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Close loop separation process for the recovery of Co, Cu, Mn, Fe and Li from spent lithium-ion batteries

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ABSTRACT

Lithium-ion batteries (LIBs) are essential energy source used in advanced electronic gadgets for getting constant and continuous power supply. Huge amount of spent LIBs are generated after their end use. LIBs contain metals, organics and plastics which require proper treatment before disposal. Keeping in view of stringent environmental regulations, limited natural resources and energy crisis, adopting recycling will not only protect the environment and pacify the gap between demand and supply but also conserve the natural resources. Present paper reports a complete process for the recycling of LIBs to recover metals and materials as value added products fulfilling zero waste concept. Initially, the spent LIBs were crushed and beneficiated by wet scrubbing process to separate cathodic material, plastic and metallic fractions. The cathodic material contained 20% Co and 2.4% Li along with other impurities (Mn, Fe, Cu). The cathodic material obtained from different LIBs were homogenized and put to leaching studies to optimize various process parameters viz. effect of leachant concentration, temperature, time, etc. About 97% Co and 99.99% Li were leached using 2 M H_2SO_4 and 10% H_2O_2 at room temperature, in 2 h maintaining pulp density 75 g/L. Kinetics for leaching of Co fitted well with "Chemical reaction control dense constant size cylindrical particles model", i.e. $1 - (1 - X)^{1/2} = Kct$. The leach liquor obtained was further processed to recover Mn and Fe using $(NH_4)_2S_2O_8$ as a precipitant whereas 99.99% Cu was extracted using LIX 84 IC at eq. pH 2, O/A ratio 1/1 and mixing time 5 min. Further, from the leach liquor depleted with Mn, Fe and Cu, ~98% Co was extracted using 20% Cyanex 272 at pH 4.8 in 10 min maintaining phase ratio (O/A) 1/1 in two stages, leaving Li in the raffinate. From the pure Co solution, value added products as metal and salt were produced using electrowinning/evaporation/precipitation techniques. The TCLP test of leached residue shows the presence of metals within permissible limit and the effluent generated was treated in an effluent treatment plant (ETP) with standard procedure and recycled to the system. The developed clean process is economical as well as environment friendly and has potential to be translated in industry after scale-up studies.

1. Introduction

Lithium-ion batteries (LIBs) are essential component of modern technology and are widely used as electrochemical source of power in mobile phones, laptops, video-cameras, etc. due to their characteristic light weight, high energy density and good performance. They contain a cathode, an anode, organic electrolyte and a separator [1]. Lithium cobalt oxide ($LiCoO_2$), lithium manganese oxide ($LiMn_2O_4$), lithium nickel oxide ($LiNiO_2$) or related oxides are most commonly used cathodic material for almost all types of commercial LIBs [2]. Among the above mentioned cathodic material, $LiCoO_2$ is most widely used in LIBs because of its high energy density, operating voltage and good electrochemical performance.

Presence of Li and Co in waste: Metals such as Co and Li present in the LIBs, are commercially important. In the upcoming decade, the global demand of Co and Li are expected to rise three times more compared to their current demand [3]. They have diverse range of metallurgical and chemical applications varying from aircraft engines to rechargeable batteries. Co finds its applications in aircraft engine, magnets, super alloy making, carbides, rechargeable batteries, etc. whereas Li is used in the production of medicines related to psychological disorders like manic-depressive psychoses, mood swings, etc [4]. The presence of Co

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Table 1
Hydrometallurgical recovery of metals from spent batteries.

Target Metals	Salient Features	References
Co & Li	Almost 99% Co and Li were leached out using 4 M HCl at 80 °C, S/L ratio of 1:10 in 1 h. PC-88A was used for the effective separation of Co and Li from the leach liquor.	[11]
Co & Li	A reductive leaching technique using HNO_3 with H_2O_2 achieved more than 95% dissolution of Co and Li from waste LIBs with activation energy 12.5 kcal/mol and 11.4 kcal/mol, respectively.	[12]
Co & Ni	Solvent extraction followed by electrochemical processes has been studied to separate of Co and Ni from spent batteries. Electrowinning of Ni was carried out at 250 A/m^2, pH 3–3.2 and 50 °C with 87% current efficiency whereas for Co current efficiency of 96% at 250 A/m^2, pH 4–4.2 and 50 °C was used.	[13]
Co & Li	Complete dissolution of Co and Li was achieved using H_2SO_4 and 15% H_2O_2within 10 min at 75 °C maintaining pulp density 50 g/L.	[14]
Co & Li	92% of the Co was recovered as $CoSO_4$ by using ethanol at a volume ratio of 3:1 whereas the remaining cobalt (8%) was precipitated as $Co(OH)_2$ by increasing the pH up to 10 by adding LiOH. 90% Li was recovered as Li_2SO_4 by the addition of ethanol at 3:1 volume ratio.	[15]
Co, Li, Mn & Ni	A hydrometallurgical path to selectively recover Zn and Mn from other base metals viz. Ni, Cu, Al, Cd, Li and Co from spent alkaline batteries has been investigated. The process mainly comprises of sorting batteries, their dismantling followed by leaching using H_2SO_4 and finally separation by liquid–liquid extraction using Cyanex 272.	[16]
Co	Complete recovery of Co from spent LIBs was noticed with current efficiency 96.9% at pH 5.4 applying potential −1.00 V and a charge density of 10 °C/cm^2.	[17]
Co, Mn, Ni & Li	More than 99% of Co, Mn, Ni and Li were leached with 4 M HCl at 80 °C in 1 h. Mn was recovered as MnO_2 and $Mn(OH)_2$ from the leach liquor using $KMnO_4$ whereas as Ni was selectively extracted using dimethylglyoxime. Co was precipitated as hydroxide at pH 11 using 1 M NaOH and Li present in the raffinate was precipitated as Li_2CO_3 by addition of Na_2CO_3 solution.	[2]
Co & Li	More than 90% Co and 100% Li recovered using 1.25 M citric acid with 1% H_2O_2 at S/L of 20 g/L within 30 min at 90 °C.	[1]
Co	Reductive leaching of Co was carried out 2 M H_2SO_4 and 6% H_2O_2 at 60 °C, S/L ratio of 100 g/L. From the leach liquor selective extraction of Co was achieved with 50% saponified 0.4 M Cyanex 272 at an equilibrium pH ∼6.	[18]
Co & Li	96.3% Co and 87.5% Li present in spent LIBs were dissolved using 2 M H_2SO_4 and 2% H_2O_2. Co present in the leach liquor was precipitated as $CoC_2O_4{\cdot}2H_2O$ by adding $(NH_4)_2C_2O_4$ whereas Li_2CO_3 precipitate was obtained by adding Na_2CO_3.	[19]
Co	95% Co has been achieved by using 0.5 M glycine, 0.02 M ascorbic acid and 0.2 g $LiCoO_2$ as leachant in a batch extractor in 360 min at 80 °C.	[20]
Li, Co, Ni & Mn	An acid leaching process for effective recovery of metals from the mixed-cathode materials has been developed. More than 95% of Li, Co, Ni, and Mn were leached out using 0.5 M citric acid and 1.5% H_2O_2 at 90 °C in a mixing time of 60 min maintaining 20 g/L pulp density.	[21]
Li	Novel process for recovery of Li from spent LIBs has been reported. The electrode materials obtained by mechanical separation are pyrolysed under vacuum atmosphere. During this process Li gets released in the form of Li_2CO_3 from the crystal structure due to the disintegration of the oxygen framework. As a result, 81.90% Li recovered with 99.7% purity at 973 K in 30 min with a pulp density of 25 g/L.	[22]
Li	A process has been developed for the selective leaching and separation of Li from cathode scrap of LIBs using formic acid. Li was recovered as Li_2CO_3 with 99.9% purity leaving Ni, Co and Mn in the leachate.	[23]
Li, Ni & Co	Solvent extraction process for the selective recovery of Li, Co and Ni with high purity has been developed. Selective extraction of Co and Ni was achieved leaving 99.9% Li in the raffinate. Further selective scrubbing of Ni was carried out using $NiSO_4$. 99.5% Ni and 99.2% Co were obtained in two counter-current stripping stages.	[24]
Al, Co & Li	A process for the separation Al, Co and Li from spent Li-ion batteries using manual dismantling, acid leaching, precipitation and solvent extraction has been developed. About 55% Al, 80% Co and 95% Li were leached from the cathode. Precipitation of Al was carried out using NH_4OH at pH 5. The filtrate containing Co and Li obtained was subjected to extraction using Cyanex 272. Around 85% Co was separated leaving Li in the raffinate.	[25]
Cu, Co & Ni	A novel process to recover metals from a mixture of spent LIBs and NiMH batteries was investigated. The spent batteries were initially dismantled and then separation of aluminum substrate and electrolyte was done. The powder including $LiCoO_2$, copper oxides, metal nickel and hydrogen storage alloy and their oxides were leached using 3 M H_2SO_4 + 3% H_2O_2 at 70 °C, S/L = 1:15 for 5 h. From the leach solution, rare earths (RE) were precipitated as sodium RE double sulfate whereas Cu was extracted with 10% Acorga M5640 at pH 1.5–1.7, Co and Ni were extracted using 1 M Cyanex272 at pH 5.1–5.3 and 6.3–6.5, respectively.	[26]
Co	A hydrometallurgical process for the recovery of a pure and marketable $CoSO_4$ solution LIBs has been reported. 93% Co and 94% Li were leached out at 100 g L pulp density using 2 M H_2SO_4, 5% of H_2O_2 in 30 min at 75 °C. From the leach solution, 85.42% Co was recovered using 1.5 M Cyanex 272 at O/A ratio of 1.6 at pH 5 whereas the co-extracted Li was scrubbed from the Co-loaded organic using 0.1 M Na_2CO_3. Finally, the $CoSO_4$ solution with 99.99% purity was obtained.	[27]
Co & Li	Preparation of LiCoO2 from spent LIBs was studied, which involved the separation of electrode materials by ultrasonic treatment followed by acid leaching, precipitation of Co and Li, further the preparation of LiCoO2 cathode materials. 99.4% Co and 94.5% Li were recovered. The LiCoO2 prepared showed good electro-chemical performance.	[28]

and Li in the active cathodic material of LIBs is quite high compared to their natural resource which makes it a potential secondary resource [5].

Hazardous effect of spent LIBs: Spent LIBs collected as municipal waste are environmentally unacceptable due to presence of various hazardous materials. LIBs consist of metals (∼5–25%), organic chemicals (∼15%) and plastics (∼7%) which cannot be disposed-of unless these contents are properly treated [6,7]. Land filling of LIBs may lead to leaching of metals (Co, Li, Fe and Cu) into the soil and pollute the ground water whereas incineration is illegal practice done by unorganized sector to make metals from e-waste including LIBs which leads to the generation of dioxins and furan gases that has adverse affect on the environment [8,9]. Presence of plastics and organic material in LIBs will contaminate water bodies and affect aquatic life as well as human beings. Therefore, proper treatment of LIBs is necessary prior to its disposal to the environment.

Recycling of LIBs: In India and few other countries, recycling of LIBs is a big challenge due to improper collection system, illegal recycling by unorganized sector as well as lack of cost-effective technology for processing such scraps. As these LIBs contain metals, organic chemicals and plastics, it requires proper treatment to remove the hazardous content before disposal. For India, if the pre-deployment scenario is compared to the post deployment benefits, it could be observed that LIBs are collected from various sources and randomly chopped to get metals. During the course of processing, the cathodic material containing $LiCoO_2$ gets discarded and contaminates the soil. Moreover, the heterogeneous nature of batteries (branded, local and cheaper) received from the municipal waste containing impurities puts forward a great challenge for selective recovery of metals from LIBs and their purification.

LIBs are usually treated by mechanical processing, pyrometallurgy, hydrometallurgy, bio-hydrometallurgy or a blending of these techniques, to recover metals [10]. Hydrometallurgical processes are considered suitable for metal recovery from spent LIBs because of low energy requirement, high purity product and minimal air emission. Several researchers have studied and reported the recovery of Co, Li, Mn and Ni from spent LIBs using hydrometallurgical route (leaching/solvent extraction/precipitation or combination of one or two