Acquisition of Co metal from spent lithium-ion battery with emulsion liquid membrane technology using cyanex 272 as extractant

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Abstract. Lithium-ion batteries are the most common type to be used as energy source in mobile phone. The amount of lithium-ion battery wastes is approximated by 200 – 500 ton/year. In one lithium-ion battery, there are 5 – 20% of cobalt metal, depend on the manufacturer. One of the way to recover a valuable metal from waste is leaching process then continued with extraction. Spent lithium-ion batteries will be characterized with EDX and AAS, the result will show the amount of cobalt metal with form of LiCoO2 in the cathode. Hydrochloric acid 4 M, temperature 80°C, and reaction time 1 hour condition give out the best leaching efficiency for both Co and Mn metals, 88.54% and 89.28% respectively. For extraction, the best extraction efficiency achieved when feed phase pH is 5 for Co and 6 for Mn. This study will discuss the leaching and extraction process and compare the efficiency for both processes.

1. Introduction
Every year, 2 billion cells of lithium ion battery are produced. Lithium ion is used because it has a lot of advantages compared to other material such as Ni Cd (Nickel Cadmium). It has bigger capacity, no memory effect, does not contain toxic substances compared to others so it is more environmentally friendly [1]. Lithium ion batteries speed of charging is considered fast if compared to other type of battery, durable, and has a high power compact in a lighter packaging. However, behind all of its advantages, there is a potential hazard in lithium ion battery and can harm the user because it contains flammable substances and high pressure so it can’t be thrown away into the environment without any proper treatment beforehand.

Lithium ion batteries consist of heavy metals, organic chemicals and plastics in the proportion of 5-20% cobalt, 5-10% nickel, 5-7% lithium, 15% organic chemicals and 7% plastics, the composition varying slightly with different manufacturers. Some methods to recover cobalt are liquid-liquid extraction, electrowinning, emulsion liquid membrane, vaporization, and hydroxide precipitation. In this study, leaching is used to recover cobalt, to dissolve lithium ion battery wastes with leaching agent and continued with emulsion liquid membrane to extract cobalt metal from leachant.

Leaching is a solid-liquid extraction method where the separation of solid cobalt mixed with leaching agent so the metal inside can be dissolved into the leaching agent. Strong acids like sulphuric acid and hydrochloric acid were often used as leaching agent. There is a previous study about recovering cobalt

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metal from lithium ion battery, comparing three reagents as leaching agents which are sulphuric acid, hydroxylamine hydrochloride, and hydrochloric acid [2]. Between three reagents stated, hydrochloric acid is the most suitable and effective with more than 99% cobalt metal leached in a hydrochloric acid 4 M in 80°C temperature, and stirring time of 1 hour.

Emulsion liquid membrane have some attractive features, for example, simple operation, high efficiency, extraction and stripping in one stage, larger interfacial area, scope of continuous operation. By extracting and stripping in one stage, it will reduce reaction time and reagents needed unlike liquid-liquid extraction method [3]. Emulsion liquid membrane is the right choice because it has the highest degree of separation and can be applied in a large scale [4].

Extractants have been used in prior studies to recover cobalt metal with emulsion liquid membrane system are Cyanex 272, Cyanex 921, tributyl phosphate (TBP), and PC-88A. From three extractants stated, Cyanex 272 is the most selective toward cobalt existence. Each extractant has different efficiency depend on leaching agent used. The reason of using Cyanex 272 is to investigate cobalt metal extraction efficiency with hydrochloric acid as leaching agent and using kerosene as diluent in emulsion liquid membrane system. In this study, hydrochloric acid is used as leaching agent, Cyanex 272 as extractant, kerosene as diluent, SPAN 80 as surfactant, and H₂SO₄ as stripping agent.

2. Experimental

2.1. Materials
Lithium ion batteries that are used are from cellphone batteries various brand sold at the market (Samsung, iPhone, Xiaomi, and LG). Hydrochloric acid used as leaching agent, Cyanex 272 as extractant. Commercial kerosene with density of 830 kg/m³ used as diluent. SPAN 80 used as surfactant, and H₂SO₄ as stripping agent. All the materials were immediately used without reprocessing to purify the materials.

2.2. Experimental procedure
Initial step is preparation of materials. One of the preparation that needed to be done is soaking lithium ion batteries into sodium chloride solution to emptied the remaining electrical charge inside the batteries which may still be inside. Next step is leaching process with varying leaching agent which has been specified before. Solution after leaching (called leachant) then filtered to get rid of solid components which can’t dissolve. After filtered, leachant then analysed of cobalt and manganese metal content with AAS (Atomic Absorption Spectroscopy). Next step is to extract cobalt and manganese metals using emulsion liquid membrane technology. The extraction process done with mixing feed phase, membrane phase, and receiving phase with pH of feed phase being varied. After extraction process is done, solution from feed phase will be analysed with AAS to determine cobalt and manganese metals extraction percentage.

3. Results and discussion

3.1. Characterization lithium-ion battery waste
3.1.1. Soaking in sodium chloride solution. Before opening the battery’s casing, the battery need to be soaked in sodium chloride solution 1%wt first with the intention of emptying the remaining electrical charge which may still be inside the battery for 24 hours. There is a chance that there is a remaining electrical charge, even though the batteries used are damaged. The remaining electrical charge need to be emptied so when the battery casing is opened, it won’t cause any harm such as the ignited fire. Using sodium chloride solution with too high concentration will decrease battery’s voltage faster but a leakage may happen, which is the sodium chloride solution entered the casing. This leakage affecting electrodes inside the battery contaminated with salt solution. Besides, LiPF₆ in the electrolyte may react with water and forming HF and will bring negative effect for the next process. To reduce reactivity during soaking process, sodium chloride 1%wt solution is used because it won’t cause a leakage. The reactions are electrolysis with sodium chloride solution as shown below:
Reaction (1) and (3) are electrolysis reactions and primer reactions of soaking lithium ion battery into sodium chloride solution. During soaking process, there are bubbles formed. Based on reaction (1) until (7) there are some gases formed, Cl$_2$, H$_2$, and O$_2$. Those reactions also formed white foam which is Al(OH)$_3$ around the battery and the cause of leakage is reaction (3) [5].

3.1.2. Characterization of battery cathode powder. To characterize lithium ion battery waste with EDX and AAS analysis, cathode sheet scraped and crushed, after that filtered with 100 mesh filter so the result is cathode powder with size as small as possible so leaching process will be more effective, to make leaching efficiency high, it needs a particle with the size 100 mesh [1]. Table 1 shows AAS analysis result with the amount of cobalt metal in cathode battery powder is 164.38 mg/g and manganese metal is 77.79 mg/g. This goes with previous study by Shin, et al. (2005), in general range of cobalt metal content in lithium ion battery is 5 – 20% weight, depends on the battery’s manufacturer.

| Substances          | Analysis Result (ppm) | mg/g Sample |
|---------------------|-----------------------|-------------|
| Co (cobalt)         | 8218.75               | 164.38      |
| Mn (manganese)      | 3889                  | 77.79       |

3.2. Leaching with hydrochloric acid
Leaching process is perform to dissolve solid cobalt metal contained in the battery cathode powder by using hydrochloric acid as a leaching agent to dissolve the cobalt metal. The usage of hydrochloric acid is varied in concentration, while other operating conditions such as stirring speed, temperature, solid/liquid ratio, and stirring time are maintained according to the optimum results of the prior study. It is aimed to obtain optimum hydrochloric acid concentration with other parameters are kept constant so that the results obtained will be accurate.

Leaching, or sometimes called solid-liquid extraction, is one of the method to separate the dissolved fraction (solute or leachant) from a solid material by a liquid solvent. Solute (in this study is cobalt metal) diffuses from within the solid to the solvent environment (in this study is hydrochloric acid) so that in the solvent, it will contain cobalt metals that are successfully leached [6]. The chemical reaction that occurs in the leaching process using hydrochloric acid is shown in equation (8) [7].

$$4 \text{LiCoO}_2 + 12 \text{HCl} \rightarrow 4 \text{LiCl} + 4 \text{Co(Cl)}_2 + 6 \text{H}_2\text{O} + \text{O}_2$$

(8)

In this study, the ratio of solid : liquid is 1 g : 20 ml due to research of Zhang et al. (1998), the optimum result of leaching using hydrochloric acid is when the ratio of solid : liquid is 1 g : 20 ml. Figure 1 shows effect of hydrochloric acid concentration to leaching cobalt and manganese metals efficiency.
Figure 1. Effect of hydrochloric acid concentration to leaching cobalt and manganese metals efficiency (stirring speed 500 rpm, S/L = 1g/20ml, temperature 80°C, stirring time 60 mins)

The result of efficiency calculation shows that hydrochloric acid with concentration 4 M is the most efficient concentration to dissolve cobalt metal that is up to 88.54%. This efficiency is not the same with previous study conducted by Zhang et al. (1998) when leaching using hydrochloric acid with operating conditions of 80°C, 500 rpm stirring rate, stirring time for 1 hour, that can be produced 99% efficiency to cobalt. This can occur due to the possibility of a temperature deviation during leaching process. However, when compared to leaching efficiency of other hydrochloric acid concentrations, the results of this study are still appropriate because the highest efficiency is when using 4 M hydrochloric acid.

The solution of leaching of cobalt metal using hydrochloric acid is colored pink. Pink color indicates the presence of cobalt metal ions in aqueous solutions of hydrochloric acid and water, giving rise to a pink color. The darker the color of the leaching result, the more the cobalt metal ion content in the solution [8].

While leaching cathode powder, not only cobalt metal get leached but also manganese. As shown from figure 1, the highest leaching efficiency for manganese reached 89.28%. This can happen because there is manganese metal in the cathode battery so when the solution is mixed and heated, manganese metal got leached. For manganese metal leaching, the reaction shows in equation (9) [9].

\[ 4 \text{LiMnO}_2 + 12 \text{HCl} \rightarrow 4 \text{MnCl}_2 + 4 \text{LiCl} + 6 \text{H}_2\text{O} + \text{O}_2 \] (9)

If the percentage of leaching using 3 M and 4 M hydrochloric acid is compared, the 3 M concentration has a lower efficiency. This can happen because when the acid concentration is increased, the number of protons will increase as well and replace more Co\(^{2+}\) ions. On the other hand, when hydrochloric acid is present between the solid and liquid phases, the gradient of H\(^+\) concentration between the solid and liquid phases with the solution increases significantly and causes increased diffusion velocity. Both of these can speed up the leaching process and provide higher leaching efficiency values. When the leaching reaction has reached equilibrium, the efficiency of the Co and Mn metal leaching reaches its maximum point. This occurs because the speed of diffusion will not change again even when the concentration of hydrochloric acid used is increased, and the Co\(^{2+}\) and Mn\(^{2+}\) ion has been replaced [10]. It appears that in this study, the equilibrium point of leaching using hydrochloric acid was at a concentration of 4 M because when using a concentration of 5 M hydrochloric acid, leaching efficiency decreased.
3.3. Extraction with emulsion liquid membrane technology
Extraction process begins by making an optimum emulsion phase (10% w/v SPAN 80 and 0.7 M Cyanex 272). This extraction process goes in one stage with the stripping process because the extracting technology used is the emulsion liquid membrane. Then the emulsion phases that have been formed are mixed with the optimum leachant that is the result of leaching using 4 M hydrochloric acid which varied the pH of the solution, ie 3, 4, 5, and 6. The pH variation is done because Cyanex 272 is a slightly acidic extractant so the pH of the stripping solution should be less than the pH of leachant metal during the extraction process with the emulsion liquid membrane. NaOH solids added gradually to change feed phase pH until the pH reaches 3, 4, 5, and 6. The ratio of the mixing volume between the emulsion phase and the feed phase is 1 : 2. After that, the solution is stirred at 250 rpm for 15 minutes. After stirring, the mixture is both transferred to the separatory funnel for extraction and held for 15 - 30 minutes and there is a separation between the feed phase and the emulsion phase. The calculation of the efficiency of the cobalt extraction process is shown in figure 2.

![Figure 2](image_url)  
**Figure 2.** Extraction efficiency with pH 3, 4, 5, and 6 (stripping speed 250 rpm, stirring time 15 mins, room temperature)

Based on figure 2 shows that extraction efficiency for cobalt extraction for cobalt metal increasing from pH 3 to 5 but decrease at pH 6. Feed phase pH 5 is the highest between other variation which is 81.94%. Meanwhile for the highest manganese extraction efficiency is reached when feed phase pH is 6 and give out efficiency of 82.17%. A low extraction efficiency may occur due to emulsion instability. Because of when the pH is high, emulsion stability changes with the emulsion, whereas at too low pH can be explained by competing H⁺ ions with the solute due to the release of H⁺ ions from extractant to leachant [11]. Extraction rate will decrease when the pH is greater than 5 due to emulsion instability because H⁺ ions transfer phenomenon from acidic feed solution to membrane phase so that the membrane can swell and decompose. pH value between stripping solution and feed solution should be different to make a difference of chemical potential for H⁺ ions. Physical properties of the extractant will cause a reduction of the ion activity difference on both phases. Cobalt extraction process increases with increasing amount of proton concentration up to a certain concentration [12]. According figure 2, at pH 6 for cobalt extraction, the emulsion has swelled so the extraction efficiency is lower than that of pH 5.
Type and concentration selection of stripping solution appropriately is one of the determinants of extraction process efficiency with emulsion liquid membrane technology. Reaction by the stripping solution plays an important role in the extraction of solute from feed solution to stripping solution in emulsion liquid membrane process. Based on prior study by Kumbasar (2012), performance of Na₂CO₃, H₂SO₄, and HCl as stripping solution was compared. In the first ten minutes, the best stripping solution sequence is Na₂CO₃ > H₂SO₄ > HCl. However, after the first ten minutes, emulsion stability while using Na₂CO₃ is changed so that its extraction efficiency is reduced so that the sequence of extraction efficiency at the end of process from highest to lowest is H₂SO₄ > Na₂CO₃ > HCl.

4. Conclusion

- Concentration of hydrochloric acid as leaching agent to produce the best leaching efficiency both for Co and Mn is 4 M with operating conditions 500 rpm stirring speed, stirring time 1 hour, temperature 80°C, and S/L = 1 g/20 ml.
- Highest extraction efficiency was obtained when extractant concentration Cyanex 272 was 0.7 M, SPAN 80% w/v surfactant, stripping agent concentration H₂SO₄ 0.1 M, and pH of the feed phase for cobalt is 5 and for manganese is 6.

5. References

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