Improvement of metal separation process from synthetic hydrochloric acid leaching solution of spent lithium ion batteries by solvent extraction and ion exchange

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Abstract: Spent lithium-ion batteries (LIBs) are good secondary resources for recycle and reuse. To develop a process for the separation of Cu(II), Co(II), Mn(II), Ni(II) and Li(I) with high purity from spent LIBs and circumvent some drawbacks of the previous work, solvent extraction and ion exchange experiments were done in this work. The synthetic hydrochloric acid leaching solution of 3 M was employed. Compared to Aliquat 336 (*N*-Methyl- *N, N, N*-trioctyl ammonium chloride), extraction with Cyanex 301 (bis(2,4,4-trimethylpentyl) dithiophosphinic acid) led to selective extraction of Cu(II) over other metal ions. Employing ion exchange with TEVA-SCN resin can completely separate Co(II) over Mn(II). After adjusting the pH of Co(II) free raffinate to 3, Mn(II) was quantitatively extracted by the mixture of Alamine 336 (mixture of tri-octyl/decyl amine) and PC 88A (2-ethylhexyl hydrogen-2-ethylhexylphosphonate) with two stage cross-current extraction. The synthesized ionic liquid (ALi-CY) was used for complete extraction of Ni(II), whereas Li(I) remained in final raffinate. The metal ions in the loaded organic phase were completely stripped with the proper agents (5% aqua regia for Cu(II), 5% NH_3 for Co(II), weak H_2SO_4 solution for Mn(II) and Ni(II) stripping, respectively). The experimental results revealed that purity of the metal ions in stripping solution was higher than 99.9%. A flowsheet was suggested to separate metal ions from the HCl leaching solutions of spent LIBs.

Keywords: spent lithium-ion batteries, solvent extraction, ion exchange, separation

1. Introduction

Manufacture of lithium ion batteries (LIBs) needs the supply of pure compounds of cobalt, manganese and nickel. Since the ores containing nickel and cobalt are depleting, the recovery of these metals from spent LIBs is a kind of sustainable strategy (Nan et al., 2005; Xu et al., 2008; Chagnes and Pospiech, 2013; Wang et al., 2015; Ordoñez et al., 2016; Zheng et al., 2018). The combination of hydrometallurgical and pyro-metallurgical steps would increases the recovery efficiency of valuable metals present in spent LIBs. However, hydrometallurgical processes should be employed to produce pure metals and compounds. Therefore, separation of the metal ions from the leaching solution is of vital importance in the recovery of valuable metals. For this purpose, precipitation, ion exchange and solvent extraction are largely employed during the separation step (Zhu et al., 2012; Joulié et al., 2013; Chen et al., 2015; Xin et al., 2016; Chiu and Chen, 2017; Torkaman et al., 2017).

Metal ions such as Ni(II) and Mn(II) can be separated from weak acidic solution by extraction with organophosphorus acidic extractants, whereas the separation of Cu(II) and Co(II) can be carried out from strong HCl solution by using amines (Zhao et al., 2010; Suzuki et al., 2012; Torkaman et al., 2017; Yao et al., 2018). In addition, the synergistic effect of the mixture containing amine and organophosphorus acids for metal extraction has been also reported (Jakovljevic et al., 2004; Liu et al., 2015; Gmar et al., 2020; Nguyen and Lee, 2020a). Furthermore, ionic liquids (IL) such as ALi-CY (Fortuny et al., 2012), ALi-D2 (Tran et al., 2020), ALi-SCN (Preston, 1982; Nayl, 2010) synthesized by reacting

Aliquat 336 (*N*-Methyl- *N, N, N*-trioctylammonium chloride) with Cyanex 272 (bis(2,4,4-triethylpentyl)phosphinic acid), D2EHPA (di(2-ethylhexyl)phosphoric acid) and NaSCN showed their extraction power for metal ions and hydrogen ions (Le et al., 2019). In particular, these ILs can be employed to separate metal ions from the leaching solutions of spent LIBs which contains Co(II), Ni(II), Mn(II) and Li(I) (Preston, 1982; Nayl, 2010; Tran et al., 2020; Nguyen and Lee, 2020b).

Since the aqueous chemistry of Co(II) and Cu(II) in concentrated HCl solution is similar, it is not easy to completely separate these two metal ions. We reported a process to separate Co(II), Cu(II), Mn(II), Ni(II) and Li(I) present in the synthetic HCl leaching solution of spent LIBs by employing solvent extraction (Nguyen and Lee, 2020a). Although the process looks simple and has some advantages, the drawbacks of this process are co-extraction of metal ions during the separation in Cu(II)/Co(II) and Mn(II)/Ni(II). Therefore, the purity of the desired metal ions in each stripping solution was not high. In order to overcome these drawbacks, we modified the reported process. First, we investigated the possibility of complete separation of Cu(II) from the leaching solution of spent LIBs. Secondly, ion exchange was employed to separate Co(II) and Mn(II) from the solution. The complete and selective extraction of Mn(II) and Ni(II) was also explored.

In this work, ILs synthesized from Aliquat 336 and mixture of Alamine 336 (mixture of tri-octyl/decyl amine) and organophosphorus acids such as D2EHPA, PC 88A (2-ethylhexyl hydrogen-2-ethylhexylphosphonate), Cyanex 272 and Cyanex 301 (the main constituent is bis(2,4,4-trimethylpentyl) dithiophosphinic acid) were used to separate the metal ions in the synthetic hydrochloric acid leaching solutions. The separation behavior of metal ions was examined by varying the concentration of extractants and the acidity of the solution. The extraction and stripping conditions for the separation of Cu(II), Co(II), Mn(II) and Ni(II) were investigated. McCabe-Thiele diagrams for the stripping were constructed and batch simulation experiments for the multi-stage extraction were performed. TEVA-SCN resin which was synthesized from TEVA and NaSCN was employed to slectively load Co(II) over Mn(II) from the stripping solution. Finally, a process for the separation of Cu(II), Co(II), Mn(II), Ni(II) and Li(I) with high purity from the spent LIBs was proposed.

2. Experimental

2.1. Reagents and chemicals

Commercial extractants such as Aliquat 336 (93%) and Alamine 336 (95%) were supported by BASF Co., while Cyanex 272 (85%) was bought from Daihachi Chemicals. Co. D2EHPA (95%), PC 88A (95%), and Cyanex 301 (70%) were products of Cytec Inc. These extractants were used without further purification. Organic phases were prepared by diluting the extractants with kerosene (Daejung Co., > 90%). Decanol (Daejung Co., > 98%) was added into the organic solutions (10%v/v) as a modifier to avoid the formation of a third phase when needed. Ionic liquid, ALi-CY ($R_4N \cdot A$) was synthesized by contacting an equimolar concentration of Aliquat 336 and Cyanex 272 in kerosene in a beaker, then 0.5 M NaHCO$_3$ was added to the solution (Fortuny et al., 2012). The mixture was stirred to eliminate CO$_2$ gas and promote the formation of ALi-CY. During the synthesis of ALi-CY, the transfer of chloride ions from the organic to the aqueous was verified by precipitation of chloride ion as AgCl using AgNO$_3$.

The composition of the synthetic leaching solution is shown in Table 1 (Nguyen and Lee, 2020a). The concentration of HCl in the synthetic solution was adjusted to 3 M. The synthetic solutions were prepared by dissolving the corresponding amount of metal chlorides such as CoCl$_2$·6H$_2$O (Junsei Co., > 97%), CuCl$_2$·2H$_2$O (Daejung Co., > 97%), MnCl$_2$·4H$_2$O (Daejung Co., > 98%), NiCl$_2$·6H$_2$O (Kakuri Co. Kyoto Japan, > 96%) and LiCl (Daejung Co., > 98%) in 3 M HCl solution. Sodium chloride (Jedia Co. Ohio USA, > 99%) was also added to adjust the concentration of chloride ion in the solution. HCl (Dae Jung Chemicals, Korea, 35%) and H$_2$SO$_4$ (Dae Jung Chemicals, Korea, 95%) solutions were diluted by doubly distilled water to desirable concentrations. The pH of the solution was adjusted by using sodium hydroxide (Duksan Co., >99%) solution. NH$_3$ (Junsei Co., 28%) solution was employed as a eluant agent and all the employed chemicals were of analytical grade.

A commercial TEVA resin (Trialkyl methylammonium chloride, Eichrom, particle size 100-150 μm, USA) was used without any treatment. The active component of the TEVA resin is an aliphatic quaternary amine, which has properties similar to those of typical strong base anion exchange resins. A

resin named TEVA-SCN was prepared by contacting 1 g TEVA resin many times with a sufficient amount of 2 M NaSCN (Daejung Co., > 98.0%) until the resin was saturated. After synthesis, TEVA-SCN was washed with water and then employed for ion exchange experiments. Scheme 1 illustrates the transformation of TEVA-SCN resin from the corresponding commercial TEVA resin.

Table 1. The composition of metal ions in the synthetic solution

Metal ions	Cu(II)	Co(II)	Mn(II)	Ni(II)	Li(I)
mg/L	150.0	938.0	150.0	100.0	150.0
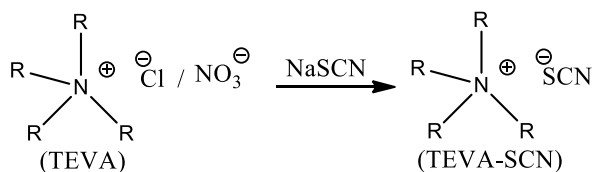
Denote. R = C_8H_{17} and $C_{10}H_{21}$

Scheme 1. The synthesis of TEVA-SCN from commercial TEVA resin

2.2. Solvent extraction and ion exchange procedures

The extraction and stripping experiments were performed by mixing equal volume of aqueous and organic phase (each 20 mL) in a screwed cap bottle. When needed, the volume ratio of the two phases was varied. The mixtures were stirred for 30 minutes using a Burrell wrist action shaker (model 75, USA) at ambient temperature (22 ± 1°C). After shaking, solutions were poured into glass separatory funnels for phase separation. Inductively coupled plasma-optical emission spectrometry (ICP-OES, Spectro Arcos) was used to measure the metal concentration in the aqueous phase before and after extraction. Most of the experiments have been done duplicately with an error of ± 5%.

Based on the mass of the metal ions in the aqueous phase before extraction $[M]_i$ and after extraction $[M]_{aq}$, the extraction percentage (%E) of a metal ion was calculated as:

$$\%E = \frac{([M]_i - [M]_{aq}) \times 100}{[M]_i}.$$

The stripping percentage of a metal ion was calculated as:

$$\%stripping = \frac{[M]^*_{aq} \times 100}{[M]_{org}},$$

where $[M]_{org}$ and $[M]^*_{aq}$ are the mass of a metal ion in the loaded organic phase before stripping and in the aqueous phase after stripping, respectively. Experimental procedure for the batch simulation of the four stage counter-current extraction is shown in scheme 2.

Batch ion exchange experiments were done by putting some amount of resins into 20 mL synthetic leaching solution. The samples were shaken in a shaking incubator (HB-201SF, Hanbeak Scientific Co.) for 12 hours at room temperature (22 ± 1°C). The stirring speed was fixed at 400 rpm. After filtering the resin by filter paper, the concentration of metals in the solution was measured by ICP-OES and the concentration of metals loaded into resin was obtained by mass balance.

3. Results and discussion

3.1 Separation of Cu(II) from solutions containing Co(II), Mn(II), Ni(II) and Li(I)

3.1.1 Cu(II) extraction by Aliquat 336

The hydrochloric leaching solution of LIBs generally contains metals such as Li(I), Cu(II), Co(II), Mn(II), Ni(II) (Wang and Friedrich, 2015; Porvali et al., 2019). In this work, a synthetic leaching solution of spent LIBs with 3 M HCl was employed. Table 1 lists the composition of Cu(II), Co(II), Mn(II), Ni(II) and Li(I) in the solution. Our previous work showed that Aliquat 336 was able to selectively extract Cu(II) from other metal ions. Batch simulation experiments on the three stage counter-current extraction with Aliquat 336 resulted in the extraction of only 71.6% of Cu(II) (Nguyen and Lee, 2020a). In order to completely extract Cu(II), we did batch simulation experiments for the four stages counter-current

extraction. Table 2 represents the concentration of the metal ions in each stage and the overal extraction percentage during the these batch simulation exeperiments with 0.3 M Aliquat 336 at unity phase ratio. The complete extraction of Cu(II) was accomplished, leaving Mn(II), Ni(II) and Li(I) in the raffinate. However, a small amount of Co(II) (6.5%, 60.7 mg/L) was also co-extracted into the organic phase. Since the aqueous chemistry of Cu(II) and Co(II) in hydrochloric acid solution is quite similar, it is not easy to separate the two metal ions by either scrubbing or stripping (Nguyen and Lee, 2020a). Therefore, we did some experiments to find out extraction system by which only Cu(II) can be seletively extracted.
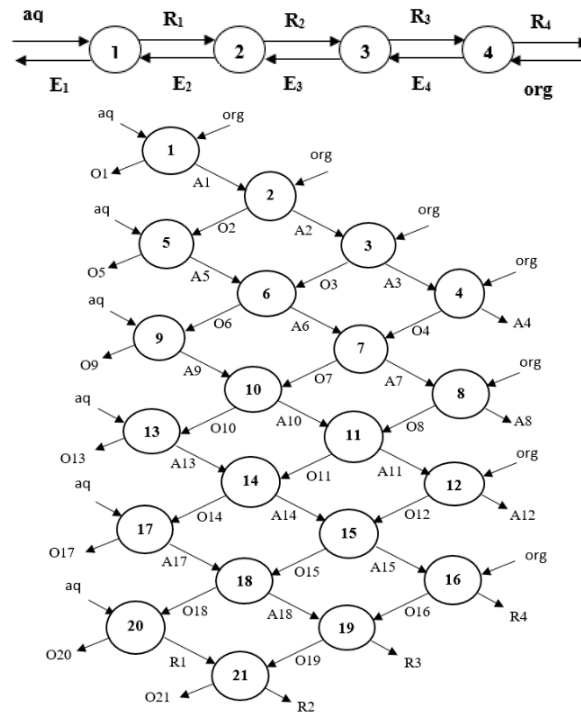
*Denote: aq = feed solution; org = fresh solvent; A/(R) = raffinate; E = extract flow; O = loaded organic phase

Scheme 2. Batch simulation of four stages counter-current extraction

Table 2. Results from batch simulation experiments for four stages counter-current extraction by 0.3 M Aliquat 336 at an unity phase ratio.

| Metal ions	Co(II)	Ni(II)	Cu(II)	Mn(II)	Li(I)
Stock solution, mg/L	938.0	100.0	150.0	150.0	150.0
Raffinate 1, mg/L	938.1	99.9	89.2	149.9	153.2
Raffinate 2, mg/L	957.6	102.6	48.8	154.1	154.8
Raffinate 3, mg/L	951.3	102.7	16.6	153.7	152.7
Raffinate 4, mg/L	877.2	106.7	0	155.3	157.8
Overall %E	6.5	0	100	0	0

3.1.2. Cu(II) extraction by Cyanex 301

Cyanex 301 shows a selectivity for Cu(II) over other metal ions such as Co(II), Ni(II), Mn(II) from strong acidic medium (Fleitlikh et al., 2018; Lee and Lee, 2019). For this reason, Cyanex 301 was selected and its concentration was varied from 0.02 to 0.3 M. **Fig. 1** indicates that Cyanex 301 can selectively extract Cu(II) over other metal ions. This is attributed to the high affinity between Cu(II) and sulfur atoms in the funtional group of Cyanex 301. According to HSAB (hard soft acid base) principle, Cu(II) is a soft acid and the sulfur atom of Cyanex 301 is a soft base and thus they have a strong tendency to interact. The extraction reactions of Cu(II) by Cyanex 301 are represented as Eqs. (1) and (2) (Fleitlikh et al., 2018):

$$Cu^{2+}_{(a)} + 2HA_{(o)} = CuA_{2(o)} + 2H^+_{(a)} \tag{1}$$
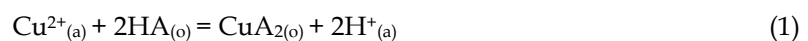
where HA = Cyanex 301.

The structure of Cu-Cyanex 301 complex can be proposed in scheme 3.
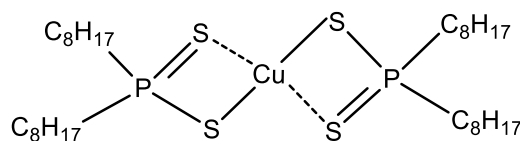
Scheme 3. Structure of Cu-Cyanex301 complex (Wieszczycka and Tomczyk, 2011)

According to the literature (Fleitlikh et al., 2018), Cu(II) in the loaded Cyanex 301 can be reduced to Cu(I) by the oxidation action of Cyanex 301. This reduced Cu(I) can undergo polymerization reaction as represented in Eq. (2):

$$2nCuA_{2(o)} = 2(CuA)_{n(o)} + nA-A_{(o)} \tag{2}$$
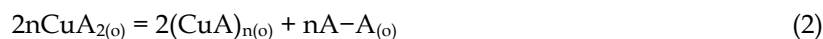
Eqs. (1) and (2) show the reason why Cyanex 301 has a selectivity for Cu(II) extraction and stripping of Cu(II) from the loaded Cyanex 301 is difficult.
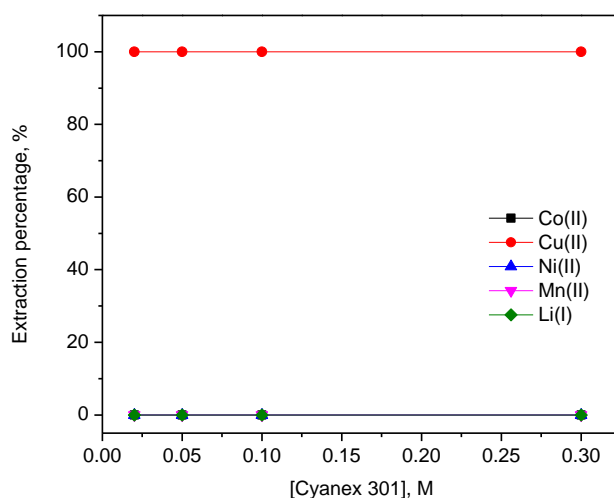

Fig. 1. Effect of Cyanex 301 concentration on extraction of metal ions from 3 M HCl solution. Conditions: [Cyanex 301] = 0.02-0.3 M; diluent: kerosene; [metals]: Cu(II),Co(II), Mn(II), Ni(II) and Li(I) = 150, 938.0, 150.0, 100 and 150.0 mg/L, respectively; O/A = 1

3.1.3. Cu(II) stripping from the loaded Cyanex 301

Aqua regia solution can efficiently strip Cu(II) from the loaded Cyanex 301 (Lee and Lee, 2019). Because of some harmful effect of aqua regia on the enviroment, aqua regia diluted with water was employed in these experiments. First, the loaded organic phase was prepared by contacting the synthetic leaching solutions with 0.02 M Cyanex 301. The concentration of Cu(II) in the loaded phase was 150.0 mg/L and no other metal ions were extracted. Stripping results showed that 95.3 % of Cu(II) was stripped from the 0.02 M loaded Cyanex 301 by using 5% aqua regia. In this case, Cu(I) which was linked with the sulfur-containing ligands might be oxidized by aqua regia solution to generate Cu(II). This accelerated the stripping efficiency due to the stronger hydration of Cu(II) complexes in the aqueous phase compared to Cu(I) and thus ion with high charge density would preferentially distribute to the aqueous phase (Lommelen et al., 2019). The concentration and purity of Cu(II) in the stripping solution was 143.0 mg/L and 99.9%, respectively. In terms of the separation degree and the purity of Cu(II) in the stripping solution, Cyanex 301 is superior to Aliquat 336.

3.2 Separation of Co(II) from the Cu(II) free raffinate

3.2.1. Co(II) extraction

After separation of Cu(II) by Cyanex 301, Co(II), Mn(II), Ni(II) and Li(I) are left in the raffinate and their concentrations are 938.0 mg/L, 150.0 mg/L, 100 mg/L and 150.0 mg/L, respectively. Our previous

work showed that addition of 2 M NaCl to the raffinate was necessary to selectively extract Co(II) from the raffinate by Aliquat 336. After three stage of counter-current extraction by 1.0 M Aliquat 336 at a O/A phase ratio of 2, 98.8% Co(II) and 36.9% Mn(II) were extracted (Nguyen and Lee, 2020a). In this work, batch simulation experiments of four stage counter-current extraction were done in order to completely extract Co(II). In these experiments, 10% (v/v) of decanol was added to the organic as a phase modifier and 2 M NaCl was also added to the feed solution. Table 3 shows that Co(II) was completely extracted by 1.0 M Aliquat 336 by four stages of counter current extraction. However, 29.9% of Mn(II) was aslo co-extracted at this condition.

Table 3. Results from batch simulation experiments for four stages counter-current extraction by 1.0 M Aliquat 336 at an A/O ratio of 1/2

Metal ions	Co(II)	Ni(II)	Mn(II)	Li(I)
Stock solution, mg/L	938.0	100.0	150.0	150.0
Raffinate 1, mg/L	120.2	100.4	118.5	149.9
Raffinate 2, mg/L	11.9	93.7	88.6	147.4
Raffinate 3, mg/L	0	99.9	61.1	154.3
Raffinate 4, mg/L	0	115.9	37.7	160.8
Overall %E	>99.9	0	29.9	0

3.2.2. Co(II) stripping

Stripping of Co(II) from 1.0 M loaded Aliquat 336 was tested by using HCl solution. The concentration of HCl was varied from 0.1 to 2.0 M and the obtained results are displayed in Table 4. The data indicated that both Co(II) and Mn(II) was stripped by a HCl solution in the studied range and the stripping percentage decreased with the increase in HCl concentration. In our experimental range, 0.1 M HCl was the best condition for the stripping of Co(II) and Mn(II) from 1.0 M loaded Aliquat 336. The stripping percentage of Co(II) and Mn(II) was 62.0 % and 34.8%, respectively.

McCabe–Thiele diagram for the stripping of Co(II) from the 1.0 M loaded Aliquat 336 by 0.1 M HCl was constructed by varying the volume ratio of the two phases from 5/1 to 1/5. In these experiments, the loaded Aliquat 336 was prepared from the batch simulation experiments for four stage counter-current extraction as shown in scheme 2 and Co(II) concentration in the loaded organic phase was 538.9 mg/L. McCabe–Thiele plot in Fig. 2 indicates that four stages counter-current stripping is necessary for the complete stripping of Co(II) at an A/O ratio of 3/1.

Table 4. Stripping percentage of Co(II) and Mn(II) from the loaded 1.0 M Aliquat 336. ([Co(II)] and [Mn(II)] in the loaded phase: 538.9 and 44.8 mg/L, respectively)

Concentration of HCl, M	Stripping percentage, %	
	Co(II)	Mn(II)
0.1	62.0	34.8
0.3	61.0	33.9
0.5	59.4	32.2
1.0	57.5	30.2
2.0	51.1	29.3

3.3. Separation of Co(II) from Mn(II) by using ion exchange TEVA-SCN

3.3.1. Loading behavior of Co(II) and Mn(II) into anion exchanger

Ion exchange was employed for selective separation of Co(II) and Mn(II) from the stripping solution of 0.1 M HCl. The concentration of Co(II) and Mn(II) in the stripping solution was 538.9 and 44.8 mg/L, respectively. Although the HCl concentration in the stripping solution was mild (0.1 M), TEVA, an anion exchange resin was employed on the basis of the reported literature (Nguyen and Lee, 2020a,b).
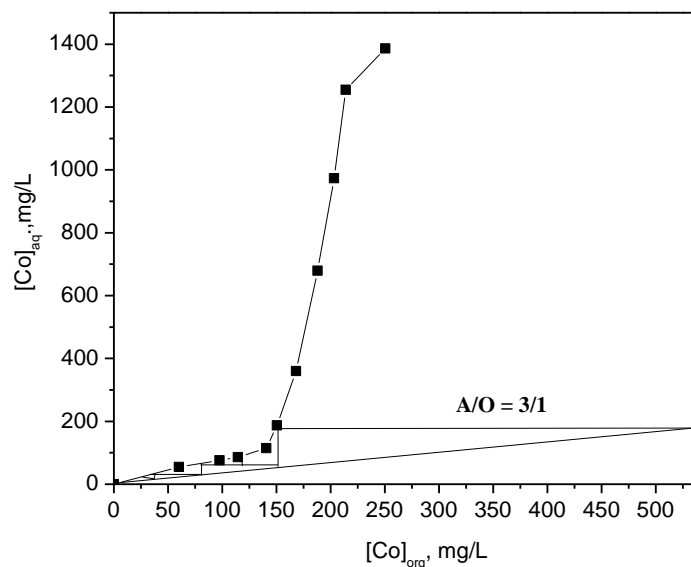
Fig. 2. McCabe Thiele diagram for the stripping of Co(II) from 1.0 M Aliquat 336 by 0.1 M HCl solution

The adsorption capacity of TEVA and TEVA-SCN resins was compared in this work. The concentration of the resins was kept at 15 g/L and the shaking time was 12 hours. Fig. 3 shows that Mn(II) was not loaded at all into TEVA-SCN resin, while 3.2% Mn(II) was loaded into TEVA resin. Furthermore, the loading percentage of Co(II) into TEVA-SCN (52.4%) was higher than that into TEVA (3.3%). The stronger adsorption of Co(II) into TEVA-SCN is ascribed to the stronger tendency of SCN⁻ to form complexes with Co(II) compared to chloride ion (Diebler and Högfeldt, 1983; Gammons and Seward, 1996; Lee and Oh, 2004). In addition, the difference in complex formation of Co(II) and Mn(II) with SCN⁻ resulted in their different adsorption towards TEVA-SCN and thus Co(II) can be selectively adsorbed. Therefore, TEVA-SCN was selected for the separation and purification of Co(II) from the stripping solution. The loading reaction of Co(II) can be represented as Eq. (3).

$$Co^{2+}_{(a)} + 2Cl^-_{(a)} + 4R_4N \cdot SCN_{(o)} = (R_4N)_2Co(SCN)_{4(o)} + 2R_4N \cdot Cl_{(o)} \qquad (3)$$
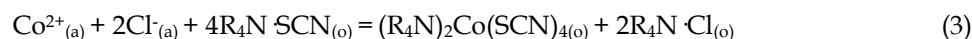
where $R_4N \cdot SCN$ represent TEVA-SCN resin.

To investigate the effect of time on the loading of Co(II) and Mn(II) into TEVA-SCN resin, 10 g/L of resin was contacted with the stripping solution of 0.1 M HCl ([Co] = 538.9 and [Mn] = 44.8 mg/L) by
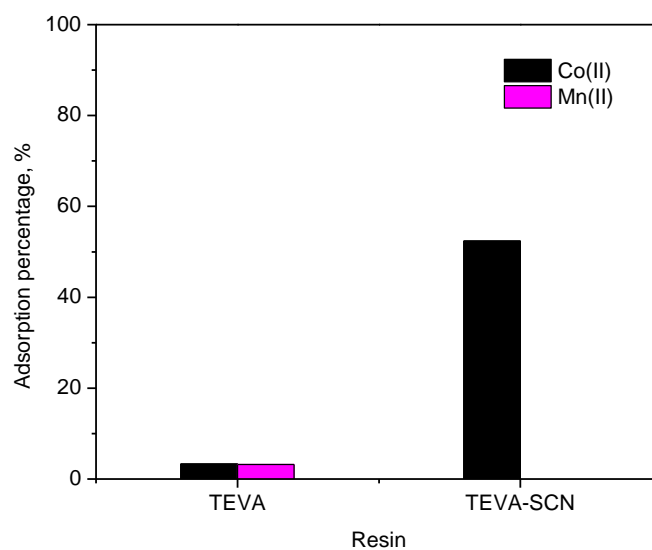

Fig. 3. Comparison between adsorption capacity of TEVA and TEVA-SCN anion exchange resin for separation of Co(II) and Mn(II). Conditions: Feed solution, mg/L: Co(II)-538.9, Mn(II)-44.8; [resin] = 15 g/L; Shaking time: 12h

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varying shaking time from 1 to 24 hour and the results are displayed in Fig. 4. This figure shows that the concentration of Co(II) in the aqueous phase was 350.1 and 318.7 mg/L after 1 and 12 hours of loading time by TEVA-SCN resin. These result indicated that loading percentage of Co(II) steadily increased from 35.4 to 40.8% as shaking time increased from 1 to 12 hour and then constant, while that of Mn(II) was negligible. Therefore, 12 hours was chosen as the optimum shaking time.
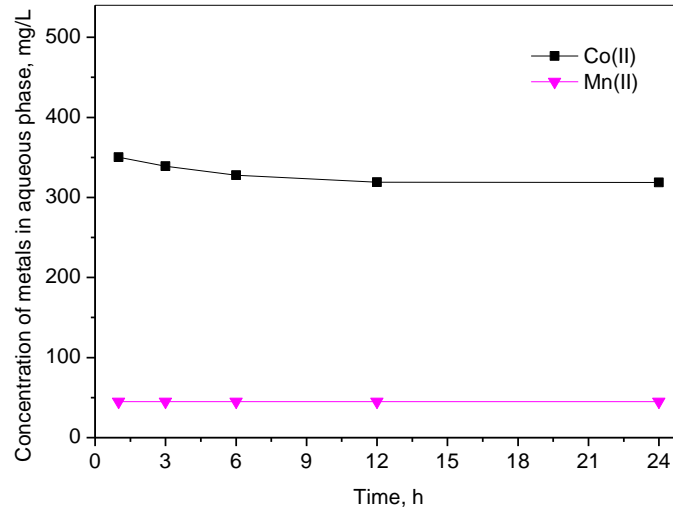

Fig. 4. Effect of time on Co(II) and Mn(II) adsorption by TEVA-SCN resin. Conditions: Feed solution, mg/L: Co(II)- 538.9, Mn(II)-44.8; [resin] = 10 g/L; Shaking time: 12h

The concentration of TEVA-SCN resin was varied from 2 to 30g/L and the experimental results are illustrated in Fig. 5. These experiments were conducted with the stripping solution containing Co(II) and Mn(II) as mentioned above in 12 hours. The results show that concentration of Co(II) in the aqueous phase gradually decreased from 448.1 to 39.6 mg/L with the increase of the concentration of TEVA-SCN resin from 2 to 30 g/L. The loading percentage of Co(II) was calculated according to the difference in concentration of metals in the aqueous phase before and after adsorption and steadily increased from 16.8 to 92.7% when the concentration of TEVA-SCN resin increased from 2 to 30 g/L, while that of Mn(II) was insignificant. The sharp increase of Co(II) adsorption was assigned to the effect of an excess dosage of resin. The SCN⁻ functional group of TEVA-SCN resin may be considered as an accelerant for the formation of $Co(SCN)_4^{2-}$ complex which have strong affinity with the positive charge center of the resin.
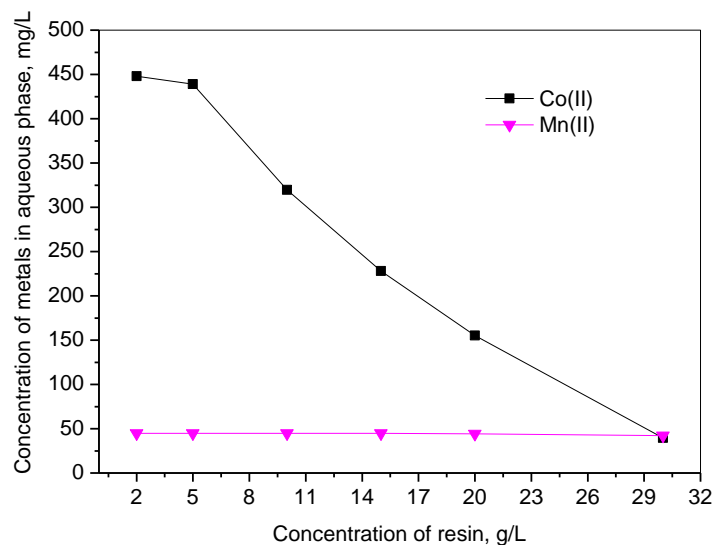

Fig. 5. Effect of concntration of TVEA-SCN resin on Co(II) and Mn(II) adsorption. Conditions: Feed solution, mg/L: Co(II)- 538.97, Mn(II)-44.77; [resin] = 2-30 g/L; Shaking time:12h

The loading capacity of TEVA-SCN for Co(II) was measured. These experiments were conducted by contacting 1 g of TEVA-SCN with 50 mL of the stripping solution containing Co(II) (538.9 mg/L) and Mn(II) (44.8 mg/L) several times until the amount of metal in the resin became constant. The cumulative amount of the metal loaded into the resin was calculated by the difference in the concentration of metal in the solution after each stage of contact. The results are shown in Fig. 6. The cumulative loading of Co(II) increased with the increase of the contact stage and became constant after five stages. The loading capacity of TEVA-SCN resin for Co(II) from 0.1 M HCl stripping solution was found to 19.8 mg per g of resin.
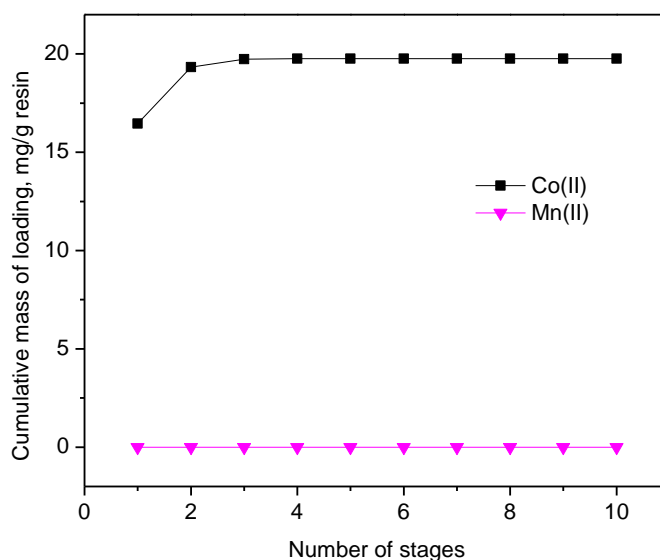

Fig. 6. Loading capacity of TEVA-SCN resin for Co(II) and Mn(II). Conditions: Feed solution, mg/L: Co(II)-538.9, Mn(II)-44.8; resin: 1g; Shaking time: 12h

3.3.2. Elution of Co(II) from the loaded resin

A ammonia solution was effective in stripping Co(II) from the loaded ALi-SCN, which was synthesized by reacting Aliquat 336 and NaSCN (Nguyen and Lee, 2020b). Moreover, NH_3 has a strong tendency to form complexes with Co(II). Therefore, ammonia solution was chosen as an eluant for Co(II) from the loaded TEVA-SCN resin. First, the loaded resin was prepared by contacting the stripping solution with 20 g/L of TEVA-SCN. In elution experiments, the concentration of NH_3 was varied from 1 to 10 %.

Fig. 7 shows that the elution percentage of Co(II) from the loaded TEVA-SCN was gradually increased to 54.1% with the increase of NH_3 concentration to 5% and then constant with the further increase of NH_3 concentration. Since the amount of Co(II) loaded into the resin depends on the resin concentration during loading, the effect of resin concentration on the elution was investigated. For this purpose, the loaded TEVA-SCN resin was obtained by varying its concentration from 1 to 20 g/L. These loaded resins were eluted by 5% NH_3 solution. The elution percentage of Co(II) decreased steadily from 100% to 54.1% with an increase of the loaded resin concentration from 1 to 20 g/L. This indicates that the concentration of Co(II) in the stripping solution decreased from 538.9 to 291.5 mg/L when the loaded resin concentration increased from 1 to 20g/L (see Fig. 8). Co(II) was completely eluted as long as the concentration of the loaded resin was below 2 g/L. By employing ion exchange with TEVA-SCN, Co(II) was completely separated from Mn(II) from the stripping solution and pure Co(II) solution with purity higher than 99.9% was recovered.

3.4 Separation of Mn(II) from the Co(II) free raffinate

A mixture of Alamine 336 and D2EHPA was effective in separating Mn(II) and Ni(II) from weak HCl solution of pH 3.0 (Nguyen and Lee, 2020a). To compare the extraction and the separation of Mn(II) over Ni(II) and Li(I), mixtures of Alamine 336 and D2EHPA/ PC 88A/ Cyanex 272 (in which mole fraction of organophosphorus acidic extractant was kept at 0.8) were tested. In these experiments, the
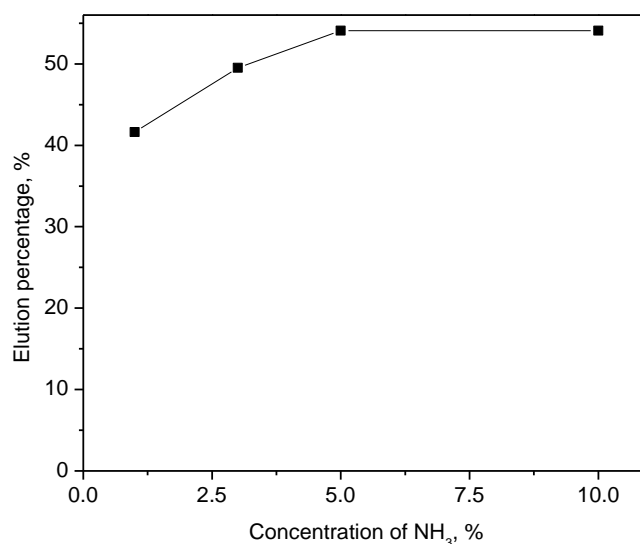
Fig. **7.** Effect of NH_3 concentration on the elution of Co(II) from the loaded TEVA-SCN resin at room temperature ([resin] = 20 g/L)
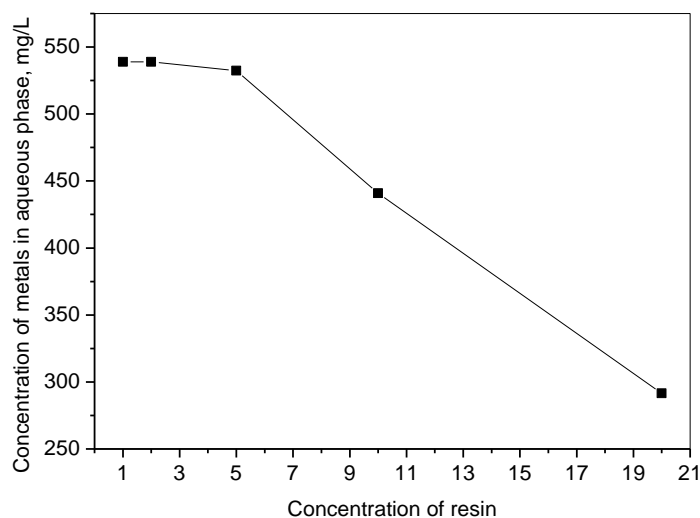

Fig. 8. Effect of loaded TEVA-SCN resin concentration on the elution of Co(II). Conditions: Eluant: 5% NH_3; [loaded TEVA resin] = 20 g/L

composition of the raffinate was 105.2 mg/L Mn(II), 100 mg/L Ni(II) and 150 mg/L Li(I) in 3 M HCl with 2 M NaCl. First, the pH of the raffinate was adjusted to 3 by adding concentrated NaOH solution. In these experiments, 10% decanol was added as a modifier. Fig. 9 shows the variation in the extraction of Mn(II), Ni(II), and Li(I) with the nature of the mixture. Although the extraction percentage of Mn(II) by mixture of Alamine 336 and Cyanex 272/ D2EHPA was higher than that by the mixture Alamine 336 and PC 88A, Ni(II) was also extracted by the mixtures of Alamine 336 and Cyanex 272/D2EHPA. Namely, 2 M mixture of Alamine 336 and Cyanex 272/(D2EHPA) can extract 100% (91.3%) Mn(II) and 8.1%/(7.8%) Ni(II), respectively. Although the mixture of Alamine 336 and PC 88A led to lowest extraction percentage of Mn(II) (77.2%), no Ni(II) was extracted at all. The formation of stable complexes of Mn(II) with PC 88A anions may represent this selective extraction. The equilibrium pH (pH_{eq}) was measured after extraction and the results are shown in Table 5. The pH_{eq} value of aqueous phase after extraction by three mixtures was in following order: Alamine 336 + D2EHPA (pKa = 3.24) < Alamine 336 + PC 88A (pKa = 4.51) < Alamine 336 + Cyanex 272 (pKa = 6.37). The increase of pH_{eq} by the mixture Alamine 336 and PC 88A/ Cyanex 272 was related to the extraction of hydrogen ion in aqueous phase by Alamine 336 (Hoh et al., 1984; Sarangi et al., 2006). Hence, the addition of Alamine 336 can controll

the pH values of solution and thus Mn(II) extraction percentage can be maintained. The extraction reaction of Mn(II) by the mixture of Alamine 336 and PC 88A can be represented as follows:

$$Mn^{2+}_{(a)} + 2Cl^-_{(a)} + (HA)_{2(o)} + 2R_3N_{(o)} = MnA_{2(o)} + 2R_3NHCl_{(o)} \tag{4}$$

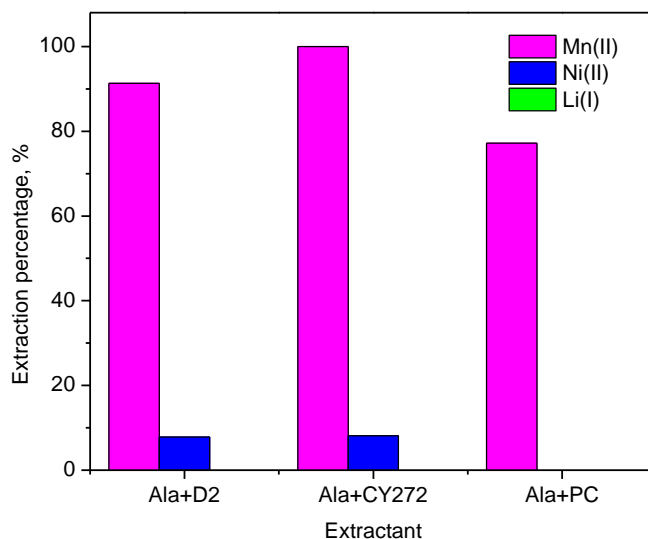where HA and R_3N represent PC 88A and Alamine 336, respectively.

Fig. 9. Effect of the nature of the extractants on the extraction of metals Mn(II), Ni(II), Li(I). Conditions: [mixture] = 2 M, mole faction of acidic extractant = 0.8; diluent: kerosene with 10% v/v decanol as modifier; A/O = 1; pH = 3; the mixture of Alamine 336 and D2EHPA/Cyanex 272 /PC 88A was denoted as Ala+D2/Ala+CY272/Ala+PC; [Mn]:[Ni]:[Li] = 105.2: 100:150 mg/L

Table 5. The equilibrium pH value after Mn(II) extraction by the mixture of Alamine 336 and D2EHPA / PC 88A/ Cyanex 272

Extractant	Alamine 336 and D2EHPA	Alamine 336 and PC 88A	Alamine 336 and Cyanex 272
pH$_{eq}$	2.23	3.15	4.49

McCabe–Thiele diagram for the extraction of Mn(II) by 2.0 M mixture of Alamine 336 and PC 88A was constructed by varying the volume ratio of the two phases from 5/1 to 1/5 and is shown in Fig. 10. In these experiments, the aqueous phase contained 105.2 mg/L Mn(II) and 2 M NaCl and its pH was 3. Fig. 10 shows that two stages of cross-current extraction are enough for complete extraction of Mn(II) at an A/O ratio of 2/3. Subsequently, batch simulation experiments for the Mn(II) extraction by 2 M mixture of Alamine 336 and PC 88A were conducted. Table 6 shows that 97.8 % Mn(II) was extracted by two stages cross–current extraction, while Ni(II) and Li(I) were not extracted at all in these conditions. Therefore, it is possible to comletely separate Mn(II) from Co(II) free raffinate by extraction with the mixture of Alamine 336 and PC 88A. After these batch simulation experiments, the equilibrium pH was 3.15. Employment of three stages cross–current extraction would completely extract Mn(II).

Table 6. Results from batch simulation experiments for the two stage cross–current extraction of metals by 2.0 M mixture of Alamine 336 and PC 88A from the Co(II) free raffinate at an A/O ratio of 2/3

Metal ions	Li	Ni(II)	Mn(II)
Stock solution, mg/L	150	100	105.3
Stage 1, raffinate, mg/L	150	100	19.4
Stage 2, raffinate, mg/L	150	100	2.3
Overall % E	0	0	97.8

Sulfuric acid solution was selected as a stripping solution for the Mn(II) in the loaded mixture of Alamine 336 and PC 88A. The concentration of Mn(II) in the loaded mixture was 102.9 mg/L. In the stripping experiments, the concentration of H_2SO_4 was varied from 0.3 to 2.0 M. The ratio of the organic to the aqueous phase was unity. Table 7 shows that sulfuric acid solution could completely strip Mn(II) from the loaded mixture of Alamine 336 and PC 88A.
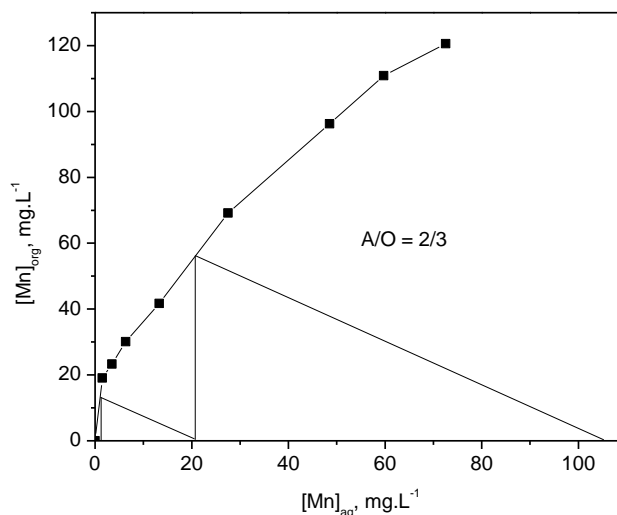

Fig. 10. McCabe Thiele diagram for the extraction of Mn(II) from the Co(II) free raffinate. Conditions: O/A = 1/5-5/1; [Mn] = 105.2 mg/L; [decanol] =10 vol.%; diluent: kerosene; [mixture of Alamine 336 and PC 88A] = 2 M, mole faction of PC 88A = 0.8; pH = 3

Table 7. Stripping percentage of Mn(II) from the loaded mixture of Alamine 336 and PC 88A by H_2SO_4

Concentration of H_2SO_4, M	Stripping percentage, %
0.3	100
0.5	100
1.0	100
2.0	100

3.5. Separation of Ni(II) from the Mn(II) free raffinate

3.5.1. Ni(II) extraction

After the extraction of Mn(II), the concentration of Ni(II) and Li(I) in the raffinate was 100.0 mg/L and 150.0 mg/L and solution pH was 3.15. In general, Li(I) is not extracted from weak HCl solution by organophosphrous extractants and control of solution pH is essential to maintain high extraction performance of Ni(II) (Tait, 1993; Singh et al., 1999; Nguyen and Lee, 2020b). Ionic liquids like ALi-CY can efficiently extract either metal ions or hydrogen ions (Le et al., 2019; Tran and Lee, 2020). Therefore, ALi-CY was selected in this work to extract Ni(II) from the Mn(II) free raffinate. In order to compare the extraction efficiency of Ni(II), Cyanex 272 was also tested. Fig. 11 shows that the concentration of ALi-CY affects the extraction of Ni(II), while the effct of Cyanex 272 concentration is negligible. Namely, Ni(II) extraction increased from 56.8 to 100% when the concentration of ALi-CY increased from 0.01 to 0.1 M. By contrast, extraction percentage of Ni(II) by Cyanex 272 was lower than 20% in the same concentration range from 0.01 to 0.1 M. Li(I) was not extracted at all in these experiments. The equilibrium pH after extraction by 0.1 M ALi-CY was 7.98. The increase in the equilibrium pH is due to the extraction of hydrogen ions (Fortuny et al., 2012; Le et al., 2019; Tran and Lee, 2020). After the extraction of Ni(II), only Li(I) left in the raffinate.

3.5.2 Ni(II) stripping

Our previous data showed that sulfuric acid solution was better than HCl solution as a stripping agent for Ni(II) from the loaded ALi-CY (Nguyen and Lee, 2020b). The concentration of Ni(II) in the loaded

ALi-CY was 100 mg/L. Fig. 12 shows that stripping percentage of Ni(II) gradually decreased with the increase of H_2SO_4 concentration from 0.1 to 2.0 M. The complete stripping of Ni(II) from the loaded organic phase is possible by using 0.1 M H_2SO_4.
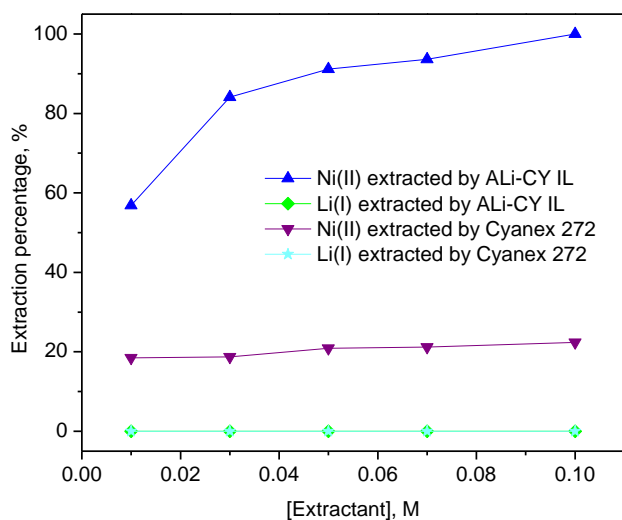

Fig. 11. Comparison on metal extraction ability between IL(ALi-CY) and Cyanex 272. Conditions: [extractant] 0.01-0.1 M; diluent: kerosene; A/O = 1; [Ni] = 100 mg/L; [Li] = 150 mg/L; pH = 3.15
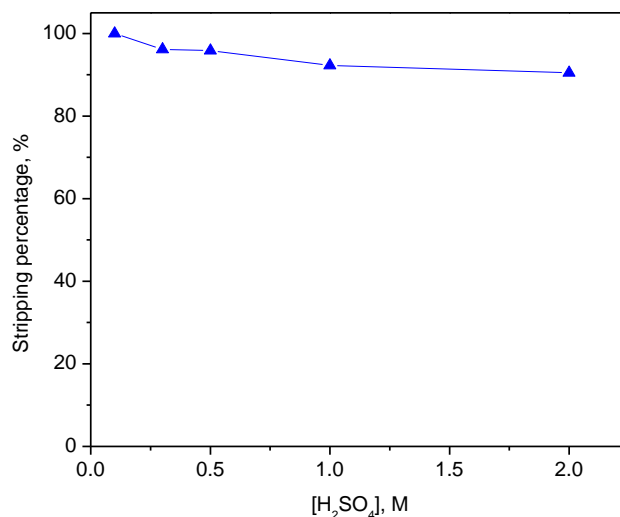

Fig. 12. Effect of H_2SO_4 concentration on the stripping of Ni(II) from 0.1 M ALi-CY loaded organic phase. Conditions: [H_2SO_4] = 0.1-2.0 M; A/O = 1; [Ni] = 100 mg/L

3.6. Integrated process

Based on our obtained results in this work, a conceptual process flowsheet was proposed for the separation of Cu(II), Co(II), Ni(II), Mn(II), and Li(I) from the synthetic 3.0 M hydrochloric acid leaching solution of spent LIBs by solvent extraction and ion exchange and is shown in Fig. 13. The optimum conditions for separation of each metal are listed in Table 8. First, Cu(II) can be selectively separated by using low concentration of Cyanex 301. The Cu(II) in the loaded of Cyanex 301 can be stripped by moderate aqua regia solution. In order to enhance the extraction percentage of Co(II), 2 M NaCl was added to the raffinate and most of Co(II) can be extracted into Aliquat 336. However, the loaded Aliquat 336 contains not only Co(II) but also a small amount of Mn(II) (44.8 mg/L). The Co(II) and Mn(II) in the loaded Aliquat 336 were completly stripped by dilute HCl solution. Ion exchange of this stripping solution with TEVA-SCN results in selective loading of Co(II) and thus the separation of Co(II) and Mn(II) can be accomplished. The Co(II) in loaded resin can be eluted with 5% NH_3 solution. The purity

of Co(II) in the eluant solution was 99.9%. By adjusting the pH of the Co(II) free raffinate to 3.0, Mn(II) can be selectively extracted by the mixture of Alamine 336 and PC 88A in which the mole fraction of PC 88A is 0.8. The Mn(II) in the loaded mixture can be stripped by a H$_2$SO$_4$ solution. After extraction of Mn(II), ALi-CY can extract completely Ni(II) and leave Li(I) in the final rafinate. The purity of Cu(II), Co(II), Mn(II) and Ni(II) in the stripping solution was higher than 99.9%. Since Li(I) and Na(I) are remained in the raffinate after the extraction of Ni(II), Li(I) compounds can be recovered from the raffinate.
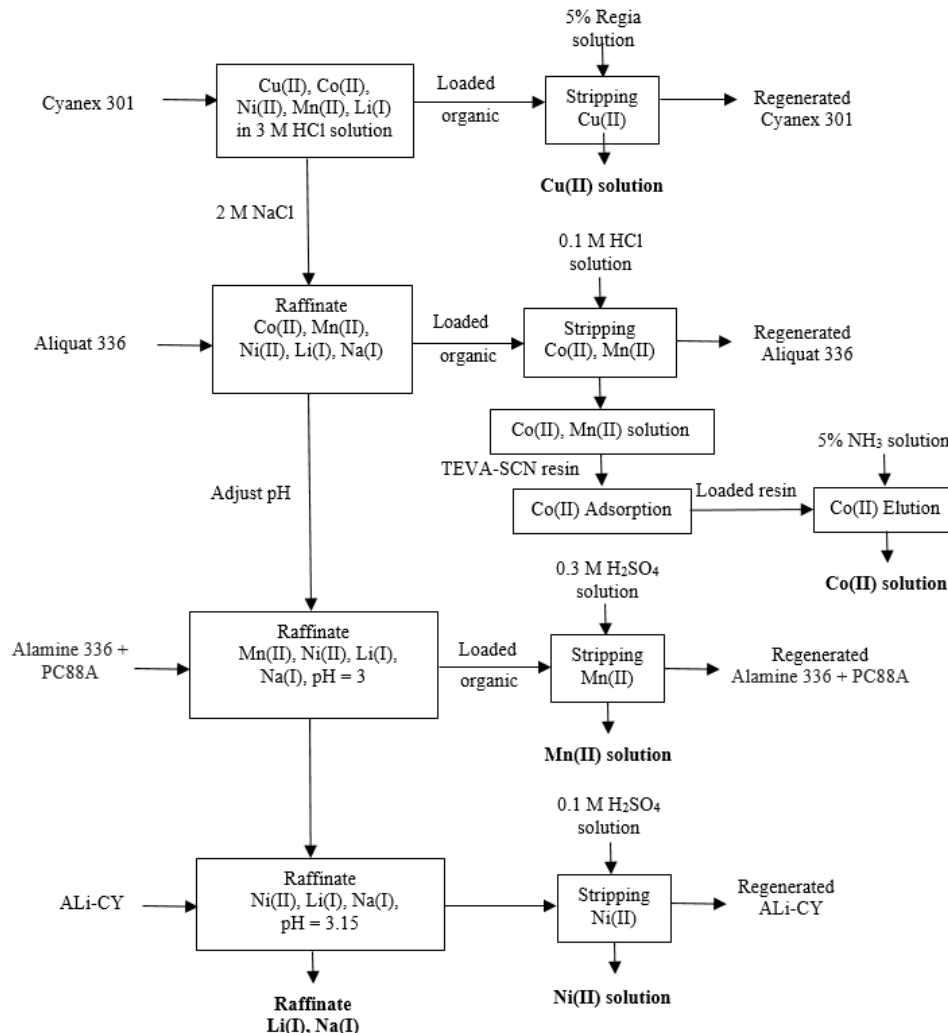

Fig. 13. The proposed flowsheet for the separation of Cu(II), Co(II), Mn(II), Ni(II) and Li(I) from the synthetic 3.0 M hydrochloric acid leaching solution of spent LIBs

From the obtained results, it can be seen that almost complete separation of the metals can be possible in each step by using solvent extraction with commercial extractants and ionic liquids synthesized from commercial extractants. Modifying TEVA by contacting NaSCN enhanced both the loading capacity and selectivity for Co(II) and thus the purity of Co(II) increased. Besides, the separation degree in each step of both solvent extraction and ion exchange is so high that pure solution of each metal can be recovered. This is prospective in terms of the feasibility of manufacture of advanced materials from the corresponding stripping solution and the final raffinate. On the basis of economics and enviroment, the use of the mixture of PC88A and Alamine 336 would circumvent the saponification of organophosphorous extractants for the control of the equilibrium pH. Along these lines, the employment of synthesized IL like ALi-CY also brought some advantage on the basis of extractbility and stability of solution pH compared to respective acidic extractant. Table 9 compares the obtained results between the data reported in the previous work (Nguyen and Lee, 2020a) and this work in terms of selectivity for metal separation.

Table 8. Mass balance and the variation in the extraction and stripping of metals from the synthetic solution duirng each separation step

Process	Detail	Cu(II)	Co(II)	Mn(II)	Ni(II)	Li(I)
Feed solution	Synthetic leaching solution, 3 M HCl, mg/L	150	938	150	100	150
Cu(II) separation	Extraction: 0.02 M Cyanex 301, A/O = 1, %	100	<LOD	<LOD	<LOD	<LOD
	Stripping: 5% aqua regia, A/O = 1, %	>95.3	-	-	-	-
Co(II) separation	Extraction: 1.0 M Aliquat 336, A/O = 1/2 with four stage counter-current extraction, %	-	>99.9	29.9	<LOD	<LOD
	Ion exchange: TEVA-SCN, 538.9 mg/L Co(II) and 44.8 mg/L Mn(II) in 0.1 M HCl, %	-	>99.9	0	<LOD	<LOD
	Eluting: 5% NH$_3$, [resin] = 2g/L, %	-	>99.9	-	-	-
Mn(II) separation	Extraction: 2 M mixture of Alamine 336 and PC 88A, A/O = 2/3 with two stage cross-current extraction, pH = 3, %	-	-	>97.8	<LOD	<LOD
	Stripping: 0.3 M H$_2$SO$_4$, %	-	-	> 9.99	-	-
Ni(II) separation	Extraction: 1.0 M ALi-CY, A/O = 1, pH = 3.15, %	-	-	-	>99.9	<LOD
	Stripping: 0.1 M H$_2$SO$_4$, %	-	-	>99.9	-	-
Li(I) in rafinate	Final raffinate, mg·L^{-1}	-	-	-	-	150
Purity, %		>99.9	>99.9	>99.9	>99.9	-
*Note: 2 M Na(I) is present in final raffinate; "<LOD" denotes under limit of detection.						

Table 9. Comparison on the improvement of separation and selectivity for the recovery of metals from leaching solution of spent LIBs

Metals in leaching solution	Previous work (Nguyen and Lee, 2020a)	This study
Cu(II): Co(II): Mn(II): Ni(II): Li(I) = 150:938:150:100:150 mg/L in 3 M HCl	-The co-extraction of some ions such as Cu(II)/ Co(II) and Mn(II)/ Ni(II) was obseeved during separation process. - Ni(II), Li(I) and Na(I) were left in final raffinate. - The separation degree of metal ions was not high, resulting in low purity.	- Most of the metal ions were completely separated in each step. - Applying ion exchange with TEVA-SCN resin can enhance both the loading capacity and selectivity of Co(II). - Li(I) and Na(I) were left in final raffinate, thus compound of Li(I) can be recovered. - Purity of Cu(II), Co(II), Mn(II), Ni(II) was over 99.9%.

4. Conclusions

Solvent extraction and ion exchange experiments were done to improve the separation degree of the previoulsy reported process for the recovery of metal ions with high purity from 3 M HCl leaching solution of LIBs containing Cu(II, Co(II), Mn(II), Ni(II) and Li(I). The separation degree and selectivity of metal ions in each step of this work was greatly improved compared to the reported process. Firstly, Cu(II) ions were completely extracted over other metal ions by Cyanex 301 and then the Cu(II) in the loaded organic was quantitatively stripped by 5%(v/v) aqua regia solution. Most of Co(II) and a small amount of Mn(II) were loaded into Aliquat 336 phase after the four stage counter-current extraction. The application of TEVA-SCN resin showed some merits in either selectivite loading or purification of Co(II) from the HCl stripping solution containing Mn(II). Co(II) in the loaded resin was successfully eluted by 5% NH$_3$ solution. Among three binary mixtures (Alamine 336 and D2EHPA/Cyanex 272/PC 88A), Mn (II) was selectively extracted over Ni(II) and Li(I) from the Co(II) free raffinate by the mixture

of Alamine 336 and PC 88A at initial pH of 3. The Mn(II) in the loaded organic phase was completely stripped by 0.3 M H_2SO_4. ALi-CY solution can completely extract Ni(II), while Li(I) was left in the final raffinate. Ni(II) was completely stripped from the loaded phase by 0.1 M H_2SO_4. In most of cases, IL and amine played an important role for controling solution pH in extraction of Mn(II) and Ni(II). Our experiments indicated that the purity of the metal ions in the stripping solutions was higher than 99.9%. A flowsheet was proposed to separate the five metal ions by solvent extraction and ion exchange on the basis of our data.

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