Available online at www.sciencedirect.com
ScienceDirect
Trans. Nonferrous Met. Soc. China 33(2023) 1282−1295
Transactions of Nonferrous Metals Society of China
www.tnmsc.cn

A novel green synergistic extraction formulation based on D2EHPA for recovering nickel from nickel plating effluent

Ying-peng LI[1], Xiu-yu LUO[2], Zhong-bing WANG[1], Qian GUAN[1],
Chen-quan NI[3], Jie-fei ZHANG[1], Chun-li LIU[1], Hai-yan JI[1], Xu-biao LUO[1], Gui-sheng ZENG[1]

1. National-Local Joint Engineering Research Center of Heavy Metals Pollutants Control and Resource Utilization,
Nanchang Hangkong University, Nanchang 330063, China;
2. Fujian College of Water Conservancy and Electric Power, Yongan 641836, China;
3. Key Laboratory of Biohydrometallurgy of Ministry of Education,
School of Minerals Processing and Bioengineering, Central South University, Changsha 410083, China

Received 9 December 2021; accepted 14 April 2022

Abstract: A new green synergistic extraction agent (di-2-ethylhexyl phosphoric acid (D2EHPA)−decanol) was developed to recycle Ni(II) from nickel plating effluent. The results show that the D2EHPA−decanol mixture carrier provided a significant synergistic effect in the process. When sulfonated kerosene or sunflower seed oil was used as a diluent, the single extraction efficiency of Ni(II) reached 97.8% and 97.1%, respectively. After three-times extraction, the Ni(II) concentration in the nickel plating effluent decreased to below 1 mg/L. Additionally, in the stripping stage, the stripping efficiency of Ni(II) in the D2EHPA−decanol mixed carrier was larger than that of D2EHPA. Mechanism studies indicate that the polar groups (—OH) from decanol initially break the hydrogen bonds in the D2EHPA dimer structure. Afterwards, van der Waals forces shorten the bond length of P—O to form electron-rich centers of O atoms. Finally, a new P—O—Ni structure is formed through interactions between P—O bond and nickel ions under electrostatic forces.

Key words: synergistic extraction; wastewater; nickel; D2EHPA; green diluent

---

1 Introduction

Nickel is widely used in many processes and products, such as electroplating and electroless plating, as catalysts, in metallic alloys, and in batteries [1−3]. With its rapid economic growth, China has become the world largest consumer and importer of nickel resources, which may accelerate the depletion of China’s mineral resources [4]. In addition, high concentrations of nickel compounds in the environment may cause serious damages to human health [5−7]. Therefore, recycling of nickel resources is a very important issue for health and environment.

In recent years, the removal and recovery of heavy metals from plating effluents has been of great concern. The conventional technologies for treating wastewater containing heavy metals are mainly based on chemical precipitation, ion exchange method, electrodialysis, and solvent extraction. However, the chemical precipitation method requires the addition of chemical substances that produce sludge containing a lot of heavy metals, resulting in secondary pollution [8]. In the ion exchange method, the ion exchange resin is not resistant to elevated temperatures and may be easily oxidized and fail to properly function [9].

Corresponding author: Gui-sheng ZENG, Tel/fax: +86-791-83953373, E-mail: zengguisheng@hotmail.com;
Zhong-bing WANG, E-mail: wzbing@126.com
DOI: 10.1016/S1003-6326(23)66182-5

The electrodialysis method is highly selective and does not produce sludge. However, this process is highly energy consuming and expensive with side reactions [10]. Solvent extraction is the most commonly-used method to separate and concentrate metal ions in aqueous solutions [11,12]. However, when a single extractant is used as a carrier in the extraction system, the load capacity for metal ions is weak. Therefore, to improve the extraction efficiency, often one or more substances acting as synergists (synergistic extractant) are added to the system [13]. For example, ZHOU et al [14] used Cyanex 572 (a phosphorus-based chelating extractant) and n-octyl diphenyl phosphate (ODP) to extract Th(IV) from the leaching solutions of rare earth residues. They found a synergistic enhancement factor as large as 12.40 at a mole ratio of 1:2. Moreover, the addition of a synergist may increase the stripping efficiency and the selectivity of the extraction process. WU et al [15] used di-isobutyl ketone (DIBK) and di(1-methyl-heptyl) methyl phosphonate (P350) for selective extraction of hafnium (Hf) on zirconium (Zr). The separation factor in the process reached 17.6. In addition, it was found that 82.2% of Zr can be stripped using 1.5 mol/L H_2SO_4 solution, reducing the consumption of sulfuric acid.

Diluent is an important component in the organic phase of the solvent extraction process. Solvent extraction systems commonly use petroleum-based organic solvents as diluents [16], such as sulfonated kerosene, chloroform, and dichloromethane. However, these diluents are hazardous, non-renewable, non-biodegradable, and flammable typically. With consideration of environmental pollution and for the development of green processes, several studies have suggested use of plant oils as replacement for petroleum-based organic solvents. Although CHANG et al [17] used D2EHPA and tri-n-butyl phosphate (TBP) in vegetable oil-based organic solvents to extract more than 98% of Cu(II) in aqueous solutions, there is no research on the effects of organic phase regeneration on synergistic extraction processes. SULAIMAN and OTHMAN [18] used LIX63–D2EHPA synergistic extraction system with palm oil as a diluent to successfully extract 75% of Ni(II) from the electroplating effluent containing Ni(II) at a concentration of 4156 mg/L. However, for the stripping process, usage of 4 mol/L HNO_3 solution could strip only 79% of nickel from the loaded organic phase. At the same time, the extraction efficiency of Ni(II) using regenerated palm oil-based organic phase was observed only at 2%. Furthermore, to the best of our knowledge, the detailed study of Ni(II) extraction from the nickel plating effluent through green synergic binary mixture of D2EHPA–decanol system has not been proposed.

Herein, we studied the process parameters for extracting Ni(II) from nickel plating effluent with a synergistic extraction system composed of D2EHPA-decanol mixed carrier. We also investigated the effects and mechanism of different kinds of plant oils and their mixing ratios with sulfonated kerosene on the extraction efficiency of Ni(II). Finally, we discussed the mechanism of the synergistic extraction and the recycling process of the organic phase. It is a promising alternative for the extraction of valuable heavy metals from industrial effluents.

2 Experimental

2.1 Materials

Nickel plating effluent sample was obtained from Nanchang City, Jiangxi Province, China. The effluent sample was dark green with a pH value of 3.57. Atomic absorption spectrophotometry (AAS) and ion chromatography (IC) analytical techniques were used to characterize the chemical composition of the effluent. The results of analyses are presented in Table 1. The sources and grades of the chemicals used in this study are provided in the Supplementary Material (SM).

Table 1 Chemical compositions of nickel plating effluent (mg/L)

Ni^{2+}	K^+	Al^{3+}	Cu^{2+}	PO_4^{3-}	NO_3^-	Cl^-	F^-	SO_4^{2-}
3673	206.4	28.7	90.6	98.5	102.3	62.4	684.9	872.8

2.2 Characterization

The characterization methods are presented in the Supplementary Material.

2.3 Experimental procedures and parameters

We studied the following variables: Carrier and synergist types, concentration of D2EHPA (0.15−0.9 mol/L), decanol content (5%−45%, volume fraction), the pH of the aqueous phase

(0.64−5.58), time (from 30 s to 90 min), type of stripping acid, concentration of stripping acid (0.4−2.5 mol/L), diluents type, and mixing ratio. All experiments were performed at A/O ratio of 1:1 and room temperature ((25±1) °C). The specific experimental procedures are given in the Supplementary Materials.

2.4 Calculations

The saponification degree (S_d), extraction efficiency (E), distribution ratio (D), stripping efficiency (S), and synergistic enhancement factor (R) were calculated using the following equations [19,20]:

$$S_d = \frac{C_{NaOH} \cdot V_{aq}}{C_{D2EHPA} \cdot V_{org}} \times 100\% \tag{1}$$

$$E = \frac{C_i V_i - C_{aq} V_{aq}}{C_i V_i} \times 100\% \tag{2}$$

$$D = C_{org} / C_{aq} \tag{3}$$

$$S = \frac{C_s V_s}{C_{org} V_{org}} \times 100\% \tag{4}$$

$$R = D_{mix} / (D_{D2EHPA} + D_{Decanol}) \tag{5}$$

where C_i, C_{aq}, C_s, and C_{org} are the concentrations (in mg/L) of Ni(II) in input effluent feed phase, aqueous phase after extraction, aqueous phase after steam stripping, and organic phase, respectively; V_i, V_{aq}, V_s, and V_{org} are the volumes of feed aqueous phase, aqueous phase after extraction, stripping solution, and organic phase, respectively. In Eq. (5), D_{mix}, D_{D2EHPA}, and $D_{Decanol}$ are the distribution ratios of D2EHPA and decanol mixture, D2EHPA alone, and decanol alone, respectively.

2.5 Statistical analysis

All the data in the current study were presented as mean ± standard deviation. Analysis of Variance (ANOVA) was conducted to evaluate the differences among different tests. All the analyses were performed using SPSS software, version 24.0.

3 Results and discussion

3.1 Extraction experiments

3.1.1 Effects of carrier and synergist types on Ni(II) extraction

The results of experiments conducted with different carriers and synergists on the extraction efficiency of Ni(II) are shown in Fig. 1. Acidic extractant could extract Ni(II) from nickel plating effluent (Fig. 1(a)). The extraction effect of the neutral extractant on Ni(II) was negligible. At the same time, D2EHPA provided an extraction efficiency of 45.8%. This observation is because D2EHPA has a high acidity constant, good solubility, and protonation degree. Therefore, the H atom of the hydroxyl group in D2EHPA can be easily replaced by Ni(II). The extraction efficiency determined for LIX63, an acidic chelating oxime type, was found to be 41.6%. However, the process with the acidic chelating oxime extractant in the extraction and stripping extraction stages takes a long time [21]. Although Cyanex 302 (bis(2,4,4-trimethylpentyl) monothiophosphinic

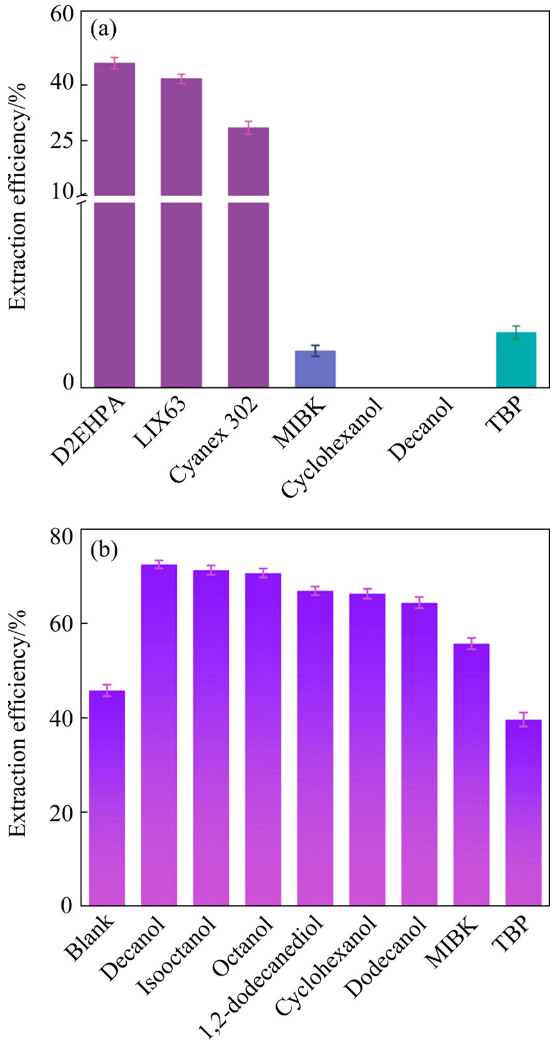

Fig. 1 Effects of various carrier and synergist types on Ni(II) extraction efficiency: (a) Carrier; (b) Synergist ($C_{carrier}$: 0.5 mol/L, C_{D2EHPA}: 0.5 mol/L, synergist: 10% (volume fraction), diluent: sulfonated kerosene, pH: 3.57, and time: 15 min)

acid) provided an extraction efficiency value of 31.6%, alkylphosphinic acid extractants are very easily oxidized and decomposed, especially in the presence of Fe(III) or Cu(II). Furthermore, the concentration of stripping acid has been found to be as high as 6 mol/L [22]. Based on the maximum extraction efficiency values of Ni(II), substance D2EHPA was selected as the most suitable carrier in the synergistic extraction system.

Synergistic extraction is a way to increase the extraction efficiency. When two molecules of carrier transfer the metal ions from the aqueous phase to the organic phase, the extraction efficiency becomes greater than that using each of the carriers alone, which is called synergy effect. It was observed that D2EHPA produces a significant synergistic extraction effect with the added alcohols and methyl isobutyl ketone (MIBK). The reason for this effect is that both alcohols and MIBK are strongly polar chemical compounds, promoting sufficient contacts between the aqueous and organic phases (Fig. 1(b)). Among them, the D2EHPA−decanol synergistic extraction system revealed the greatest extraction efficiency of 72.5%. The extraction system of D2EHPA−TBP has an antagonistic effect on the extraction of Ni(II), because the solvation carrier is weakly basic in nature and can extract neutral metal complexes or alkali metals [23]. In addition, the combination of acidic-solvating properties may reduce the acidity of the membrane phase and the degree of protonation of the carrier complex, and prevent the formation of the metal−organic complexes in tetrahedral or octahedral structures [24].

Based on the extraction efficiency of Ni(II) and the maximum synergistic effects, decanol was selected as the synergistic extractant for the following experiments.

3.1.2 Effects of D2EHPA concentration and saponification degree on Ni(II) extraction

The concentration of D2EHPA is a very important variable in the extraction experiments. In the experiments, the extraction efficiency of Ni(II) increased with the increase of D2EHPA concentration (Fig. 2(a)). This observation is due to the increase in the extractant concentration, causing an increase in the number of D2EHPA molecules that provide more coordination groups to combine with Ni(II), allowing Ni(II) to enter into the organic phase. When the concentration of C_{D2EHPA} increased from 0.75 to 0.9 mol/L, the extraction efficiency of Ni(II) slightly increased. Considering the economic and environmental costs, the concentration C_{D2EHPA} of 0.75 mol/L was selected for further experiments. At the same time, when the concentration of D2EHPA increased from 0.15 to 0.75 mol/L, the pH of the aqueous phase linearly decreased in the extraction equilibrium conditions (Fig. 2(b)). When the concentration of D2EHPA reached 0.75 mol/L, the pH value of equilibrium aqueous phase tended to be stable. This behavior is due to the overall extraction of metal ions from aqueous media by D2EHPA, expressed as Reaction (6) [25]:

$$\mathrm{Me}^{m+}_{(\mathrm{aq})} + n(\mathrm{HA})_2 \rightleftharpoons \mathrm{MeA}_m(\mathrm{HA})_{2n-m(\mathrm{org})} + m\mathrm{H}^+_{(\mathrm{aq})} \tag{6}$$

where n is a stoichiometric constant and $(\mathrm{HA})_2$ represents D2EHPA molecule.

According to Reaction (6), the D2EHPA molecules exchange protons with the metal ions present in the aqueous phase. The extraction of metal ions causes an increase in the aqueous phase acidity or decreases the pH of the solution.

Because H^+ ions are released into the aqueous phase during the extraction process, the pH value of this phase decreases, which is not beneficial to the metal extraction process. Therefore, the extractant is saponified to keep the pH value stable during the extraction process. At D2EHPA concentration of 0.75 mol/L, the effect of saponification degree on the extraction efficiency of Ni(II) was studied. In the experiments, the optimal saponification degree was observed to be 50% (Fig. 2(c)). When the saponification degree continues to increase, the extraction efficiency of Ni(II) decreases instead. After saponification of D2EHPA, the saponified extractant forms a water-in-oil microemulsion in an organic phase. When the saponification degree is 50%, the water content in the microemulsions reaches to a critical value. Further increase in the saponification degree will cause break down of the water-in-oil microemulsion structure [26]. At the same time, when the saponified D2EHPA was used to extract Ni(II), the pH of the aqueous phase at equilibrium slightly decreased compared with the initial pH (Fig. 2(d)). This behavior can be due to the chemical reactions presented in Reactions (7) and (8) during the extraction process of saponified D2EHPA:

$$2\mathrm{NaOH}_{(\mathrm{aq})} + (\mathrm{HA})_{2(\mathrm{org})} \rightleftharpoons 2\mathrm{NaA}_{(\mathrm{aq})} + 2\mathrm{H_2O} \tag{7}$$

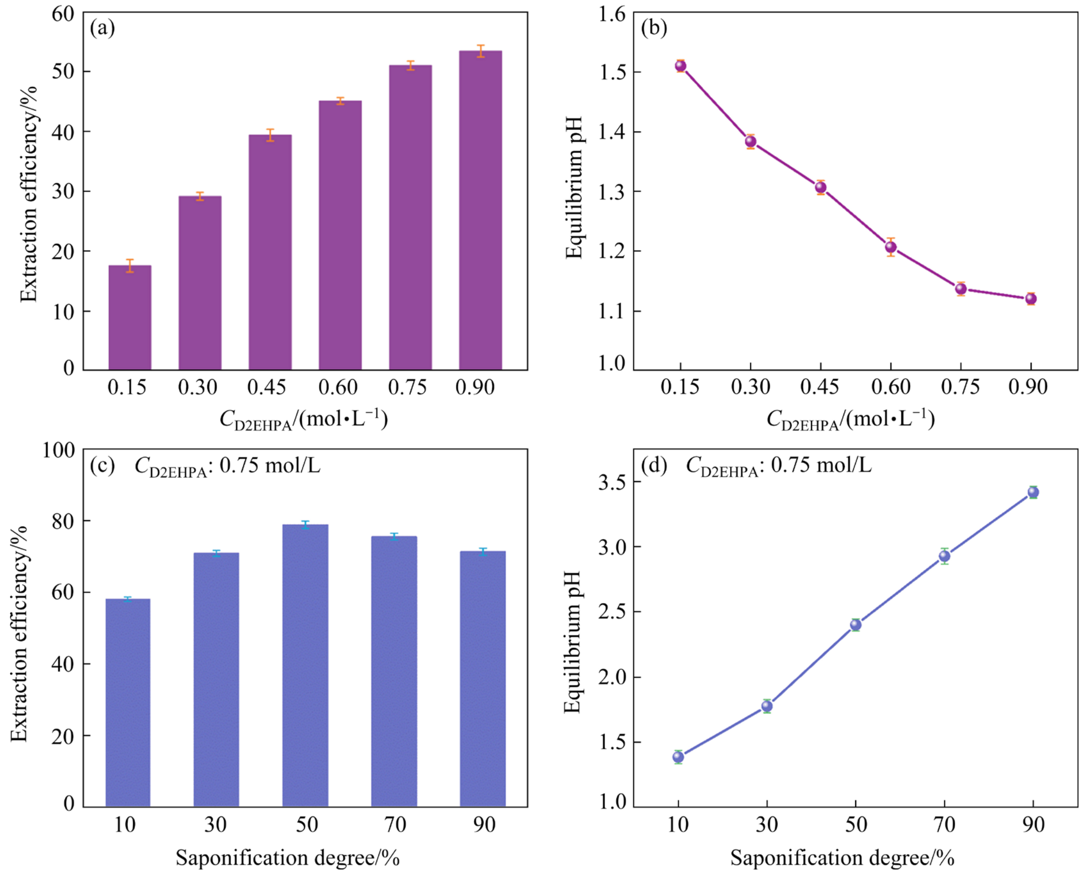

Fig. 2 Effects of D2EHPA concentration (a, b) and saponification degree (c, d) on extraction efficiency (a, c) and equilibrium pH (b, d) (Diluent: sulfonated kerosene, pH: 3.57, and time: 15 min)

$$m\mathrm{NaA}_{(\mathrm{org})}+\mathrm{Me}^{m+}_{(\mathrm{aq})} \rightleftharpoons \mathrm{MeA}_{m(\mathrm{org})}+m\mathrm{Na}^{+}_{(\mathrm{aq})} \tag{8}$$

This extraction process could be described as “neutralization–ion exchange” mechanism. Initially, acid-base neutralization reaction occurs, followed by the cation exchange process. In this “neutralization–ion exchange” process, no H^{+} ion is released. Therefore, decrease in the pH of the aqueous phase after the extraction is relatively small. The lower acidity of the aqueous phase favors the extraction reaction represented in Reaction (6).

3.1.3 Equilibrium slope analysis

The organophosphorus extractants, such as D2EHPA, PC88A, and Cyanex 272 form organometallic complex in the form of $\mathrm{MeA}_{m}(\mathrm{HA})_{2n-m}$ with the molecules of metals during extraction process, as presented earlier in Reaction (6).

For extraction of Ni(II), this reaction can be written as Reaction (9):

$$\mathrm{Ni}^{2+}_{(\mathrm{aq})}+n(\mathrm{HA})_{2(\mathrm{org})} \rightleftharpoons \mathrm{NiA}_2(\mathrm{HA})_{2n-2(\mathrm{org})}+2\mathrm{H}^{+}_{(\mathrm{aq})} \tag{9}$$

K_{ex} is given by Eq. (10):

$$K_{\mathrm{ex}}=\frac{[\mathrm{NiA}_2(\mathrm{HA})_{2n-2}]_{(\mathrm{org})}\cdot[\mathrm{H}^{+}]^{2}_{(\mathrm{aq})}}{[\mathrm{Ni}]^{2+}_{(\mathrm{aq})}\cdot[(\mathrm{HA})_2]^{n}_{(\mathrm{org})}} \tag{10}$$

Substitution of the distribution ratio (D) into Eq. (10) gives

$$D=\frac{K_{\mathrm{ex}}\cdot[(\mathrm{HA})_2]^{n}_{(\mathrm{org})}}{[H^{+}]^{2}_{(\mathrm{aq})}} \tag{11}$$

Taking the logarithm on both sides of Eq. (11) results in Eq. (12):

$$\lg D=n\lg[(\mathrm{HA})_2]_{(\mathrm{org})}+\lg\left[\frac{K_{\mathrm{ex}}}{[\mathrm{H}^{+}]^{2}_{(\mathrm{aq})}}\right] \tag{12}$$

Plot of $\lg D_{\mathrm{Ni}}$ versus $\lg[(\mathrm{HA})_2]$ (accordance with Fig. 2(a)) at pH 3.57 (initial pH of nickel plating effluent), shown in Fig. 3, was used to calculate the number of D2EHPA molecules. At pH 3.57, the slope was found to be 0.9669 (R^2=0.9969), indicating that the number of D2EHPA molecules was 1. Thus, the Ni extraction reaction can be represented as Reaction (13):

$$\mathrm{Ni}^{2+}_{(\mathrm{aq})}+(\mathrm{HA})_{2(\mathrm{org})} \rightleftharpoons \mathrm{NiA}_{2(\mathrm{org})}+2\mathrm{H}^{+}_{(\mathrm{aq})} \tag{13}$$

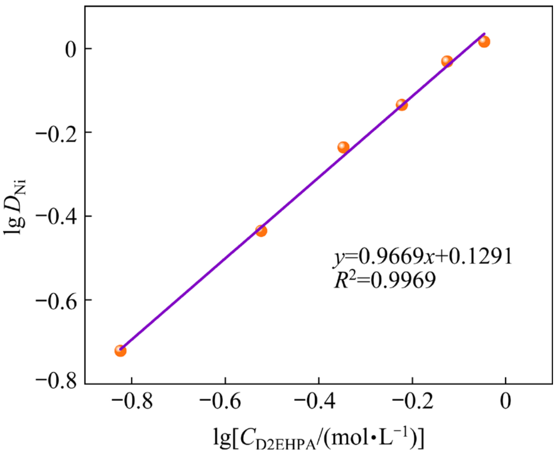

Fig. 3 Effect of D2EHPA concentration on distribution of Ni at pH 3.57 in kerosene at 25 °C and A/O ratio of 1:1 (Diluent: sulfonated kerosene, pH: 3.57, and time: 15 min)

3.1.4 Quantitative analysis with FTIR spectra

To verify the results obtained from the analysis in Section 3.1.3, a quantitative analysis with FTIR spectra was performed on the Ni(II)-loaded D2EHPA according to the procedures described by CHANG et al [17]. The analysis is based on the highly polar phosphoryl bond ($P=O$) of D2EHPA molecules that easily interacts with Ni(II). Figure 4(a) shows the phosphoryl band at 1217 cm^{-1} [27] in different concentrations of free-D2EHPA (D2EHPA not loaded with Ni(II)), diluted in sulfonated kerosene, from 300 to 900 mmol/L. As exhibited in Fig. 4(a), transmittance decreases with the increase of free-D2EHPA concentration. To determine the concentration of D2EHPA in the Ni(II)-loaded solution, a calibration curve was obtained from plot in Fig. 4(a), which allowed us to identify the transmittance versus D2EHPA concentration (Fig. S1(a) in SM). Figure 4(b) shows the FTIR transmittance bands associated with $P=O$ group (1217 cm^{-1}) in D2EHPA loaded with different $[Ni]_{org}$ (57.4−187.3 mmol/L). Based on the relative intensity of phosphoryl bands from Fig. 4(b), the free-D2EHPA concentration can be obtained from Fig. S1(a) in SM. The concentration of Ni–D2EHPA was then calculated by subtracting the corresponding free-D2EHPA concentration from the total D2EHPA concentration used, which was 900 mmol/L. By plotting [Ni–D2EHPA] against $[Ni]_{org}$ (Fig. S1(b) in SM), a slope value of 1.98 was obtained, indicating a constant stoichiometric ratio of D2EHPA to Ni(II) of 2:1. This result indicates that Ni(II) is solvated with one molecule of the dimeric form of D2EHPA with the formation of NiA_2 complexes in D2EHPA. This confirms the results obtained from both the equilibrium slope analysis.

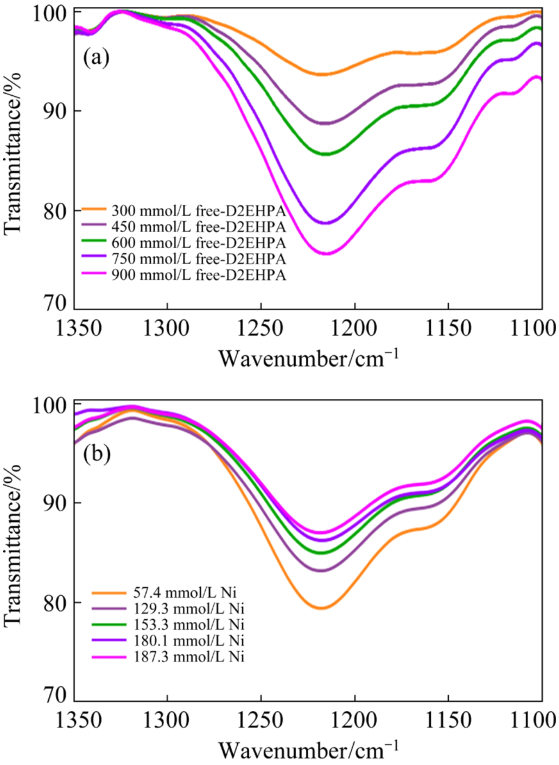

Fig. 4 Quantitative analysis with FTIR: (a) FTIR transmittance associated with $P=O$ group in D2EHPA standard solutions; (b) FTIR transmittance bands associated with $P=O$ group in DIEHPA organic phase loaded with Ni(II) (Diluent: sulfonated kerosene, and time: 15 min)

3.1.5 Effects of D2EHPA−decanol mixture concentration on Ni(II) extraction

Figure 5 depicts the volume fraction of decanol required to produce maximum synergy with different concentrations of D2EHPA in the extraction system. When the concentration of D2EHPA increased in range of 0.30−0.90 mol/L and the volume fraction of decanol was 5%−45% (volume fraction), the extraction efficiency of Ni(II) increased from 53.5% to 98.3%. At the same time, the extraction efficiency of Ni(II) reached a plateau (97.8%) when C_{D2EHPA} was 0.75 mol/L with decanol content of 35% (volume fraction). We obtained a synergistic enhancement factor ($R_{Ni,max}$) value of 11.89 using Eq. (5). Furthermore, more decanol was required to obtain the maximum synergistic effect

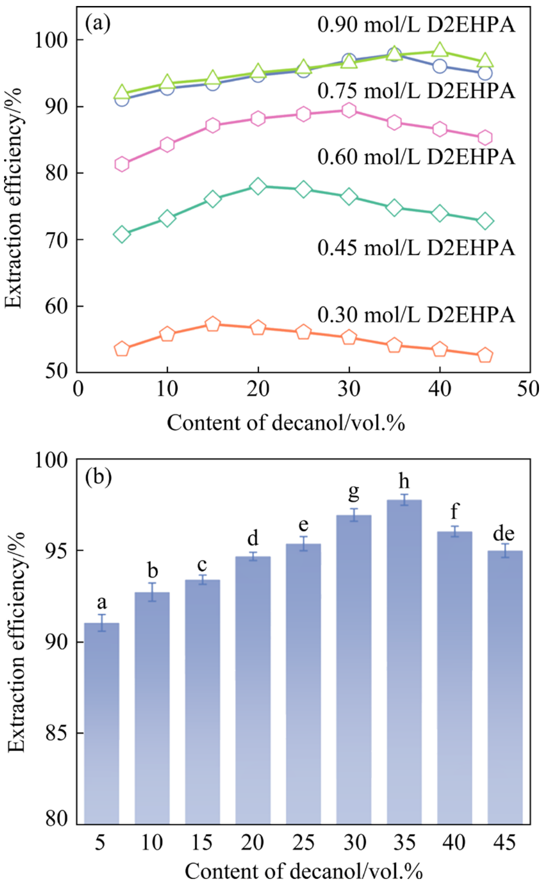

Fig. 5 Effects of D2EHPA−decanol mixture concentration on Ni(II) extraction efficiency: (a) C_{D2EHPA}=0.30−0.90 mol/L; (b) C_{D2EHPA}=0.75 mol/L (S_d: 50%, diluent: sulfonated kerosene, pH: 3.57, and time: 15 min; in (b), each point is expressed as mean±SD (n=3), and different letters show significant differences at $p<0.05$)

when D2EHPA concentration increased. After reaching the peak value, the extraction efficiency of Ni(II) decreased. This behavior is due to the polar groups provided by decanol molecules, causing coupling among D2EHPA molecules and providing more D2EHPA extraction sites. However, excessive decanol tends to wrap D2EHPA molecules and plays a shielding role against the extraction of Ni(II) [28]. Thus, based on these experimental results, the concentration C_{D2EHPA} of 0.75 mol/L and the decanol relative amount of 35% (volume fraction) were considered for the experiments.

3.1.6 Effects of initial pH and extraction time on Ni(II) extraction efficiency

The pH of the system is an important factor affecting the extraction efficiency of Ni(II). In the experiments, Ni(II) extraction efficiency increased with increasing of the initial pH of the nickel plating effluent (Fig. 6). This behavior could be due to the presence of fewer H^+ ions in the aqueous solution. The more favorable organophosphorus acidic extractants release more H^+ ions [29]. When pH was 3.57 (initial pH of effluent), the system in the presence of decanol could extract 97.8% of Ni(II) in the effluent. When the pH value increased to 5.58, the extraction efficiency only slightly increased by 0.4%. At the same time, when only D2EHPA alone was added as the extractant, system required a higher initial pH for extracting Ni(II). At a pH of 0.64 and D2EHPA concentration of 0.75 mol/L, the process could only extract 53.5% of Ni(II) from the effluent. However, D2EHPA accompanied by decanol could increase the extraction efficiency at lower pH conditions. At pH 0.64, the extraction efficiency was determined as 85.1%. Therefore, it was speculated that the D2EHPA−decanol synergistic extraction system provides a great potential in the treatment of the effluent under lower pH conditions.

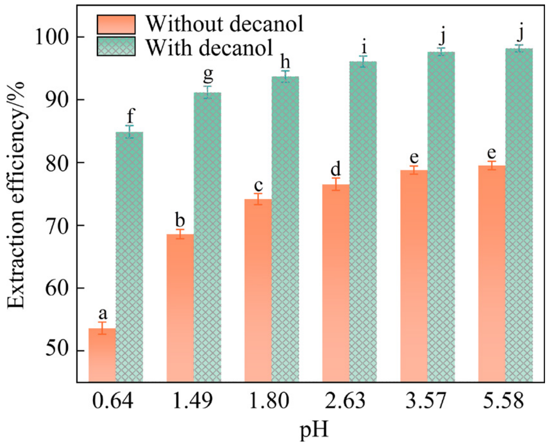

Fig. 6 Effects of initial pH on Ni(II) extraction efficiency (C_{D2EHPA}: 0.75 mol/L, decanol: 35% (volume fraction), S_d: 50%, diluent: sulfonated kerosene, and time: 15 min; each point is expressed as mean±SD (n=3), and different letters show significant differences at $p<0.05$)

The effects of extraction time on the extraction efficiency for Ni(II), as displayed in Fig. 7, revealed a relatively short time required for the extraction reaction to reach equilibrium conditions, because in the extraction process, the equilibrium time for the aqueous and organic phases depends on the mass transfer rate. A faster mass transfer leads to a shorter time needed for the process to reach the equilibrium conditions. As Fig. 7 reveals, the equilibrium can be reached in almost 6 min of the extraction process.

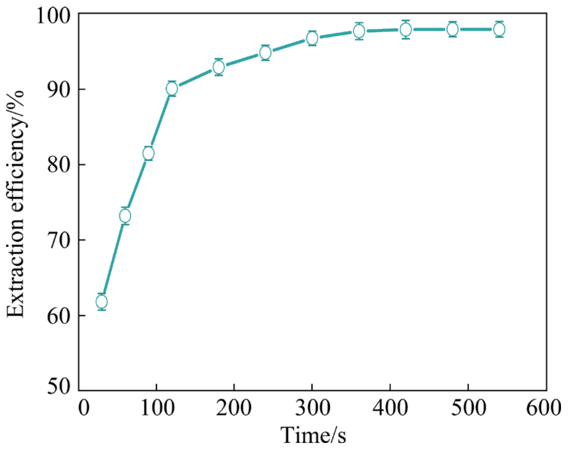

Fig. 7 Effects of extraction time on Ni(II) extraction efficiency ($C_{\rm D2EHPA}$: 0.75 mol/L, decanol: 35% (volume fraction), $S_{\rm d}$: 50%, diluent: sulfonated kerosene, and pH: 3.57)

3.2 Stripping process

From the experiments, we observed that the D2EHPA−decanol synergistic system provides a higher extraction efficiency. Stripping is the inverse reaction of extraction. In the entire extraction process, stripping is a considerable step to back extract nickel from the loaded organic phase and then recycle organic phase [29]. To explore the peelability of the D2EHPA−decanol synergistic extraction system, we conducted the following study.

3.2.1 Effects of stripping acid type on Ni(II) stripping efficiency

The effects of several inorganic acids at a concentration of 0.5 mol/L on the Ni(II) stripping process were studied. The results are presented in Table 2. Under the same concentrations, the stripping efficiency depends on the anion type in the order of NO_3^- > SO_4^{2-} > Cl^-. The results are attributed to the smallest charge and hydration energy of NO_3^- anion. Thus, this anion offers the weakest interaction with the water molecules, making it easier to break the bond for complexation with Ni(II). This characteristic leads to a larger stripping efficiency.

Table 2 Effects of stripping acid type on extraction efficiency (E) and stripping efficiency ($S_{\rm t}$) of Ni(II) ($C_{\rm D2EHPA}$: 0.75 mol/L, $S_{\rm d}$: 50%, diluent: sulfonated kerosene, pH 3.57, time: 6 min, and $C_{\rm acid}$: 0.5 mol/L)

Stripping acid	E/%	$S_{\rm t}$/%
HNO_3	78.5	72.2
HCl	78.9	65.5
H_2SO_4	77.5	69.3

The better performance of SO_4^{2-} compared with Cl^- can be explained by the difference in their ionic radius ($R_{Cl^-} < R_{SO_4^{2-}}$). Smaller ion gives stronger attraction and greater enthalpy of hydration. Therefore, smaller Cl^- anion provides a larger enthalpy of hydration compared with SO_4^{2-}. Sulfate anion with smaller enthalpy of hydration can weaken the interactions between water molecules, destroying the complete bonding of Ni(II). From these experimental observations and theoretical consideration, HNO_3 was chosen as the stripping agent.

3.2.2 Effects of HNO_3 concentration on Ni(II) stripping efficiency

The results of various stripping acid concentrations on the extraction of Ni(II) reveal that the stripping efficiency of Ni(II) increases with the increase of HNO_3 concentration (Fig. 8). This observation is due to the cation exchange reaction between H^+ ions in the stripping agent and Ni(II) present in the organic phase during the stripping process. The increase of H^+ concentration shifts the stripping reaction balance to the right. Moreover, an increase in the chemical potential difference promotes the exchange of Ni(II) with H^+ ion [30]. Moreover, when the same concentration of HNO_3 was used as the stripping acid to strip Ni(II), a larger stripping efficiency with the addition of

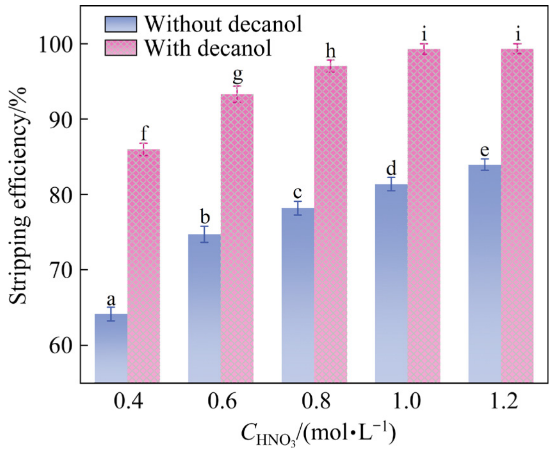

Fig. 8 Effects of HNO_3 concentration on Ni(II) stripping efficiency ($C_{\rm D2EHPA}$: 0.75 mol/L, decanol: 35% (volume fraction), $S_{\rm d}$: 50%, diluent: sulfonated kerosene, pH: 3.57, and time: 6 min; each point is expressed as mean±SD (n=3), and different letters show significant differences at p<0.05)

decanol was observed. The reason for this result is that decanol is an electron donor molecule attracting more H^+ ions from HNO_3. Delivery of more H^+ ions into the organic phase increases the efficiency of the available H^+ ions. Therefore, based on these results, 1 mol/L HNO_3 solution was selected as the stripping agent for the subsequent experiments.

3.3 Synergistic extraction mechanism

3.3.1 FTIR and UV−vis spectroscopy analyses

On occasions of low acidity, the extraction of metal ions with D2EHPA is mainly achieved by cations exchange between hydrogen atoms on the hydroxyl groups and metal ions. However, in the actual extraction process, D2EHPA molecules undergo intermolecular association through hydrogen bonds to form a dimer structure in which two bonds of O---H—O and O—H---O form between two D2EHPA molecules. This phenomenon causes the oxygen atoms to be connected to the hydrogen atoms, attracting almost all the electrons available in the hydrogen atoms. This makes the oxygen and the phosphorus atoms with almost the same numbers of electrons. As a result, the electron withdrawing ability of P atoms is weakened, causing the P—O bonds to get longer. Moreover, the electron density around the oxygen atoms decreases, which is not favorable to the combination of the extractant molecules and the metal ions.

The results of FTIR and UV−vis spectroscopy examinations performed on D2EHPA before and after mixing with decanol are displayed in Fig. 9. The stretching vibration peak for P—O bond shows red-shift in the FTIR spectra (Fig. 9(a)), shifting from 1033 to 1043 cm^{-1} [31]. This shift indicates that when decanol was added to D2EHPA, the polar functional groups of —OH in decanol weaken the hydrogen bonds connecting D2EHPA dimer molecules. As a result, the effects of hydrogen bond on P—O become weaker and the bond length of P—O gets shorter. Meanwhile, the electron density around the oxygen atoms become larger. These changes lead to the formation of complexes between the extractant molecules and the metal ions.

The UV−vis spectra in Fig. 9(b) reveal an increase in the electron activity in the O atom due to the weakening of hydrogen bonds on the P═O bonds. This phenomenon reduces the amount of energy required for the n→π* transition, so that the absorption peak of n→π* moves to the longer wave direction [32].

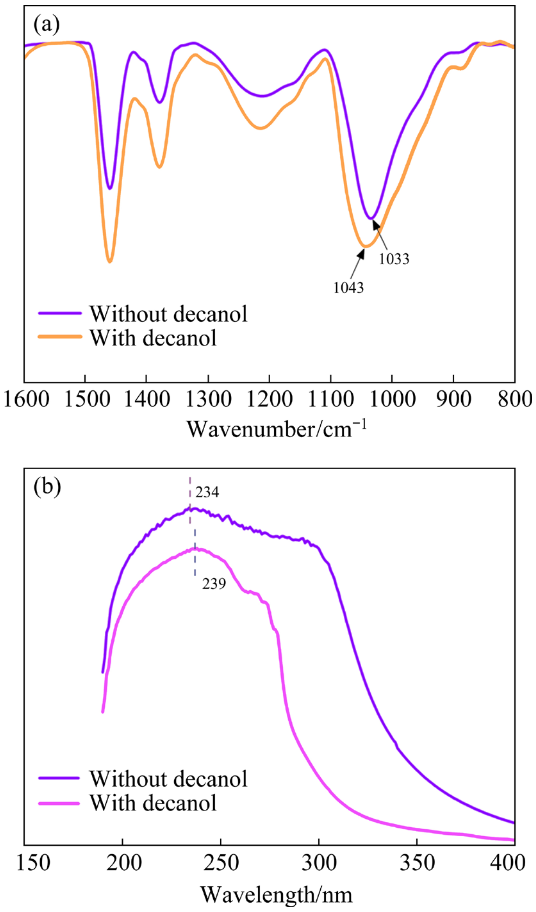

Fig. 9 FTIR (a) and UV−vis (b) spectra of D2EHPA in presence and absence of decanol

3.3.2 XPS analysis

To explore how D2EHPA molecules interact with decanol molecules, XPS analysis was further performed on D2EHPA in the presence and absence of decanol. The results are presented in Table 3 and Fig. 10. Oxygen atoms in the D2EHPA molecule without decanol exist in the forms of P═O [33], P—O [34], and C—O [35] groups. After the addition of decanol, the percentage of C—O in D2EHPA increases from 4.99% to 10.80%, demonstrating that the R' groups provided by decanol destroy the P—O bond in the D2EHPA dimer structure, forming a hydrogen bond with O atoms.

According to the above analytical results, it is speculated that the polar group of —OH provided by decanol synergistically breaks down the intermolecular hydrogen bonds between D2EHPA

Table 3 Peak positions, FWHM (full-width at half maximum), and relative contents from curve fitting of O 1s for XPS examinations of D2EHPA in presence and absence of decanol

Bond	Without decanol		
	Peak position/eV	FWHM/eV	Relative content/%
P═O	530.78	1.60	64.99
C—O	532.61	3.02	4.99
P—O	529.27	1.41	30.03
Bond	**With decanol**		
	Peak position/eV	FWHM/eV	Relative content/%
P═O	530.83	1.53	57.01
C—O	532.44	5.85	10.80
P—O	529.31	1.55	32.19

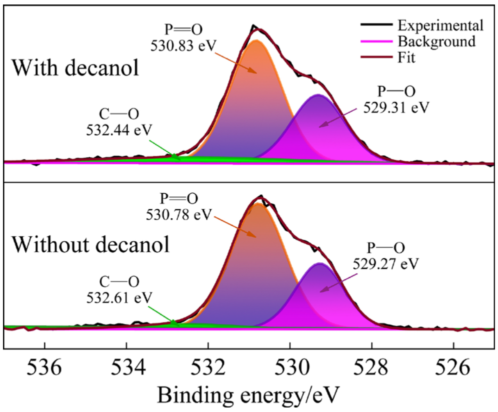

Fig. 10 Typical deconvoluted peaks of O 1s in D2EHPA molecules in presence and absence of decanol

molecules, weakening the attraction of the hydrogen bond to P—O and shortening the P—O bond length. Thus, the electron density around the oxygen atoms increases, leading to the formation of complexes between the extractant molecules and the metal ions. In addition, the R' groups ($C_{10}H_{21}$—) in the decanol molecules destroy the P—O bonds in the D2EHPA dimer structure, forming a bond with O (Fig. 11).

3.4 Effects and mechanism of different plant oil–sulfonated kerosene mixtures as diluents on Ni(II) extraction

To promote the green process with D2EHPA–decanol extraction system, different kinds of plant oil–sulfonated kerosene mixtures were used as diluents for the synergistic extraction process. The ratio of vegetable oil in the added diluent was varied from 10% to 100%. Among the five kinds of plant oils, the addition of 70% sunflower seed oil revealed relatively good extraction performance ($E_{70\%}$=84.52%) (Fig. 12(a)). However, when the sunflower seed oil was completely used as diluent, the extraction efficiency of the synergistic system dropped to 40.2%. This behavior may be attributed to the higher viscosity of sunflower seed oil than that of sulfonated kerosene, causing mass transfer resistance during the Ni(II) extraction process. Therefore, the influence of temperature on the extraction efficiency when sunflower seed oil was used as a diluent was investigated (Fig. S2 in SM). As exhibited in Fig. S2 in SM, the extraction efficiency of Ni(II) did not change significantly with increasing temperature. Therefore, the viscosity effect could not be the reason of the decrease in the extraction efficiency. Furthermore, a higher concentration of the nitric acid solution is required to strip Ni(II) loaded in sunflower seed oil (Fig. 12(b)). This behavior is due to the compatibility phenomenon. Because of the non-polar nature of plant oils, oil molecules tend to interact with the nickel solution, resulting in Ni(II) with relatively stronger stability in the extractant that requires relatively larger concentration of H^+ ions.

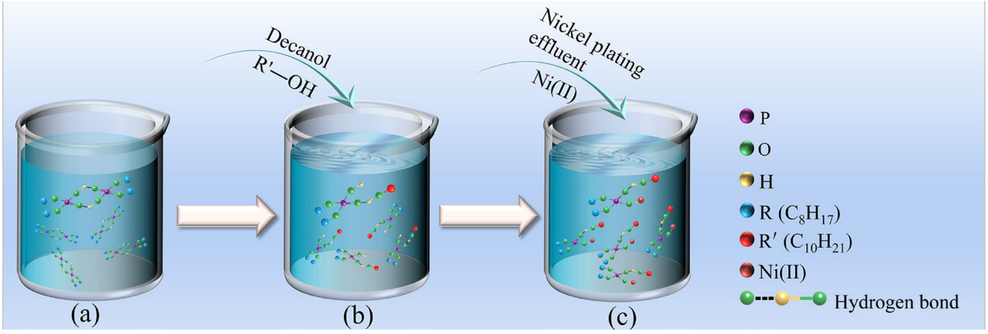

Fig. 11 Schematic diagram of D2EHPA–decanol synergistic extraction of Ni(II): (a) D2EHPA molecules; (b) Disruption of hydrogen bonds through addition of decanol; (c) Synergistic extraction of Ni(II)

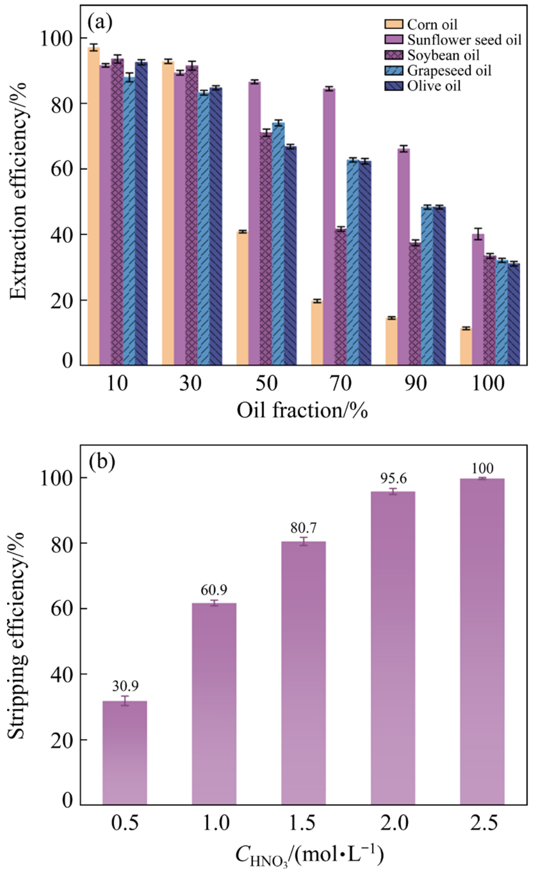

Fig. 12 Effects of different plant oil–sulfonated kerosene mixtures as diluents on Ni(II) extraction efficiency: (a) Effect of mixing ratio; (b) Stripping efficiency values at various HNO_3 contents (C_{D2EHPA}: 0.75 mol/L, decanol: 35% (volume fraction), S_d: 50%, pH: 3.57, and time: 30 min)

Additionally, when sunflower seed oil was used as diluent without decanol, Ni(II) extraction efficiency in 90 min was determined to be 32.7%. When decanol was allowed to react with D2EHPA for 30 and 90 min and then the extraction process was conducted, the Ni(II) extraction efficiency reached 40.2% and 97.1%, respectively. At the same time, the FTIR spectra in Fig. 13 reveal the stretching vibration peak for P—O bond shifting more obviously with longer mixing time. Therefore, we speculate that when sunflower seed oil is used as a diluent, the reason for the lower extraction efficiency is that D2EHPA and decanol are not completely mixed.

3.5 Performance with impurity ions and extraction

To investigate the selectivity of the extraction system, D2EHPA and D2EHPA−decanol mixed carriers were used to extract nickel plating effluent under the same experimental conditions. The extraction efficiency of each metal ion is shown in Fig. S3 of Supplementary Material. When sulfonated kerosene was used as a diluent, the extraction preference ratios [36] (compared by extraction percentage) of Ni to each of Cu, Al, and K were found as 4.13, 3.37, and 7.86 for the D2EHPA−decanol synergistic extraction case and 4.08, 3.45, and 7.71 for the D2EHPA case. When sunflower seed oil was used as a diluent, the extraction preference ratios (compared by extraction percentage) of Ni to each of Cu, Al, and K were determined as 4.09, 3.48, and 7.89 for the D2EHPA−decanol synergistic extraction case and 4.01, 3.62, and 7.97 for the D2EHPA case. These results show that when decanol is added to D2EHPA for synergistic extraction of nickel plating effluent, the extraction efficiency of Ni(II) as well as impurity ions increases; however it does not significantly change the selectivity of D2EHPA to extract impurity ions.

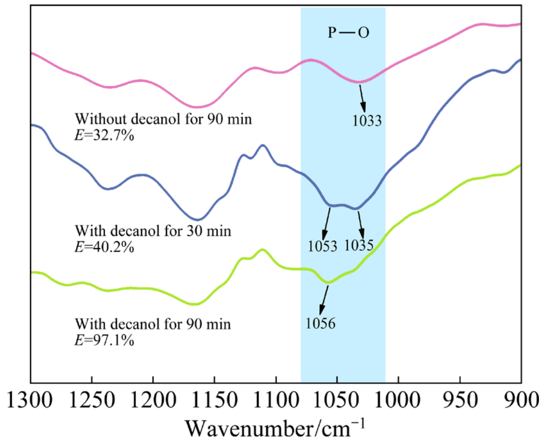

Fig. 13 FTIR spectra of sunflower seed oil without decanol and mixed with decanol for 30 and 90 min

3.6 Effects of organic phase recycling on Ni(II) extraction

After completing one cycle of the extraction and stripping process, the organic phase was recovered and saponified before continuing the extraction cycles. The specific process is presented in the Supplementary Material. Figure 14 shows the extraction efficiency of regenerated organic phase to extract Ni(II) from nickel plating effluent. The Ni(II) compound present in the effluent was successfully extracted after the organic phase was recycled for 3 cycles (Fig. 14). After the extraction, the organic phase loaded with Ni(II) was stripped using HNO_3 solution. The stripping solution was then evaporated and crystallized at 80 °C for 24 h. The XRD patterns of the product are shown in Fig. S4 of Supplementary Material.

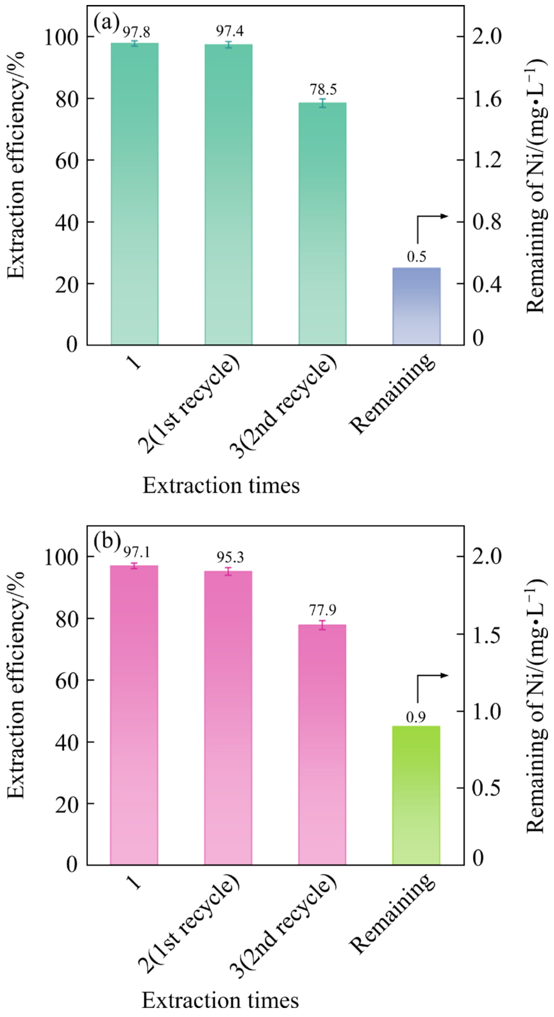

Fig. 14 Effects of organic phase recycling on Ni(II) extraction performance: (a) Sulfonated kerosene as diluent; (b) Sunflower seed oil as diluent (C_{D2EHPA}: 0.75 mol/L, decanol: 35% (volume fraction), S_d: 50%, and pH: 3.57)

4 Conclusions

(1) When sulfonated kerosene or sunflower seed oil was used as diluent, the single-stage extraction efficiency reached 97.8% and 97.1%, respectively, with a mixture composition of 0.75 mol/L D2EHPA and 35% (volume fraction) decanol. After three extractions, the Ni(II) concentration in the nickel plating effluent was decreased to below 1 mg/L.

(2) D2EHPA−decanol mixed carrier had a better strippability than D2EHPA. In D2EHPA−decanol mixed carrier, using sulfonated kerosene as diluent, and 1.0 mol/L HNO_3 could reach 100% stripping efficiency of Ni(II) loaded in the organic phase. Moreover, 2.5 mol/L HNO_3 could achieve the same stripping efficiency of Ni(II) when using sunflower oil as diluent.

(3) The mechanism of synergistic extraction is that the —OH functional groups in decanol molecules destroy the intermolecular hydrogen bonds in the D2EHPA dimers. As a result, the effects of hydrogen bonds on P—O become weaker and the bond length of P—O becomes shorter. Hence, the electron population of the oxygen atoms becomes denser, resulting in much easier complex formation between the extractant molecules and the metal ions.

Acknowledgments

The authors gratefully acknowledge the financial support from the National Natural Science Foundation of China (No. 52064038), and the Key Research and Development Program of Jiangxi Province, China (No. CK202002472).

Supplementary material

Supplementary material in this paper can be found at: http://tnmsc.csu.edu.cn/download/23-p1282-2021-1584-Supplementary_materials.pdf.

References

[1] TSAI T H, CHOU Hao-wei, WU Y F. Removal of nickel from chemical plating waste solution through precipitation and production of microsized nickel hydroxide particles [J]. Separation and Purification Technology, 2020, 251: 117315.

[2] LIU Fan, ZHOU Hong-yu, PAN Zhi-cheng, LIU Yang, YAO Gang, GUO Yong, LAI Bo. Degradation of sulfamethoxazole by cobalt−nickel powder composite catalyst coupled with peroxymonosulfate: Performance, degradation pathways and mechanistic consideration [J]. Journal of Hazardous Materials, 2020, 400: 123322.

[3] EL N A, KAZAK C. Preparation and characterization of novel nano-structured porous nickel alloy composite induced by electroless deposition and its performance in the hydrogen separation [J]. Separation and Purification Technology, 2016, 160: 73−80.

[4] ZENG Xian-lai, XU Ming, LI Jin-hui. Examining the sustainability of China's nickel supply: 1950—2050 [J]. Resources, Conservation and Recycling, 2018, 139: 188−193.

[5] YUAN Xue-hong, XUE Nan-dong, HAN Zhi-guang. A meta-analysis of heavy metals pollution in farmland and urban soils in China over the past 20 years [J]. Journal of Environmental Sciences-China, 2021, 101: 217−226.

[6] JIANG Bao, SU De-chun, WANG Xiao-qing, LIU Ji-fang, MA Yi-bing. Field evidence of decreased extractability of copper and nickel added to soils in 6-year field experiments [J]. Frontiers of Environmental Science & Engineering, 2018, 12: 71−77.

[7] YU Ling-yun, LI Rui-li, WU Hai-lun, ZHANG Shan-fa, CHAI Min-wei, SHEN Xiao-xue, HONG Mei, LIN Hai. Selective removal of Cu^{2+} ion in aqueous solution by poly (Acrylic Acid/Acrylamide) hydrogel [J]. Chinese Journal of Analytical Chemistry, 2020, 48: e20098−e20106.

[8] KURNIAWAN T, CHAN G, LO W H, BABEL S. Physico-chemical treatment techniques for wastewater laden with heavy metals [J]. Chemical Engineering Journal, 2006, 118: 83−98.

[9] NEKOUEI R, PAHLEVANI F, ASSEFI M, MAROUFI S, SAHAJWALLA V. Selective isolation of heavy metals from spent electronic waste solution by macroporous ion-exchange resins [J]. Journal of Hazardous Materials, 2019, 371: 389−396.

[10] ZHAO Zhi-yuan, SHI Shao-yuan, CAO Hong-bin, LI Yu-jiao, BRUGGEN B. Comparative studies on fouling of homogeneous anion exchange membranes by different structured organics in electrodialysis [J]. Journal of Environmental Sciences-China, 2019, 77: 218−228.

[11] HUANG Ting, WANG Yong-xi, HU Hui-ping, HU Fang, LUO Yu-qing, LIU Shi-jun. Phase separation in solvent extraction of cobalt from acidic sulfate solution using synergistic mixture containing dinonylnaphthalene sulfonic acid and 2-ethylhexyl 4-pyridinecarboxylate ester [J]. Transactions of Nonferrous Metals Society of China, 2019, 29: 1107−1116.

[12] HU Jiu-gang, CHEN Qi-yuan, HU Hui-ping, YIN Zhou-lan. Synergistic extraction of zinc from ammoniacal solutions using β-diketone mixed with CYANEX923 or LIX84I [J]. Transactions of Nonferrous Metals Society of China, 2012, 22: 1217−1223.

[13] GUAN Qing-jun, SUN Wei, ZHOU Gui-ying, LIU Jia-peng, YIN Zhi-gang. Recovery of cobalt and nickel in the presence of magnesium and calcium from sulfate solutions by Versatic 10 and mixtures of Versatic 10 and Cyanex 301 [J]. Transactions of Nonferrous Metals Society of China, 2016, 26: 865−873.

[14] ZHOU Hai-yue, DONG Ya-min, WANG Ya-bin, ZHAO Ze-yuan, XIAO Yu, SUN Xiao-qi. Recovery of Th(IV) from leaching solutions of rare earth residues using a synergistic solvent extraction system consisting of Cyanex 572 and n-octyl diphenyl phosphate (ODP) [J]. Hydrometallurgy, 2019, 183: 186−192.

[15] WU Ming, HE Hong-yang, XU Fei, XU Zhi-gao, ZHANG Wen-jie, HE Zheng-yan, QU Jun, CHI Ruan, HUANG Ling-yun. High-efficient and selective extraction of Hf over Zr with DIBK-P350 synergistic extraction system [J]. Separation and Purification Technology, 2019, 212: 255−261.

[16] SOEEZI A, ABDOLLAHI H, SHAFAEI S, RAHIMI E. Extraction and stripping of Cu and Ni from synthetic and industrial solutions of Sarcheshmeh Copper Mine containing Cu, Ni, Fe and Zn ions [J]. Transactions of Nonferrous Metals Society of China, 2020, 30: 518−534.

[17] CHANG Siu-hua, TENG T, ISMAIL N. Extraction of Cu(II) from aqueous solutions by vegetable oil-based organic solvents [J]. Journal of Hazardous Materials, 2010, 181: 868−872.

[18] SULAIMAN R, OTHMAN N. Synergistic green extraction of nickel ions from electroplating waste via mixtures of chelating and organophosphorus carrier [J]. Journal of Hazardous Materials, 2017, 340: 77−84.

[19] RAHMAN H, JUSOH N, OTHMAN N, ROSLY M, SULAIMAN R, NOAH N. Green formulation for synthetic dye extraction using synergistic mixture of acid-base extractant [J]. Separation and Purification Technology, 2019, 209: 293−300.

[20] SONG Yun-feng, HE Li-hua, ZHAO Zhong-wei, LIU Xu-heng. Separation and recovery of lithium from Li_3PO_4 leaching liquor using solvent extraction with saponified D2EHPA [J]. Separation and Purification Technology, 2019, 229: 115823.

[21] BARNARD K R, URBANI M D. The effect of organic acids on LIX®63 stability under harsh strip conditions and isolation of a diketone degradation product [J]. Hydrometallurgy, 2007, 89: 40−51.

[22] HU Fang, HU Hui-ping, LUO Yu-qing, WANG Yong-xi, YANG Jin-peng, HU Jiu-gang. The separation of Ni(II) over base metal ions in acidic polymetallic medium: Synergistic extraction and structural evidence [J]. Hydrometallurgy, 2018, 181: 240−247.

[23] TALEBI A, TENG T, ALKARKHI A, ISMAIL N. Nickel ion coupled counter complexation and decomplexation through a modified supported liquid membrane system [J]. RSC Advances, 2015, 5: 38424−38434.

[24] PARHI P K, CERRETANI L. Supported liquid membrane principle and its practices: A short review [J]. Journal of Chemistry, 2012, 2013: 1−11.

[25] KUMARI A, PANDA R, LEE Jin-young, THRIVENI T, JHA M, PATHAK D. Extraction of rare earth metals (REMs) from chloride medium by organo-metallic complexation using D2EHPA [J]. Separation and Purification Technology, 2019, 227: 115680.

[26] SUN Min, LIU Shi-jun, ZHANG Yun-ran, LIU Mei, YI Xin, HU Jiu-gang. Insights into the saponification process of di(2-ethylhexyl) phosphoric acid extractant: Thermodynamics and structural aspects [J]. Journal of Molecular Liquids, 2019, 280: 252−258.

[27] HAGHSHENAS F D, DARVISHI D, ETEMADI S, EIVAZI H A, KESHAVARZ A E, SALARDINI A. Interaction between TBP and D2EHPA during Zn, Cd, Mn, Cu, Co and Ni solvent extraction: A thermodynamic and empirical approach [J]. Hydrometallurgy, 2009, 98: 143−147.

[28] ZHANG Guo-zhi, CHEN De-sheng, ZHAO Wei, ZHAO Hong-xin, WANG Li-na, WANG Wei-jing, QI Tao. A novel D2EHPA-based synergistic extraction system for the recovery of chromium(III) [J]. Chemical Engineering Journal,

2016, 302: 233−238.

[29] YING Zi-wen, HUO Man-xing, WU Gui-xuan, LI Jie, JU Yun, WEI Qi-feng, REN Xiu-lian. Recovery of vanadium and chromium from leaching solution of sodium roasting vanadium slag by stepwise separation using amide and EHEHPA [J]. Separation and Purification Technology, 2021, 269: 118741.

[30] WANG Ning, WANG Qi, LU Wen-juan, RU Miao-yan, YANG Yan-zhao. Extraction and stripping of platinum(IV) from acidic chloride media using guanidinium ionic liquid [J]. Journal of Molecular Liquids, 2019, 293: 111040.

[31] AZIZITORGHABEH A, RASHCHI F, BABAKHANI A. Stoichiometry and structural studies of Fe(III) and Zn(II) solvent extraction using D2EHPA/TBP [J]. Separation and Purification Technology, 2016, 171: 197−205.

[32] HU Ying-tian, WEN Yi-zhang, WANG Xiao-ping. Novel method of turbidity compensation for chemical oxygen demand measurements by using UV–vis spectrometry [J]. Sensors and Actuators B: Chemical, 2016, 227: 393−398.

[33] DESIMONI E, CASELLA G I, MORONE A, SALVI A M. XPS determination of oxygen-containing functional groups on carbon-fibre surfaces and the cleaning of these surfaces [J]. Surface and Interface Analysis, 1990, 15: 627−634.

[34] FOLKESSON B, SUNDBERG P. A reinvestigation of the binding energy versus atomic charge relation for oxygen from X-ray photoelectron spectroscopy [J]. Spectroscopy Letters, 1987, 20: 193−200.

[35] ZOU Lie-zhao, SHAO Peng-hui, ZHANG Kai, YANG Li-ming, YOU Deng, SHI Hui, PAVLOSTATHIS S G, LAI Wei-qiang, LIANG Da-hao, LUO Xu-biao. Tannic acid-based adsorbent with superior selectivity for lead(II) capture: Adsorption site and selective mechanism [J]. Chemical Engineering Journal, 2019, 364: 160−166.

[36] LIU Chong, HSU P C, XIE Jin, ZHAO Jie, WU Tong, WANG Hao-tian, LIU Wei, ZHANG Jin-song, CHU S, CUI Yi. A half-wave rectified alternating current electrochemical method for uranium extraction from seawater [J]. Nature Energy, 2017, 2(4): 17007.

一种基于 D2EHPA 的新型绿色协同萃取配方用于从镀镍废液中回收镍

李英朋 [1]，罗秀玉 [2]，王忠兵 [1]，关 乾 [1]，倪晨权 [3]，张捷菲 [1]，刘春力 [1]，姬海燕 [1]，罗旭彪 [1]，曾桂生 [1]

1. 南昌航空大学 重金属污染物控制与资源化国家地方联合工程研究中心，南昌 330063；
2. 福建水利电力职业技术学院，永安 641836；
3. 中南大学 资源加工与生物工程学院 生物冶金教育部重点实验室，长沙 410083

摘　要：开发一种新型绿色协同萃取剂(二-2-乙基己基磷酸(D2EHPA)−癸醇)用于从镀镍废液中回收 Ni(II)。结果表明，D2EHPA−癸醇混合载体在萃取过程中表现出显著的协同效果。当磺化煤油或葵花籽油为稀释剂时，Ni(II)的单级萃取率分别达到 97.8%和 97.1%。经过 3 次萃取后，镀镍废水中 Ni(II)浓度降至 1 mg/L 以下。另外，在反萃取阶段，Ni(II)在 D2EHPA−癸醇混合载体中的反萃取效率高于 D2EHPA。机理研究表明，癸醇提供的极性基团(—OH)会破坏 D2EHPA 二聚体结构中的氢键，导致 P—O 键在范德华力的作用下变短，同时形成氧原子富电子中心，最后，P—O 与 Ni 离子在静电力促使下形成新的 P—O—Ni 结构。

关键词：协同萃取；废水；镍；D2EHPA；绿色稀释剂

(Edited by Bing YANG)