A greener approach for valuable metal recovery from the waste lithium-ion batteries

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Introduction

The rapid growth in lithium-ion batteries (LIBs) demand for various emerging applications, such as electric vehicles and energy storage systems, will result in waste and disposal problems in the next few years as these batteries reach end-of-life (EoL). The spent LIBs also include 5−20 wt % cobalt (Co), 1−7 wt % lithium (Li), 5−15 wt % nickel (Ni) and 10-15 wt % manganese (Mn), the composition varying slightly with different manufacturers (Shin, 2005). Co is considered a rare and strategic metal as it is relatively expensive, and the natural resources are primarily limited to the Democratic Republic of the Congo and Zambia. There is a unique opportunity to utilize these end-of-life (EoL) batteries as a secondary source to recover this valuable metal. Over the years, various recycling processes, including pyrometallurgy, hydrometallurgy, and bioleaching, have been developed to effectively recover metals from spent batteries. The hydrometallurgy method has been considered as a facile, safe, and efficient process to extract and recover valuable metals from spent LIBs. However, as leaching reagents, conventional inorganic acids (HCl, H_2SO_4 and HNO_3) are not considered environment-friendly. The current need is to use greener solvents to reduce secondary pollution and negative impact on the environment. The chelation process has emerged as a green approach for metal recovery from waste material. Aminopolycarboxylic acids are popularly known for their chelation efficiency and have been used widely for contaminants/ heavy metal removal from soil (Chauhan, 2015). A similar approach will be used in this study to recover valuable metals from waste batteries using these chelating agents. This research will focus on developing a close-loop recycling process to recover critically-rare metals from spent lithium-ion batteries using a greener approach.

In the present study, EDTA has been used as a lixiviant for metal extraction from spent LIBs for the first time. Most of the processes available in the literature focus on the recovery of transition metals present in the cathode material (Li, Co, Ni and Mn). In contrast, current collectors (Al and Cu) are separated before leaching, which requires extra process steps. In our process, the crushed sample is used as it is before any pre-treatment. The feed sample contains both anode and cathode material. In a recent study, Peeters et al. that the current collector (Cu) can be used as a cost-effective reductant during Co (III) extraction using DES. A similar approach has been used and the current collector (Cu) present in the feed was also recovered during the process (Peeters, 2020).

Material and methods

Crushed Spent LIBs were provided by Exigo (E-waste recycling plant), Panipat. The crushed powder was directly used as feed material without any further treatment. The feed material contained batteries of mobiles, tablets and laptops. The elemental composition of the feed sample was determined by microwave plasma atomic emission spectrometry (MP-AES). The feed sample was digested in aqua regia (HCl:HNO_3 = 3:1) for the complete dissolution of metals present in the feed. Ethylenediaminetetraacetic acid (EDTA) (Fisher Scientific) was used as an extractant for the chelation experiments. Sulfuric acid (H_2SO_4, 98% pure) (Merck) and sodium hydroxide (NaOH) (Merck) was employed for pH adjustment during the experiments. The double-distilled water of high purity (Millipore apparatus) was used in all the experiments. Various characterization studies (energy dispersive X-ray analysis, scanning electron microscopy, X-ray diffraction, inductively coupled plasma spectrophotometry) of spent LIBs powder and residues were performed for qualitative and quantitative analysis of the samples. Dechelation of the metal complexes was done by adjusting the solution pH to the acidic range; therefore sulfuric acid was added to the filtrate to attain pH 2–3. Precipitation time of 6 h was provided to allow the maximum precipitation and settling of EDTA (Jadhao, 2016).

Results and discussion

The feed sample was digested entirely in aqua regia solution (HCl:HNO_3 = 3:1) for 1.5 h at 180°C. The elemental composition of the feed sample is presented in Table 1.

Table 1. Elemental composition of the feed LIB sample.

Element	Li	Co	Cu	Mn	Al	Ni
Wt%	2.9	25.3	3.2	1.3	0.98	0.6

The effect of various process parameters, viz., temperature, pH, L'S ratio, and EDTA concentration, on the extraction efficacy was studied. The results showed that increasing the temperature or L:S ratio has a positive effect or shows an increment in the extraction efficiency up to a specific temperature or L:S ratio, after which it levels off. Thus, a temperature of 90^{o}C and an L:S ratio of 20 was optimized for performing the experiments. The effect of pH and EDTA concentration show increasing extraction efficiency up to a specific pH and concentration, and thereafter it shows a decrease in the extraction efficiency. So, the pH value of 10 and EDTA concentration of 0.8 M were optimized from these experiments. At optimized process conditions, more than 90% of Li, Co and Cu was extracted. More than 94% EDTA was recovered during the deceleration process which was recycled in the subsequent chelation cycles.

Conclusions

An environmentally benign process was developed to efficiently recover valuable metals (Li and Co) from waste LIBs using the chelating agent EDTA. It was observed that the presence of current collector metal (Cu) was beneficial for the Co from LIBs. Cu acts as a reducing agent during the leaching process, which eliminates the need to add a reducing agent as inorganic acids; H_2O_2 is required for efficient extraction of Co. The method is eco-friendly as EDTA can be easily recovered and reused; thus, no secondary pollutants were generated. UV-Vis analysis was carried out to understand the plausible reaction mechanism. EDTA was effectively used as an extractant and more than 90% of Li, Co and Cu were recovered.

References

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