



Resource recovery of critically-rare metals by hydrometallurgical recycling of spent lithium ion batteries

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ABSTRACT

The increasing demand for critical metals and mounting pressure on the environmental impact of solid waste disposal have widely attracted the recycling of spent lithium ion batteries (LIBs). Although the hydrometallurgical recycling of LiCoO₂ cathode materials from spent LIBs has been commonly investigated, the studies on LiNi_xCo_yMn_zO₂ type cathode materials are infrequent. Hence, the present work is focused on sulfuric acid leaching of LiNi_xCo_yMn_zO₂ cathode material for resource recovery of all the critical and rare metals from spent LIBs. The process parameters viz., pulp density, acid concentration, the dosage of reducing agent (i.e., H₂O₂), time, and temperature have been optimized for leaching of cathode powder (of weight composition: 7.6% lithium, 20.48% cobalt, 19.47% manganese, and 19.35% nickel). The maximum 92% lithium and nickel, 68% cobalt, and 34.8% manganese could be leached while leaching a 5% pulp density in 3.0 M H₂SO₄ without H₂O₂ at 90 °C. Leaching efficiencies of metals were found to be increased within 30 min and reaching to > 98% by adding 4 vol% H₂O₂ even at a lower temperature, 50 °C. Thereafter selective precipitations of manganese and nickel were carried out from leach liquor using KMnO₄ and C₄H₈N₂O₂ as suitable precipitants, respectively. Subsequently, a 2-stage solvent extraction using 0.64 M Cyanex 272 (50% saponified) at equilibrium pH 5.0 and O:A of 1:1 was employed for recovery of a highly pure solution of CoSO₄. Finally, lithium could be precipitated at Li⁺:Na₂CO₃ of 1.2:1.0 and a process flow-sheet has been proposed for the recycling of spent LIBs.

1. Introduction

Electronic (e-)waste is the fastest growing solid waste problem worldwide, challenging the global sustainability [1]. The spent lithium ion batteries (LIBs) are one of such e-waste which has intrinsic domination for implementing new technologies in modern electronic devices, laptops, personal computers, and electric vehicles due to the attractive electro-chemical properties of high energy density, long service life, modest size and weight ratio [2–4]. The spent LIBs usually contain significant amounts of hazardous pollutants of organic substances and inorganic compounds of heavy metals. An improper disposal/management of waste streams (spent LIBs) presents serious threats to the human health, environment, and biota [5,6]. The weight ratio of critically-rare metals in waste materials (LIBs) is valuable to be recycled for their re-use in the manufacturing of new materials along with the alleviation of environmental adversity and promising economic benefits [7–11]. Henceforth, the development of efficient recycling technologies has paid great attention in recent times.

A variety of methods for recycling of spent LIBs to extract the

critical and rare metals (i.e., cobalt, lithium, and nickel) have been studied by involving the pyro/hydro/bio metallurgical processes, which have been recently reviewed by Choubey et al. [12] and Lv et al. [13]. The biometallurgy is yet to be up-scaled for processing of spent materials due to the adversity of high metal concentrations to incubate the microbes [8,9]. The pyrometallurgical operations have been adopted by several commercial organizations (Inmetco, Umicore, and Xstrata), but the burning of binder and organic electrolytes is costly due to high energy requirement and loss of the critical metal (lithium) into the slag [14]. Alternatively, the hydrometallurgical process follows dismantling, physical separation, crushing, acid (inorganic/organic) leaching of cathodic materials with or, without additives for metals extraction in soluble form, which undergo for separation and purification steps [4,12–16]. Usage of organic acids viz., citric acid, succinic acid, oxalic acid, ascorbic acid, malic acid [2,17–21] have been considered eco-friendly instead of using strong inorganic acids viz., sulfuric acid, hydrochloric acid, and nitric acid [4,16,22–27]. Use of organic acids gave similar leaching efficiency to inorganic acids, albeit their applications are discouraged due to relatively high costs and difficulties in metals

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Table 1
Summary of the works carried out using $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ cathode material for recycling of spent LIBs.

Material	Lixiviant and chemicals used	Salient features and efficiency	Reference
LiCoO ₂	Organic acids	> 96% cobalt and 98% Li was recovered using 1.5 M C ₆ H ₈ O ₇ + 1 vol% H ₂ O ₂ at 90 °C under the optimized conditions of 80 min, 70 °C, 2.0 M reductant dosage 0.6 g/g, and pulp density 50 g/L	[2]
	H ₂ SO ₄ + H ₂ O ₂	2.0 M H ₂ SO ₄ + 5 vol% H ₂ O ₂ at a pulp density of 100 g/L and 75 °C yielded 99% Li and 70% Co in 60 min	[4]
	H ₃ PO ₄ + H ₂ O ₂	> 99% extraction of Co and Li was obtained at optimal condition: 0.7 M H ₃ PO ₄ with 4 vol% H ₂ O ₂ at pulp density 2%, 40 °C, time 60 min	[7]
	Organic acids	> 90% cobalt and 100% Li could be recovered using 1.25 M C ₆ H ₈ O ₇ + 1 vol% H ₂ O ₂ at 90 °C	[18]
	HNO ₃ + H ₂ O ₂	> 95% Li and Co were leached in reducing environment with activation energy 11.4 kcal/ mole and 12.5 kcal/mole, respectively.	[23]
	Various acids	Leaching with 4.0 M HCl at 80 °C yielded better leaching efficiency (~99%) of Li and Co in comparison to sulfurous acid and hydroxylamine hydrochloride	[24]
	H ₂ SO ₄ + H ₂ O ₂	96% Co and 87% Li were leached in 2.0 M H ₂ SO ₄ solution with 2 vol% H ₂ O ₂	[25]
	HCl	> 99% of all metals (Li, Co, Ni, and Mn) were leached out with 4.0 M HCl solution at 80 °C in 60 min and subsequently precipitated in different forms for metals recovery	[26]
	Tri-chloro acetic acid (TCA) + H ₂ O ₂	Leaching with 3.0 M TCA and 4 vol% H ₂ O ₂ at 5% pulp density, 60 °C yielded 93% Ni, 91.8% Co, 89.8% Mn and 99.7% Li in 30 min	[28]
	Lixiviant: NH ₄ OH + reductant: (NH ₂) ₂ S + buffer (NH ₄) ₂ CO ₃	Leaching at the ratio of NH ₄ OH:(NH ₂) ₂ S:(NH ₄) ₂ CO ₃ = 1.0:0.5:1.0 at 80 °C for 60 min yielded the maximum Cu, Co, and Ni, leaving Al and Mn undissolved in leach residue	[29]
Only LiNi _x Co _y Mn _z O ₂ type cathode material separated from the spent LIBs	H ₂ SO ₄ + H ₂ O ₂	All the concerned metals (Li, Ni, Co and Mn) leached > 99% under the conditions: 1.0 M H ₂ SO ₄ , 1 vol% H ₂ O ₂ , 4% pulp density, 60 min, 40 °C, by following the surface controlled dissolution mechanism	[30]
	C ₆ H ₈ O ₇ + H ₂ O ₂	> 95% of Li, Co, Ni, and Mn were obtained at 90 °C in 60 min while leaching at 2% pulp density in 0.5 M citric acid + 1.5 vol% H ₂ O ₂	[31]

separation from leach liquor [7]. Due to this, sulfuric acid leaching is most preferable being a cheaper and less-toxic lixiviant [27]. Although plenty of recycling studies on sulfuric acid leaching of spent LIBs containing LiCoO₂ cathode materials have been carried out, a few deals with second generation cathode materials of LiNi_xCo_yMn_zO₂ (those conditions are summarized by literature survey in Table 1) [2,4,7,18,23–31]. Recently, Yang et al. [32] employed the sulfuric acid leaching in presence of H₂O₂ which was followed by a facile co-extraction of manganese, nickel, and cobalt using solvent extraction with D2EHPA, leaving lithium into the raffinate. Subsequently, the co-stripped metals into 0.5 M H₂SO₄ solution used to directly regenerate the cathode materials, is a simple process, however, the authors failed to achieve the desired proportionate of recycled metals for regeneration of LiNi_xCo_yMn_zO₂. Hence, a systematic study for recycling the LiNi_xCo_yMn_zO₂ material will be useful to efficiently recover rare metals from the LIBs.

In the present study, sulfuric acid leaching of the cathode material in presence of the reducing agent, hydrogen peroxide has been investigated first. The optimization of leaching conditions has been carried out by varying the parameters viz., acid concentration, pulp density, H₂O₂ dosage, temperature, and time. As the article deals with the process optimization studies, leaching kinetics has been not included for the sake of brevity. Subsequently, the leach liquor has been processed for the separation and recovery of rare metals by selective precipitation and solvent extraction techniques. Finally, a flow sheet for the entire recycling process of spent LIBs has been proposed using simple operating steps that can lead to the sustainable management of this electronic waste and mitigation of rare metals supply risks.

2. Experimental

2.1. Dismantling of spent LIBs and collection of cathode powder

Spent LIBs of discarded laptops, personal computers, and smart phones were collected from a local vendor and dismantled manually after discharging and soaking in brine solution for 24 h. Thereafter removal of plastic cases was followed by unfolding of anode and cathode to collect the copper and aluminum foils separately. The black powder of the active-cathode material was then separated from

aluminum foil by a heat treatment at 300 °C for 1 h in a muffle furnace. It needs to clarify here that not any specific proportionate of spent batteries was considered because at the higher scale it would be difficult to maintain any fixed proportionate due to the availability of raw materials to be processed. Hence, they were taken arbitrarily to get the mixture of cathode materials. Thus collected powdery cathode material was homogenized and analyzed before making stock to be used in this study. The metal composition of the stock sample is given in Table 2.

2.2. Reagents

Sulfuric acid (Lab-Scan Analytical Science, 98% purity) was used to prepare the solution of desired concentrations to be used as lixiviant for leaching of the cathode material. Hydrogen peroxide (Sigma Aldrich, 30% purity) was used as the reducing agent during leaching studies. The reagents potassium permanganate (Sigma Aldrich, 97% purity), dimethylglyoxime (Sigma Aldrich, 99% purity), and sodium carbonate (Sigma Aldrich, 99.9% purity) were used as the precipitating agents for manganese, nickel, and lithium, respectively from the leach liquor. Sodium hydroxide solution (4.0 M from the pellets supplied by Riedel-deHaën and Lab Scan) prepared in distilled water was used for pH adjustments, wherever required, and saponification of the organic extractant (Cyanex 272; 85% purity, Sp. gr. 0.92 supplied by Cytec, Canada) for solvent extraction of cobalt. The recovered products in the form of precipitates were washed with distilled water before the characterization studies. All reagents used were of analytical grade and without further purification.

2.3. Leaching studies

All the leaching studies were performed in a 500 mL 3-neck flat bottom flask with a magnetic stirrer, a temperature sensor with a controller, and a glass condenser fitted onto the middle neck of the flask

Table 2
Chemical composition of cathode material used for leaching.

Elements	Li	Co	Ni	Mn	Cu	Fe	Non-metals
Wt.%	7.6	20.48	19.35	19.47	0.004	0.05	balance

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