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Solvent extraction and separation of cobalt from leachate of spent lithium-ion battery cathodes with N263 in nitrite media

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Abstract: To effectively separate and recover Co(II) from the leachate of spent lithium-ion battery cathodes, we investigated solvent extraction with quaternary ammonium salt N263 in the sodium nitrite system. NO_2^- combines with Co(II) to form an anion $[Co(NO_2)_3]^-$, and it is then extracted by N263. The extraction of Co(II) is related to the concentration of NO_2^-. The extraction efficiency of Co(II) reaches the maximum of 99.16%, while the extraction efficiencies of Ni(II), Mn(II), and Li(I) are 9.27%–9.80% under the following conditions: 30vol% of N263 and 15vol% of iso-propyl alcohol in sulfonated kerosene, the volume ratio of the aqueous-to-organic phase is 2:1, the extraction time is 30 min, and 1 M sodium nitrite in 0.1 M HNO_3. The theoretical stages require for the Co(II) extraction are performed in the McCabe–Thiele diagram, and the extraction efficiency of Co(II) reaches more than 99.00% after three-stage counter-current extraction with Co(II) concentration of 2544 mg/L. When the HCl concentration is 1.5 M, the volume ratio of the aqueous-to-organic phase is 1:1, the back-extraction efficiency of Co(II) achieves 91.41%. After five extraction and back-extraction cycles, the Co(II) extraction efficiency can still reach 93.89%. The Co(II) extraction efficiency in the actual leaching solution reaches 100%.

Keywords: cobalt; N263; sodium nitrite; extraction; iso-propyl alcohol; spent lithium-ion battery

1. Introduction

As a transition metal, cobalt has unique properties, including heat resistance, strength, and magnetism. In the early 20th century, cobalt was employed in various alloy, medical, and chemical industries. It is a critical raw material in high-grade pigments, and plays an important role in medical, automotive, and defense applications [1]. With the development of the battery industry, the global cobalt market becomes mainly related to the rechargeable battery industry, which accounts for 58wt% of cobalt consumption. The growth in the battery market is driven by smartphones, laptops, and a range of electronics, as well as the popularity of electric vehicles [2–3]. At present, lithium-ion batteries (LIBs) exhibit advantages such as high energy density, long cycle life, simple charging and maintenance, and environmental friendliness. Meanwhile, lithium-ion batteries are also regarded as the battery of choice for next-generation hybrid electric vehicles (HEVs) and plug-in hybrid electric vehicles (PHEVs) [4–5].

However, the service life of LIBs in small electronic products is almost less than 3 years, while those in electric vehicles last 5–10 years [6–7]. Therefore, high production of lithium-ion batteries is expected. Until 2020, China produced about 5×10^5 t of waste LIBs [8–9]. As a strategic and expensive material, cobalt usually accounts for about 15wt% of LIB cathode materials. However, according to statistics, less than 10wt% of the LIBs used in China's consumer electronics products are recycled, and LIBs are usually idle or buried [10]. In addition, accumulating large amounts of cobalt is a critical challenge to environmental issues. Therefore, Co(II) recovery from LIB materials for resource utilization are economically and environmentally beneficial. However, the existing technology still faces practical problems [2].

Most of the recyclable value of waste batteries is in cathode materials. Several methods for treating waste Li have been proposed, including pyrometallurgy, bio-metallurgy, and hydrometallurgy [11–12]. In pyrometallurgy, acetylene black, organic electrolytes, and binder are usually completely burned to facilitate metal leaching, which requires high energy consumption. The treatment cycle in the bio-metallurgical process needs a long time, and it is difficult to cultivate the required bacteria [13–14]. In hydrometallurgy,

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✉ Corresponding author: Chunlin He E-mail: helink1900@126.com electrodes are removed after a series of mechanical pretreatments and then dissolved in acid [15–16]. Afterward, the metals are separated and recovered by extraction [17], adsorption [18], and co-precipitation [11] in the solution. Therefore, hydrometallurgical processes have the advantages of high efficiency and energy saving and can provide better metal recovery [19].

Solvent extraction exhibits high efficiency, easy back-extraction, convenient operation, and low energy consumption. Nowadays, solvent extraction for separating and recovering Co(II) is an attractive research topic. The commonly used extractants are phosphonic acids and amines (Cyanex 301 [20], TOA [21], Aliquat 336 [22]). Several researchers have reported that Co(II) reacts with Cl^- (introduced via hydrochloric acid) to form $[CoCl_4]^{2-}$ anion complexes and then is recovered with Aliquat 336 [23]. However, the extraction by introducing Cl^-, which is generally performed in chloride media, exhibits some limitations. For instance, the addition of Cl^- via hydrochloric acid greatly increases the concentration of acid in the solution and the corrosive effect on the equipment is also increased. The extractant (N263) is usually used to separate Co(II) and Ni(II) in the Cl^- system [24]. However, other metals, such as Mn(II), also tend to form complex anions with Cl^- [25], yielding competitive extraction. Therefore, there is a need to find highly selective and efficient separation systems to improve the extraction efficiency of Co(II) from leachate of spent LIB cathodes under milder acidic conditions.

In addition, it was reported that Co(II) could efficiently complex with nitrite to form anionic complexes [26]. However, nitrite-assisted Co(II) extraction has been scarcely reported. In our work, ascorbic acid and nitric acid were employed as co-leaching reagents [27]. Due to the reduction potential of ascorbic acid, nitrate ions in the solution are reduced to nitrite ions to enhance the extraction efficiency of Co(II). We used the quaternary ammonium extractant N263 to effectively separate and recover Co(II) ions from the Li-ion battery cathode materials by leaching solution under low-acidic conditions, expecting to establish a suitable process to selectively recover Co(II) and avoid effects of Ni(II), Mn(II), and Li(I). The effects of the sodium nitrite concentration, H^+ concentration, modifier type, extractant concentration, phase ratio, contact time, and temperature on the Co(II) extraction were investigated, and the extraction mechanism was revealed.

2. Experimental

2.1. Materials

The extractant was methyl trioctyl ammonium chloride (N263; 97% purity); Besides, we used the following chemicals: nitric acid (HNO_3; analytical grade purity), ascorbic acid ($C_6H_8O_6$; purity ≥99.7%, Guangdong Guanghua Sci-Tech Co., Ltd., China), sodium nitrite ($NaNO_2$; 99%), Co(II) nitrate hexahydrate ($Co(NO_3)_2\cdot 6H_2O$; 98.5%), Ni(II) nitrate hexahydrate ($Ni(NO_3)_2\cdot 6H_2O$; 98%), Mn(II) nitrate hexahydrate ($Mn(NO_3)_2\cdot 6H_2O$; 98%), and Li(I) nitrate ($LiNO_3$; 99%). The third-phase modifier iso-propyl alcohol (≥99.7%) and the sulfonated kerosene were supplied by Shanghai Maclin Biochemical Technology Co., Ltd., China. Other analytical grade organic reagents were used in this work without further purification. Spent LIB packs used in buses were obtained from the Shanghai Momiji New Energy Technology Co., Ltd., China.

The battery material was first disassembled, cleaned, and dried, and the electrode powder was collected to obtain the actual leaching composition by the experimental leaching method of Chen *et al.* [27], as shown in Table 1. The leached solution was used directly in the experiments exploring Co(II) extraction from the actual solution. Also, the composition of the aqueous solution in the extraction experiment was prepared using nitrate, and the concentration of metal ions in the aqueous solution was 0.5 and 0.8 g/L.

Table 1. Composition of the real leaching solution mg/L

Li	Mn	Co	Ni
1163	3534	2493	6450

2.2. Methods

The organic phase was composed of N263/modifier/sulfonated kerosene. Solvent extraction and separation experiments were performed in a thermostated shaking box. The type of extractants and modifiers, the acid concentration (0.01 to 0.4 M), the concentration of sodium nitrite (0 to 6 M), extraction time (5 to 90 min), and extraction temperature (25, 30, 35, 40, and 45°C) were investigated. Also, the relationship among the three N263/modifier/sulfonated kerosene ratios was investigated. To explore the separation of Co(II) from the actual leachate solution, we used the following leaching conditions: 0.5 M ascorbic acid and 0.5 M HNO_3; the solid/liquid (S/L) was 20 g/L at 70°C for 1 h [27]. The phases were left to stand in the separation funnel for 10 min after extraction, and the extracted organic phases (30vol% N263 and 15vol% iso-propyl alcohol in sulfonated kerosene, $[Co^{2+}] = 0.8$ g/L, 1 M $NaNO_2$, the volume ratio of the aqueous-to-organic phase (A/O) = 2:1, extraction time (t) = 30 min, temperature (T) = 25°C, and $[HNO_3] = 0.1$ M) were collected for the next back-extraction experiments. In the back-extraction experiments, various back-extraction agents, such as NaCl, NH_4Cl, NaOH, NH_3H_2O, H_2O, HNO_3, H_2SO_4, and HCl, were used for the back-extraction of Co(II). The effects of the concentration (0.5 to 2.5 M), equilibration temperature (25, 30, 35, 40, and 45°C), and equilibration time (5 to 60 min) of back-extraction agents on back-extraction efficiency, were also explored to determine the best back-extraction conditions.

After the phase separation, the aqueous phase was collected and diluted with 0.1 M HNO_3 to prevent the precipitation of metal ions by hydrolysis under low acidic conditions and the introduction of impurity ions. At the same time, the ion concentration in the organic phase was calculated by the mass balance method. The inductively coupled plasma-atomic emission spectrometry (ICP-AES) measurement method was used to investigate the concentration of metal ions. The experimental results were calculated using Eqs. (1)–(5):

$$D = \frac{C_{\text{org}}}{C_{\text{aq}}} \times \frac{V_{\text{aq}}}{V_{\text{org}}} \tag{1}$$

$$E = \frac{D}{D + (V_{\text{aq}}/V_{\text{org}})} \times 100\% \tag{2}$$

$$S = \frac{M'_{\text{aq}}}{M'_{\text{org}}} \times 100\% \tag{3}$$

$$Q = C_{\text{org}} \times \frac{V_{\text{aq}}}{V_{\text{org}}} \tag{4}$$

$$\beta_{1/2} = \frac{D_1}{D_2} \tag{5}$$

where D, E, S, Q, and $\beta_{1/2}$ are the distribution ratio, the extraction efficiency, the back-extraction efficiency, the extraction capacity, and the extraction separation coefficient of the two metals, respectively. C_{org} (mg/L) and C_{aq} (mg/L) represent the metal ion concentrations obtained in the loaded organic and loaded aqueous solution, respectively. V_{org} (L) and V_{aq} (L) represent the volume of the loaded organic and loaded aqueous phases, respectively. M'_{org} (g) and M'_{aq} (g) denote the mass of loaded organic and aqueous phase metal ions, respectively.

2.3. Characterization

The extraction mechanism of Co(II) with N263 was investigated using a Fourier transform infrared spectrometer (FT-IR racer 100, Shimadzu, Japan), and the formation of metals in solution was analyzed using an ultraviolet absorption spectrometer (UV 3600Plus, Japan). The concentration of metal ions in the solution was analyzed by an ICP-AES (ICPS-7510, Shimadzu, Japan) instrument. X-ray photoelectron spectroscopy (XPS) measurements were performed on 0.5 g of dried potassium bromide (KBr) with a drop of organic phase using an ESCALAB 250XI spectrophotometer (Thermos Fisher Scientific, USA).

3. Results and discussion

3.1. Solvent extraction

3.1.1. Effect of extractants and modifiers

The extraction of Co(II) with primary amine salt (N1923), tertiary amine salt (N235) [28], and quaternary ammonium salt (N263) [22] is shown in Fig. 1(a). The effect of the modifier type (iso-octanol, iso-propyl, and sec-octanol) on the extraction of Co(II), Ni(II), Mn(II), and Li(I) is shown in Fig. 1(b). As demonstrated in Fig. 1(a), the extraction efficiency of Co(II) with N263 reaches 83.34%, which is higher than those with N1923 and N235. Compared with N1923 and N235, N263 can bind many anionic complexes, exhibiting a stronger extraction ability of Co(II). Fig. 1(b) indicates that the extraction of Co(II) with iso-propyl alcohol is more efficient than with sec-octanol and iso-octanol. In addition, the extraction efficiency of Co(II) without a modifier is 63.50%, but the extraction of Co(II) is significantly improved in the presence of a modifier. Also, the extraction efficiencies of Ni(II), Mn(II), and Li(I) are about 10.00%. The extractant N263 cannot be completely dissolved in kerosene without modifier due to its high viscosity and poor mobility, which affects the combination of N263 and solution complex anions (Fig. S1). The results show that the modifier can better dissolve N263 in kerosene and increase the solubility and the extraction efficiency of Co(II). The addition of iso-propyl alcohol enables the dissolution of N263 in the diluent and prevents the generation of the third phase with a higher completion degree of the extraction reaction. Therefore, the addition of iso-propyl alcohol efficiently separates Co(II).

3.1.2. Effect of the sodium nitrite concentration

The effects of $NaNO_2$ concentration on the extraction efficiencies of Co(II), Ni(II), Mn(II), and Li(I) and on the pH in the Co(II) solution are presented in Fig. 2. The results show that the extraction efficiency of Co(II) is affected by the change in the $NaNO_2$ concentration, and the extraction efficiency of Co(II) reaches 77.76% with the addition of 1 M $NaNO_2$. As the $NaNO_2$ concentration further increases, the Co(II) extraction efficiency decreases, possibly due to the re-

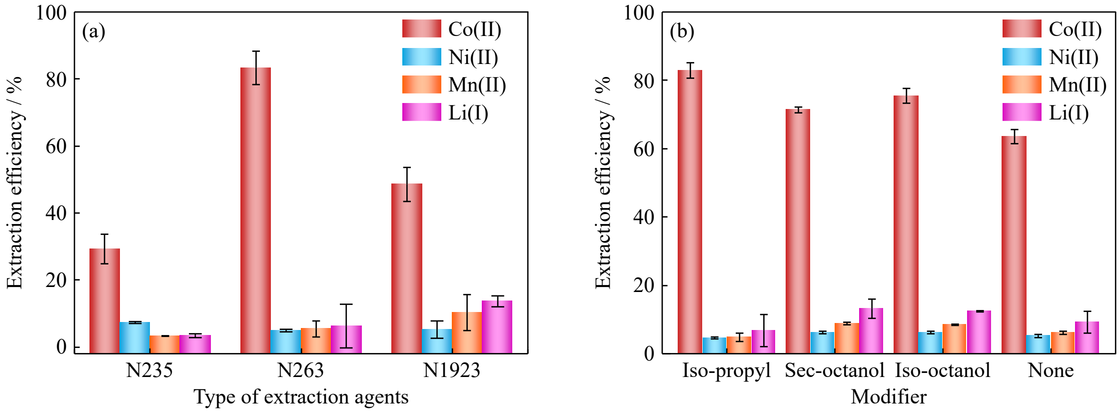


Fig. 1. Effect of different extractants and modifiers on the extraction of Co(II), Ni(II), Mn(II), and Li(I): (a) effect of N235, N1923, and N263; (b) effect of modifiers (iso-propyl alcohol, sec-octanol, and iso-octanol) (conditions: 20vol% N263, 10vol% iso-propyl in sulfonated kerosene, 1 M $NaNO_2$, A/O = 10:1, t = 1 h, T = 25°C, [HNO_3] = 0.1 M, and [Co^{2+}] = 0.5 g/L).

straining of the high nitrite concentration on ion exchange [26,29]. However, the extraction efficiencies of Ni(II), Mn(II), and Li(I) continue to rise with the $NaNO_2$ concentration increasing. In addition, excess $NaNO_2$ consumes more hydrogen ions, changing the solution pH. For instance, the pH value is 4.5 and 5.3 at a $NaNO_2$ concentration of 1 and 6 M, respectively. To prevent metal precipitation, it is important to control the quantity of $NaNO_2$. Therefore, according to the complexation ability of metal ions with nitrite, Co(II) has a strong extraction ability and reaches the maximum value at a $NaNO_2$ concentration of 1 M. Based on this, the subsequent tests were carried out with 1 M $NaNO_2$.

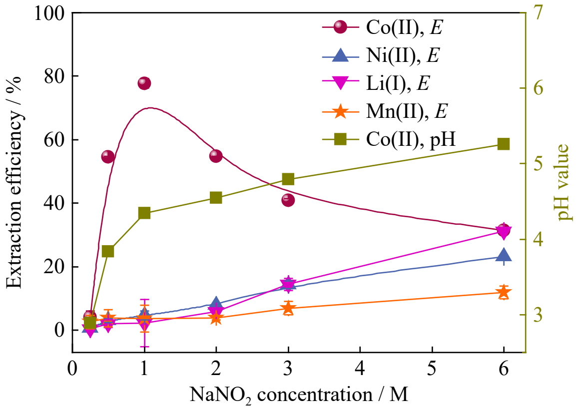


Fig. 2. Effect of the $NaNO_2$ concentration on the extraction efficiency (*E*) and pH value (conditions: 20vol% N263, 10vol% iso-propyl in sulfonated kerosene, A/O = 10:1, *t* = 1 h, *T* = 25°C, $[HNO_3]$ = 0.1 M, and $[Co^{2+}]$ = 0.5 g/L).

3.1.3. Effect of acidity

Fig. 3(a) illustrate the effect of different acid concentrations on the extraction efficiency of Co(II), and Fig. 3(b) describe the extraction of Co(II), Ni(II), Mn(II), and Li(I) by the change in solution pH after the addition of $NaNO_2$ in the HNO_3 system. Fig. 3(a) depicts that the Co(II) extraction efficiency exhibits a downward trend with the acid concentration increasing. Therefore, high acidity is not favorable for the extraction of Co(II), and there is only little effect of the type of acids on it. In highly acidic solution, $NaNO_2$ would react with hydrogen ions to produce NO_2 and NO, as shown in Eq. (6):

$$2NO_2^- + 2H^+ = NO_2\uparrow + NO\uparrow + H_2O \quad (6)$$

Fig. 3(b) shows the pH value and the extraction of Co(II), Ni(II), Mn(II), and Li(I) at different concentrations of HNO_3 with 1 M sodium nitrite. In the 0.01 M HNO_3 solution, 98.63% of Co(II) can be extracted, and the pH value approaches 5.5. However, 0.1 M HNO_3 was chosen to conduct the experiment to avoid the hydrolysis of metals.

3.1.4. Effect of the N263 and iso-propyl alcohol ratio

To investigate the optimal relationship between N263 and iso-propyl, Fig. 4 indicates that the extraction efficiency of Co(II) increases with the proportion of N263 and reaches a balance of about 84.25% at a volume ratio of 1.5:1. Therefore, an N263 and iso-propyl alcohol ratio of 1.5:1 was chosen for subsequent experiments.

3.1.5. Effect of the N263 concentration

Fig. 5 presents the extraction efficiencies of Co(II), Ni(II), Mn(II), and Li(I) as a function of the N263 concentration. The extraction efficiency of Co(II) increases with the N263 concentration increasing from 10vol% to 50vol%, as shown in Fig. 5. The extraction efficiency achieves equilibrium when the N263 concentration reaches 30vol%. It also exhibit good selectivity for extracting Co(II) from Co(II), Ni(II), Mn(II), and Li(I). The pure extractant (N263) is pale yellow solid with a certain viscosity (viscosity is negatively correlated to mobility). Therefore, the higher the concentration of N263, the higher the viscosity, resulting in poorer contact properties between the organic and aqueous phases, which affects the extraction efficiency [30]. Considering the extraction of Co(II) and the extractant cost in detail, 30vol% N263 was selected as the optimal extraction condition in this work.

3.1.6. Effect of the phase ratio

To investigate the separation effect of Co(II), Fig. 6 shows the effect of the A/O ratio. Fig. 6 illustrates that the extraction efficiency of Co(II) increases with the A/O ratio decreasing from 10:1 to 2:1. When the A/O ratio is 2:1, the extraction efficiency of Co(II) reaches the maximum of 99.16%, while the extraction efficiencies of Ni(II), Mn(II), and Li(I) is 9.27%–9.80%. A higher amount of the organic

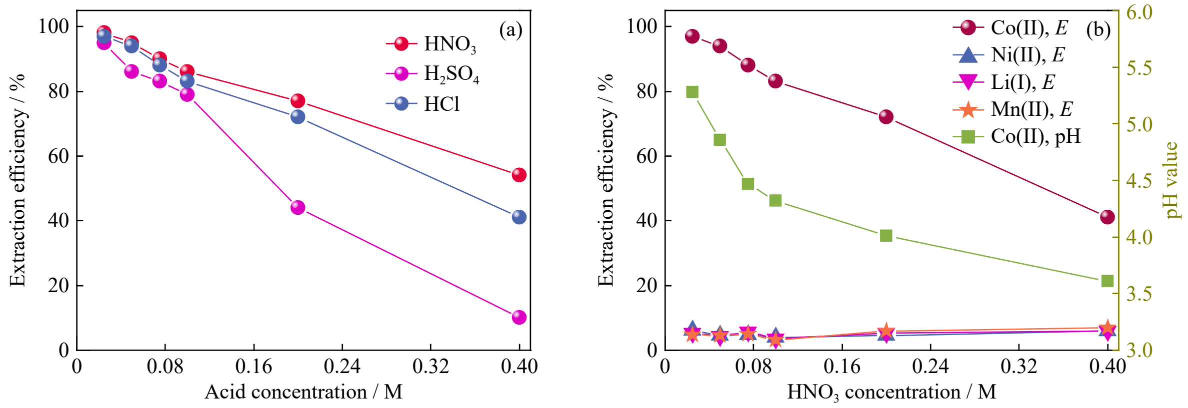


Fig. 3. (a) Effect of the acid concentration on the Co(II) extraction; (b) effect of the HNO_3 concentration on the extraction of Co(II), Ni(II), Mn(II), and Li(I) and pH in the HNO_3 system (conditions: 20vol% N263, 10vol% iso-propyl alcohol in sulfonated kerosene, 1 M sodium nitrite, A/O = 10:1, *t* = 1 h, *T* = 25°C, and $[Co^{2+}]$ = 0.5 g/L).

phase could yield a higher extraction and separation efficiency of Co(II) but may lead to inappropriate usage and waste of the organic phase. Therefore, an A/O ratio of 2:1 was used in subsequent experiments considering the economic cost of the extractant.

3.1.7. Effect of the extraction time

Fig. 7 shows the extraction kinetics, and the results indicate that when the extraction time increases from 5 to 15 min, the Co(II) extraction efficiency increases from 93.75% to 99.18%, which shows that the extraction equilibrium time is 15 min. The extraction efficiencies of Ni(II), Mn(II), and Li(I) are less than 7.12% over the whole investigated time range. Therefore, the optimum separation of Co(II) is achieved at 15 min. However, to reach an adequate contact time, we fixed the extraction time to 30 min in all experiments.

3.1.8. Effect of the extraction temperature

The effect of temperature on the extraction efficiency of metal ions is shown in Fig. 8. As temperature increases, the extraction efficiency of Co(II) decreases. This may occur due to the partial transformation of NO_2^- to NO_2 and NO at high temperature, which are then released in the air, yielding a lower concentration of NO_2^- in solution. Moreover, the ex-

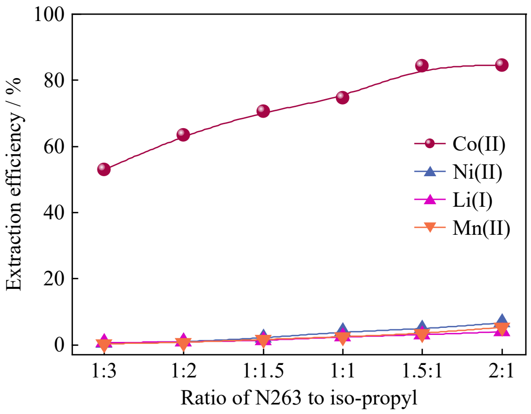


Fig. 4. Effect of the N263 and iso-propyl alcohol ratio on the extraction efficiencies of Co(II), Ni(II), Mn(II), and Li(I) (conditions: 20vol% N263, 10vol% iso-propyl alcohol in sulfonated kerosene, 1 M $NaNO_2$, A/O = 10:1, t = 1 h, T = 25°C, [HNO_3] = 0.1 M, and [Co^{2+}] = 0.8 g/L).

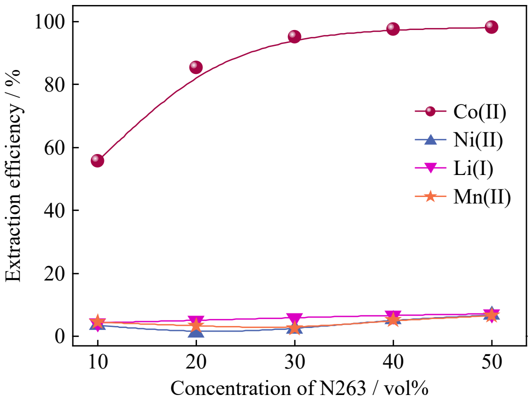


Fig. 5. Extraction efficiencies of Co(II), Ni(II), Mn(II), and Li(I) versus the N263 concentration (conditions: the organic phase contains N263, iso-propyl alcohol, and sulfonated kerosene, 1 M $NaNO_2$, A/O = 10:1, t = 1 h, T = 25°C, [HNO_3] = 0.1 M, and [Co^{2+}] = 0.8 g/L).

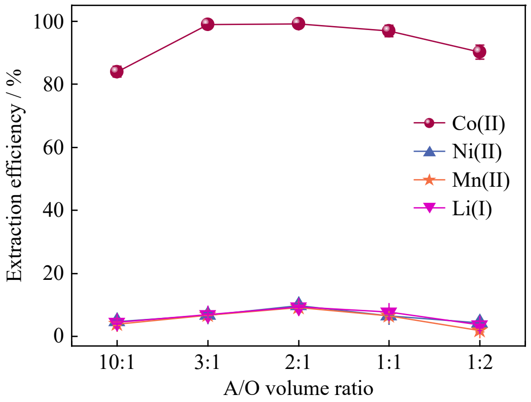


Fig. 6. Effect of the aqueous-to-organic phase (A/O) volume ratio on the extraction efficiencies of Co(II), Ni(II), Mn(II), and Li(I) (conditions: 30vol% N263, 15vol% iso-propyl alcohol in sulfonated kerosene, 1 M $NaNO_2$, t = 1 h, T = 25°C, [HNO_3] = 0.1 M, and [Co^{2+}] = 0.8 g/L).

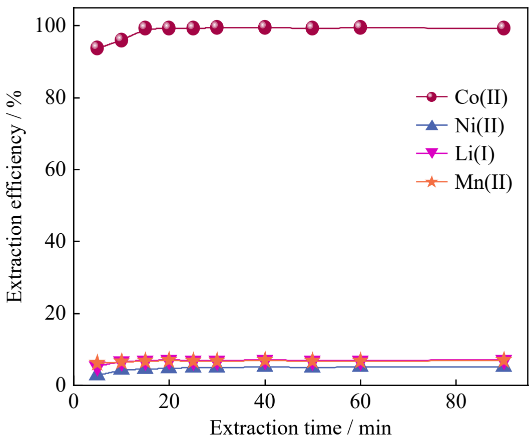


Fig. 7. Effect of the extraction time on the extraction efficiencies of Co(II), Ni(II), Mn(II), and Li(I) (conditions: 30vol% N263 and 15vol% iso-propyl alcohol in sulfonated kerosene, 1 M sodium nitrite, A/O = 2:1, T = 25°C, [HNO_3] = 0.1 M, and [Co^{2+}] = 0.8 g/L).

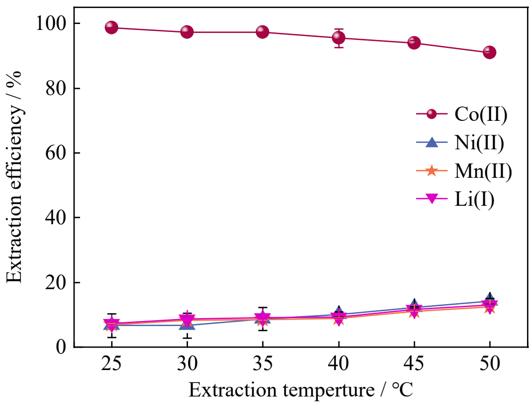


Fig. 8. Effect of the extraction temperature (conditions: 30vol% N263 and 15vol% iso-propyl alcohol in sulfonated kerosene, 1 M $NaNO_2$, t = 30 min, A/O = 2:1, [HNO_3] = 0.1 M, and [Co^{2+}] = 0.8 g/L).

traction efficiencies of Ni(II), Mn(II), and Li(I) continue to rise because Ni(II), Mn(II), and Li(I) interact with NO_2^- relatively little at the initial temperature (25°C). As the temperature increases, the viscosity and surface tension decrease while the diffusion increases, enhancing the binding between metal ions and NO_2^- and slightly improving the extraction efficiency [31–32]. However, the Co(II) extraction efficiency decreases with temperature in our study, while the extraction efficiencies of Ni(II), Mn(II), and Li(I) increase, resulting in the highest separation coefficients of cobalt and other metals at 25°C. The $\beta_{\text{(Co/Li)}}$, $\beta_{\text{(Co/Mn)}}$, and $\beta_{\text{(Co/Ni)}}$ separation coefficients reach 1140.95, 1171.70, and 1547.31, respectively (Table S1). To ensure efficient Co(II) separation, we performed experiments at room temperature.

3.1.9. Effect of the high concentrations of Co(II)

The relationship between the $NaNO_2$ concentration and the extraction capacity of Co(II) is shown in Fig. 9. When the concentration of Co(II) is below 3000 mg/L, the extraction capacity firstly increases with the $NaNO_2$ concentration increasing from 0.25 to 1 M and then decreases, exhibiting the highest value at the $NaNO_2$ concentration of 1 M. When the Co(II) concentration is 4000 and 5000 mg/L and the $NaNO_2$ concentration exceeds 2 M, the extraction capacity of Co(II) reaches an equilibrium. The extraction capacity of Co(II) further increases when the Co(II) concentration is higher than 5000 mg/L and the $NaNO_2$ concentration exceeds 1 M. More cobalt ions require more nitrite ions to form a complex, which is more conducive to extraction. It can be concluded that the concentration of $NaNO_2$ needs to be adjusted according to the concentration of Co(II).

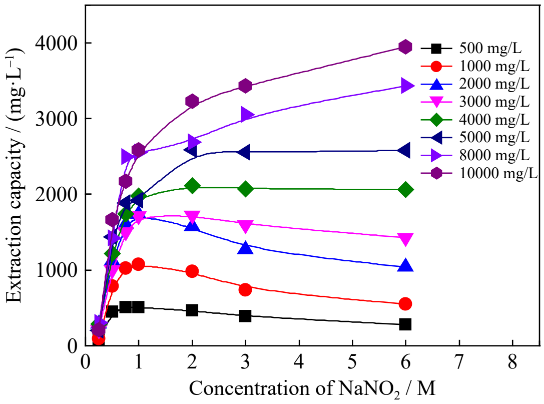


Fig. 9. Effect of the $NaNO_2$ concentration on the extraction capacity of Co(II) for different Co(II) concentrations (conditions: 30vol% N263 and 15vol% iso-propyl alcohol in sulfonated kerosene, A/O = 10/1, 1 M $NaNO_2$, t = 30 min, T = 25°C, and $[HNO_3]$ = 0.1 M).

3.2. Back-extraction tests

Fig. 10(a) presents the effect of the back-extractant type on Co(II) back-extraction, and Fig. 10(b) shows the effect of the HCl concentration on the back-extraction efficiency of Co(II). The effects of temperature and time are shown in Fig. 10(c) and Fig. 10(d), respectively.

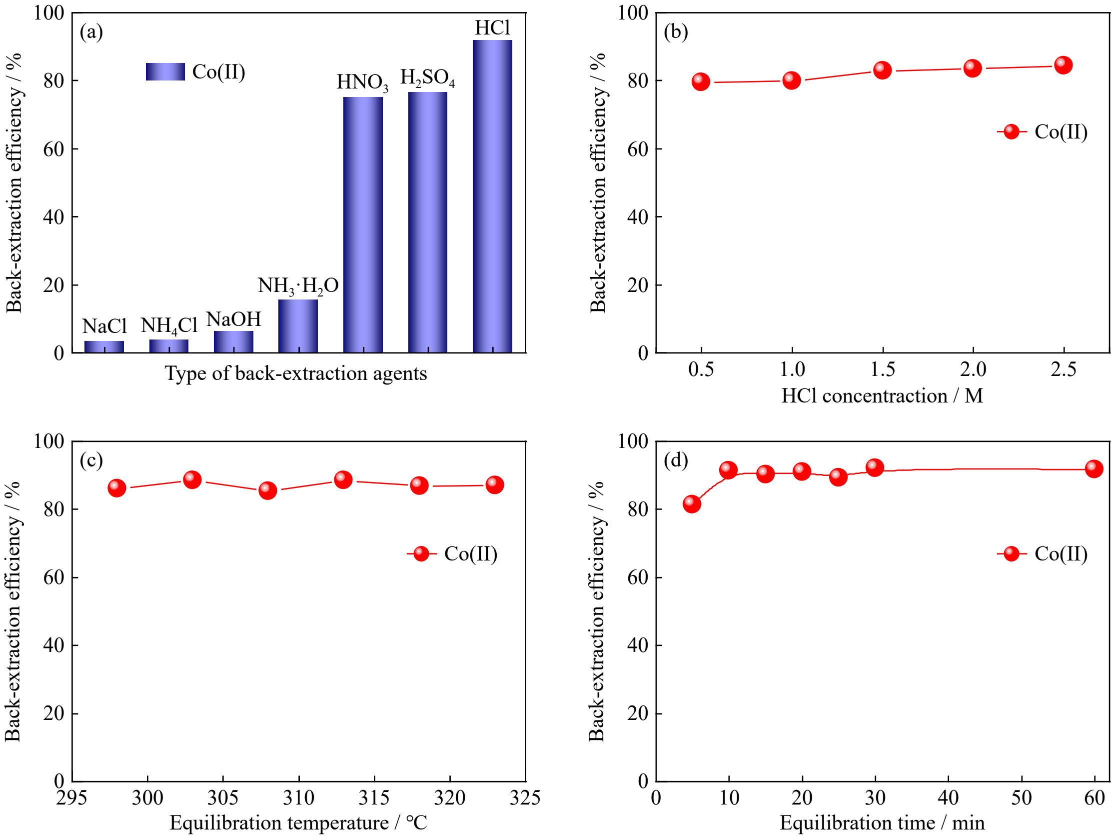


Fig. 10. Effects of various parameters on the Co(II) back-extraction efficiency: (a) comparison of seven back-extraction agents; (b) HCl concentration (as a back-extraction agent); (c) equilibration temperature, (d) equilibration time (conditions: $[Co^{2+}]_{org}$ = 0.8 g/L, [HCl] = 1.5 M, A/O = 1:1, t = 30 min, and T = 25°C).

Fig. 10(a) indicates that the optimal back-extraction efficiency of Co(II) from the loaded organic phase is in the presence of HCl at a concentration of 1.5 M. Under acidic conditions, Cl^- can more efficiently exchange with Co(II) complex anions ($(Co(NO_2)_n^{2-n}$) compared to NO_3^- and SO_4^{2-}, as shown in Eq. (7):

$$R_4N^+ \cdot Co(NO_2)_n^{2-n} + Cl^- = Co^{2+} + nNO_2^- + R_4NCl \tag{7}$$

Furthermore, HCl is convenient due to its many available sources and moderate price, and it largely prevents the hydrolysis of metal ions under acidic conditions. Therefore, the subsequent back-extraction experiments were performed with HCl as a back-extraction agent. The back-extraction efficiency of Co(II) increases slowly with the HCl concentration, as shown in Fig. 10(b), indicating that the HCl concentration has little effect on the back-extraction efficiency. Considering the obtained data on the back-extraction efficiency of Co(II) and ecological aspects, 1.5 M HCl was selected as the appropriate back-extraction agent concentration. The back-extraction efficiency of Co(II) remains unchanged with the temperature, as shown in Fig. 10(c), so the back-extraction process is performed at room temperature. Fig. 10(d) shows that 91.41% of Co(II) is stripped in 10 min, indicating that the back-extraction of Co(II) exhibits fast kinetics.

3.3. Extractant reusability

Extractant reusability is shown in Fig. 11. The organic phase was obtained after back-extraction with 1.5 M HCl. After five extraction and back-extraction cycles, the extraction efficiency of the organic phase decrease only by 3.80%, and the extraction efficiency of the organic phase still reach 93.89%, indicating that the extracted organic phase shows good reusability and can be recycled many times.

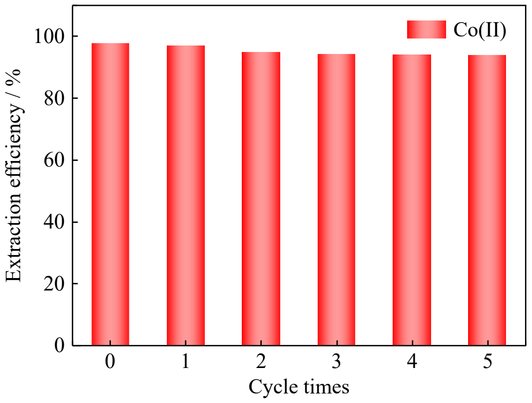


Fig. 11. Recycling of extractants (conditions: $[Co^{2+}]$ = 2 g/L; back-extraction agent, 1.5 M HCl; A/O = 1:1; t = 30 min).

3.4. Analysis of the extraction mechanism

3.4.1. Composition of cobalt complexes

The plot of lg$D$ vs. lg[N263] is illustrated in Fig. 12. The extraction is performed at a Co(II) concentration of 2 and 3 g/L, an extractant amount of 0.04, 0.1, 0.14, 0.2, 0.3, and 0.4 mL), and the A/O ratio of 10:1.

In the nitrite solution, Co(II) easily forms an anion complex with NO_2^- and performs ion exchange with N263. The complex formation and reactions of Co(II) in the nitrite medium can be expressed as follows [26]:

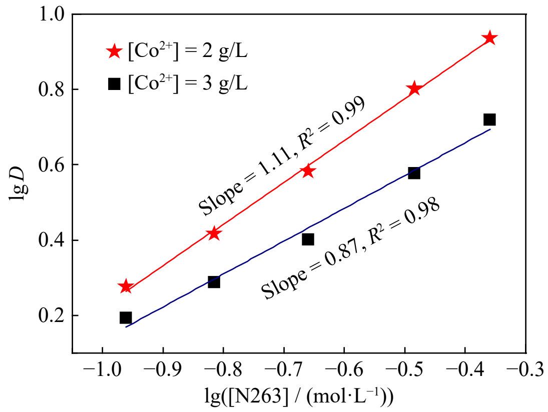


Fig. 12. Effect of the N263 concentration on the cobalt distribution ratio.

$$Co^{2+} + nNO_2^- = Co(NO_2)_n^{2-n} \tag{8}$$

As Fig. 12 shows, the relationship between lg$D$ and lg[N263] is linear, with slopes of 1.11 and 0.87 at a Co(II) concentration of 2 and 3 g/L, respectively. The former value is close to 1; therefore, the value of "n" should be 3 according to Eq. (9), indicating that 1 M N263 would be consumed when 1 M Co(II) is extracted.

$$\begin{aligned} &Co(NO_2)_n^{2-n} + (n-2)(R\cdot NO_2^-) = \\ &\quad R_{(n-2)} \cdot Co(NO_2)_n^{2-n} + (n-2)NO_2^- \end{aligned} \tag{9}$$

$$R_4NCl + Co(NO_2)_3^- = R_4N^+ \cdot Co(NO_2)_3^- + Cl^- \tag{10}$$

where n and R denote the coordination number of nitro-complexes and the fixed-ionic-group of the anion exchanger (N263: R_4NCl), respectively.

3.4.2. FT-IR characterization of the organic phase

The FT-IR spectra of pure and Co-loaded organic phases are shown in Fig. 13. The absorption peak of the three organic phases at 2954 cm^{-1} represents the asymmetric stretching vibration of $-CH_3$; 2923 and 2854 cm^{-1} are asymmetrical and symmetrical stretching vibrations of $-CH_2$, respectively. Furthermore, the peaks of $-CH_3$ deformation vibration and $-CH_2$ interfacial bending vibration appear at 1377 and 1462 cm^{-1}, respectively. The characteristic absorption peak of saturated hydrocarbons with long carbon chains ($n \geq 4$ in $-(CH_2)_n^-$) is at 724 cm^{-1}. By comparing the chromatograms of N263 and the mixed organic phase, the characteristic peak of N263 is almost unchanged after the addition of iso-propyl alcohol and kerosene, indicating that iso-propyl alcohol is only used as a modifier to dissolve N263 in kerosene without interaction. The broad, blunt peak at 3400 cm^{-1} and the peak at 1639 cm^{-1} are typical absorption peaks of –OH [33–35]. There is also an obvious absorption peak of NO_2^- at 1271 cm^{-1} [29]. Comparing the organic phase before and after extraction, it is found that the organic phase loaded with Co(II) shows a new peak at 1315 cm^{-1}, which is due to the shift of the peak caused by the complexation reaction and the combination of cobalt and nitrite. In summary, the reaction principle of the extraction process is as follows [4]: the quaternary ammonium salt extractant N263 is an anionic extractant, and the Cl^- anions in

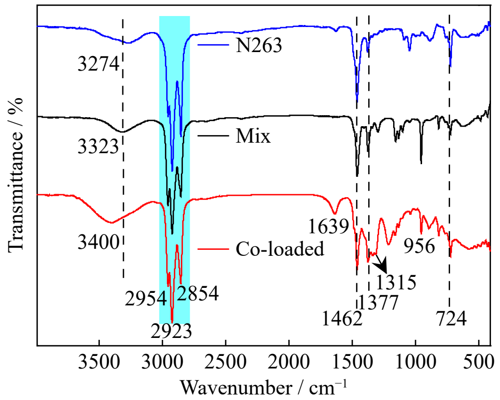
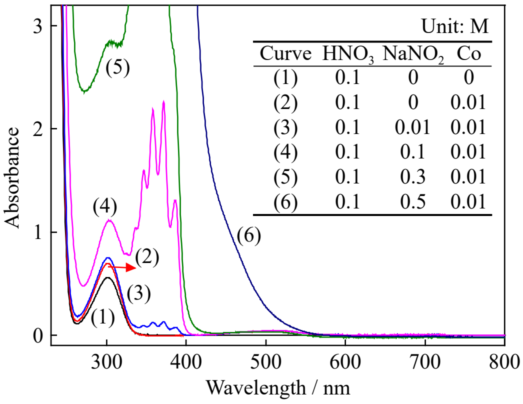


Fig. 13. FT-IR spectra of pure and Co-loaded organic phases.



Curve	HNO_3	$NaNO_2$	Co
(1)	0.1	0	0
(2)	0.1	0	0.01
(3)	0.1	0.01	0.01
(4)	0.1	0.1	0.01
(5)	0.1	0.3	0.01
(6)	0.1	0.5	0.01

Fig. 14. UV absorption spectra of Co(II) in the $NaNO_2$–HNO_3 solution.

the extracted quaternary ammonium salt N263 are replaced by $Co(NO_2)_3^-$ anions via an ion-exchange reaction.

3.4.3. UV characterization

Fig. 14 illustrates the UV broadband absorption spectra of Co(II) in the $NaNO_2$–HNO_3 solution. As shown in Fig. 14, the nitrate absorption peak appears at 300 nm, and the peak intensity gradually increases when cobalt nitrate is added. Curves (1) and (2) show that there is a weak peak at 510 nm, which is attributed to Co(II). Moreover, four sharp peaks from 350 to 400 nm appear in curves (3) to (6). The peak at 350 nm originates from nitrite (NO_2^-) ions [36], and the remaining peak could be from the complexes formed by cobalt and nitrite. However, as the amount of $NaNO_2$ increases, the intensities of the four absorption peaks gradually increase. In curve (6), the absorption peak is too strong, leading to the disappearance of the Co(II) peak at 510 nm [37]. The UV spectra prove that Co(II) complexes with $NaNO_2$.

3.4.4. XPS characterization of the organic phase and the structural mechanism

X-ray photoelectron spectroscopy (XPS) was used to study the valence states of ions in the organic phases before and after extraction. Fig. 15(a) and (b) shows the peak values of Co 2p and N 1s before and after extraction, respectively. Based on the FT-IR, UV, and XPS analyses, we propose in Fig. 15(c) a schematic of the Co(II) extraction mechanism by N263.

As shown in Fig. 15(a), the Cl 2p peak in the organic phase before extraction almost disappears after extraction due to the ion exchange effect, leading to the presence of Cl^- ions in the solution. In addition, the absorption peaks of C 1s, O 1s, and N 1s are enhanced after extraction, and the absorption peaks of Co 2p confirm that Co(II) is successfully extracted. Therefore, an ion-exchange relationship exists be-

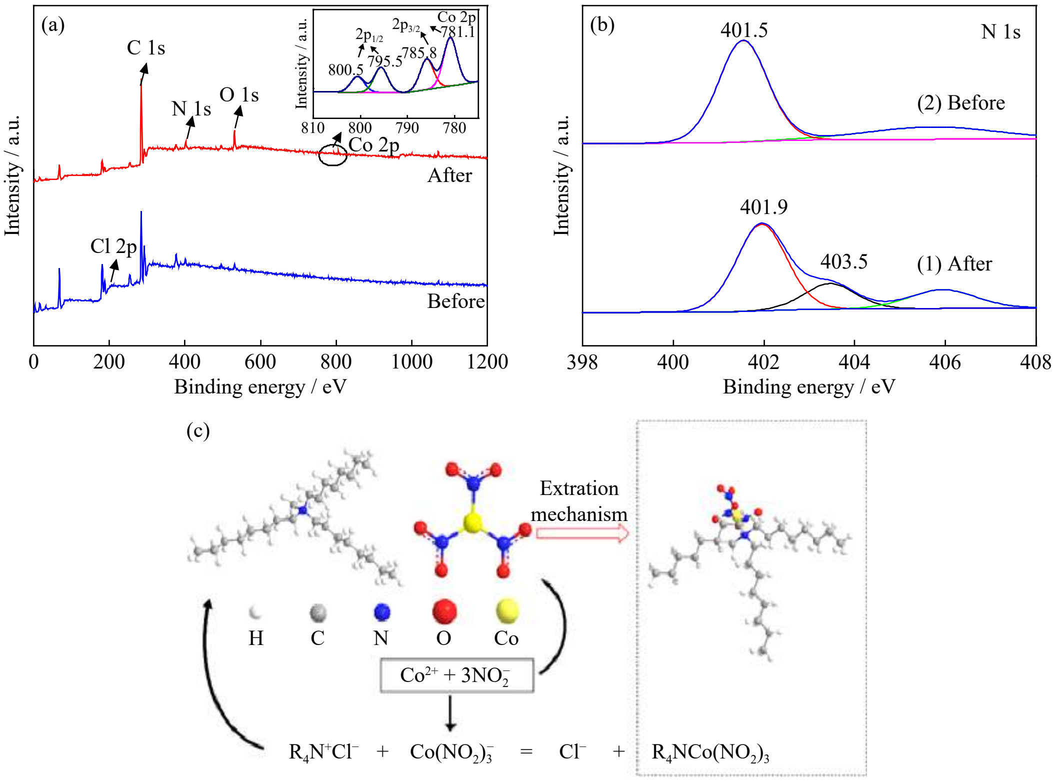


Fig. 15. (a) XPS survey spectra of the extraction agent before and after adsorption and enlarged spectra of Co 2p; (b) enlarged spectra of N 1s of the extraction agent before and after adsorption; (c) the mechanism of the Co(II) extraction by N263.

tween the anionic complex formed by cobalt, nitrite, and the extractant. The weak intensity of Co 2p, Cl 2p, and N 1s peaks is mainly due to the lack of the organic phase during preparation [38]. The 2p of all cobalt atoms in the organic phase after extraction is further illustrated in Fig. 15(a). The binding energies at 781.1 and 795.5 eV are related to the possible spin states $2p_{3/2}$ and $2p_{1/2}$, respectively. Ultimately, the $2p_{3/2}$ and $2p_{1/2}$ separation and the satellite structure indicate the presence of elements in the cobalt chemical environment [39].

To explore the extraction mechanism more conveniently, the N 1s spectra before and after extraction indicate the presence of quaternary amine groups (R_4N^+) at 401.5 eV, as shown in Fig. 15(b). After extraction, the peak of the quaternary amine group (R_4N^+) shifts to 401.9 eV, and the position of the quaternary amine group (R_4N^+) increases by 0.4 eV, illustrating a large number of Co(II) anionic complexes interacting with the quaternary amine groups. In addition, the absorption peak of $-NO_2$ appears at 403.5 eV after extraction, which may be because Co(II) and NO_2^- ions are combined and extracted into the organic phase, indicating that the extraction mechanism is ion exchange [29].

Therefore, combined with the slope analysis, it can be estimated that the extractant and complex are combined in a ratio of 1:1. The UV, FT-IR, and XPS results show that Co(II) reacts with NO_2^- to form $Co(NO_2)_3^-$, and the extraction mechanism of Co(II) is an anion-exchange reaction. In conclusion, the extracted complex is identified as $[R_4NCo(NO_2)_3]$, and the mechanism of the Co(II) extraction by N263 is shown in Fig. 15(c).

3.5. Distribution isotherms and extraction in simulated solution

To determine the number of theoretical extraction stages in actual industrial operation, we measured the McCabe–Thiele diagrams for cobalt by equilibrium extraction distribution isotherms in the A/O ratio range of 1:2 to 3:1, as shown in Fig. 16(a). According to the actual concentration of metal ions in the solution after leaching (Table 1), the simulated solution is shown in Table 2. Fig. 16(b) depicts the metal ion extraction efficiency in the simulated mixed solution.

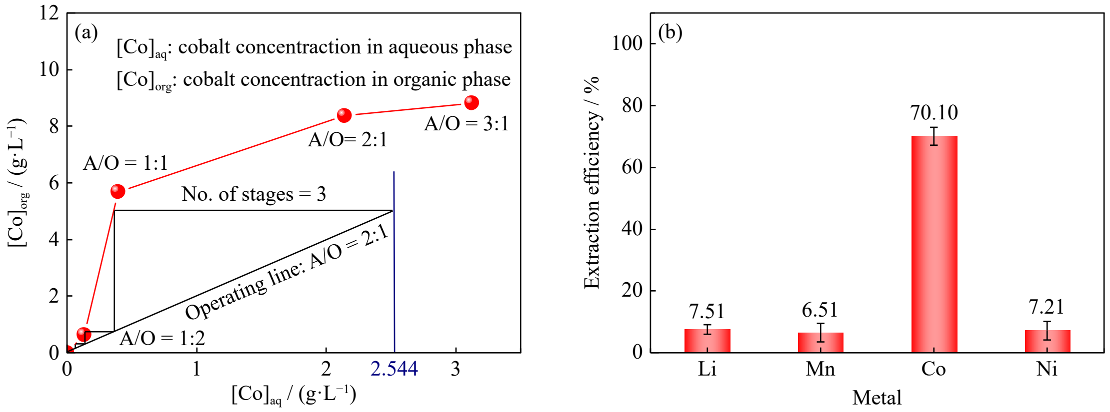


Fig. 16. **(a) Co(II) extraction distribution isotherm and McCabe–Thiele diagrams; (b) the extraction efficiency of the simulated mixed solution (30vol% N263 and 15vol% iso-propyl alcohol in sulfonated kerosene, 1 M sodium nitrite, t = 30 min, T = 25°C, and $[HNO_3]$ = 0.1 M).**

Table 2. **Composition of the simulated solution** mg/L

Li	Mn	Co	Ni
1224	3547	2544	6977

Note: 30vol% N263 and 15vol% iso-propyl alcohol in sulfonated kerosene, 1 M $NaNO_2$, t = 30 min, A/O = 2:1, and $[HNO_3]$ = 0.1 M.

According to the McCabe-Thiele diagram (Fig.16(a)), the simulated Co(II) content in the solution is 2544 mg/L. The extraction efficiency of Co(II) is 70.10% (Fig. 16(b)). Three or more theoretical extraction stages are needed to theoretically extract more than 99% of Co(II) under the following conditions: an A/O ratio of 2:1, 30vol% N263 and 15vol% iso-propyl alcohol in sulfonated kerosene, 1 M sodium nitrite, t = 30 min, T = 25°C, and $[HNO_3]$ = 0.1 M.

3.6. Extraction in real leaching solution

In this study, the separation effect on Co(II) in the actual leaching solution was investigated using the following leaching conditions: 0.5 M ascorbic acid and 0.5 M HNO_3, S/L of 20 g/L, temperature of 70°C, and time of 1 h [27]. We conducted real solution leaching tests with the concentrations of Co(II), Ni(II), Mn(II), and Li (I) given in Table 1. Combined with Fig. 9, which shows that the optimal concentration of sodium nitrite is 1 M at a Co(II) concentration of 2493 mg/L, the extraction efficiency of Co(II) in the actual leaching solution is 100%, as shown in Fig. 17.

Due to the reduction potential of ascorbic acid, nitrate ions in the solution are reduced to nitrite ions [27]. After $NaNO_2$ is added, NO_2^- is introduced to combine with Co(II) more effectively to form an anionic complex for ion exchange. The extraction efficiencies of Li(I), Mn(II), and Ni(II) are 15.04%, 12.11%, and 12.32%, respectively.

Table S2 illustrates the extraction efficiency by simulating the concentration of metal ions to study the effects of ascorbic acid in the actual solution. Condition 1: when 0.5 M HNO_3 and 0.5 M ascorbic acid are used, the metal ion extraction efficiency is 0, indicating that ascorbic acid does not interact with metal ions in the solution. The extraction efficiency of Co(II) is 62.99% under condition 2: 0.5 M HNO_3 and 1 M $NaNO_2$. The extraction efficiency of Co(II) increases to 94.24% after the addition of ascorbic acid under condition 3: 0.5 M HNO_3, 0.5 M ascorbic acid, and 1 M $NaNO_2$. The presence of ascorbic acid as a reducing agent in the solution contributes to the Co(II) extraction, and it reaches 100% in the actual solution (Fig. 17). Therefore, the $NaNO_2$ system with N263 can effectively extract and separate Co(II) from the solution of ascorbic acid and HNO_3.

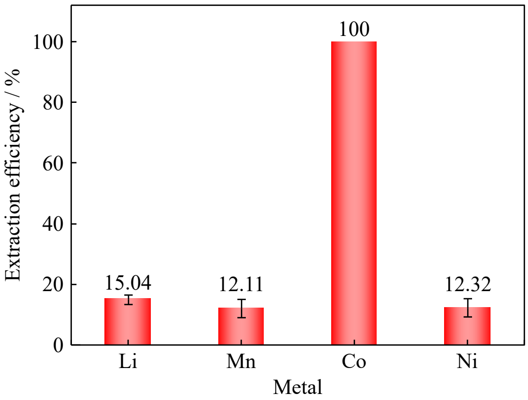


Fig. 17. Application of the actual leaching solution (30vol% N263 and 15vol% iso-propyl alcohol in sulfonated kerosene, 1 M sodium nitrite, $t = 30$ min, and $T = 25°C$).

According to Fig. 17, Co(II) can be effectively extracted by N263, but about 10.00% of Li (I), Mn(II), and Ni(II) ions still exist. We performed back-extraction with 1.5 M HCl at an A/O of 1:1, as stated in Table S3, to better separate and recover Co(II). The obtained ultimate Co(II) purity can reach 97.98%, and a good separation effect is indicated.

4. Conclusion

We demonstrate the feasibility of the extraction and separation of Co(II) from the acidic leaching solution of LIBs cathode materials with quaternary ammonium extractant (N263) in the nitric acid system. Three different extractants and three modifiers are selected for comparison, and N263 and iso-propyl alcohol exhibit excellent Co(II) separation abilities. The results show that under the conditions of an A/O ratio of 2:1, 30vol% N263, and 15vol% iso-propyl alcohol in the sulfonated kerosene extraction systemwith an extraction time of 30 min, 0.1 M HNO_3, and 1 M $NaNO_2$, the extraction efficiency of Co(II) from the actual leaching solution reaches 100%. According to the analysis of the McCabe–Thiele diagram, the extraction efficiency of Co(II) reaches more than 99.00% after a three-stage counter-current extraction. More than 97.70% of Co(II) could be back-extracted from the organic phase with 1.5 M HCl when the A/O ratio is 1:1. Furthermore, adding ascorbic acid to the solution improves the Co(II) extraction efficiency and could separate Co(II) from Ni(II), Mn(II), and Li (I) via back-extraction. The purity of Co(II) reaches 97.98%.

Finally, it is found that in solution with different Co(II) concentrations, the extraction efficiency of Co(II) is related to the change in the concentration of $NaNO_2$, where a higher Co(II) concentration requires a higher $NaNO_2$ concentration. FT-IR, XPS, UV, and slope analyses confirmed that the structure of the extracted complex is $[R_4NCo(NO_2)_3]$ and that the mechanism of the Co(II) extraction by N263 is an anion-exchange reaction.

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Conflict of Interest

The authors declare no potential conflict of interest.

Supplementary Information

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References

[1] E. Peek, T. Åkre, and E. Asselin, Technical and business considerations of cobalt hydrometallurgy, *JOM*, 61(2009), No. 10, p. 43.

[2] Q. Dehaine, L.T. Tijsseling, H.J. Glass, T. Törmänen, and A.R. Butcher, Geometallurgy of cobalt ores: A review, *Miner. Eng.*, 160(2021), art. No. 106656.

[3] M. Chandra, D.W. Yu, Q.H. Tian, and X.Y. Guo, Recovery of cobalt from secondary resources: A comprehensive review, *Miner. Process. Extr. Metall. Rev.*, 43(2022), 6, p. 679.

[4] B. Wassink, D. Dreisinger, and J. Howard, Solvent extraction separation of zinc and cadmium from nickel and cobalt using Aliquat 336, a strong base anion exchanger, in the chloride and thiocyanate forms, *Hydrometallurgy*, 57(2000), No. 3, p. 235.

[5] R. Golmohammadzadeh, F. Faraji, and F. Rashchi, Recovery of lithium and cobalt from spent lithium ion batteries (LIBs) using organic acids as leaching reagents: A review, *Resour. Conserv. Recycl.*, 136(2018), p. 418.

[6] M.K. Tran, M.T.F. Rodrigues, K. Kato, G. Babu, and P.M. Ajayan, Deep eutectic solvents for cathode recycling of Li-ion batteries, *Nat. Energy*, 4(2019), No. 4, p. 339.

[7] W.Y. Wang, C.H. Yen, and J.K. Hsu, Selective recovery of cobalt from the cathode materials of NMC type Li-ion battery by ultrasound-assisted acid leaching and microemulsion extraction, *Sep. Sci. Technol.*, 55(2020), No. 16, p. 3028.

[8] X.H. Zheng, Z.W. Zhu, X. Lin, *et al.*, A mini-review on metal recycling from spent lithium ion batteries, *Engineering*, 4(2018), No. 3, p. 361.

[9] X.L. Zeng, J.H. Li, and N. Singh, Recycling of spent lithium-ion battery: A critical review, *Crit. Rev. Environ. Sci. Technol.*, 44(2014), No. 10, p. 1129.

[10] F. Gu, J.F. Guo, X. Yao, P.A. Summers, S.D. Widijatmoko, and P. Hall, An investigation of the current status of recycling spent

lithium-ion batteries from consumer electronics in China, *J. Clean. Prod.*, 161(2017), p. 765.

[11] L. Sun and K.Q. Qiu, Organic oxalate as leachant and precipitant for the recovery of valuable metals from spent lithium-ion batteries, *Waste Manage.*, 32(2012), No. 8, p. 1575.

[12] A.M. Bernardes, D.C.R. Espinosa, and J.A.S. Tenório, Recycling of batteries: A review of current processes and technologies, *J. Power Sources*, 130(2004), No. 1-2, p. 291.

[13] L. Li, J. Ge, R.J. Chen, F. Wu, S. Chen, and X.X. Zhang, Environmental friendly leaching reagent for cobalt and lithium recovery from spent lithium-ion batteries, *Waste Manage.*, 30(2010), No. 12, p. 2615.

[14] J.Q. Xu, H.R. Thomas, R.W. Francis, K.R. Lum, J.W. Wang, and B. Liang, A review of processes and technologies for the recycling of lithium-ion secondary batteries, *J. Power Sources*, 177(2008), No. 2, p. 512.

[15] L. Chen, X.C. Tang, Y. Zhang, L.X. Li, Z.W. Zeng, and Y. Zhang, Process for the recovery of cobalt oxalate from spent lithium-ion batteries, *Hydrometallurgy*, 108(2011), No. 1-2, p. 80.

[16] M.B.J.G. Freitas, V.G. Celante, and M.K. Pietre, Electrochemical recovery of cobalt and copper from spent Li-ion batteries as multilayer deposits, *J. Power Sources*, 195(2010), No. 10, p. 3309.

[17] J.G. Kang, G. Senanayake, J. Sohn, and S.M. Shin, Recovery of cobalt sulfate from spent lithium ion batteries by reductive leaching and solvent extraction with Cyanex 272, *Hydrometallurgy*, 100(2010), No. 3-4, p. 168.

[18] H.Y. Wang, K. Huang, Y. Zhang, *et al.*, Recovery of lithium, nickel, and cobalt from spent lithium-ion battery powders by selective ammonia leaching and an adsorption separation system, *ACS Sustainable Chem. Eng.*, 5(2017), No. 12, p. 11489.

[19] X.P. Chen, Y.B. Chen, T. Zhou, D.P. Liu, H. Hu, and S.Y. Fan, Hydrometallurgical recovery of metal values from sulfuric acid leaching liquor of spent lithium-ion batteries, *Waste Manage.*, 38(2015), p. 349.

[20] N. Ocaña and F.J. Alguacil, Cobalt–manganese separation: The extraction of cobalt(II) from manganese sulphate solutions by cyanex 301, *J. Chem. Technol. Biotechnol.*, 73(1998), No. 3, p. 211.

[21] B. Pośpiech and W. Walkowiak, Separation of copper(II), cobalt(II) and nickel(II) from chloride solutions by polymer inclusion membranes, *Sep. Purif. Technol.*, 57(2007), No. 3, p. 461.

[22] A.H. Blitz-Raith, R. Paimin, R.W. Cattrall, and S.D. Kolev, Separation of cobalt(II) from nickel(II) by solid-phase extraction into Aliquat 336 chloride immobilized in poly(vinyl chloride), *Talanta*, 71(2007), No. 1, p. 419.

[23] H.C. Kao and R.S. Juang, Kinetic analysis of non-dispersive solvent extraction of concentrated Co(II) from chloride solutions with Aliquat 336: Significance of the knowledge of reaction equilibrium, *J. Membr. Sci.*, 264(2005), No. 1-2, p. 104.

[24] M. Majdan, J. Mierzwa, and P. Sadowski, On the separation of Co and Ni from chloride media with Aliquat 336-TBP and Aliquat 336-TOPO, *Monatsh. Chem.*, 128(1997), No. 2, p. 113.

[25] N.A. Milevskii, I.V. Zinov'eva, Y.A. Zakhodyaeva, and A.A. Voshkin, Separation of Li(I), Co(II), Ni(II), Mn(II), and Fe(III) from hydrochloric acid solution using a menthol-based hydrophobic deep eutectic solvent, *Hydrometallurgy*, 207(2022), art. No. 105777.

[26] Y.Z. Wei, T. Arai, M. Kumagai, and Q.M. Feng, Adsorption behavior of various metal ions in nitrite medium and separation of some metals by anion exchange, *J. Ion Exch.*, 14(2003), Suppl., p. 305.

[27] H. Chen, S. Gu, Y.X. Guo, *et al.*, Leaching of cathode materials from spent lithium-ion batteries by using a mixture of ascorbic acid and HNO_3, *Hydrometallurgy*, 205(2021), art. No. 105746.

[28] J.R. Ju, Y.L. Feng, H.R. Li, *et al.*, Separation of Cu, Co, Ni and Mn from acid leaching solution of ocean cobalt-rich crust using precipitation with Na_2S and solvent extraction with N_{235}, *Korean J. Chem. Eng.*, 39(2022), No. 3, p. 706.

[29] Y.J. Yang, Y.N. Yang, C.L. He, *et al.*, The adsorption and desorption behavior and mechanism research of cobalt, nickel and copper in nitrite–sulfuric acid system, *Sep. Sci. Technol.*, 57(2022), No. 12, p. 1848.

[30] Z.S. Liu, J. Huang, Y.M. Zhang, *et al.*, Separation and recovery of vanadium and aluminum from oxalic acid leachate of shale by solvent extraction with Aliquat 336, *Sep. Purif. Technol.*, 249(2020), art. No. 116867.

[31] K. Wang, G.Q. Zhang, M.Z. Luo, and M. Zeng, Separation of Co and Mn from acetic acid leaching solution of spent lithium-ion battery by Cyanex272, *J. Environ. Chem. Eng.*, 10(2022), No. 5, art. No. 108250.

[32] A.A. Nayl, M.M. Hamed, and S.E. Rizk, Selective extraction and separation of metal values from leach liquor of mixed spent Li-ion batteries, *J. Taiwan Inst. Chem. Eng.*, 55(2015), p. 119.

[33] H.E. Rizk, Y.A. El-Nadi, and N.E. El-Hefny, Extractive separation of scandium from strongly alkaline solution by quaternary ammonium salt, *Solvent Extr. Ion Exch.*, 38(2020), No. 3, p. 350.

[34] H. Zhang, C.M. Li, X.J. Chen, *et al.*, Layered ammonium vanadate nanobelt as efficient adsorbents for removal of Sr^{2+} and Cs^+ from contaminated water, *J. Colloid Interface Sci.*, 615(2022), p. 110.

[35] J.J. Meng, C.L. He, Y.J. Li, *et al.*, Enhanced adsorption and separation of gallium using silica-based P507-TBP/SiO_2-P adsorbent from sulfuric acid solution, *Microporous Mesoporous Mater.*, 314(2021), art. No. 110859.

[36] L.Z. Jiao, D.M. Dong, W.G. Zheng, *et al.*, Determination of nitrite using UV absorption spectra based on multiple linear regression, *Asian J. Chem.*, 25(2013), No. 4, p. 2273.

[37] H. Benalia and D. Barkat, Solvent extraction studies of cobalt(II) by capric acid from sodium sulfate solution, *J. Dispersion Sci. Technol.*, 38(2017), No. 9, p. 1247.

[38] J. Cañón and A.V. Teplyakov, XPS characterization of cobalt impregnated SiO_2 and γ-Al_2O_3, *Surf. Interface Anal.*, 53(2021), No. 5, p. 475.

[39] G. Kowalski, J. Pielichowski, and M. Grzesik, Characteristics of polyaniline cobalt supported catalysts for epoxidation reactions, *Sci. World J.*, 2014(2014), art. No. 648949.