

# Ion Exchange for the Purification of Co(II) or Ni(II) from Acidic and Ammonia Solutions in the Recycling of Spent Lithium-Ion Batteries

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**Abstract:** The recycling of critical metals like cobalt and nickel from spent lithium-ion batteries (LIBs) is of immense importance in sustainable manufacturing. This work aims to purify Co(II) and Ni(II) present in acidic and ammonia solutions using ion exchange. AG-1-X8 resin modified with thiocyanate anions ( $R_4N^+SCN^-$  resin) was used to separate a small amount of Co(II) from HCl and  $H_2SO_4$  solutions containing Ni(II) and Si(IV) at pH 3, and the effect of factors such as pulp density, shaking time, and Ni(II) concentration on the adsorption of Co(II) was investigated. The difference in the adsorption behaviour of metal ions onto the  $R_4N^+SCN^-$  resin from HCl and  $H_2SO_4$  solutions was insignificant. Increasing the Ni(II) concentration in the feed negatively affected the loading efficiency of Co(II). The complete elution of the metals from the loaded resin was attained with a 5%  $NH_3$  solution. Purolite C100 resin was selected for the purification of Co(II) from a 10% (v/v)  $NH_3$  solution containing a small amount of Ni(II), and the best conditions for the complete adsorption of both Co(II) and Ni(II) were determined. Selective elution of Ni(II) over Co(II) from the loaded resin was achieved by dilute  $H_2SO_4$  solution. The purity of Co(II) in the solution after elution with 2.0 mol/L  $H_2SO_4$  from the Ni(II) free resin was higher than 99.99%. Ion exchange was effective for purifying a weak acidic or ammonia solution in which there is a significant difference in the Co(II) and Ni(II) concentrations.

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**Keywords:** lithium-ion batteries, cobalt, nickel, ion exchange, purification

## 1. INTRODUCTION

The shift from traditional energy resources (e.g., natural gas, oil, and coal) to clean energy systems such as electric vehicles (EVs), solar photovoltaic (PV) plants, and wind farms to reduce global greenhouse gas emissions has resulted in the rapidly growing consumption of critical metals like cobalt, nickel, and lithium in recent years [1-5]. According to an International Energy Agency (IEA) report, the demand for minerals for clean energy technologies could increase by at least four times by 2040, relative to 2020 [5,6]. Currently, a large amount of spent lithium-ion batteries (LIBs) from EVs are being discarded, an amount that could total 464,000 tons in 2025 [7]. Taken together, these spent LIBs contain large

amounts of valuable metals (e.g., Ni: 5-10%, Co: 20%, and Li: 5-7%) [8]. Therefore, finding ways to recover these valuable metals from spent LIBs is a sustainable strategy to address the shortages in critical metals [9,10].

Many processes have been developed for the recycling of spent LIBs, based on pyrometallurgy, hydrometallurgy, and biometallurgy, and their combinations [11-14]. In general, hydrometallurgical routes (e.g., leaching, solvent extraction, ion exchange, or precipitation) are often necessary to recover pure metals or their compounds [15-17]. And it is difficult to find extractants, stripping agents, and precipitants which are selective for target metal ions present in low concentration [18-20]. Therefore, ion exchange is generally employed for the purification of the raffinate or filtrate after solvent extraction or precipitation, so that pure solutions containing the target metal ions can be obtained [16].

In our previous studies, metallic alloys containing Co, Ni, Cu, Mn, Fe, and Si generated from the smelting reduction of

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spent LIBs were leached by HCl or H<sub>2</sub>SO<sub>4</sub> solutions [21,22]. The separation of metal ions from these leachates containing Co(II), Ni(II), Cu(II), Mn(II), Fe(III), and Si(IV) was accomplished using selective extractants and precipitants. In the HCl medium, Fe(III) and Cu(II) ions from the leachate were extracted by D2EHPA and Cyanex 301 and the two metals from the loaded phases were stripped by aqua regia solution. The Co(II) from the raffinate containing Mn(II), Ni(II), and Si(IV) was recovered by extraction with ALi-SCN and subsequent stripping with an NH<sub>3</sub> solution. For the H<sub>2</sub>SO<sub>4</sub> leaching solution, Cu(II) ions were extracted by ALi-Cyanex301 and then stripped by HNO<sub>3</sub> solution. Sequentially, both Fe(III) and Co(II) present in the raffinate containing Mn(II), Ni(II), and Si(IV) were extracted by ALi-SCN. The separation of Co(II) and Fe(III) from the loaded ALi-SCN was achieved with an NH<sub>3</sub> solution as the stripping agent. In this step, both Co(II) and Fe(III) were stripped into the aqueous solution, and Fe(III) ions were precipitated to iron(III) hydroxide because of the solution pH.

In both the HCl and H<sub>2</sub>SO<sub>4</sub> leaching solutions, Mn(II) from the raffinate containing Ni(II) and Si(IV) was selectively precipitated to MnO<sub>2</sub> by adding NaClO solution. Although the purity of Ni(II) in the final raffinate (pH=3) and of Co(II) in the 10% (v/v) NH<sub>3</sub> stripping solution was 99%, a small amount of the other metal ions were still present. Thus, further studies are necessary for the purification of Ni(II) and Co(II) from these solutions.

Few works have reported the purification of Ni(II) or Co(II) from weak acidic and NH<sub>3</sub> solutions by ion exchange. Therefore, the ion exchange behavior of Ni(II), Co(II), and Si(IV) was investigated to obtain pure solutions from the final raffinate and stripping solution of our previous works.

For this purpose, HCl or H<sub>2</sub>SO<sub>4</sub> solutions containing Co(II), Ni(II), and Si(IV) with pH 3 were prepared to simulate the final raffinates after the solvent extraction of Cu(II), Fe(III), and Co(II) from the leaching solutions of spent LIBs. The stripping solution was simulated by a 10% (v/v) NH<sub>3</sub> solution, which was employed to strip Co(II) and Fe(III) from the loaded ALi-SCN. The effect of several variables, such as the nature of the ion exchange resins, the concentration of metal ions, and reaction time, on the separation of the metal ions was investigated. The elution of the metal ions from the loaded resins was also studied. The obtained results provide important information on the recovery of valuable metals with high purity from spent LIBs.

## 2. EXPERIMENTAL

### 2.1 Reagents and Chemicals

For the purification of Ni(II), synthetic Ni(II) solutions were prepared by dissolving sulfate or chloride salts of metals such as CoCl<sub>2</sub>·6H<sub>2</sub>O (Junsei Chemical Co., >99%, Japan), NiCl<sub>2</sub>·6H<sub>2</sub>O (Yakuri Pure Chemicals Co., >99%, Japan), CoSO<sub>4</sub>·7H<sub>2</sub>O (Daejung Chemical & Metals Co., >99%, Korea), NiSO<sub>4</sub>·6H<sub>2</sub>O (Daejung Chemical & Metals Co., >99%, Korea), Na<sub>2</sub>SiO<sub>3</sub> solution (Daejung Chemical & Metals Co., >99%, Korea) in doubly distilled water. Then the solution pH of these aqueous solutions was adjusted to 3 by adding H<sub>2</sub>SO<sub>4</sub> (Daejung Chemical & Metals Co., >95%, Korea) or HCl solution (Daejung Chemical & Metals Co., 35%, Korea). For the purification of Co(II) from the NH<sub>3</sub> solution (Junsei Chemical Co., 28%, Japan) containing Ni(II), the metal chlorides were dissolved in 10% NH<sub>3</sub>

**Table 1.** Physico-chemical characteristics of the ion exchange resins used in this work

Resins	Type	Strength	Crosslink/ Polymer support	Ionic form	Dry mesh size	Moisture retention, %	Wet bead size, μm
AG-1-X8	Anion exchange	Strong	8%	Chloride	100-200	-	106-180
AG-50W-X4	Cation exchange	Strong	4%	Hydrogen	100-200	-	106-250
Diphonix	Chelating ion- exchange	Strong	Styrene- divinylbenzene	Hydrogen	-	60-70	297-707
Purolite C100	Cation exchange	Strong	Styrene- divinylbenzene)	Sodium	-	44-48	300-1200
Dianion <sup>®</sup> WA21J	Anion exchange	Weakly basic porous	Styrene- divinylbenzen	Polyamine - free base	-	40-52	300-1180

solution. All the employed chemicals were of analytical grade.

Commercial ionic exchange resins such as AG-1-X8 resin (Bio-Rad Laboratories, Inc., USA), AG-50W-X (Bio-Rad Laboratories, Inc., USA), Diphonix (Eichrom Industries, France), Purolite C100 (Purolite International Limited, Hounslow, Middlesex, UK), and Dianion WA21J (Sigma-Aldrich company Ltd., USA) were used without any treatment. The physico-chemical characteristics of the ion exchange resins are presented in Table 1.

**Preparation of modified AG-1-X8 resin:** 1.0 g of AG-1-X8 resin was contacted several times with an adequate amount of 2.0 mol/L NaSCN (Daejung Chemical & Metals Co., >98%, Korea) until the resin was saturated. The modified resin with a thiocyanate form ( $R_4N^+SCN^-$ ) was washed with doubly distilled water and then employed in the ion exchange experiments.

### 2.2 Experimental procedures

Batch ion-exchange experiments were performed by putting some amount of the resins into 20 mL of synthetic Ni(II) or Co(II) solution. The samples were shaken in a shaking incubator (HB-201SF, Hanbeak Scientific Co., Korea) for 6 hours (hrs) at room temperature ( $22 \pm 1^\circ\text{C}$ ), except for investigating the effect of shaking time on the loading efficiency of the metal ions by the resins. Shaking speed was controlled at 200 rpm. After filtering the resin with filter paper, the concentration of the metal ions in the solution was measured by Inductively coupled plasma-optical emission spectrometry (ICP-OES, Spectro Arcos, Cleve, Germany) and the concentration of metal ions loaded into the resin was obtained by mass balance. Most of the experiments were performed two times with an error of around  $\pm 5\%$ .

Based on the mass of the metal ions in the aqueous phase

before adsorption  $[M]_i$  and after adsorption  $[M]_{aq}$ , the adsorption percentage (%Ads) of a metal ion was calculated, as:  $\%Ads = \frac{([M]_i - [M]_{aq}) \times 100}{[M]_i}$ . The elution percentage of a metal ion was calculated as:  $\%elution = \frac{[M]_{aq}^* \times 100}{[M]_{resin}}$ , where  $[M]_{resin}$  and  $[M]_{aq}^*$  are the mass of a metal ion in the loaded resin before elution and in the aqueous phase after elution, respectively.

**Determining the loading capacity of a resin:** 1 g resin was consecutively contacted with a fresh solution containing metal ions under a specific condition until the amount of metal ions loaded onto the resin became constant. The loading capacity data was used to determine the Langmuir isotherm constant.

## 3. RESULTS AND DISCUSSION

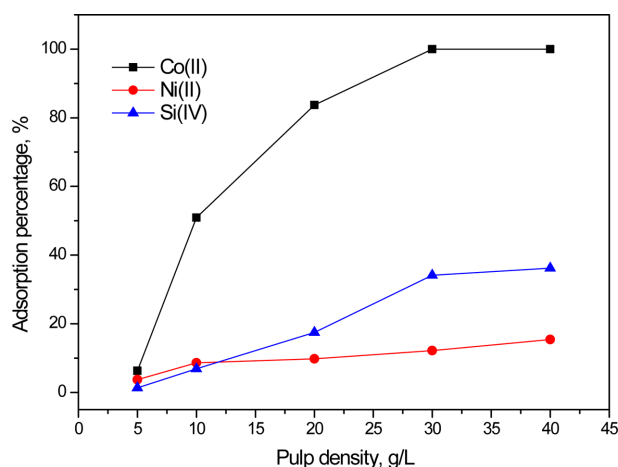
3.1 Purification of Ni(II) from a synthetic acidic solution containing Co(II) and Si(IV)

3.1.1 Effect of pulp density on modified AG-1-X8 resin

The metal ion concentrations in the synthetic pH 3 HCl solution were 1000 mg/L for Ni(II), 30 mg/L Co(II), and 50 mg/L Si(IV). Since Co(II) and Ni(II) ions in HCl solution at low concentration mainly exist as cationic species such as  $Co^{2+}$ ,  $CoCl^+$ ,  $Ni^{2+}$ , and  $NiCl^+$ , it is difficult to separate these two ions using cation exchange resins [23-25]. It is known that Co(II) can form anionic complexes with chloride ions when the concentration of chloride ions is higher than 6 mol/L. The complex formation constants of Co(II) and Ni(II) with chloride and thiocyanate ions are listed in Table 2 [15,25]. This table shows that the thiocyanate ion has a stronger tendency to form anionic complexes with Co(II) than with Ni(II). In order to exploit this difference in complex

**Table 2.** Stability constants of metal complexes with chloride and thiocyanate ions at  $25^\circ\text{C}$  [26,28]

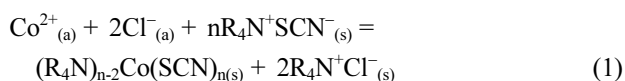
Reaction	logK	Reaction	logK
$Co^{2+} + Cl^- = CoCl^+$	0.22	$Co^{2+} + 3SCN^- = [Co(SCN)_3]^-$	4.0
$Co^{2+} + 2Cl^- = CoCl_2$	-3.95	$Co^{2+} + 4SCN^- = [Co(SCN)_4]^{2-}$	3.9
$Co^{2+} + 3Cl^- = CoCl_3^-$	-3.02	$Ni^{2+} + SCN^- = [NiSCN]^+$	2.2
$Co^{2+} + 4Cl^- = CoCl_4^{2-}$	-9.06	$Ni^{2+} + 2SCN^- = [Ni(SCN)_2]^0$	2.4
$Ni^{2+} + Cl^- = NiCl^+$	-1.29	$Ni^{2+} + 3SCN^- = [Ni(SCN)_3]^-$	2.6
$Co^{2+} + SCN^- = [CoSCN]^+$	2.5	$Ni^{2+} + 4SCN^- = [Ni(SCN)_4]^{2-}$	2.1
$Co^{2+} + 2SCN^- = [Co(SCN)_2]^0$	1.8		



**Fig. 1.** Effect of pulp density of the modified AG-1-X8 resin on the loading of Co(II), Ni(II) and Si(IV). Feed solution: Co(II) = 30 mg/L, Ni(II) = 1,000 mg/L, Si(IV) = 50 mg/L; pH = 3; shaking time = 6 hrs; shaking speed = 200 rpm.

formation tendency, AG-1-X8 resin, an anion exchange in chloride form was selected, and its structure was modified by replacing chloride with thiocyanate ions. With this modification, the thiocyanate ions transferred to the aqueous phase can form anionic complexes with Co(II), which can be selectively loaded into the anion exchange resin.

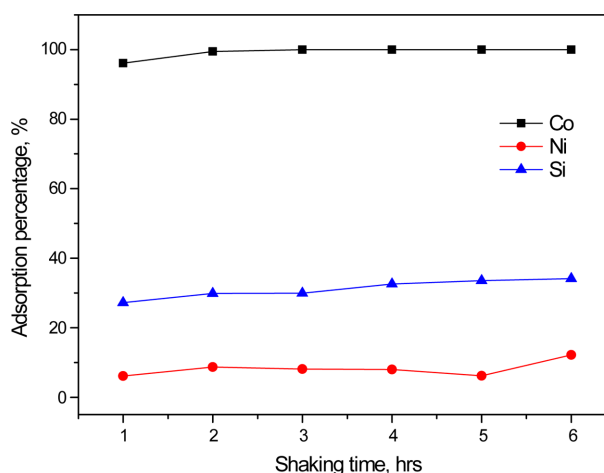
To investigate the effect of the modification of AG-1-X8 resin ( $R_4N^+SCN^-$ ) on the loading, the pulp density of the modified AG-1-X8 resin was varied from 5 to 40 g/L by fixing the reaction time at 6 hrs. In Fig. 1, most of the Co(II) was loaded into the  $R_4N^+SCN^-$  resin at 30 g/L, while the loading percentage of Ni(II) and Si(IV) increased from 3.7 and 1.3% to 15.4 and 36.2%, respectively in the range of the pulp density of the resin. From the obtained results, 30 g/L pulp density of  $R_4N^+SCN^-$  resin was selected for further studies. The selective adsorption of Co(II) into  $R_4N^+SCN^-$  is attributed to the stronger tendency of thiocyanate ions to form complexes with Co(II) than Ni(II) (see Table 2) [26-28]. The loading reaction of Co(II) can be represented as Eq. (1).



where  $R_4N^+SCN^-$  represents the modified AG-1-X8 resin and  $n$  is equal to 3 or 4.

### 3.1.2 Effect of shaking time

The effect of shaking time on the loading of Co(II), Ni(II),

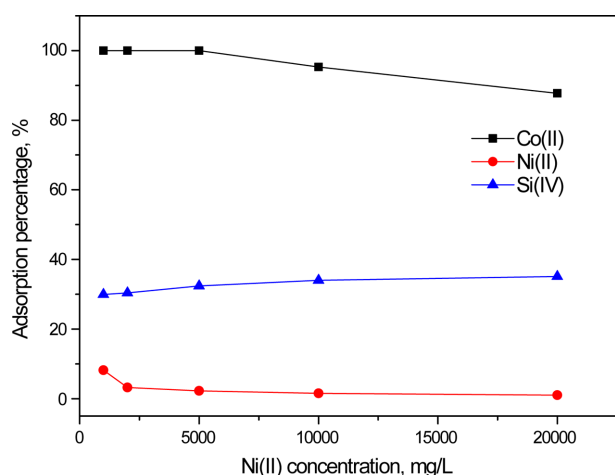


**Fig. 2.** Effect of shaking time on the loading of Co(II), Ni(II), and Si(IV) into the modified AG-1-X8 resin. Feed solution: Co(II) = 30 mg/L, Ni(II) = 1,000 mg/L, Si(IV) = 50 mg/L; pH = 3; pulp density of the resin = 30 g/L; shaking speed = 200 rpm.

and Si(IV) into  $R_4N^+SCN^-$  resin from the HCl solution at pH 3 was investigated by varying the reaction time from 1 to 6 hrs at 30 g/L pulp density and 200 rpm shaking speed. Fig. 2 shows that Co(II) was completely loaded after 3 hrs of shaking time, whereas the loading percentage of others increased from 6.1 to 12.2% for Ni(II) and from 27.2 to 34.1% for Si(IV) as shaking time increased to 6 hrs. These results agree well with the adsorption reaction of Co(II) proposed in Eq. (1), which can be ascribed to the strong affinity between the anionic Co(II) complex and the cations of the resin. Therefore, the reaction time of 3 hrs was chosen as the optimum shaking time for the removal of Co(II) from the solution.

### 3.1.3 Effect of Ni(II) concentration

To consider the effect of Ni(II) concentration on the selective adsorption of Co(II) over Ni(II) and Si(IV) by  $R_4N^+SCN^-$  resin, the concentration of Ni(II) in the pH 3 HCl solution was varied from 1,000 to 20,000 mg/L, while the concentrations of Co(II) and Si(IV) were fixed at 30 and 50 mg/L, respectively. Experiments were conducted at the resin pulp density of 30 g/L for 3 hrs and 200 rpm. As shown in Fig. 3, Co(II) was completely loaded into the resin when Ni(II) concentration was in the range of 1,000 to 5,000 mg/L, and then decreased to 87.7% with a further increase in Ni(II) concentration. Although the adsorption percentage of Ni(II) in the solution decreased from 8.2 to 1.0% with the

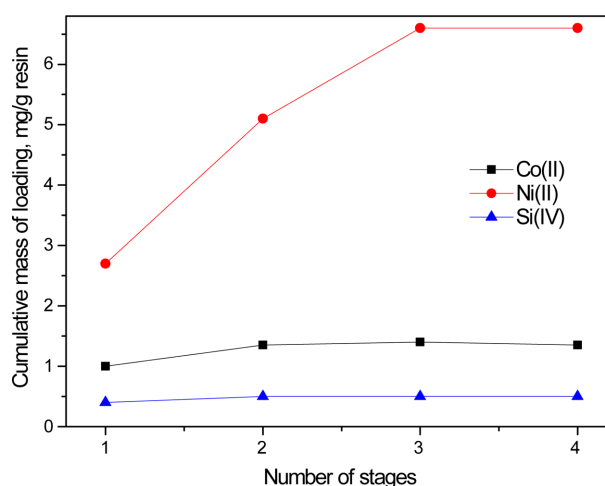


**Fig. 3.** Effect of the concentration of Ni(II) on the selective loading of Co(II) into the modified AG-1-X8 resin. Feed solution: Co(II) = 30 mg/L, Si(IV) = 50 mg/L; pH = 3; pulp density of the resin = 30 g/L; shaking time = 3 hrs, shaking speed = 200 rpm.

increasing Ni(II) concentration, the loaded amount of Ni(II) rose significantly from 82 to 200 mg per 30 g of the resin. Meanwhile, the adsorption percentage of Si(IV) slightly increased from 29.9 to 35.1%. These results indicate that increasing the concentration of Ni(II) in the solution can hinder the selective adsorption of Co(II) into the resin, resulting in a decrease in the adsorption efficiency of Co(II) into the resin. This indicates that it is possible to separate a small amount of Co(II) present in a Ni(II) solution by ion exchange with modified AG-1-X8 resin, and that the optimum conditions for the selective loading of Co(II) depend on the concentration of both Co(II) and Ni(II).

### 3.1.4 Loading capacity of the modified AG-1-X8 resin

The loading capacity of the modified AG-1-X8 resin for Co(II), Ni(II), and Si(IV) was measured by contacting 1 g of  $R_4N^+SCN^-$  with 50 mL of the pH 3 HCl solution containing Co(II) (30 mg/L), Ni(II) (1,000 mg/L), and Si(IV) (50 mg/L) several times, until the amount of metal in the resin became constant. The cumulative amount of metal loaded into the resin was measured by the difference in the concentration of metal in the solution after each stage of contact. Fig. 4 indicates that the cumulative loading of Co(II) increased as the contact stage increased and became constant after three stages. The loading capacity of the  $R_4N^+SCN^-$  resin for Co(II) from the solution was found to be 1.4 mg per g of the



**Fig. 4.** Loading capacity of the modified AG-1-X8 resin for Co(II), Ni(II) and Si(IV). Feed solution: Co(II) = 30 mg/L, Si(IV) = 50 mg/L; pH = 3; shaking time = 3 hrs, shaking speed = 200 rpm.

resin, while that for Ni(II) and Si(IV) was 6.6 and 0.5 mg per g of resin, respectively. This data on the loading capacity can explain the increase in the loading percentage of Ni(II) when the concentration of Ni(II) increased from 1,000 to 20,000 mg/L as shown in Fig. 3.

### 3.1.5 Elution of the metal ions from the modified AG-1-X8 resin

Since Co(II) has a strong tendency to form complexes with  $NH_3$ , Co(II) loaded into  $R_4N^+SCN^-$  resin can be eluted by using  $NH_3$  solution [15]. Therefore, an ammonia solution was employed for the elution of Co(II) from the loaded  $R_4N^+SCN^-$  resin. Firstly, the loaded resin was prepared by contacting the pH 3 synthetic solution with  $R_4N^+SCN^-$  resin at a pulp density of 30 g/L, and a reaction time of 3 hrs. Subsequent elution experiments were conducted with  $NH_3$  solutions. The results revealed that Co(II) and Ni(II) were completely eluted by 5%  $NH_3$  solution within 1 hr, while the elution of Si(IV) was negligible.

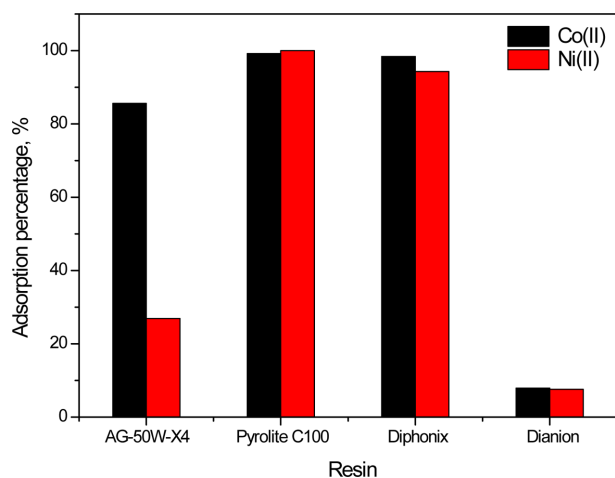
From the obtained results, the most suitable conditions for the purification of 1,000 mg/L Ni(II) from pH 3 HCl solution containing 30 ppm Co(II) and 50 ppm Si(IV) were  $R_4N^+SCN^-$  resin with a 30 g/L of pulp density for 3 hrs. In this condition, the loading percentages of Co(II), Ni(II), and Si(IV) were 100%, 8.1% and 29.9%, respectively. Since there is little difference in the chemical behaviour of these metal ions in pH 3 HCl and  $H_2SO_4$  solutions, these conditions were

also used to test the purification of Ni(II) from H<sub>2</sub>SO<sub>4</sub> solution whose composition was 1,000 mg/L Ni(II), 30 mg/L Co(II), and 50 mg/L Si(IV) at pH 3. Our results showed that the adsorption percentages of Co(II), Ni(II), and Si(IV) were 100, 15.6, and 13.0%, respectively. The elution of metal ions from the loaded resin with the H<sub>2</sub>SO<sub>4</sub> solution was also accomplished using 5% NH<sub>3</sub> solution for 1 hr. These results confirm that the purification of Ni(II) from both HCl and H<sub>2</sub>SO<sub>4</sub> solutions containing a small amount of Co(II) and Si(IV) using R<sub>4</sub>N<sup>+</sup>SCN<sup>-</sup> resin is possible. After the ion exchange, the recovery of Ni(II) from solutions containing Si(IV) can be performed using a precipitation method or electrowinning [29].

### 3.2 Purification of Co(II) from an ammonia solution containing a small amount of Ni(II)

#### 3.2.1 Screening of resins

In ammonia solution, Co(II) and Ni(II) have a strong tendency to form positive complexes with NH<sub>3</sub> such as [Co(NH<sub>3</sub>)<sub>6</sub>]<sup>2+</sup> and [Ni(NH<sub>3</sub>)<sub>6</sub>]<sup>2+</sup>. Hence, cation exchange resins such as AG-50W-X and Purolite C100 were employed to compare their selective adsorption. Other resins like diphonix and dianion WA21J were also employed in this work. The concentrations of Co(II) and Ni(II) in 10% NH<sub>3</sub> solution were adjusted to 1,000 and 30 mg/L, respectively. The pulp density of the resins was kept at 20 g/L, and shaking time and speed were 6 hrs and 200 rpm, respectively.



**Fig. 5.** Comparison on the loading of Co(II) and Ni(II) into cation exchange resins. Feed solution: Co(II) = 1,000 mg/L and Ni(II) = 30 mg/L; pulp density of the resin = 20 g/L; shaking time = 6 hrs; shaking speed = 200 rpm.

Fig. 5 shows that the adsorption percentage of Co(II) and Ni(II) was in the order of Purolite C100 > Diphonix > AG-50W-X4 > Dianion. The adsorption percentage of the metal ions is related to the functional groups of each resin, which resulted in some differences in the interaction between the metal ions and the resins. The loading reaction of Co(II) and Ni(II) onto these cationic resins can be represented as Eq. (2).

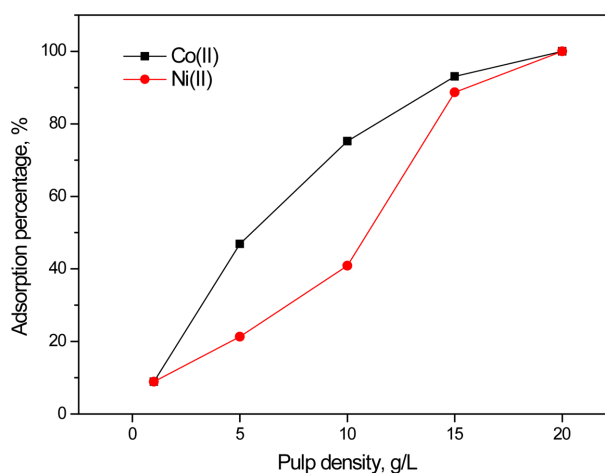


where Me is Co(II) or Ni(II) and R-H represents the cationic resin.

The screening results indicate that the selective adsorption of one metal ion over the other was difficult. Therefore, complete adsorption of both Co(II) and Ni(II) from the solution into the resin, and then the selective elution, was investigated further. In this work, Purolite C100 resin was chosen for the purification of Co(II) from NH<sub>3</sub> solution containing a small amount of Ni(II).

#### 3.2.2 Effect of pulp density of the resin

To investigate the effect of the pulp density of Purolite C100 on the adsorption of Co(II) and Ni(II) from the 10% NH<sub>3</sub> solution, the pulp density of the resin was varied from 1 to 20 g/L. The concentrations of the metals in the solutions were 1,000 mg/L Co(II) and 30 mg/L Ni(II). Experiments

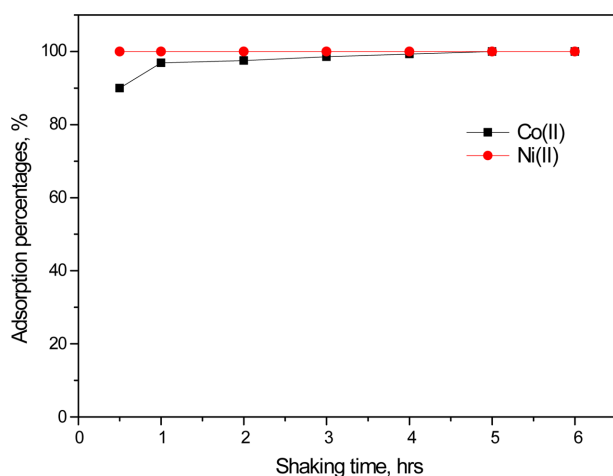


**Fig. 6.** Effect of the pulp density of Purolite C100 resin on the loading of Co(II) and Ni(II) from the 10% NH<sub>3</sub> solution. Feed solution: Co(II) = 1,000 mg/L and Ni(II) = 30 mg/L; shaking time = 6 hrs; shaking speed = 200 rpm.

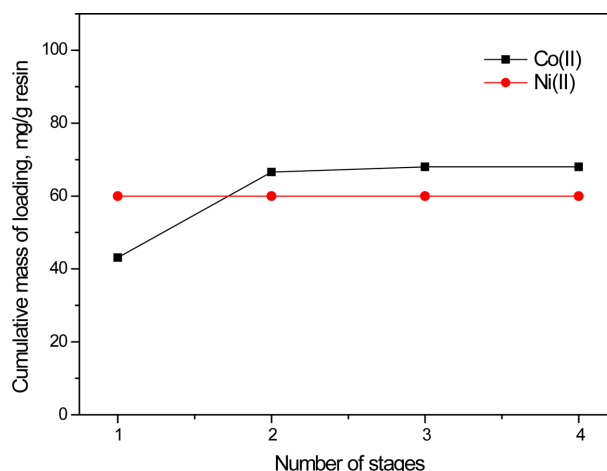
were conducted for 6 hrs and at 200 rpm. As shown in Fig. 6, the adsorption percentages of both Co(II) and Ni(II) gradually increased from 10 to 100% as the resin pulp density increased from 1 to 20 g/L. Excess dosage of the resin was responsible for the sharp increase in the loading of Co(II) and Ni(II) in these experiments. To completely load both metal ions into the resin, 20 g/L pulp density resin was selected for further studies.

### 3.2.3 Effect of shaking time

The effect of shaking time on the loading of Co(II) and Ni(II) from 10% NH<sub>3</sub> solution containing 1,000 mg/L Co (II) and 30 mg/L Ni(II) was investigated by varying shaking times from 0.5 to 6 hrs. The experiments were carried out at a 20 g/L resin pulp density and 200 rpm shaking speed. Fig. 7 indicates that the loading percentage of Co(II) steadily increased from 90 to 100% as the shaking time increased from 0.5 to 5 hrs and then became constant, while that of Ni(II) was complete in the studied range. As presented in Eq. (2), the NH<sub>3</sub> alkaline solution facilitates ion exchange between the hydrogen ions of the Purolite C100 and metal cations. However, ammonium ions generated by the reactions (see Eq. (3)) can compete with metal ions for adsorption onto the resins, and an increase in the shaking time was required to reach equilibrium. Therefore, 5 hrs was selected as the optimum reaction time.



**Fig. 7.** Effect of shaking time on the loading of Co(II) and Ni(II) from 10% NH<sub>3</sub> solution. Feed solution: Co(II) = 1,000 mg/L and Ni(II) = 30 mg/L; pulp density of the Purolite C100 resin = 20 g/L; shaking speed = 200 rpm.



**Fig. 8.** Loading capacity of Purolite resin for Co(II) and Ni(II) from 10% NH<sub>3</sub> solution. Feed solution: Co(II) = 1,000 mg/L and Ni(II) = 30 mg/L; pulp density of Purolite C100 resin = 20 g/L; shaking time = 5 hrs; shaking speed = 200 rpm.

### 3.2.4 Loading capacity of Purolite C100

To determine the loading capacity of Purolite C100 for Co(II) and Ni(II) from 10% NH<sub>3</sub> solution, 1 g of the resin was contacted with 50 mL of the solution containing 1,000 mg/L of Co(II) and 30 mg/L of Ni(II) several times until the amount of the metal ion loaded into the resin became constant. The cumulative amount of metal loaded into the resin was verified by the difference in the concentration of metal ions in the solution after each stage of contact. Fig. 8 shows that the cumulative loading of Co(II) increased as the contact stage increased, and became constant after three stages, while that of Ni(II) steadily increased. The loading capacity of Purolite C100 resin for Co(II) from the solution was found to be 68 mg per g of resin, and that for Ni(II) was 60 mg per g of resin.

### 3.2.5 Elution of Ni(II) and Co(II) from the loaded Purolite C100

#### *Selective elution of Ni(II) over Co(II) from the loaded Purolite C100*

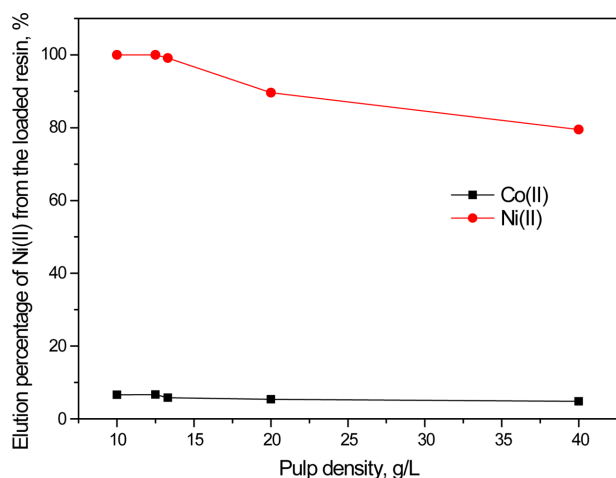
To selectively elute Ni(II) over Co(II) from the loaded Purolite C100, dilute acidic solutions of HCl and H<sub>2</sub>SO<sub>4</sub> were employed. In this work, 0.1 mol/L acid solution was tested with 20 g/L pulp density loaded resin for 2 hrs shaking time and 200 rpm shaking speed. Our results showed that there was little difference in the elution percentage of Co(II) and Ni(II) from the HCl and H<sub>2</sub>SO<sub>4</sub> solutions. Specifically, the

elution percentages of Co(II) and Ni(II) were 5.4 and 89.6% from the H<sub>2</sub>SO<sub>4</sub> solution, and 4.4% and 86.6% from the HCl solution, respectively. These results showed that Ni(II) can be selectively eluted over Co(II) from loaded Purolite C100 by dilute acid solutions. The difference in the interaction strength of the functional groups (sulfonate groups) in the resin with the metal ions could explain the selective elution of Ni(II) over Co(II). The elution reaction of metal ions from the loaded resin by acidic solutions can be written as



Although increasing the acid concentration of the eluting solution can raise the elution of Ni(II) from the resin, it would also increase that of Co(II). Therefore, to completely elute Ni(II) from the loaded resin, 0.1 mol/L H<sub>2</sub>SO<sub>4</sub> solution was selected and the pulp density of the loaded resin was varied from 10 to 40 g/L. Experiments were conducted for 2 hrs shaking time at 200 rpm shaking speed. As presented in Fig. 9, Ni(II) was completely eluted from the loaded resin at the loaded resin pulp density of 12.5 g/L, while the elution percentage of Co(II) was below 6.6% in the studied range.

The effect of shaking time on the complete elution of Ni(II) over Co(II) was also considered, for experimental conditions of 12.5 g/L pulp density of the loaded Purolite C100 with 0.1 mol/L H<sub>2</sub>SO<sub>4</sub>. Our results revealed that the decreasing the shaking time from 2 to 1 hrs led to a decrease in the elution percentage of Ni(II) from the resin, from 100 to 95.2%. Therefore, a shaking time of 2 hrs was selected as the



**Fig. 9.** Effect of the pulp density of the loaded Purolite resin on the elution of Co(II) and Ni(II). Eluant: 0.1 M H<sub>2</sub>SO<sub>4</sub>; shaking time = 2 hrs, shaking speed = 200 rpm.

optimum for the selective elution of Ni(II) over Co(II). Thus, the optimum conditions for the selective elution of Ni(II) over Co(II) from loaded Purolite C100 with 0.1 mol/L H<sub>2</sub>SO<sub>4</sub> solution were a loaded resin pulp density of 12.5 g/L and 2 hrs shaking time.

#### *Elution of Co(II) from Ni(II) free loaded Purolite C100 resin*

To recover Co(II) after the elution of Ni(II) from the loaded Purolite C100, HCl and H<sub>2</sub>SO<sub>4</sub> solutions of 1.0 and 2.0 mol/L were employed with a loaded resin pulp density of 20 g/L for 2 hrs and at 200 rpm. Our results showed that the elution percentage of Co(II) increased from 29.0 to 49.1% for the HCl solution, and 30.5 to 52.8% for the H<sub>2</sub>SO<sub>4</sub> solution, as the acid concentration was increased from 1.0 to 2.0 mol/L. These results indicate that the difference in the elution percentage of Co(II) by HCl and H<sub>2</sub>SO<sub>4</sub> solutions was trivial.

Next, the effects of shaking time (from 2 to 3 hrs) and the pulp density of the loaded resin (from 50 to 20 g/L) on the elution of Co(II) were investigated. Our results revealed that the elution percentage of Co(II) was below 61% and it was difficult to completely elute Co(II) from the resin by varying these factors. Therefore, continuous elution experiments for Co(II) from the loaded resin using 2.0 mol/L acid solutions were conducted using a column. Co(II) was completely recovered after 60 BV and the purity of the eluting solution was higher than 99.99%.

The obtained results indicated that Purolite C100 can be employed in the high purity purification of Co(II) from NH<sub>3</sub> solutions containing a small amount of Ni(II). This process has some advantages, including the recovery of Co(II) solutions with high purity, simple and continuous operation, with two steps for complete adsorption and selective elution, and the regeneration of NH<sub>3</sub> solutions. With these advantages, this process can be employed in real operations for the purification of Co(II) from NH<sub>3</sub> solutions in the presence of Ni(II).

## 4. CONCLUSIONS

This study investigated the use of ion-exchange resins like AG-1-X8 modified with thiocyanate anions, and Purolite C100, for the purification of Ni(II) and Co(II) from synthetic



acidic and ammonia solutions. The effect of parameters such as the pulp density of the resin, Ni(II) concentration, and shaking time on the selective adsorption of Co(II) over others by the modified AG-1-X8 resin was studied. The best conditions for the complete adsorption of Co(II) from solutions containing 1,000 mg/L Ni(II), 30 mg/L Co(II), and 50 g/L Si(IV) were determined to be 30 g/L pulp density and 3 hrs shaking time. Increasing the Ni(II) concentration in the solutions decreased the adsorption efficiency of Co(II). There was little difference in the adsorption behavior of Co(II) into modified AG-1-X8 resin from HCl and H<sub>2</sub>SO<sub>4</sub> solutions. Metal ions from the loaded resin were quantitatively eluted by 5% NH<sub>3</sub> solution.

In the purification of Co(II) from 10% (v/v) NH<sub>3</sub> solution containing a small amount of Ni(II) by Purolite C100 resin, the optimum conditions for the complete adsorption of the two metals were resin pulp density of 20 g/L at a shaking time of 5 hrs. The loading capacity of Purolite C100 for Co(II) and Ni(II) from solution was 68 and 60 mg per g of resin, respectively. Ni(II) was selectively eluted from the loaded Purolite C100 by using 0.1 mol/L H<sub>2</sub>SO<sub>4</sub> solution under conditions of loaded resin pulp density of 12.5 g/L and 2 hrs. The elution of Co(II) from the resin after the selective elution of Ni(II) was achieved by using 2.0 mol/L H<sub>2</sub>SO<sub>4</sub> solution, and the purity of Co(II) in the solution was higher than 99.99%. Thus, ion exchange can be employed to purify Co(II) and Ni(II) from acidic and ammonia solutions, which result from the separation processes of spent LIBs.

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