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Separation and recovery of Co(II) and Li(I) from spent lithium-ion mobile phone batteries

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ABSTRACT

In the present work, a process for recovery of Co(II) and Li(I) from spent lithium-ion mobile phone batteries was developed by using leaching, precipitation and solvent extraction. The leaching efficiency of Co(II) and Li(I) was investigated with respect to HCl concentration, temperature, and time. Most of Co(II) and Li(I) were dissolved from spent lithium-ion batteries under optimum leaching conditions: 4 M HCl, 50°C, 1.5 hrs and pulp density of 10 g/L. Separation and recovery of Co(II) and Li(I) from the HCl leaching solution can be carried out by precipitation and solvent extraction. Cobalt oxalate was precipitated from the HCl leaching solution by adding oxalic acid at pH = 3, leaving Li(I) in the aqueous solution. In the case of solvent extraction, trioctylamine (TOA) was used to selectively extract Co(II) over Li(I) from the HCl leaching solution, and then Co(II) from the loaded TOA was stripped using distilled HCl solution. In term of recovery efficiency of Co(II) and loss of Li(I), precipitation was recommended as a suitable method to separate and recover Co(II) and Li(I) from the leaching solution of spent lithium-ion mobile phone batteries.

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1 INTRODUCTION

Lithium is an indispensable element in the manufacture of the electrode materials for batteries and in the other fields such as ceramic glass, enamels, adhesive, lubricant greases, metal alloys, air-conditioning, and dyeing (Nguyen and Lee, 2018). Cobalt powders have been used in steel for cutting tools, in abrasion strengthened composites and in alkaline rechargeable batteries (Nguyen and Lee, 2015). Increasing demand of cobalt and lithium in

electronic products leads to depletion of natural resources of these metals and producing a large number of electronic wastes. The spent lithium-ion batteries is defined as hazardous wastes because they cause serious harm to the environment and human's health (Wang *et al.*, 2012). Therefore, it is important to develop a process for the recovery of cobalt and lithium from secondary resources, namely spent lithium ion batteries (Wang and Zhou, 2002; Wang *et al.*, 2009; Kang *et al.*, 2010; Nguyen and Lee, 2015). Both pyro-metallurgy and

hydrometallurgy were used to recover lithium and other metals from spent lithium-ion batteries (Meshram *et al.*, 2016; Ordoñez *et al.*, 2016; Swain, 2016). Since pyro-metallurgy processes require intensive investment and cause environment pollution, hydrometallurgy processes are considered to be promising methods in term high recovery efficiency, simple operation and low cost.

In order to recover lithium and other metals, spent lithium-ion batteries were pretreated by physical processes including dismantling, crushing, screening, magnetic separation, washing, and thermal pretreatment (Quintero-Almanza *et al.*, 2019). Subsequently, hydrometallurgical processes consisting of acid leaching, ion exchange, solvent extraction, chemical precipitation, and electro-chemical processes were employed to separate and recover metals from the lithium-ion batteries. Generally, the most common positive and negative electrode materials in the lithium-ion batteries for consumer electronics are lithium cobalt oxide (LiCoO_2) and graphite, respectively (Zhang *et al.*, 1998). Therefore, acid leaching was commonly used to leach Li(I) and Co(II) from the active cathode materials. Leaching of lithium and other metals from the spent lithium-ion batteries using various reagents was reviewed in previous paper (Nguyen and Lee, 2018). According to reported data, sulfuric acid solution was commonly used to leach Li(I) and other metals from the spent lithium-ion batteries owing to high selectivity of Li(I). However, the main disadvantage of sulfuric acid leaching is low leaching efficiency of Co(I) from spent lithium-ion batteries. Hydrochloric acid leaching was known to be effective for dissolving Co(I) and few information on leaching of Co(II) and Li(I) from spent lithium-ion mobile phone batteries was reported in literatures. Thus, HCl leaching solution was used to investigate leaching efficiency of Co(II) and Li(I) from the spent lithium-ion mobile phone batteries in the present study. After leaching, separation and recovery of Co(II) and Li(I) from the HCl leaching solution was carried out by precipitation and solvent extraction.

2 MATERIALS AND METHODS

2.1 Materials and reagents

The powder samples used in this study were collected from spent lithium-ion batteries of mobile phones. Hydrochloric acid (Merck) and hydrogen peroxide (PubChem) were used as leachate and reductant, respectively. Oxalic acid (PubChem) was used to precipitate Co(II) from leaching liq-

uors of spent lithium-ion batteries. NaOH (Sigma-Aldrich) was used for adjusting the solution pH. Commercial extractant, TOA (Sigma-Aldrich), was used without further purification, and kerosene (Merck) was used as a diluent.

2.2 Preparation of powder samples

Spent lithium-ion mobile phone batteries were discharged firstly to prevent the dangers of short-circuits and spontaneous combustion. The spent lithium-ion batteries were dismantled to different parts such as cathode, anode, separator, and plastic case. After collecting black active materials from cathodes and anodes, these powder samples were placed in a furnace and calcined at 500°C for 1 hr to remove organic components. The calcined powder samples were used in leaching experiments.

2.3 Leaching and precipitation procedures

The calcined powder samples were employed as a feed for the hydrochloric acid leaching experiments. Pure HCl solution was dissolved in doubly distilled water to prepare leaching solutions. Leaching experiments of powder samples were conducted by taking 100 mL of HCl solution with desired acidity in a 250 mL of three-neck round bottom flask with a magnetic stirrer bar in a heating mantle. In all leaching experiments, the weight ratio of powder samples to leachant (pulp density) was fixed at 10 g/L. After the required reaction period, the slurries were filtered by filter papers. The concentration of metals in leaching solutions was measured by inductively coupled plasma optical emission spectrometers (ICP-OES, Spectro Arcos). Leaching percentage of metals was calculated based on Eq. (1).

$$\text{Leaching percentage} = \frac{\text{mass of metal in leaching solution}}{\text{mass of metal in powder sample}} \times 100 \quad (1)$$

The extraction experiments were carried out by mixing 10 mL of organic and aqueous phases and the mixtures were shaken for 30 min. After shaking, the organic and aqueous phases were separated using separating funnels. The concentration of metals in the aqueous solutions was measured by ICP-OES.

Precipitation of Co(II) from the HCl leaching solutions was prepared by following procedure. The aqueous containing Co(II) was mixed with oxalic acid at specific mole ratio. The pH of the mixing solutions was adjusted by using NaOH or HCl solution. After obtaining the certain value of pH, the mixed solutions were continuously stirred for 30

min. The precipitate products were separated by filter papers. Precipitation percentage of metals was calculated based on Eq. (2).

$$\text{Precipitation percentage} = \frac{\text{mass of metal in solution after precipitating}}{\text{mass of metal in solution before precipitating}} \times 100 \quad (2)$$

3 RESULTS AND DISCUSSION

3.1 Leaching of Co(II) and Li(I) from spent lithium-ion mobile phone batteries

3.1.1 Effect of HCl concentrations

In order to investigate the effect of HCl concentration on leaching percentage of Co(II) and Li(I) from the spent lithium-ion batteries, a series of leaching experiments were performed by varying HCl concentration from 0.5 to 4 M for 2 hrs at 50°C. Variation in leaching percentage of Co(II) and Li(I) with HCl concentration was shown in Fig. 1. The leaching efficiency of Co(II) was

strongly affected by HCl concentrations. The leaching percentage of Co(II) steadily increased from 47.3 % to 96.4 % with an increase of HCl concentration from 0.5 to 4 M while most of Li(I) was dissolved at any HCl concentration range. The obtained results agree well with these reported results in literatures (Wang *et al.*, 2012; Jha *et al.*, 2013). The main phase of powder materials of spent lithium-ion batteries was LiCoO₂ thus leaching reaction of Co(II) and Li(I) with HCl was represented as Eq. (3). The increasing acid concentration in leaching solutions brings incremental amount of proton, resulting in replacement more Co(II) and Li(I) (Guo *et al.*, 2016). Therefore, leaching efficiency of Co(II) increased with HCl concentration increase. According to the obtained results, 4 M HCl solution was considered as an optimum condition for leaching Co(II) and Li(I).

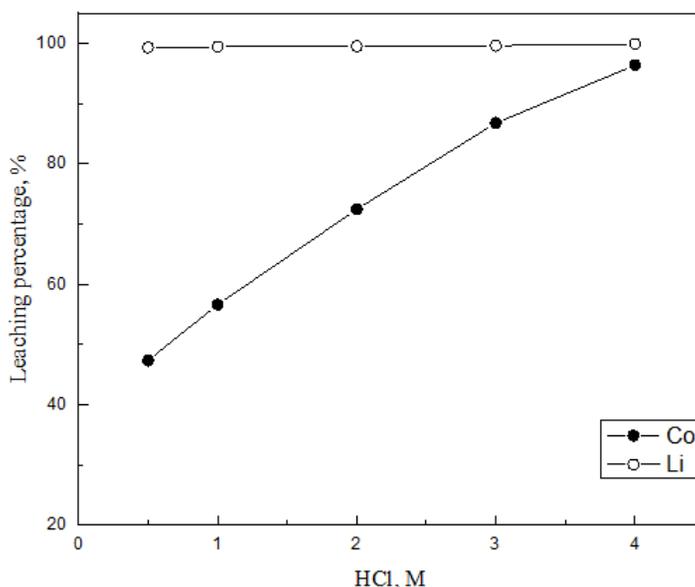
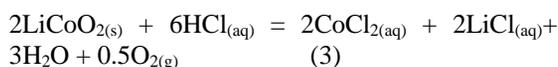


Fig. 1: Effect of HCl concentration on leaching percentage of Co(II) and Li(I) from spent lithium-ion mobile phone batteries. [HCl] = 0.5-4 M, temperature = 50 °C, pulp density = 10 g/L, time =2 hrs

3.1.2 Effect of leaching temperature

The effect of temperature on leaching efficiency of Co(II) and Li(I) from spent lithium-ion batteries was investigated in the range temperature of 25-90 °C. In these experiments, other leaching parameters were fixed at 4 M HCl, pulp density of 10 g/L and leaching time of 2hrs. The leaching percentage of Co(II) and Li(I) steadily rose to 96.4 and 99.5 %, respectively with an increase of temperature up to

50°C and then reached to a plateau with further increase of temperature (Fig. 2). In HCl leaching process, the ionization velocity of proton increased with the increase of temperature, leading to acceleration the reaction velocity (Guo *et al.*, 2016). This reason can explain why leaching percentage of Co(II) and Li(I) increased with temperature increase. The results from Fig. 2 indicated that complete leaching of Co(II) and Li(I) was obtained when the temperature leaching was higher than

50°C. However, temperature leaching at 50°C was suggested as the best temperature for leaching of

Co(II) and Li(I) in term leaching efficiency and cost operation.

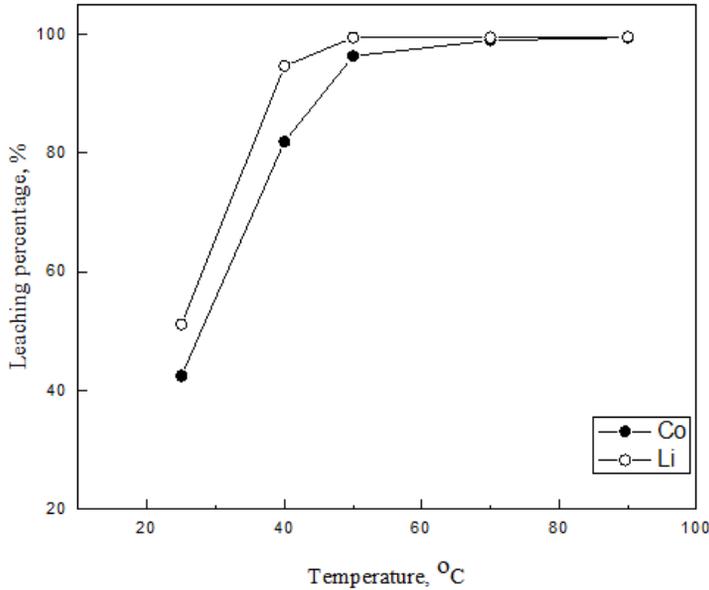


Fig. 2: Effect of temperature on leaching percentage of Co(II) and Li(I) from spent lithium-ion mobile phone batteries. [HCl] = 4 M, temperature = 25-90°C, pulp density = 10 g/L, time = 2 hrs

3.1.3 Effect of reaction time

In order to study the effect of time on leaching percentage of Co(II) and Li(I), leaching experiments were studied in the reaction time range of 0.5-2.5 hrs. All experiments were performed at 4 M HCl, pulp density of 10 g/L and leaching temperature of 50°C. The obtained results were shown in Fig. 3.

The leaching percentage of Co(II) and Li(I) increased from 81.6 and 91.2 % to 99.5 and 97.1 %, respectively when leaching time rose from 0.5 to 1.5 hrs. After 1.5 hrs, the leaching behavior of these metals was nearly constant. Thus, leaching time of 1.5 hrs was chosen as the optimum condition in the present study.

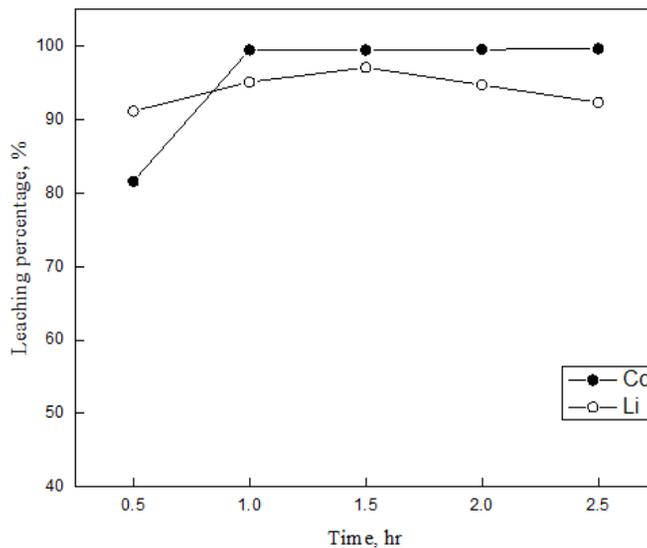


Fig. 3: Effect of time on leaching percentage of Co(II) and Li(I) from spent lithium-ion mobile phone batteries. [HCl] = 4 M, time = 0.5-2.5 hrs, pulp density = 10 g/L, temperature = 50°C

3.2 Separation and recovery of Co(II) and Li(I) from leach liquors

3.2.1 Separation of Co(II) and Li(I) from the leach liquors by precipitation method

The leaching solution used in these experiments was prepared under the optimum conditions: 4 M HCl, leaching time of 1.5 hrs, leaching temperature of 50°C and pulp density of 10 g/L. The concentration of Co(II) and Li(I) in the leaching solution was 933 and 259 mg/L, respectively. It has been reported that acidity influenced precipitation efficiency of Co(II) as cobalt oxalate (Wang and Zhou, 2002; Chen *et al.*, 2011). Therefore, the effect of solution pH on precipitation behavior of Co(II) was investigated by neutralizing leaching solution to pH = 2-7 using NaOH solution. Oxalic acid was mixed with leaching solution at H₂C₂O₄/Co²⁺ mole ratio of 4. Fig. 4 shows the effect of pH on precipitation percentage of Co(II) and Li(I). It can be seen that most

of Co(II) was precipitated in the pH range of 2-7 while the co-precipitation of Li(I) was lower than 7 % at any pH range. The precipitation reaction of Co(II) and oxalic acid was represented in Eq. (4). Based on the obtained results, the precipitation of Co(II) from leaching solution was suggested at pH = 3 as the best condition owing to high precipitation efficiency and low loss of Li(I).



The effect of H₂C₂O₄/Co²⁺ mole ratio on precipitation percentage of Co(II) was also studied in the range H₂C₂O₄/Co²⁺ mole ratio of 1- 4 at pH = 3. It can be seen from Fig. 5 that precipitation efficiency of Co(II) rose from 27.1 to 94.9 % with increase of H₂C₂O₄/Co²⁺ mole ratio from 1 to 4. The co-precipitation of Li(I) was negligible at any mole ratio. It can be concluded that complete separation of Co(II) from the HCl solution containing Li(I) by precipitation method under condition: [H₂C₂O₄]/[Co²⁺] mole ratio of 4 and pH of 3.

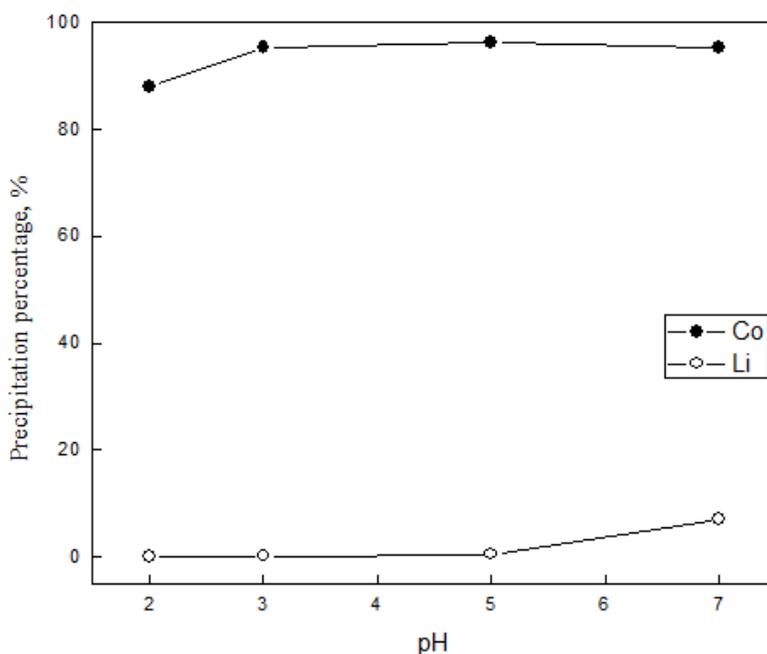


Fig. 4: Effect of pH on precipitation percentage of Co(II) and Li(I) from leaching liquors of spent lithium-ion mobile phone batteries. Leaching solution: Co(II) = 933 mg/L, Li(I) = 259 mg/L, 4 M HCl; Precipitation condition: pH = 2-7, [H₂C₂O₄]/[Co²⁺] = 4

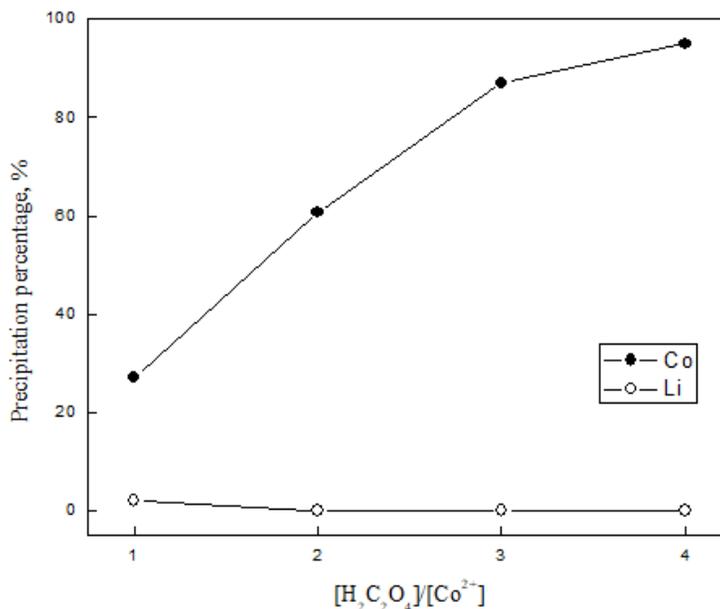
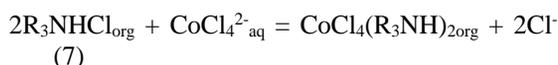
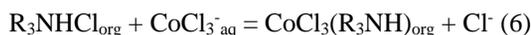


Fig. 5: Effect of [H₂C₂O₄]/[Co²⁺] mole ratio on precipitation percentage of Co(II) and Li(I) from leaching liquors of spent lithium-ion mobile phone batteries. Leaching solution: Co(II) = 933 mg/L, Li(I) = 259 mg/L, 4 M HCl; Precipitation condition: pH = 3, [H₂C₂O₄]/[Co²⁺] = 1-4

3.2.2 Separation of Co(II) and Li(I) from the leach liquors by solvent extraction

The leaching solution containing 933 mg/L of Co(II) and 259 mg/L of Li(I) used in these experiments was prepared under the optimum conditions: 4 M HCl, leaching time of 1.5 h, leaching temperature of 50°C and pulp density of 10 g/L. The previous study investigated that TOA can extract Co(II) from sulfuric acid solution (Nguyen *et al.*, 2018). Therefore, TOA was used to investigate extraction behavior of Co(II) from the HCl leaching solution in the present study. The influence of TOA concentration on the extraction of Co(II) from 4 M HCl leaching solution containing Li(I) was studied by varying TOA concentration from 0.03 to 0.1 M. The concentration of Co(II) and Li(I) in the leaching solution was 933 and 259 mg/L, respectively, and the organic to aqueous phase ratio was unity. Fig. 6 showed that extraction percentage of Co(II) increased from 22.6 to 55.3 % with an increase of TOA concentration from 0.03 to 0.1 M while that of Li(I) was lower than 10 % at any TOA concentration range. It means that TOA was effective to

selective extraction of Co(II) over Li(I) from the HCl leaching solution. CoCl₃⁻ and CoCl₄²⁻ were predominant in the 4 M HCl solution so they can be extracted by anionic extractant (Nguyen *et al.*, 2015). The extraction reactions between Co(II) and TOA (R₃N) were represented in Eqs. (5) and (7). Previous study indicated that TOA concentration or the organic to aqueous phase ratio should be increased to increase extraction efficiency of Co(II) by TOA (Nguyen *et al.*, 2018). Complete stripping of Co(II) from TOA was obtained using distilled water. After separation of Co(II) by TOA, Li(I) remained in the raffinate as final lithium solution which can be used to produce lithium metal or lithium compounds.



where aq and org denote aqueous and organic phase, respectively.

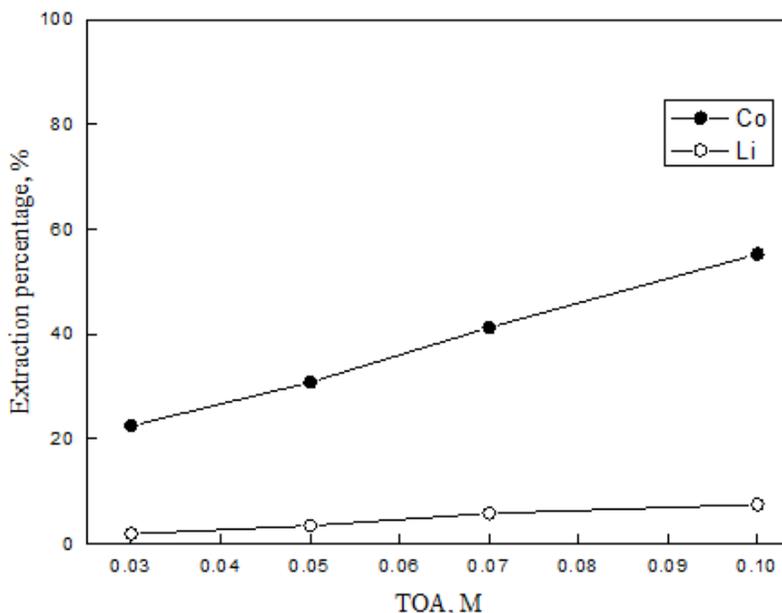


Fig. 6: Effect of TOA concentration on extraction of Co(II) and Li(I) from HCl leaching solution by TOA. Leaching solution: Co(II) = 933 mg/L, Li(I) = 259 mg/L, 4 M HCl; Organic: TOA = 0.03-0.1 M, O/A = 1/1

A process for separation and recovery of Co(II) and Li(I) from the spent lithium-ion mobile phone batteries was shown in Fig. 7. Although both solvent extraction and precipitation can selectively extract Co(II) over Li(I) from the leaching solution,

loss of Li(I) from solvent extraction system was higher than that from precipitation. Therefore, precipitation was suggested as the better method to separate and recover Co(II) and Li(I) from the leaching solution in the the present study.

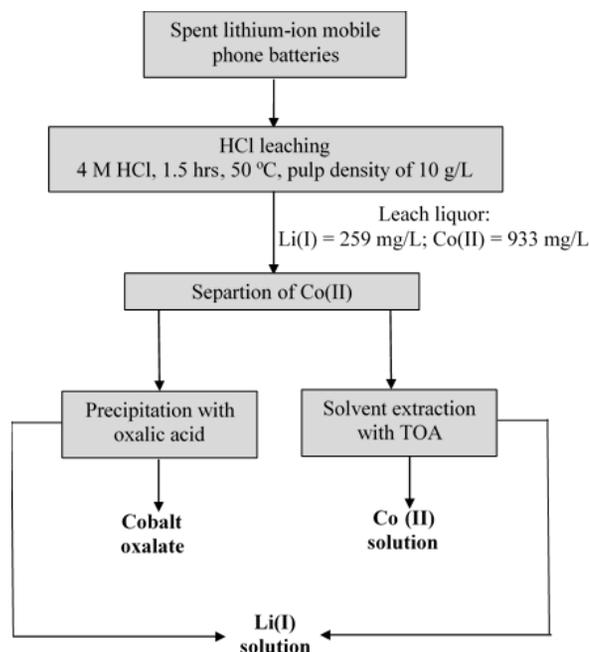


Fig. 7: A process for separation and recovery of Co(II) and Li(I) from spent lithium-ion mobile phone batteries

4 CONCLUSIONS

The recovery of Co(II) and Li(I) from the spent lithium-ion mobile phone batteries was investigated by combining HCl leaching, precipitation and solvent extraction. The leaching percentage of Co(II) and Li(I) increased with the increase of HCl concentration, time, and temperature. In the experimental condition of leaching temperature of 50°C, 4 M HCl, pulp density of 10 g/L and reaction time of 1.5 h, the leaching efficiency of Co(II) and Li(I) reached its maximum of 99.5 % and 97 %, respectively. After leaching, Co(II) and Li(I) from the HCl leaching solution was separated by precipitation or solvent extraction. Cobalt oxalate was precipitated from the HCl leaching solution by adding oxalic acid, leaving Li(I) in the aqueous solution. Precipitation percentage of Co(II) was obtained at 95% under the optimum condition while co-precipitation of Li(I) was negligible. In the case of solvent extraction, TOA was used to selectively extract Co(II) over Li(I) from the leaching solution. However, the co-extraction of Li(I) slightly increased with increase of TOA concentration. Thus, precipitation was suggested as a suitable method to separate and recover Co(II) and Li(I) from the leaching solution of the spent lithium-ion mobile phone batteries due to high recovery efficiency of Co(II) and low loss of Li(I).

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