Recovery of Lithium (Li) Salts from Industrial Effluent of Recycling Plant

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Abstract   To cope up with the supply–demand gap of lithium (Li) an essential energy element, the recycling of waste industrial effluent (generated after cobalt recycling from waste Li-ion batteries) is targeted. In industry, after the recovery of Co, Cu, Ni, and graphite from one ton of black cathodic material of Li-ion batteries about 8 m^3 of waste effluent containing 5–10 g/L Mn and 1–3 g/L Li is generated. Systematic precipitation studies were carried out using saturated alkaline solution varying Eh/pH of the effluent. Settling time 30 min and pH ~12 were found to be optimum conditions for maximum precipitation of Li (~90%) as salt. Precipitation studies for Mn/ Li with scientific validation were also carried out and discussed. The process developed has tremendous potential to be commercialized in industry after scale-up studies.

Keywords Lithium-ion batteries (LIBs) · Lithium (Li) · Precipitation · Hydrometallurgy

Introduction

Li, an essential energy element, has been extensively used in lithium-ion batteries, computer products, communication devices and other fields. Li and its compounds are usually produced from their primary resources, which is not sufficient to cope up with the amount of Li required. The limited supply of Li is not forbidding its utilization in battery production and is constantly escalating [1–4]. The requirement of Li by the battery industries is estimated to increase from 43% in 2017 to 65% in 2025 [5]. Almost one-third of Li present in the earth crust will be consumed in making electric vehicle batteries by 2050 and ultimately the Li resources are predicted

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to be entirely exhausted by 2080 [6]. Thus, to cope up with the supply–demand gap of Li, it is essential to ensure a reliable alternative source of Li. Huge amount of effluent containing substantial amount of Li is generated by battery recycling industries, where after the recovery of Co, Cu, Ni, and graphite from the black cathodic material of LIBs, the effluent is discarded. It is expected to have loss of Li in drained/ treated effluent during the final disposal. Moreover, variation in the concentration of Li is often noticed due to complex and heterogeneous nature of scrap LIBs which has limited the research work on laboratory scale rather than scale-up or commercial scale. The effluent generated during processing of LIBs showed the presence of other metals (Mn, Co, Cu, Ni) as impurities, which when disposed to the environment can cause severe damage to the aquatic life. However, recuperation of Li from industrial effluent will not only assuage the load on natural resources but also solve the problems caused to the ecosystem. Hydrometallurgical processes consisting of solvent extraction, precipitation, or adsorption have been globally applied for the recovery of Li from effluents. Researchers worked for the recovery of Li from various effluent. Table 1 summarizes different routes adopted to recover Li from wastewater [7–11]. Although studies have been carried out to recover Li from various effluent

Table 1 Different routes utilized to recover Li from wastewater

Process used	Remarks	References
Electrometallurgy	Li recovery and organic pollutant removal from industrial wastewater was proposed where an electrochemical system containing a Li-recovering electrode and an oxidant-generating electrode was used to simultaneously recover Li and decompose organic pollutants. This recovers 98.6 mol% Li and reduces organic pollutants by 65%	Kim et al. [7]
Adsorption	A magnetic Li-ion imprinted polymer, $Fe_3O_4@SiO_2@IIP$ was synthesized using novel crown ether to recover Li from wastewater. At optimum pH $= 6$ was for adsorption and polymer takes 10 min to reach complete equilibrium. About 89.8% of the Li was recovered	Luo et al. [8]
Leaching	Selective recovery of Li from spent LIBs by coupling advanced oxidation and chemical leaching processes was studied. Loss of Li was only 2.06%. Li_2CO_3 of purity 99.0% was finally obtained	Lv et al. [9]
Precipitation	Two-stage precipitation process using Na_2CO_3 and Na_3PO_4 as precipitants was developed to recover Li as 74.72% raw Li_2CO_3 and 92.21% pure Li_3PO_4, respectively from effluent	Guo et al. [10]
Precipitation	A two-step precipitation of Li_2CO_3 using CO_2 as a precipitation agent from Li-containing alkaline wastewaters was studied. At 95 °C, more than 99.5% sparingly soluble Li_2CO_3 was produced in the second step, whilst most impurities remain in the solution	Jandová et al. [11]

of recycling plant, much consideration has been made on the various methods used for recycling Li rather than its effective recovery from low concentration solution. Moreover, lack of selectivity still persists. Keeping in view of the above, CSIR-NML, Jamshedpur has developed feasible technology for battery recycling and transferred the same to different Indian industries. Based on this, the present paper reports the development of a complete process flowsheet to recover Li and Mn as a valuable product from effluent generated after Co, Cu, and Ni recycling from waste LIBs using precipitation process.

Systematic and scientific precipitation studies were carried out and after studying various process parameters, optimal condition for the maximum extraction of Li and Mn from the effluent was obtained. The metal-free effluent generated containing carbonate ions will be re-utilized. Developed process is novel and has potential approach for Li recovery from effluent generated by the recycling industries.

Materials and Method

Materials

Present work is carried out using the effluent generated after the recovery of Co, Cu, Ni, Fe, and graphite during LIBs recycling to recover Li and Mn. The effluent was chemically analyzed and found to contain about 2.31 g/L Li and 5.52 g/L Mn. The pH of the effluent generated was recorded to be ~3. Sodium hydroxide (NaOH) and sodium carbonate (Na_2CO_3), both supplied by Merck, India was used as precipitant to precipitate Mn and Li, respectively, from the generated effluent. Both the precipitating reagents were diluted to the required concentration using de-ionized water. Apart from these, H_2SO_4 used during this study (for pH adjustment) was of analytical grade (AR) supplied by Rankem, India. All chemicals used for the experimental studies were used without further purification. Samples to be analyzed were diluted using de-ionized water.

Procedure

Based on our group (CSIR-NML, Jamshedpur) experience in the area of LIBs recycling, a complete process flowsheet including pre-treatment—leaching—solvent extraction—precipitation is presented in this paper with detailed discussion regarding Li and Mn recovery. Waste LIBs were received from a recycling industry, M/s Evergreen Recyclekaro Pvt. (India) Ltd. situated at Mumbai, India. Spent LIBs were initially discharged, crushed (using scutter crusher) and further beneficiated to separate the black cathodic material. The typical analysis of metals present in this black powder is presented in Table 2.

Table 2 The composition of metals present in black powder of LIBs

Elements	Co	Mn	Li	Cu	Ni	Fe
Wt.%	15.16	6.30	2.36	1.29	1.95	0.35

Variation in the composition of metals in the black powder is generally observed due to quality and type of LIBs collected and it may range between 10–20% Co; 0.5–1.5% Fe; 1.5–3% Ni; 2.1–3.5% Li; 7.5–9.5% Mn, and 4.1–6% Cu. The leaching of metals from the black cathodic material of scrap LIBs were carried out in a three-necked closed Pyrex glass reactor fitted with a condenser using a hot plate with a temperature controlling sensor. Magnetic stirrer was used for mechanical agitation. The obtained leach liquor was subjected to solvent extraction resulting in maximum extraction of Cu and Ni using suitable extractant. Further, selective separation of Co takes place via precipitation technique. Solvent extraction and precipitation process result in complete extraction of Co, Ni, and Cu leaving Mn and Li in the raffinate. This raffinate when generated in huge quantity in recycling industries mostly discarded due to lack of viable technologies for their processing. In order to prevent the wastage of Li and Mn left in the effluent generated were collected, mixed properly and experiments for their precipitation were carried out. After selecting the precipitating reagent, optimization of suitable conditions for batch scale studies as well as validation of the same was also made so as to collect salts of Li and Mn. Satisfactory mass balance was obtained for representative test samples. The content of metals in the sample as well as in the solution generated during the experiments was analyzed using atomic absorption spectrometer (AAS) (Perkin Elmer model, Analyst 200; USA). Metrohm Basic Titrino 797 with glass pH combination electrode and automatic temperature correction was used for pH measurement.

Results and Discussion

Generation of Effluent Containing Li and Mn

Scrap LIBs were initially ensured to be completely discharged and beneficiated to separate the plastic part that floats on top, black cathodic powder which remains suspended and metallic content settles at the bottom. Among these materials, the black cathodic material mainly containing Co, Li, Mn, Cu, Ni, and graphite was used for the experimental purpose. The beneficiated black cathodic material obtained was leached using suitable concentration of sulfuric acid (H_2SO_4) in presence of an oxidizing agent, hydrogen peroxide (H_2O_2) at an elevated temperature for some time to get maximum amount of metals in the solution. It was observed that H_2SO_4 with H_2O_2 proved to be the positive lixiviant for leaching of metals. The whole slurry was filtered and the residue was washed for further analysis. More than 98% leaching of metals was achieved and the obtained leach liquor majorly contained about 15.03 g/L
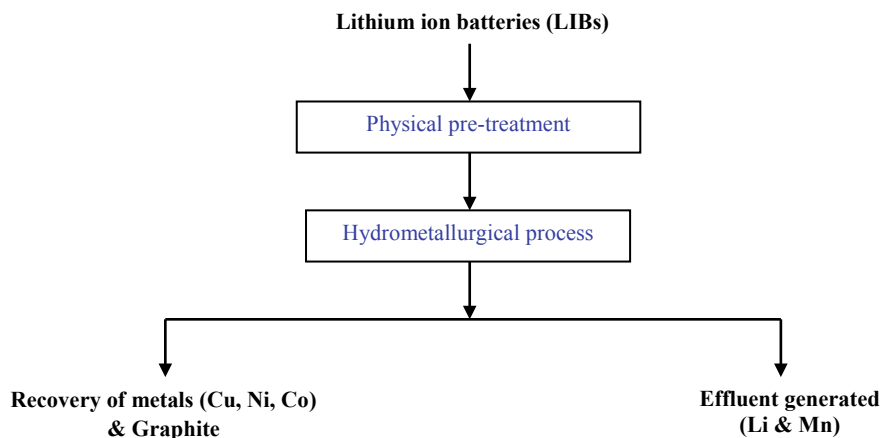
Physical pre-treatment

Hydrometallurgical process

Recovery of metals (Cu, Ni, Co) & Graphite

Effluent generated (Li & Mn)

Fig. 1 Process flow for the generation of effluent containing Li and Mn. (Color figure online)

Co; 2.2 g/L Li; 1.3 g/L Cu; 1.87 g/L Ni; and 5.5 g/L Mn. Further, Cu, Ni, and Co were selectively separated using solvent extraction technique. Major amount of Co, Ni, and Cu, as well as their metallurgical advantages, attracted industrialists towards their extraction while Li along with Mn gets disposed off as effluent (Fig. 1). Lack of cost-effective process to recover Li and Mn results in their loss. Thus, huge amount of effluent was generated which require proper treatment.

Selective Precipitation of Mn from the Effluent

The effluent obtained after extraction of Co was found to contain 2.31 g/L Li and 5.52 g/L Mn. The pH of the effluent was ~3.5. Due to low concentration of Li, the effluent was concentrated 10 times and analyzed. It was found that the content of Li and Mn increased up to 20.9 g/L and 53.1 g/L, respectively, and pH was ~4.5. For selective precipitation of Mn from this concentrated solution, optimization of the precipitation parameters was carried out including effect of pH, settling time, and temperature. Using 50% NaOH solution at room temperature, the pH of the effluent was increased up to 11, provided with constant stirring and maintaining settling time of 30 min. It was observed that ~pH 10.5; ~99.99% of Mn present in the effluent get precipitated in two stages (Fig. 2). The reaction taking place is represented by the equation below:

$$MnSO_4 + 2NaOH = Mn(OH)_2 \downarrow + Na_2SO_4 \qquad (1)$$
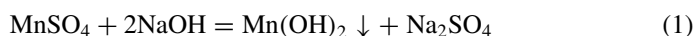
The amount of NaOH required for increasing the pH was also calculated and found that for 200 mL of effluent (containing 53.1 g/L Mn), ~2.5 g of NaOH is required to reach pH 10.5 and completely precipitate Mn from the effluent. It was noticed that
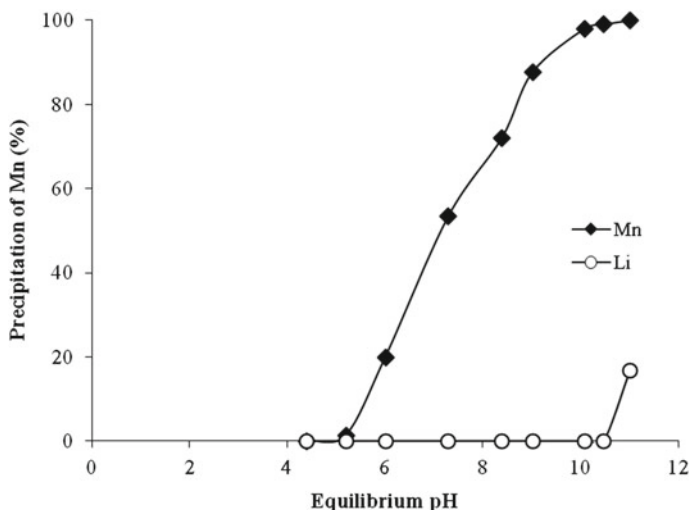
Fig. 2 Effect of pH on precipitation of Mn (Aqueous: 53.1 g/L Mn and 20.9 g/L Li; Reagent: 50% NaOH; Temp.: 30 °C; Time: 30 min; Stirring speed: 300 rpm)

beyond pH 11, minor amount of Li present in the raffinate get co-precipitated. Thus, at pH 10.5, Mn was selectively separated. The effluent was further filtered and a black precipitate of $Mn(OH)_2$ was collected. This precipitate of $Mn(OH)_2$ was dried to get MnO_2 of purity 99%. After Mn removal, the raffinate (analysed to be free from Mn) was ready for Li recovery.

Chemical Precipitation for Li Recovery

After successful recovery of Mn from the effluent, focus was made towards the Li recovery. Analysis of the raffinate (free from Mn) showed the presence of 20.88 g/L Li. Li was present as liquid phase, which was selectively precipitated as solid phase by the chemical reaction during this precipitation process. In this case, Na_2CO_3 was used to precipitate Li according to the equation:

$$Li_2SO_4 + Na_2CO_3 = Li_2CO_3 + Na_2SO_4 \qquad (2)$$
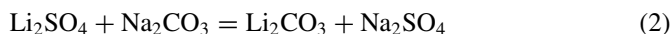
After carrying out the precipitation experiments at different conditions, it was found that temperature plays an imperative role during Li precipitation. The fact is that the solubility of Li_2CO_3 decreases with increase in temperature and thus, to reduce the loss of Li due to solubility, it is beneficial to precipitate Li at elevated temperature. Consequently, after optimizing other parameters, the effect of temperature was also studied at room temperature (30 °C), 50 and 90 °C as presented in Fig. 3. It was observed that elevated temperatures favored the rate of Li precipita-
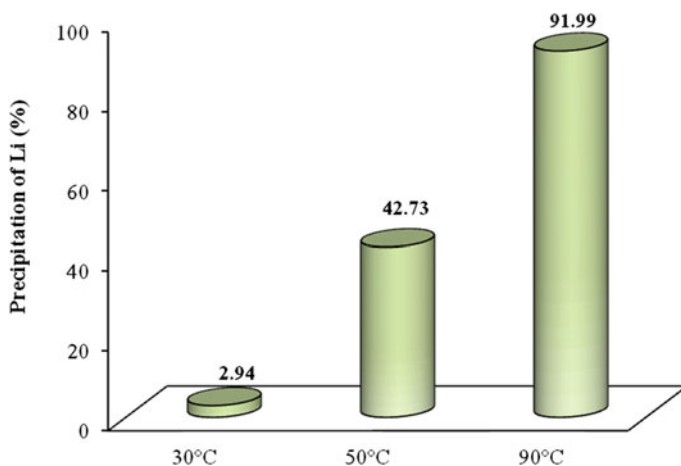
Fig. 3 Effect of temperature on precipitation of Li. (Aqueous: 20.88 g/L Li; Reagent: 50% Na_2CO_3; Time: 15 min; Stirring speed: 300 rpm). (Color figure online)

tion. In 15 min time, ~90% precipitation of Li as carbonate takes place maintaining the solution temperature 90 °C. As far as the requirement of Na_2CO_3 is concerned, it was noticed that 200 mL of 20.88 g/L Li-containing raffinate needs about 50 g of Na_2CO_3 for complete Li precipitation. The salt of Li_2CO_3 get precipitated. The obtained Li_2CO_3 was washed with hot water as water-washing decreases the possibility for the presence of impurities (containing Na^+) in Li_2CO_3 produced. The purity of obtained Li_2CO_3 salt was 99%.

In order to validate the result of Li precipitation, standard Eh–pH diagram was drawn using HSC software and presented in Fig. 4. The experimental data were validated with the theoretical Eh–pH diagrams showing the recovery of Li as carbonate usually starts at pH 9 but as optimized, carbonate of Li occurs in solution having pH range above 11.

Processing of Wastewater

It is essential to process the wastewater left after Mn and Li recovery for re-utilization or water treatment to check its suitability for disposal in the environment. If allowed to be discharged in the environment, it is essential to maintain pH of the wastewater between pH 6 and 7 for disposal. In this condition, the effluent left after Li recovery contains Na_2CO_3 and thus, the temperature was decreased to 4 °C for more than 24 h and crystals of Na_2CO_3 were collected and water was used further for the hydrometallurgical process. The content of metal ions in ppb level is required to be checked and TDS to be maintained in the range 150–200. The treated water can be utilized/recycled in the industry.
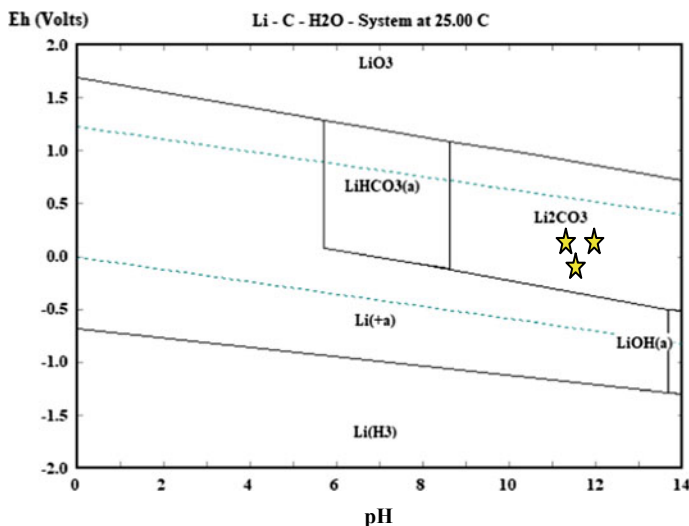
Fig. 4 Validating Eh–pH diagrams with experimental data for Li precipitation (=Li_2CO_3). (Color figure online)

Conclusions

Based on the obtained experimental results for separation and recovery of Li and Mn from the effluent generated after Co, Cu, Fe, and Ni extraction, the following conclusions can be drawn:

- Effluent containing Mn and Li were precipitated using NaOH at room temperature and Na_2CO_3 at 90 °C, respectively without using any additive.
- About 99.99% of Mn and Li were found to be selectively precipitated with purity ~99% at pH 10.5 in two stages and 12.34 in single stage, thus chances of co-precipitation was reduced.
- Temperature plays a very essential role where the solubility of Li_2CO_3 decreases with increase in temperature and thus, it is beneficial to precipitate Li at elevated temperature.
- Filtration separates the hydroxides of Mn and carbonate of Li leaving metal depleted wastewater.
- The developed process will be economical as it consumes comparatively less amount of energy and time than the processes reported previously. The complete process flowsheet is shown in Fig. 5. Lab-scale data shows feasibility of the process; however, some scale-up studies/ pilot scale studies are required before commercialization.
- After Li and Mn extraction, the effluent generated can be re-utilized in industry after the treatment and maintaining TDS and pH.
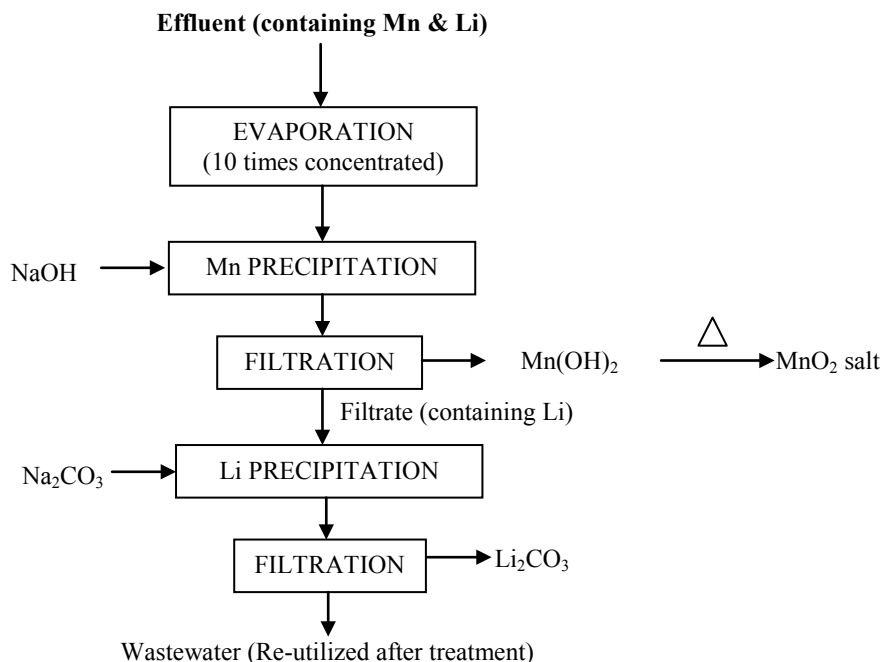
Effluent (containing Mn & Li)

Fig. 5 A complete process flowsheet for the recovery of Li and Mn from the effluent generated after LIBs processing

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