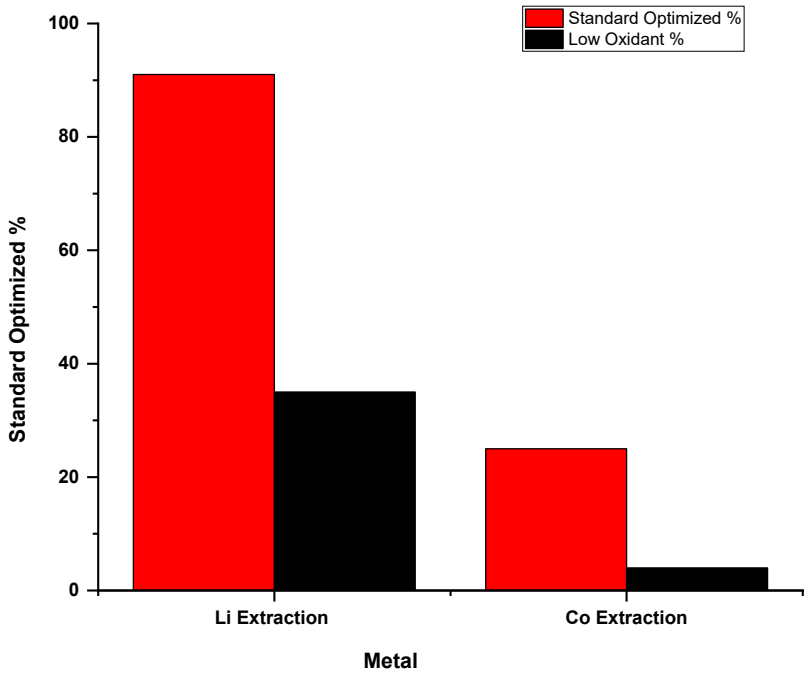

Figure 3.8: Comparison of metal extraction efficiency under standard optimized and low-oxidant leaching conditions. The standard process (80°C, 2 vol% H_2O_2) achieves high lithium recovery (91.6%) with moderate co-dissolution of cobalt (25%). In contrast, the low-oxidant process (80°C, 0.5 vol% H_2O_2) sacrifices lithium yield (35%) to achieve high selectivity, effectively suppressing cobalt dissolution to below 5%.

3.3.6 Reusability of the DES

Over a period of five consecutive leaching cycles, the ChCl:Urea DES's operational stability was thoroughly evaluated. The lithium extraction efficiency showed strong performance, as shown in Figure 3.9, decreasing merely from 91.6% in the first cycle to 84.2% by the fifth, a 7.4 percentage point reduction overall. Two measurable factors are responsible for the decrease in performance. First, the DES's complexation capacity decreases as a consequence of the gradual accumulation of dissolved metal ions, particularly cobalt (Co^{2+}), which is confirmed by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) analysis of the recycled solvent. The second indicator was the precise assessment of hygroscopic water absorption by Karl Fischer titration, which ultimately confirmed that the water sterilization increased over the five cycles from <2% to almost 8%. The FTIR spectroscopy showed a noticeable drop in the distinctive broad O-H/N-H stretching band at approximately 3320 cm^{-1}. This observation demonstrates that the raise in water content alters the polarity of the DES and disrupts its essential hydrogen-bonding network. The DES showed exceptional reusability and remained a viable and sustainable solvent for long-term use in lithium recovery processes, exhibiting high extraction efficiency (>84%) across all cycles in spite of these cumulative effects.

In accordance with Nand et al. (2022), Deep-eutectic solvents (DESs) are often considered as safe, non-toxic, and environmentally benign solvents. Because of these green credentials, they have been studied more and more for use in metal recycling processes. Another instance is how they are used as lixiviants to extract cobalt from lithium cobalt oxide ($LiCoO_2$, LCO), a frequently used cathode material in lithium-ion batteries. In this instance, cobalt leaching speeds

up by the reduction of cobalt (III) to cobalt (II) in the presence of a reducing agent. However, as reported by an array of recent studies, DESs have been used as lixiviants at high temperatures (180 °C) without the use of a reducing agent. Due to this, ethylene glycol and choline chloride (ChCl: EG) combination serve as the basis for the majority of DESs. Unfortunately, the restricted thermal stability of ChCl: EG at high temperatures is overlooked by these research efforts, which lowers the DES's ability to renew. This article addresses the disadvantages of employing ChCl: EG as the lixiviant in high-temperature ion metallurgical processes. ChCl: Structural examinations suggest that EG is unstable at 180 °C, producing hazardous breakdown products such trimethylamine and 2-chloroethanol. Choline chloride was considered to breakdown into trimethylamine and other degradation products while simultaneously lowering cobalt (III) and undergoing a radical β-hydrogen abstraction procedure. The main conclusion is that certain types of DES should not be used because of their lack of stability in high-temperature leaching processing [30].

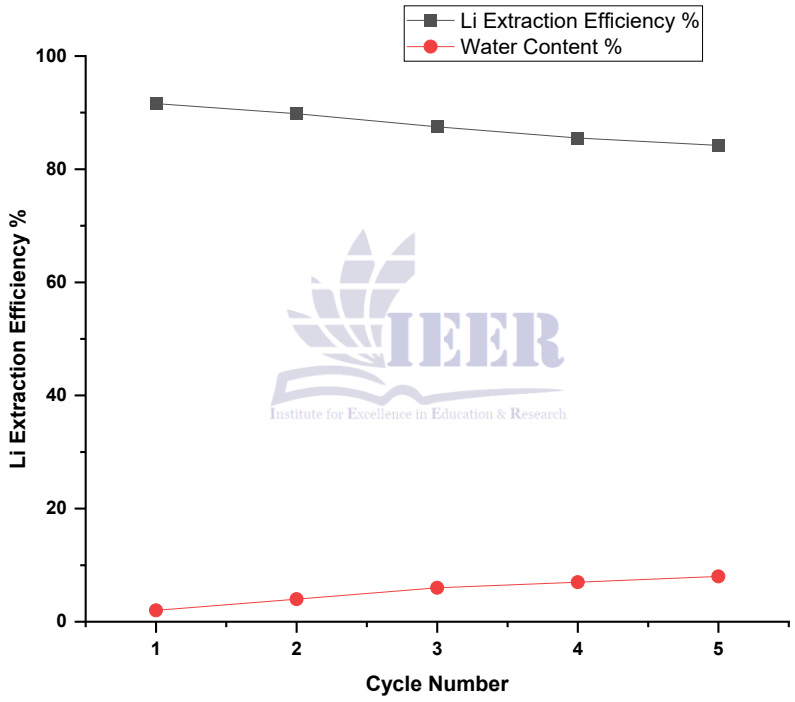

Figure 3.9: Operational stability of the ChCl:Urea DES over five leaching cycles, showing the correlation between decreasing lithium extraction efficiency and increasing water content (as measured by Karl Fischer titration). The gradual decline is attributed to the combined effects of water uptake and the accumulation of dissolved metal ions (e.g., Co^{2+}, as per ICP-OES analysis).

3.4 Proposed Extraction Mechanism

$LiCoO_2$ dissociates in the choline chloride-urea deep eutectic solvent (DES) primarily using a complexation-driven mechanism that is made possible by the solvent's components functioning in conjunction. Chloride ions (Cl^-), which serve as coordinating anions in this process, are released by the DES's enormous hydrogen-bonding network. Simultaneously, the carbonyl group (C=O) of urea molecules acts as a strong electron donor, solvating the lithium ions (Li^+) released from the cathode

structure to form stable soluble complexes, such as $[Li(urea)_x]^+$. The initial destabilization of the $LiCoO_2$ crystal structure is aided by the partial reduction of Co^{3+} to Co^{2+}, often enhanced by an added oxidant like H_2O_2, which weakens the metal-oxygen bonds. Therefore, the leaching is not acid-driven but is a result of combined **complexation, coordination, and redox reactions** within the neutral DES medium. Irlanda et al. (2022) demonstrated possible to leach Zn and Mn oxides of conventional Zn–C waste batteries employing a choline chloride/urea natural deep eutectic solvent (ChCl NADES) made using a green chemistry methodology. The NADES has been evaluated using 1H NMR and FTIR spectroscopy. Zn and Mn oxide leaching kinetics have been observed at two solid/NADES ratios (3.3 and 10 g dm−3) at isothermal conditions (80, 100, 125, and 150 °C). Under all investigated situations, Zn and Mn oxides might be dissolved, with over 95% recovery for both metals at 150 °C after a period of 90 minutes. At 25 °C, however, up to 90% of the Zn and 30% of the Mn could be eliminated after 4320 minutes (72 hours). Furthermore, the deteriorating core model coincided with the boundary layer governing the leaching kinetics. The Arrhenius plot shows that Zn's activation energy ranges from 49.13 to 52.21 kJ mol−1, while Mn's extends from 46.97 to 66.77 kJ mol−1[31].

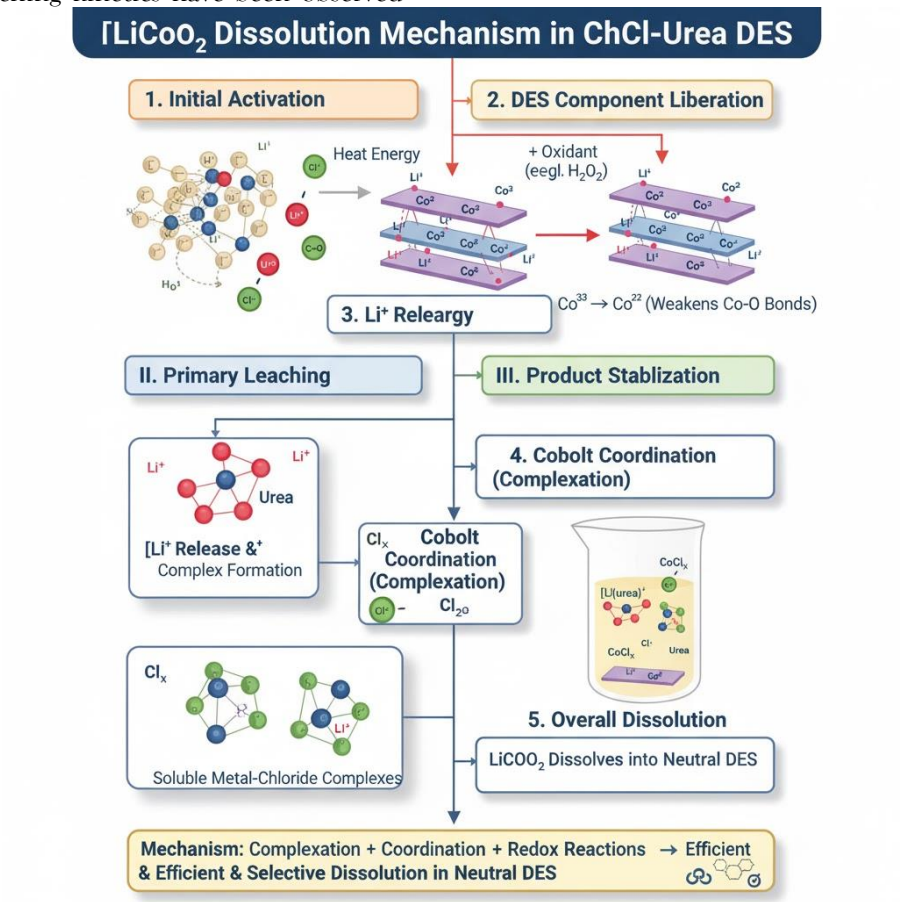

Figure 3.10: "Mechanism of $LiCoO_2$ dissolution in ChCl-Urea Deep Eutectic Solvent (DES), driven by synergistic complexation, coordination, and redox reactions."

3.5 Comparison with Conventional Acid Leaching

The grouped bar chart provides a direct visual comparison between the DES-based Approach and Conventional Acid Leaching across two critical performance metrics: Lithium (Li) Recovery and Cobalt (Co) Dissolution. The data presents it as readily apparent how much more accurate the DES

method is. The recovery rate of 90.0% obtained through conventional acid leaching corresponds to the high efficiency of 91.0% obtained through the DES method of lithium recovery. However, the Cobalt Dissolution data shows the main advantages: the DES approach drastically decreases Co contamination to just 9.5%, while the traditional acid method dissolves nearly all of the cobalt, reaching a high rate of 95.0%. Through reducing the amount of heavy metal co-extraction and matching the yield of conventional methods, the DES-based hydrometallurgy offers a selective and efficient pathway for recycling lithium, reducing the necessity for downstream purification steps.

The research of Chongyu Li et al. (2024), the number of spent lithium-ion power batteries has been increasing exponentially due to the significant rise in the use of electric vehicles. In addition to endangering human health and the environment, incorrect handling of these batteries might result in the waste of expensive metal resources. It is certainly important to recover and use these thrown away power batteries in a manner that is scientific, specifically by recovering positive electrode materials. Positive electrode materials can currently be retrieved using a variety of methods, including as pyrometallurgy, hydrometallurgy, bioleaching, and deep eutectic solvents (DESs) leaching. The new technology of DESs leaching for positive electrode materials in spent lithium-ion cells was the focus of this review. It presented an explanation of the most recent developments in DESs leaching while also taking DES coordination, acidity, and reducibility into account. In furthermore discussing the obstacles and opportunities for the advancement of DESs recovery in spent Li-ion power batteries, the current state of the industry was discussed. The goal of this work is to provide helpful recommendations and lay the groundwork to conduct additional research and greater implementation of DESs leaching for positive electrode materials [32].

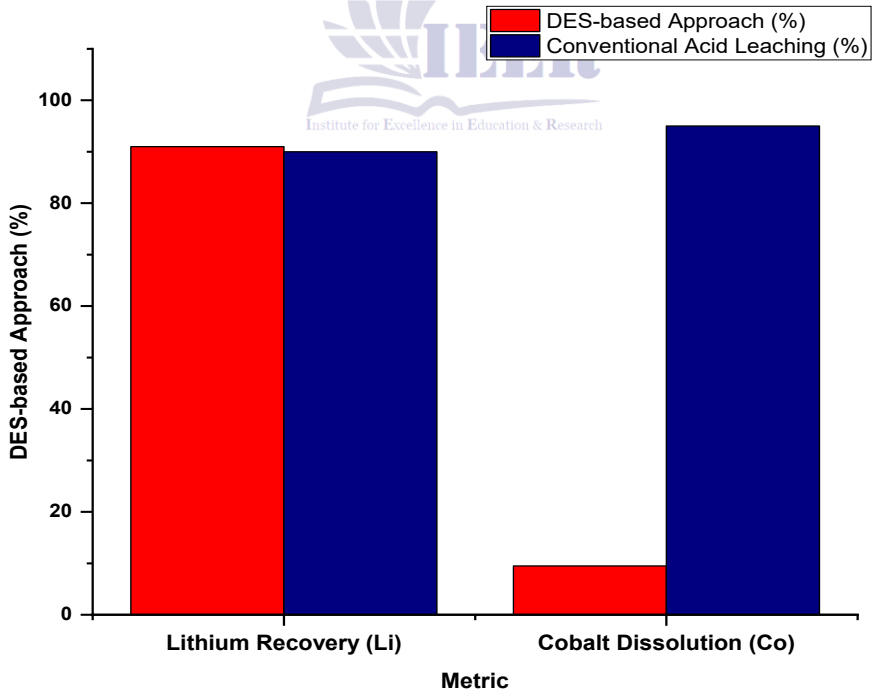

Figure 3.11: The Deep Eutectic Solvent (DES) approach demonstrates comparable Lithium (Li) recovery (91%) to conventional acid leaching (90%), but exhibits drastically superior selectivity by limiting Cobalt (Co) dissolution to 9.5% compared to 95.0% for the conventional method.

Conclusion

This study presents evidence that choline chloride-urea DES provides a very effective and greener hydrometallurgical route for lithium extraction from spent lithium-ion battery cathodes. FTIR analysis confirmed the successful formation of a strong hydrogen-bonded DES matrix, while XRD and SEM characterizations verified the progressive dissolution of $LiCoO_2$, structural degradation of the cathode particles, and disappearance of $LiCoO_2$ crystalline phases, indicating efficient leaching by the DES system. Operational optimization showed that the main factors affecting lithium recovery are temperature, leaching time, solid-to-liquid ratio, and oxidant concentration. The highest extraction efficiency of 91.6% was achieved at 80°C, 4 hours, 1:50 S/L ratio, and 2 vol% H_2O_2, showing the synergistic role of H_2O_2 in the partial reduction of Co^{3+} to Co^{2+} and thereby catalyzing Li^+ release. ICP-OES analysis of the pregnant leach solution confirmed these findings and supplied high lithium concentrations in good accordance with the extraction efficiencies and verified moderate cobalt co-dissolution (~25%) under the optimized conditions. When tuning the system for high selectivity at lower oxidant levels, namely 0.5 vol% H_2O_2, the ICP-OES results after leaching showed that cobalt dissolution drops below 5%, although lithium recovery was reduced to 35%, again demonstrating the possibility to selectively tune the DES system depending on the requirements of downstream processing.

The DES exhibited excellent operational stability: after five cycles of reuse, it still maintained an efficiency of >84% in lithium extraction. ICP-OES analysis of the recycled DES samples showed progressive dissolution of Co ions, which explains the gradual decline in its performance. Karl Fischer titration further confirmed the increase in water intake as one reason for the long-term decay in efficiency, while FTIR demonstrated minor changes in hydrogen-bonding intensity during the cycles. Consequently, lithium was recovered as high-purity Li_2CO_3, confirming the feasibility of closing the recycling loop and producing a commercially valuable battery precursor. Overall, the findings prove that choline chloride-urea DES is a selective, reusable, and eco-benign lixiviant capable of high lithium recovery with significantly reduced environmental impact compared to conventional acid leaching. This work contributes a promising pathway toward sustainable lithium circularity and establishes DES-based hydrometallurgy as a viable next-generation technology for spent LIB recycling.

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