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Selective recovery of Co(II) over Ni(II), Al(III), and Li(I) from ethylene glycol solution by solvent extraction and precipitation

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ABSTRACT

Using "green solvents" like ethylene glycol (EG) to replace water in hydrometallurgical processes is increasingly popular because of its feasibility and environmental friendliness advantages. In this study, the selective recovery behavior of Co(II) over Ni(II), Al(III), and Li(I) from mixed EG and H_2O of HCl solution was studied by a combination of solvent extraction and stripping precipitation. The results showed that Co(II) from the EG-H_2O solutions was selectively extracted over other metals by ionic liquids, in which ALi-SCN was more efficient than Aliquat 336. The presence of EG offered significant advantages in selectivity and efficiency for Co(II), whereas the effect of HCl concentration in the EG-H_2O system was negligible. The selective extraction behavior of ALi-SCN for Co(II) is due to differences in the stability and speciation of metal complexes in the EG-H_2O solution. Co(II) from the loaded ALi-SCN was directly precipitated to cobalt oxalate with above 99.9% purity under conditions: 60 min, O/A ratio of 1, and 1:2 of mole ratio of Co(II) to $H_2C_2O_4$. ALi-SCN solutions after the Co(II) precipitation can be reused several times with selective Co(II) extraction capacity at high performance. Thus, Co(II) recovery from an EG-H_2O system through continuous two steps of ALi-SCN extraction and precipitation is feasible.

1. INTRODUCTION

Cobalt (Co) is a crucial metal of rechargeable batteries like lithium-ion batteries (LIBs) due to its ability to enhance the battery life and energy density by stabilizing the battery structure during repeated charging and discharging cycles. Moreover, it is also an indispensable metal in current technologies, such as engines, robotics, drones, 3D printing, and digital technology (Martins et al., 2021). Most cobalt is used for battery production, Ni-based alloys, and other modern materials, which account for 57, 13, and 8% of cobalt total consumption, respectively (Botelho Junior et al., 2021). With the LIBs extending application in electric vehicles (EVs) and energy storage devices, the global demand for cobalt is huge and will continuously rise. As a result, a large amount of spent batteries have been discarded and have potential impacts on the environment. Therefore, the recovery of cobalt from secondary sources, especially spent LIBs not only mitigates environmental problems but also reduces the dependence on scarce metal resources, lowers production costs, and promotes a sustainable production process (Alipanah et al., 2021).

Many methods, such as pyrometallurgy, hydrometallurgy, and bio-metallurgy, have been proposed for recovering cobalt from spent LIBs (Mishra et al., 2008; Xin et al., 2009; Zeng et al., 2012; Velázquez-Martínez et al., 2019; Martins et al., 2021). Among them, hydrometallurgy is preferred for industrial application and implementation because of its immense value in terms of high-purity metal, low recovery costs, minimal environmental impact, and operational complexity (Georgi-Maschler et al., 2012; Träger et al., 2015; Pavez et al., 2018; Botelho Junior et al., 2021;). Generally, hydrometallurgical processes include leaching, liquid-liquid solvent extraction, and electrolysis/precipitation steps (Kang et al., 2010; Chen et al., 2011; Quintero-Almanza et al., 2019). However, most of the existing processes for recovering cobalt in the form of pure compounds or metal were required to raise the aqueous solution pH, leading to a significant caustic soda consumption and further steps done for the environmental treatment. Thus, new processes that could be environmentally friendly and have high metal recovery efficiency need to be explored.

The use of “green solvents” or “nonaqueous solutions” (e.g. ionic liquids (ILs), deep eutectic solvents (DES)) for the recovery of metals has attracted much attention, which showed the metal recovery efficiency and reduction of wastewater generated (Li & Binnemans, 2021). Ethylene glycol (EG) is considered a green solvent because of its properties, such as non-volatility, low flammability, and low toxicity (Prat et al., 2016; De Clercq et al., 2017). EG is one of the polar organic solvents that could be a potential solvent for replacing water as a diluent in the dissolution, separation, and recovery of metals (Batchu et al., 2020; Li et al., 2021; Nguyen et al., 2022a, 2022b). The reported studies showed that the presence of EG in leaching solutions can reduce water activity, enhancing the extraction of metal ions to organic phases (Li et al., 2018; Tran et al., 2021). Moreover, metal recovery in EG media can bring many advantages in terms of improving recovery efficiency, and selectivity and reducing wastewater generation throughout the recovery process (Nguyen et al., 2022a, 2022b).

The objective of this work is the selective recovery of Co(II) compounds with high purity from synthetic ethylene glycol-water solution simulated by the hydrochloric acid leaching solution of spent LIBs containing Ni(II), Al(III), and Li(I). To this end, an ionic liquid (ILs) like ALi-SCN synthesized from Aliquat 336 was employed to selectively extract Co(II) over other metals from the EG-water solution. The effect of factors such as ALi-SCN, HCl, and Co(II) concentrations and volume fraction of EG on the Co(II) extraction was explored. Sequentially, recovering Co(II) from loaded ALi-SCN was investigated by the precipitation method. Besides, the reusability of the extractant after the Co(II) recovery was explored. The studied results will provide important information in recovering valuable metals from spent LIBs using greener solutions.

2. MATERIALS AND METHODS

2.1. Reagents and chemicals

Synthetic leaching solutions containing Co(II), Ni(II), Al(II), and Li(II) were prepared by dissolving their corresponding chloride salts such as cobalt (II) chloride hexahydrate ($CoCl_2{\cdot}6H_2O$, Guangdong Guanghua Sci-Tech Co., 99%), lithium chloride monohydrate ($LiCl{\cdot}H_2O$, Junsei Co., > 99%), aluminum chloride hexahydrate ($AlCl_3{\cdot}6H_2O$, Shanghai Zhanyun Chemical Co., 98%), nickel(II) chloride hexahydrate ($NiCl_2{\cdot}6H_2O$, Shanghai Zhanyun Chemical Co., 98%) in the mixture of hydrochloric acid (HCl, Guangdong Guanghua Sci-Tech Co., 36-38%) and ethylene glycol ($(CH_2OH)_2$, Xilong Scientific Co., Ltd., ≥ 99.5%) solutions to desired concentrations. Oxalic acid ($H_2C_2O_4$, Shantou Xilong Chemical Factory, 99.5%) was employed as a precipitant.

A commercial extractant like *N*-Methyl-*N,N,N*-trioctylammonium chloride (Aliquat 336, Sigma Aldrich Co., 93%) was used without further purification. Kerosene (Sigma Aldrich Co., > 90%) was employed as a diluent to desired extractant concentrations and 1-octanol (Yatai Chemical Co., 98%) was added into organic phases as a modifier with 10% (v/v) concentration to prevent a third phase formed after the extraction process.

An ionic liquid as ALi-SCN ($R_4N{\cdot}SCN$) was synthesized according to the previous literature with a small modifier (Nguyen & Lee, 2021). Namely, 1.0 M Aliquat 336 ($R_4N{\cdot}Cl$) was contacted several times with 2 M ammonium thiocyanate (NH_4SCN, Xilong Scientific Co., Ltd., ≥ 98.5%) solution at equal volume of organic and aqueous phases for the complete conversion of chloride of

Aliquat 336 to thiocyanate ions and the precipitation method of Cl^- ions with silver nitrate ($AgNO_3$, Shantou Xilong Chemical Factory, > 98%) were employed to verify for the transfer of Cl^- ions between these phases. All the chemicals used for experiments were of analytical grade.

2.2. Experimental procedure and analytical methods

All experiments of solvent extraction were conducted by mixing equal volumes of aqueous and organic phases (10 mL each) in a screwed cap bottle. These mixtures were shaken within 30 min using a Burrell wrist action shaker (model 75, USA) at room temperature (30 ± 1°C). After a required contact shaking time, organic and aqueous phases were separated using glass separating funnels. Inductively coupled plasma-optical emission spectrometry (ICP-OES, Spectro Arcos) was employed to determine the concentration of metal ions in aqueous solutions. Mass balance calculations were used to verify the metal concentration in organic solutions. The pH value of the aqueous solution was measured by a thermal scientific pH meter (model A211, Orion Star, USA). The extraction percentage (*%E*) of a metal ion was calculated as:

$$\%E = \frac{([M]_i - [M]_{aq}) \times 100}{[M]_i} \quad (1)$$

where $[M]_i$ and $[M]_{aq}$ are the concentrations of the metal ions in the aqueous phase before and after extraction, respectively. It is assumed that there was no change in the volume of the two phases during experiments.

Co(II) precipitation experiments from organic phases were done by mixing the organic solution with the $H_2C_2O_4$ solution in a beaker. The mixtures were stirred using a magnetic stirrer in a heating mantle. After the required period, precipitates were collected by filtration and then dried in an oven (Oakton, Korea) at 60°C for 12 h. The precipitation percentage (X%) of Co(II) was calculated as:

$$X\% = \frac{M_o - M}{M_o} \times 100 \quad (2)$$

where M_o and M are the mass of metal ions in the organic phase before and after the precipitation, respectively.

The characteristics of Co(II) precipitates were verified by X-ray diffractometer (XRD- D8 - Advance - Bruker - USA), Fourier Transform Infrared Spectroscopy (FTIR, Shimadzu, IRAffinity-1s WL), and analytical high-resolution scanning electron microscopy (HR-SEM-JCM-7000/JEOL).

Reuse of organic solution: After Co(II) was removed from the loaded ALi-SCN phase by precipitation, the organic solution was washed several times using distilled water until the pH value of the washed water reached around 8.0. The organic solution was subsequently used in additional experiments for extracting Co(II).

All experiments were conducted in triplicate for ± 5% error range.

3. RESULTS AND DISCUSSION

3.1. Selective extraction of Co(II) from EG-H_2O solutions containing Ni(II), Al(III), and Li(I)

3.1.1. Comparison of Co(II) extraction behavior of ionic liquids from EG/H_2O solution

In our previous studies, the selective extraction of Co(II) over Ni(II), Al(III), and Li(I) from the leaching solutions of spent LIBs by using HCl or H_2SO_4 aqueous solutions can be obtained by using ionic liquids (ILs) like Aliquat 336 and ALi-SCN. The Co(II) extraction behavior of these ILs was attributed to the extraction reactions between NR_4^+ cations of Aliquat 336 and chloride or thiocyanate complex anions of Co(II) (e.g., $[CoCl_3]$, $[CoCl_4]^{2-}$, $[Co(SCN)_3]^-$, $[Co(SCN)_4]^{2-}$) (Nguyen & Lee, 2021). Therefore, in this work, the extraction behavior of Aliquat 336 and ALi-SCN for Co(II) from the system of EG and H_2O solutions simulated by the HCl leaching of spent LIBs containing Co(II), Ni(II), Al(III), and Li(I) was studied.

To compare the Co(II) extraction behavior of the ILs, the concentration of Aliquat 336 and ALi-SCN in the organic phase was kept at 0.03M and the EG-H_2O system was prepared with fixing at the volume ratio of EG to H_2O at a unity, 500 mg/L of each metal, and 1.0 M HCl. Our experimental results showed that the Co(II) extraction percentage of Ali-SCN (31.53%) was higher three times than that of Aliquat 336 (11.45%), whereas no Al(III), Ni(II) and Li(I) were extracted by these two ILs. This agreed well with previous reports that the separation degree of Co(II) to other metals by ALi-SCN is more effective than that by Aliquat 336, which was attributed to be more stable complex anions of Co(II) with SCN^- than that Cl^-, resulting the increase in the extraction efficiency of Co(II) by ILs (Table 1) (Tran & Lee, 2020; Nguyen & Lee, 2020a, 2021). The poor extraction ability of Ni(II), Al(III), and Li(I) by these ILs could be due to the stereoscopic hindrance of complexes to ILs accompanied by the competition of proton in the leaching solution (Sasic et al., 2001; Tran & Lee, 2020; Tran et al., 2021). From the obtained results, ALi-SCN was chosen for the selective extraction of Co(II) from the EG-H_2O system.

Table 1. The stability constants of metal complexes with thiocyanate ion at 25°C (Tran & Lee, 2020)

Reaction	logK	Reaction	logK
$Co^{2+} + SCN^- = [CoSCN]^+$	2.5	$Ni^{2+} + 4SCN^- = [Ni(SCN)_4]^{2-}$	2.1
$Co^{2+} + 2SCN^- = [Co(SCN)_2]^o$	1.8	$Co^{2+} + Cl^- = CoCl^+$	0.2
$Co^{2+} + 3SCN^- = [Co(SCN)_3]^-$	4.0	$Co^{2+} + 2Cl^- = CoCl_2^o$	−3.9
$Co^{2+} + 4SCN^- = [Co(SCN)_4]^{2-}$	3.9	$Co^{2+} + 3Cl^- = CoCl_3^-$	−3.0
$Ni^{2+} + SCN^- = [NiSCN]^+$	2.2	$Co^{2+} + 4Cl^- = CoCl_4^{2-}$	−9.1
$Ni^{2+} + 2SCN^- = [Ni(SCN)_2]^o$	2.4	$Ni^{2+} + Cl^- = NiCl^+$	−1.3
$Ni^{2+} + 3SCN^- = [Ni(SCN)_3]^-$	2.6		

3.1.2. *Effect of ALi-SCN concentration*

The effect of the dosage of ALi-SCN on the extraction efficiency of Co(II) from the EG-H_2O solution was considered from 0.03 to 0.3 M. Figure 1 reveals that the extraction percentage of Co(II) increased as rising ALi-SCN concentration and reached ~100% at 0.12 M. Meanwhile, the extraction percentage of Al(III), Ni(II), and Li(I) was zero. These results were ascribed to the complex formation degree of Co(II) and thiocyanate ion, such as $Co(SCN)_3^-$ and $Co(SCN)_4^{2-}$ are superior as compared to other metals, leading to the Co(II) extraction efficiency of ALi-SCN. On the other hand, the approach of metal ions and ligands based on the HSAB (hard soft acid base) principle also affects metallic extraction percentage. Ni(II) and Co(II) are known as intermediate acids, while Li(I) and Al(III) are hard acids. Thus, these metal ions have less affinity with SCN^- through different electron donor atoms (N or S atom) to form metal thiocyanate complexes and were extracted by the quaternary ammonium cation (Matveichuk et al., 2015). When Ni(II) coordinates SCN^- through the S atom, the hydrophilic N atom protrudes outwards. By contrast, Co(II) tends to combine with SCN^- through N and the hydrophobic S atom protruded outwards, which increases their affinity for the quaternary ammonium cation. This led to an increase in the extraction efficiency of Co(II) by ILs (Matveichuk et al., 2015; Nguyen & Lee, 2021). The extraction reaction of Co(II) by ILs can be expressed as (Tran et al., 2021):

$$Co^{2+}_{(a)} + 2Cl^-_{(a)} + 4R_4N\cdot SCN_{(o)} = (R_4N)_2Co(SCN)_{4(o)} + 2R_4N\cdot Cl_{(o)} \quad (3)$$

Where $R_4N\cdot SCN$ denotes ALi-SCN, (a) and (o) represent aqueous and organic phase.

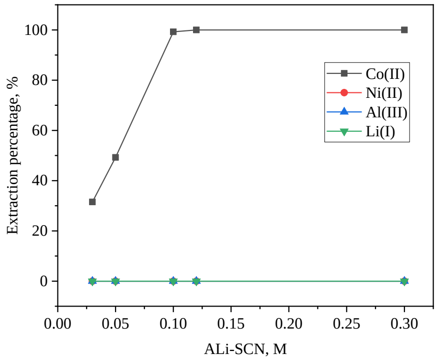

Figure 1. Effect of ALi-SCN concentration on the extraction percentage of metal ions from EG-H_2O solution

(Conditions: [ALiSCN] = 0.03-0.3 M; 1 M HCl; [each metal] = 500 mg/L; the ratio of EG to H_2O = 1:1 (v/v))

Thus, 0.12 M ALi-SCN was the best concentration for the selective separation of Co(II) over Ni(II), Al(II), and Li(I) from the EG-H_2O system.

3.1.3. *Effect of HCl concentration*

To investigate the effect of HCl concentration on the Co(II) extraction efficiency, the concentrations of HCl were varied from 0.5 to 3.0 M. In these experiments, 500 mg/L of each Co(II), Mn(II), Ni(II), and Li(I) was prepared in an EG-water mixture of 1:1 volume ratio, and the concentration of ALi-SCN in the organic solution was 0.12 M. As presented in Figure 2, the concentration of HCl insignificantly affected the Co(II) extraction percentage and no Al(III), Ni(I), and Li(I) were extracted in these experiments. Most Co (II) was extracted with 0.5 to 2.0 M HCl and then lightly decreased to 94.3% at 3.0 M HCl. The competitive extraction of hydrogen ions to the ionic liquid phase could be attributed to a deceased Co(II) extraction percentage (Nguyen & Lee, 2020b). Although the extraction efficiency of Co(II) at 1.0 M HCl (~100%) was higher than that of 0.5 M HCl (97.9%), this difference was trivial. Moreover, a mild acid is a favorable choice for solvent extraction due to decreasing acid consumption and the cost of post-treatment processes. Therefore, 0.5 M HCl was chosen for further experiments.

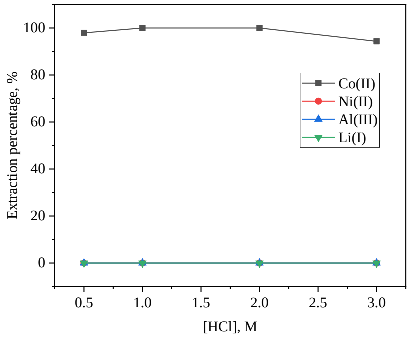

Figure 2. Effect of HCl concentration on the extraction percentage of metal ions from the EG-H_2O solution

(Conditions: [ALi-SCN]=0.12M; [HCl] =0.5-3.0 M; [each metal] = 500 mg/L; the ratio of EG to H_2O = 1:1 (v/v))

3.1.4. Effect of ethylene glycol fraction

Since the high viscosity of synthetic EG-H_2O solution could affect the solubility of metallic salts, EG volume fraction in the EG-H_2O system was varied from 20 to 80% (v/v), and the concentrations of each metal ion as Co(II), Mn(II), Ni(II) and Li(I) and HCl were fixed at 500 mg/L and 0.5 M, respectively. The concentration of ALi-SCN in the organic solution was kept at 0.12 M. Figure 3 shows that Co(II) extraction percentage increased from 90.3 to 100% when EG fraction increased from 20 to 50% (v/v) and steadily decreased to 61.6% at 80% (v/v). This might be the reduction of water activity by the presence of EG, leading to an improvement in the affinity of metal ions to the organic phase (Li et al., 2018; Tran et al., 2021). Moreover, the conversion from $[Co(H_2O)_6]^{2+}$ to $CoCl_4^{2-}/CoSCN^{2-}$ is favored in EG solution because H_2O activity decreases with the difference in the dielectric constant between EG (41.0 at 25 °C) and water (78.2 at 25 °C) (Tran et al., 2021). However, the increase in the EG fraction (higher than 60%) could cause the suppression of Co(II) extraction by increasing the viscosity of the EG-H_2O solution to result in the decrease in the contacting of Co(II) complexes with active center of the IL (Cool et al., 2024). Meanwhile, the extraction percentages of Ni(II) and Li(I) were nil. Ni(II) can form complexes like $[Ni(H_2O)_x(C_2H_6O_2)_yCl_{(6-x-y)}]^{(x+y-4)}$, which is favorable in EG compared to that in water (Tran et al., 2021). Therefore, the stability of complexes in the aqueous phase might be responsible for the low extraction efficiency of this metal by the ALi-SCN in the EG-H_2O solution. In the case of Al(III), the extraction percentage of Al(III) decreased from 12.7% to zero with the increase in the volume fraction of EG from 20 to 50%. This reveals that Al(III) extraction is suppressed in the presence of EG but is favored in aqueous solution. This might explained by the stability and formation of a small amount of Al(III)–thiocyanate–water complex during the extraction process (Bahta et al., 1997; Sasic et al., 2001). Indeed, a comparison experiment of aqueous solution with the absence of EG was conducted in the same conditions. The result indicated that 38.4% Al(III) was extracted to the ALi-SCN phase while the extraction percentage of Ni(II), and Li(I) are zero. Therefore, the presence of EG (50% v/v) in the aqueous phase is beneficial in terms of selective extraction of Co(II) over others and suppression of Al(III) extraction.

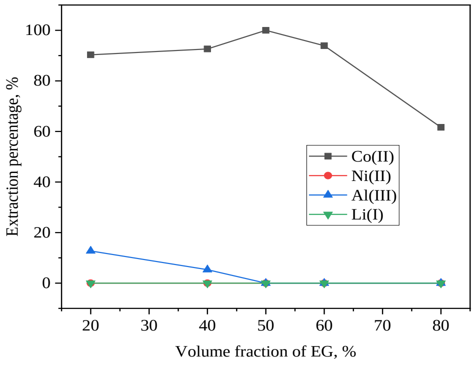

Figure 3. Effect of volume fraction of EG on the extraction percentage of metal ions

(Conditions: [ALi-SCN] = 0.12M; [HCl] = 0.5M; [each metal] = 500 mg/L; [EG] in the EG-H_2O solution = 20-80% (v/v)

3.1.5. Effect of Co(II) concentration

In the metal selective separation, the concentration of a target metal in the solution of mixed metals is a key element affecting its selective separation behavior from its solution. To investigate this point, the concentrations of Co(II) in the EG-H_2O solution containing Al(III), Ni(II), and Li(I) were varied from 50 to 500 mg/L with a 1:1 (v/v) of EG/H_2O

ratio and 0.5 M HCl and the concentration of each Al(III), Ni(II) and Li(I) was kept at 500 mg/L. Extraction experiments were performed at 0.12 M ALi-SCN.

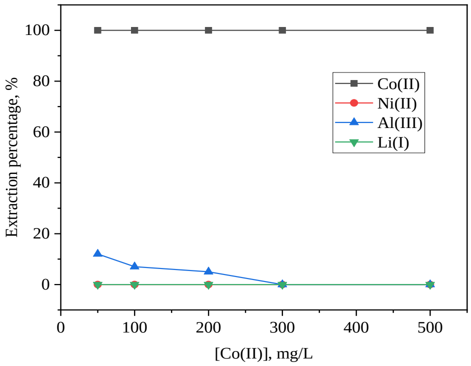

Figure 4. Effect of Co(II) concentration on the extraction percentage of metal ions from the EG-H_2O solution

(Conditions: [ALi-SCN] = 0.12M; [HCl] = 0.5M; [Co(II)] = 50-500 mg/L; [other metal] = 500 mg/L; the ratio of EG to H_2O = 1:1 (v/v))

As presented in Figure 4, full Co(II) was extracted in the range of studied Co(II) concentrations, whereas Ni(II) and Li(I) were not extracted. Meanwhile, the extraction percentage of Al(III) gradually decreased from 12% to zero with rising the Co(II) concentration from 50 to 300 mg/L. The extraction of Al(III) at below 300 mg/L Co(II) concentration can be due to high ALi-SCN concentration after the extraction of full Co(II). The extraction of Al(III) by ALi-SCN can be explained by the formation of Al(III)–thiocyanate–water system such as $Al(NCS)(H_2O)_5^{2+}$, $Al(NCS)_2(H_2O)_4^{+}$ and $Al(NCS)_3(H_2O)_3$ where SCN− is coordinated through nitrogen as a terminal ligand (logK = 0.42) (Bahta et al., 1997; Sasic et al., 2001). These complexes have a sulfur head that has such high affinity toward the ammonium center of ALi-SCN, resulting in the extraction of Al(III). In contrast, the high concentration of Co(II) can lead to the rubbing of Al(III) from the loaded organic phase due to the predominance of Co(II)-SCN complexes and their higher affinity to the organic phase. This can suggest that the selective recovery of Al(II) over Ni(II) and Li(I) from the raffinate after full Co(II) recovery can be attained by using ALi-SCN solution. From our results, the best conditions for selective extraction of Co(II) in the synthetic leaching solution containing Al(III), Ni(II), and Li(I) in the EG-H_2O solution were confirmed to be 0.12 M ALi-SCN, 1:1 (v/v) of EG/H_2O ratio in the leaching solution of 0.5 M HCl.

3.2. Precipitation of Co(II) from the loaded ALi-SCN

3.2.1. *Effect of the factors on the precipitation of Co(II) from the loaded ALi-SCN*

To consider the recovery ability of Co(II) from the loaded organic phase, the concentration of Co(II) at 500 mg/L in the loaded ALi-SCN was studied. In this study, Co(II) from the loaded ALi-SCN was directly precipitated to cobalt(II) oxalate by using oxalic acid ($C_2H_2O_4$) as a precipitant.

Effect of the solution pH: Since the precipitation of Co(II) greatly depends on the dissociation of $C_2H_2O_4$ to $C_2O_4^{2-}$ anions, the pH of the mild acid solution is essential to trigger the dissociation (Pinching & Bates, 1948). Therefore, the pH of oxalic acid solution was tested in the range of 3 to 5. The precipitation reactions were conducted at a 1:1 molar ratio of Co(II) to $H_2C_2O_4$ at room temperature for 60 min. As a result, about 96% Co(II) was precipitated from the loaded phase in the range of studied pH values. This agreed well with the previous report that the pH solutions are around 3 which is favorable for cobalt oxalate precipitation (Nguyen & Duong, 2020). The mechanism precipitation of Co(II) from the loaded ALi-SCN may be suggested by two steps: (1) the stripping of Co(II) from the organic phase to the aqueous phase; (2) the precipitation of Co(II) by oxalate ions in the aqueous phase. The stripping-precipitation reaction of Co(II) and oxalic acid was proposed in Eq. (4)

$$(R_4N)_2Co(SCN)_{4(o)} + 2R_4N{\cdot}Cl_{(o)} + C_2O_4^{2-}{}_{(aq)} = CoC_2O_{4(s)} + 4R_4NSCN_{(o)} + 2Cl^-{}_{(aq)} \quad (4)$$

Effect of the dosage of $H_2C_2O_4$: To completely precipitate Co(II) from loaded ALi-SCN, the molar ratio of Co(II) to $H_2C_2O_4$ were changed from 1:1, 1:1.5, and 1:2. Experiments were done at pH 3, 30°C for 60 min. Table 2 shows that the precipitation percentage of Co(II) increased from 96.0 to ~100% with increasing the dosage of $H_2C_2O_4$.

Effect of reaction temperature and time: To save the dosage of Co(II) precipitant, the effect of reaction temperature and time on the precipitation efficiency of Co(II) from the loaded phase was considered while keeping at 1:1.5 molar ratio of Co(II) to $H_2C_2O_4$. First, the temperature was varied from 30 to 80°C for 60 min. The obtained results showed that the precipitation percentage of Co(II) is around 97% in the range of 30-40°C temperature and then lightly reduced to 95% at 80°C (Figure 5). Thus, the increase in the reaction temperature negatively affected the precipitation of Co(II), which was ascribed to the exothermic process of the second step dissociation of oxalic acid into H^+ and $C_2O_4^{2-}$ (Pinching & Bates, 1948; Chen et al., 2016; Nayaka et al., 2016). Then, the effect of reaction time was performed with prolonging from 30 to 90 min at room temperature. As presented in Table 3, Co(II) precipitation is fast and proportional to the time reaction. Namely, the Co(II) precipitation percentage increased from 92 to 97.3% when the time reaction was prolonged from 15 to 60 min and constant with the further time.

Table 2. Effect of mole ratio of Co(II) to oxalic acid on precipitation of Co(II)

$n_{Co}: n_{H_2C_2O_4}$	Precipitation percentage (%)
1:1	96.0
1:1.5	97.3
1:2	99.0

Condition: room temperature, 60 min, $n_{Co}: n_{H_2C_2O_4}$ *= 1:1-1:2; A/O =1*

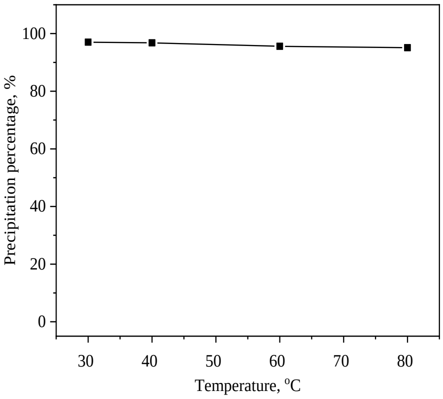

Figure 5. Effect of temperature on precipitation percentage of Co(II) from loaded ALi-SCN phase

(Conditions: [Co(II)] = 500 mg/L; 60 min; temperature = 30-80°C; $n_{Co}: n_{H_2C_2O_4}$ *= 1:1.5; A/O = 1:1)*

Table 3. Effect of reaction time on precipitation percentage of Co(II) from the loaded ALi-SCN phase

Time, min	Precipitation percentage (%)
15	92.0
30	93.9
60	97.3
90	97.5

(Conditions: [Co(II)] = 500 mg/L; temperature = 30°C; $n_{Co}: n_{H_2C_2O_4}$ *= 1:1.5; A/O = 1:1)*

Thus, the best conditions for the precipitation of Co(II) from loaded ALi-SCN were 1:2 ratio of mole ratio of Co(II) to oxalic acid, 1:1 ratio of the organic and aqueous phase, 60 min. of the reaction time, and room temperature. Under the best precipitation conditions, the pink precipitates of cobalt oxalate were obtained at higher than 99.9% purity.

3.2.2. Characteristics of cobalt(II) oxalate precipitate

The analytical methods of SEM, XRD, and FT-IR were measured to verify the morphological and structural characteristics of the precipitates. The crystal structure of the precipitates was determined to be $CoC_2O_4 \cdot 2H_2O$ with a uniform morphology (Figures 6(a)-(c)).

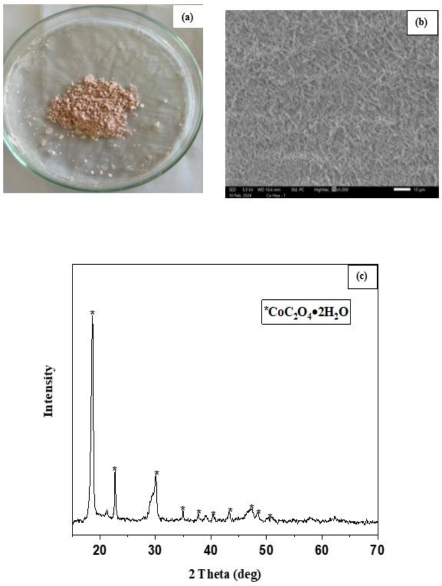

Figure 6. Powders (a), SEM images (b), and XRD pattern (c) of $CoC_2O_4 \cdot 2H_2O$ precipitates

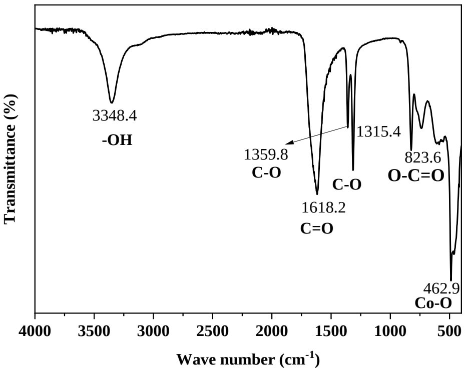

Figure 7. FTIR spectra of $CoC_2O_4 \cdot 2H_2O$ precipitates

Moreover, FT-IR spectra were used to recheck the structure of the $CoC_2O_4 \cdot 2H_2O$, which was recorded in the range of 400 to 4000 cm^{-1}. As presented in Figure 7, the broad peak at 3348.42 cm^{-1} represented the stretching vibration of the hydroxyl group (–OH) which denotes the presence of water in the compound. The absorption peak at 1618.28 cm^{-1} was attributed to the anti-symmetric carbonyl stretching band (C=O) of the $C_2O_4^{2-}$ group (Wei et al., 2018). Two observed peaks at 1359.82 cm^{-1} and 1315.45 cm^{-1} were assigned for vibrations of $C_2O_4^{2-}$ (C–O) + (C–C) and (C–O) + (O–C=O), respectively. The vibration mode of $C_2O_4^{2-}$ with O–C=O bending vibrations was shown in the peak at 819.16 cm^{-1}. The sharp peak at 462.92 cm^{-1} was ascribed to Co–O bonding presented in cobalt oxalate (Mishra et al., 2021).

Thus, our data revealed that the recovery of a pure Co(II) compound from the organic ALi-SCN phase by direct stripping-precipitation was achieved with high performance and purity. Then, cobalt oxalate could be used as a cobalt precursor to produce the cathode material for rechargeable batteries.

3.3. Reuse of organic phase

The ALi-SCN organic phase after removing Co(II) was washed several times with distilled water. The reuse capacity of the organic phase was tested by using the washed organic one for the new cycle of Co(II) extraction from the EG-H_2O solution containing Al(III), Ni(II), and Li(I). The concentration of each metal ion in the EG-H_2O system was 500 mg/L with 0.5 M HCl. The results revealed that Co(II) was fully extracted by reused ALi-SCN of 1st and 2nd reuse, but only 84.43% of Co(II) was that of 3rd reuse. In these experiments, Al(III), Ni(II), and Li(I) were not extracted. The lower extraction of Co(II) after three times the extraction can be attributed to the certain loss of SCN^- ions in the loaded phase after the reuse processes, resulting in a decrease in the complexation of Co(II) extracted to the organic phase. Therefore, the 2nd reuse of ALi-SCN is favorable for selective Co(II) extraction from the EG-H_2O solution in this work. To maintain the complete Co(II) extraction, adding a certain amount of SCN^- anions for regenerating ALi-SCN is necessary.

4. CONCLUSIONS

In this work, the Co(II) recovery process from HCl-EG-H_2O system through two simple steps consists of selectively extracting Co(II) over Ni(II), Al(III), and Li(I) by ALi-SCN and directly precipitating Co(II) from the loaded organic phase by oxalic acid. In extracting Co(II) by ALi-SCN from the HCl-EG-H2O system, control of EG volume fraction was crucial to selectively separate Co(II) and suppress the extraction of Al(III). The predominance of Co(II) species in the extraction process compared to Al(III) ones is also necessary to avoid co-extraction of Al(III). To extract selectively Co(II) from 0.5 M HCl, the best conditions are 0.12 M ALi-SCN, 1:1 A/O ratio, and 50% volume fraction of EG in the aqueous phase (it means the ratio of EG to H_2O = 1:1 (v/v)). Meanwhile, the precipitation of cobalt oxalate is easy and fast at room temperature; mole ratio of Co(II) to oxalic acid is 1:2, A/O ratio of 1, within 60 min. The precipitation efficiency is proportional to the H_2CO_4 mole. After each metal recovery process, the organic phase can be reused for selectively extracting Co(II) over other metal ions in the solution at least twice. The resynthesis of ALi-SCN should be done after the 3rd reuse of the organic phase of the process, consisting of extraction and stripping precipitation in this work. The mass balance of continuous experiments indicated that the purity of $CoC_2O_4 \cdot 2H_2O$ after precipitate from the loaded ALi-SCN phase was higher than 99.9%. Our results provide a deep sense for the selective recovery of Co from leachate containing EG by using solvent extraction with ALi-SCN and followed by direct precipitation of Co(II) with oxalate agent in the solution of pH 3.

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