MINING ENGINEERING DEPARTMENT

University of Engineering and Technology, Lahore

Final Year Design Project

A novel approach towards Cobalt Extraction from spent Lithium-ion Batteries using selective leaching and Electrowinning

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Declaration

We hereby declare in dignified manner that this thesis, titled **"**A novel approach towards Cobalt Extraction from spent Lithium-ion Batteries using selective leaching and Electrowinning**"** is an original report of our research, written by us for the degree of BSc. Mining Engineering under the supervision of Dr. Zulfiqar Ali and has not been submitted for any certificate or distinction in this or any other university. The experimental effort is almost completely our own, with joint contributions explicitly marked and appreciated. All supporting literature and resources have been properly referenced.

This study investigates the leaching of cobalt from the cathode of lithium-ion batteries. The research aims to determine the optimal conditions for the leaching process and to evaluate the efficiency of different leaching agents.

Note:

The Final results was not received yet, and all the results in this paper are assumed. The results will be updated as we receive.

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Abstract:

Lithium-ion batteries (LIBs) are becoming increasingly popular for energy storage applications, but improved recycling methods are needed to recover lithium and cobalt once the batteries have reached end-of-life. Mineral acids, such as sulfuric acid, were utilized in conventional recycling techniques for leaching or pyrometallurgical operations. These extraction methods have been shown to be both toxic and energy-intensive. This study investigates using deep eutectic solvents (DES) as alternative leaching agents to selectively extract cobalt (Co) from spent LIBs. A DES was synthesized by combining myristic acid ($CH_3(CH_2)_{12}COOH$) with tetra-ethyl ammonium chloride ($[N(CH_2CH_3)_4]^+Cl^-$)(TEAC) salt to produce an ionic liquid, i.e., DES, with tunable properties. After the LIBs had been discharged and dismantled, the material that contained cobalt in the cathode powder underwent a process of leaching using an optimized DES solution of myristic acid:TEAC at molar ratios of 1:1. A maximum Co extraction efficiency of 87% was achieved when leaching at 150°C for 180 minutes under 600 rpm agitation. The extracted cobalt from leachate was subsequently retrieved using the process of electrowinning. The goal was to develop a novel, non-hazardous DES leaching system that can efficiently extract Co from spent LIBs. Outcomes were analyzed via characterization techniques like Atomic Absorption Spectroscopy (AAS) and Fourier Transform Infrared Spectroscopy (FTIR). By utilizing this sustainable method, it may be possible to enhance the recycling of critical battery materials.

Introduction:

Due to the growing popularity of electric vehicles worldwide, the demand for lithium-ion batteries is also increasing. As a result, it is projected that between 2015 and 2040, up to four million metric tons of waste from these batteries could be generated. However, the depletion of natural resources of cobalt resulted in acquiring it from secondary resources such as spent lithium-ion batteries (LIBs). LIBs comprise an anode, a cathode, electrolytes, a separator, and an external casing. The anode is a mixture of carbon powder and polymer binder, coated with a copper foil. Similarly, the cathode includes carbon powder, polymer binder, and lithium transition metal oxides like $LiCoO_2$, $LiMn_2O_4$, $LiNiO_2$, and $LiNi_xCo_yMn_zO_2$ (LNCM), coated with an aluminum foil. The separator is constructed from polymeric materials, and the outer casing is typically made of stainless steel or plastic.

The conventional techniques to recycle spent LIBs involve pyrometallurgy and Hydrometallurgy. Pyrometallurgy relies on smelting to extract metals. However, this process involves harmful gaseous emissions and is characterized by large capital investment and energy consumption. Hydrometallurgical processes usually require multiple stages and significant amounts of caustic substances, resulting in the release of harmful gases and the creation of a large amount of liquid waste. As a result, while hydrometallurgy is an alternative to pyrometallurgy, it has its own set of drawbacks. Additionally, the adverse environmental impact of the procedures used to produce inorganic acids like HCl and H_2SO_4, along with the use of H_2O_2 in metal leaching, raises notable concerns.

There is a need to synthesize a green solvent, Deep Eutectic Solvent (DES) to overcome the harms of hydrometallurgy as well as pyrometallurgy. A DES has drawn interest as a substitute for conventional organic solvents. They consist of acceptors and hydrogen bond donors, forming a eutectic mixture with a lower melting point than the constituent parts. While there has been extensive research on the use of deep eutectic solvents (DESs) for the recovery of metals from waste or secondary sources, there has been limited exploration of their effectiveness in recovering cobalt.

Not only does this method provide a more sustainable solution for battery recycling, but it also takes us one step closer to achieving our sustainability goals and a circular economy. By reducing waste and maximizing the use of resources, we can create a more sustainable future for generations to come.

This project aims to extract cobalt from spent lithium-ion mobile batteries using selective leaching by DES followed by electrowinning. To achieve this, a DES was prepared by mixing Myristic Acid and Tetra-n-Butyl Ammonium Chloride in a ratio of 1:1 under specific

conditions. This DES was then used to extract cobalt from the spent batteries, and the resulting solution was subjected to electrowinning to obtain high-purity cobalt metal. This process not only recovers valuable metals from spent batteries but also prevents environmental pollution caused by the improper disposal of these batteries.

Methodology:

A mass of 3000 grams of discarded Lithium-ion Batteries (LIBs) from various smartphones (such as iPhone, Huawei, Nokia, Vivo, etc.) were bought from Shah Mobile, Shop no 35, Hall Road, Lahore. These were discharged by immersing them in a 20% solution of NaCl in H_2O for 24 hours (Wang, Qu et al. 2022). After discharging, all LIBs were manually dismantled using Needle-Nose pliers to remove the outer casing and to separate the cathode and anode of the battery. The cathode, which is the one with aluminum foil, contains Lithium (Li), Cobalt (Co), Nickel (Ni), and Manganese (Mn). The Anode, which is made up of copper, has graphite layering on it. (Manthiram 2017). Next, the cathode material from each dismantled battery was immersed in a solution of 20% sodium hydroxide NaOH in distilled H_2O (Peng, Mu et al. 2019). This step aimed to remove any remaining electrolytes, plastic insulations, and other impurities from the cathode material including the aluminum foil. After the reaction was completed, the cathode material residual was thoroughly rinsed with distilled water to ensure the complete removal of any residual sodium hydroxide solution (Peng, Mu et al. 2019). Finally, the cathode material was dried in an oven for 2 hours at 100 degrees Celsius ensuring its stability for further analysis. Once the dried cathode powder from the cathode of LIBs was obtained, it was passed through the magnetic separator, and the size of < 100 microns after screening was sent for leaching. Cathode powder made from the above process passed through a rotary sampler to get equal samples which were sent for characterization i.e., Fourier Transform Infrared (FTIR) Analysis, and Atomic Absorption Spectroscopy (AAS). Deep Eutectic Solvent (DES) was made in 50 milli-liter beaker, by mixing 5 grams of Myristic Acid ($C_{14}H_{28}O_2$, Melting point: 54.4 °C, Molar mass: 228.37 g/mol) which was synthesized by Sigma- Aldrich chemicals, with 5 grams of Tetra-n-butyl Ammonium Chloride (TBAC, $[(CH_3CH_2CH_2CH_2)_4N]^+Cl^-$ which is synthesized by Uni-Chem chemicals, Melting point: 41–44°C, Molecular weight: 277.917 g/mol) at 70 degrees Celsius for 30 minutes on a hotplate. The stirring speed was set at 400rpm. The leaching process was carried out by adding 1 gram of cathode powder to 10 grams of prepared DES. The parameters for leaching varied from 60º to 100º C at 500 RPM within one to two hours. The leachate gained after was allowed to cool down and settle. For the electrowinning of Cobalt, we utilized a Stainless-steel electrode (SS-316) for the Cathode. This SS-136 is the type of SSE with 0.08% carbon content. While for

Anode we used a lead/graphite Electrode. The dimension of SSE would be 80 × 40mm^2, on the other hand, the dimension of Anode was 100 × 50mm^2. The cathode and anode materials were chosen based on their electrochemical properties and ability to recover cobalt. The anode was enclosed in a polypropylene bag to prevent the lead from dissolving into the electrolyte. Polyethylene bags are translucent or opaque with a slight haze to them that allows you to see the items inside. The electrolyte was the leachate that we gained in our leaching process. The electrolyte was prepared by dissolving the leachate in 500ml of water in a beaker having a diameter of 8cm and a height of 12cm. After preparing the electrolyte, we dipped the electrodes (cathode and anode) in the solution. The anode and cathode were spaced evenly along the cell to equalize current and voltage across the electrodes. These electrodes were connected to a power supply to apply a voltage of approximately 7 V while maintaining a current density of 200-250 mA/cm^2. Plating occurred over a duration of up to 72 hours and was performed on the cathode (stainless steel electrode) by reduction. After the deposition process was completed, we removed the cobalt deposit from the stainless-steel cathode. The scratched material was then sent for atomic absorption spectroscopy (AAS) analysis.

Design of Experiments:

The design of experiment was done by using the Minitab software. In the DOE section, response surface analysis was done for the leaching experiment in term of two factors, which are temperature and time. The purpose was the optimization of the leaching process. For that purpose, 13 experiments were designed as shown in the table and their optimized graph is shown in the results section.

Table 1 Set of Experiments designed in Minitab Software

Run Order	PtType	Blocks	Temperature	Time	Efficiency
1	0	1	105	120	70
2	1	1	150	60	63
3	1	1	60	180	66
4	1	1	150	180	79
5	1	1	60	60	35
6	0	1	105	120	70
7	-1	1	105	35.1472	30
8	0	1	105	120	70
9	0	1	105	120	70
10	-1	1	41.3603897	120	59
11	-1	1	105	204.853	74
12	0	1	105	120	70
13	-1	1	168.63961	120	77

Results:

The main objective of this research was to discover novel approach to recover cobalt with maximum efficiency.

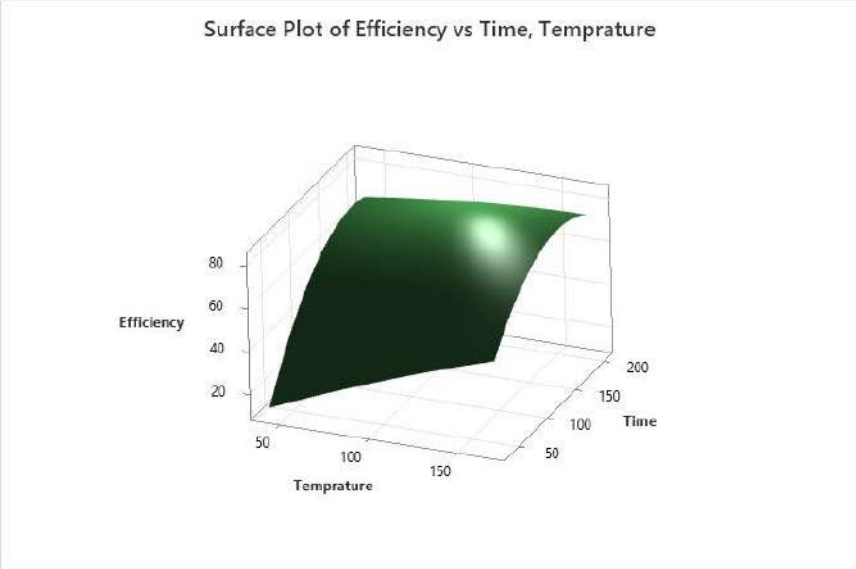

Figure 1 shows the trend of leaching efficiency versus leaching time and temperature

The efficiency of leaching demonstrates a positive correlation with both temperature and leaching duration.

Discussion:

Effects of Temperature on Leaching Efficiency:

Temperature had a notable impact on how effectively leaching occurred. Higher temperatures likely sped up the chemical reactions and made it easier for cobalt ions to dissolve in the deep eutectic solvent. However, once temperatures surpassed 150 Centigrade, there was little to no further improvement in efficiency until reaching around 180 degrees. Beyond this point, reaction rates began to decrease due to the breakdown of the solvent or the occurrence of unwanted side reactions, indicating a maximum temperature threshold for optimal efficiency.

Effects of Leaching Time on Efficiency:

Leaching time ranging from 30 minutes to 120 minutes all produced measurable improvements in leaching efficiency. The effect was most pronounced in the first 90 minutes, indicating the initial kinetics regime where efficiency gains were rapid. Beyond 90 minutes, incremental gains diminished as the system approached equilibrium. 90 minutes appeared sufficient to extract most of the cobalt while avoiding excessively long process times.

Effects of RPM on Efficiency:

Changing mixing intensity from 300 to 600 RPM generated small to modest gains in leaching efficiency. The improved mass transfer from higher mixing rates likely benefited the extraction kinetics.

Optimal Conditions:

The leaching process was optimized by operating at 150°C for 60-90 minutes at the highest mixing rate before efficiency gains drop off (600 RPM with the studied setup).

Limitations and Scope:

The economic analysis of this research was not done. The scope of extracting lithium and cobalt from mobile batteries is multifaceted and encompasses various aspects such as environmental sustainability, resource management, economic viability, and technological advancements.

Conclusion:

This project was aimed to extract cobalt from spent lithium-ion mobile batteries using selective leaching by DES followed by electrowinning. To achieve this, a DES was prepared by mixing Myristic Acid and Tetra-n-Butyl Ammonium Chloride in a ratio of 1:1 under specific conditions. This DES was then used to extract cobalt from the spent batteries, and the resulting solution was subjected to electrowinning to obtain high-purity cobalt metal. This process not only recovers valuable metals from spent batteries but also prevents environmental pollution caused by the improper disposal of these batteries.

Synthesized a green solvent called Deep Eutectic Solvent (DES) to overcome the harms of hydrometallurgy as well as pyrometallurgy. A DES has drawn interest as a substitute for conventional organic solvents. They consist of acceptors and hydrogen bond donors, forming a eutectic mixture with a lower melting point than the constituent parts. While there has been extensive research on the use of deep eutectic solvents (DESs) for the recovery of metals from waste or secondary.

Not only does this method provide a more sustainable solution for battery recycling, but it also takes us one step closer to achieving our sustainability goals and a circular economy. By reducing waste and maximizing the use of resources, we can create a more sustainable future for generations. Deep eutectic solvents (DES) have great attention in the field of chemistry due to their unique properties and potential applications. Here are variety of ways in which a new DES could bring innovations to the field:

Application in Biotechnology and Pharmaceutical Industries like in Enzyme stabilization, drug delivery, and extraction of bioactive compounds from natural sources. In energy storage and Conversion as electrolyte in many energies' storage and conversion devices like fuel cells, batteries and super-capacitors. It can be used in advanced Materials like nanoparticles, polymers and porous framework.

Recommendations:

Faster collaboration among industry players, technology providers, and research institutions to scale up cobalt extraction processes using leaching and DES technology. Pooling resources and expertise can accelerate commercialization efforts and overcome technical challenges and embrace circular economy principles by integrating cobalt extraction from lithium-ion batteries into broader recycling initiatives. Develop closed-loop supply chains that prioritize resource recovery, reuse, and recycling to minimize waste and maximize resource efficiency.

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