



Separation Science and Engineering

The separation and recovery of copper(II), nickel(II), cobalt(II), zinc(II), and cadmium(II) in a sulfate-based solution using a mixture of Versatic 10 acid and Mextral 984H☆



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ARTICLE INFO

Article history:

Received 25 May 2016

Received in revised form 12 October 2016

Accepted 19 October 2016

Available online 31 January 2017

Keywords:

Water treatment

Solvent extraction

Versatic 10 acid

Mextral 984H

Recovery

ABSTRACT

We studied the separation and recovery of copper(II), nickel(II), cobalt(II), zinc(II), and cadmium(II) from magnesium and calcium, using synergistic solvent extraction (SSX) in a typical hydrometallurgical waste solution. A mixture of Versatic 10 acid and Mextral 984H, diluted with Mextral DT100, was used to obtain fundamental data on pH and distribution isotherms, as well as the kinetics of extraction and stripping. We also investigated the main effects and interactions of common solvent extraction factors: the extraction pH at equilibrium, the temperature, and the extractant concentration. The synergistic effect for extracting metals was confirmed. The results showed that the addition of Mextral 984H enhanced the separation factors of copper, nickel, cobalt, zinc, and cadmium over magnesium and calcium. Compared with Versatic 10 acid alone, for a mixture of $0.5 \text{ mol} \cdot \text{L}^{-1}$ Versatic 10 acid/ $0.5 \text{ mol} \cdot \text{L}^{-1}$ Mextral 984H, ΔpH_{50} values of copper, nickel, cobalt, zinc, and cadmium were found to be >2.0, 3.30, 2.85, 0.95, and 1.32 pH units, respectively. The $\Delta\text{pH}_{50(\text{Zn-Mg})}$ and $\Delta\text{pH}_{50(\text{Zn-Ca})}$ values were 3.27 and 2.25, respectively, indicating easy separation and recovery of copper, nickel, zinc, cobalt, and cadmium. The extraction and stripping of copper, cobalt, zinc, and cadmium were fast, with 90% of the metal transferred in 2 min. We next studied whether the metals could be stripped from the extracted liquid selectively in sequence, by using sulfuric acid at different concentrations. The influence of the molecular structure of the oxime and carboxylic acid components upon the synergistic effects was identified by numerical analysis. Excellent separation of copper, nickel, cobalt, and zinc over magnesium and calcium was achieved with this synergistic solvent extraction system.

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1. Introduction

Wastewaters containing heavy metals like copper(II), cobalt(II), nickel(II), zinc(II), and cadmium(II) have caused serious global environmental problems. Solvent extraction (SX), a physicochemical method, is relatively convenient and cost-effective way to recover heavy metals from wastewaters, provided that the metal concentrations are reasonably high and the organic reagents are commercially available [1–6]. The concentrations of heavy metals can be largely increased by using membrane distillation (MD), as suggested by Kesime *et al.* [7], with fresh water recovered. However, no single solvent extractant is commercially available for the removal of these heavy metals together, because they have similar aqueous chemical behaviors in aqueous solutions [8–10]. Synergistic

solvent extraction (SSX), using a synergist to improve the selectivity of an extractant, could be an attractive alternative to extract all the heavy metals mentioned above from wastewaters [11,12].

SSX has attracted more and more attention since the 1960s [13,30]. In particular, acidic systems mixed with the nitrogen donor group have been found to produce strong synergistic effects on the extraction of certain metal ions [14–16]. The extraction of metals using carboxylic acids and mixtures of other extractants (a Mintek synergist or Avicea CLX50 (diisodecyl 3,5-pyridinedicarboxylate)) was studied, which form synergistic mixtures for the separation of nickel and cobalt from calcium, magnesium, and manganese [17,18]. Cheng *et al.* [19–21] and Zhu *et al.* [22] found that the combination of LIX63 (an aliphatic α -hydroxyoxime, active component 5,8-diethyl-7-hydroxy-6-dodecanone oxime) [23] with Versatic 10 acid (also known as neodecanoic acid, a mixture of several highly branched- C_{10} carboxylic acid isomers) resulted in significant synergistic shifts for nickel, cobalt, copper, zinc, and manganese, and in antagonistic shifts for calcium and magnesium. Large synergistic shifts were obtained for cobalt and zinc, which showed that the synergistic extraction system could efficiently recover lower content metals in a multi-metal solution. In another paper [24,25], the performance of two

☆ Supported by the National Major Science and Technology Program for Water Pollution Control and Treatment (2010ZX07212-006), and the International S&T Cooperation Program “Research of a New Combined Technology Based on Membrane Distillation and Synergistic Extraction for Heavy Metal Waste Water Treatment”(2014DFA90920).

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SSX systems, containing Versatic 10 acid/LIX63/TBP (tri-butyl phosphate) and Versatic 10 acid/4PC (*n*-decyl-4-pyridinecarboxylate ester) respectively, was studied in batch tests. Further, Zhu *et al.* [22] found in two steps using two different SSX systems (Versatic 10 acid/LIX63/TBP and Alamine336 (Tri-*n*-octylamine)/TBP in Shellsol D70 (100% aliphatic)) in separate circuits to separate metals gradually. Recently, the phenolic oximes reagent [26–29], which is more stable than LIX63 in copper extraction and is widely used in metal separation, was introduced into a synergistic system. These studies all provided good ideas for the recovery of the metals from sulfate acidic leach liquors or wastewater, and for efficient separation of nickel and copper from other metals. A newly developed oxime reagent Mextral 984H, which contains aldoxime and ketoxime (as metal complexant), modifiers, stabilizers, defoamer and surfactant, *etc.*, was a stable and efficient solvent for the extraction of copper or zinc from sulfuric acid solution. The commercial Mextral 984H gives better results than expected from summing the properties of its individual components, its extraction performance is better than ketoxime and stripping effect is better than aldoxime. It can form water insoluble complexes with various metallic cations. The current studies for the potential use of this extractant in the solvent mixture are on the way.

This paper studies the extraction of copper(II), nickel(II), cobalt(II), zinc(II) and cadmium(II) by Versatic 10 acid/Mextral 984H. The extractants were diluted with Mextral DT100 and added to a sulfate acid solution to learn the factors affecting extraction and optimize the extraction parameters. The application of the extractant mixture, Versatic 10 acid together with commercially readily available synergist Mextral 984H, is first concerned. When using Versatic 10 acid alone, the pH should be adjusted to a high value to recover the desirable metals while the current pH of the solution to be treated with is usually low. Also, when pH reaches 7, the solubility for the Versatic 10 acid in the aqueous solution increases heavily. In order to solve the problem, we first studied the separation effects and roles of carboxylic acids and nitrogen-containing oxime extractant mixtures. The separation and recovery of copper(II), nickel(II), cobalt(II), zinc(II), and cadmium(II) in wastewater were achieved. We verified that Versatic 10 acid/Mextral 984H is a potential synergistic system using commercially available reagents. Numerical slope analysis of the data was carried out to elucidate the mechanism of the extractants with divalent metals in the organic phase.

2. Materials and Methods

2.1. Aqueous feed solution

An aqueous feed solution, typical of hydrometallurgical wastewaters, containing ($\text{g} \cdot \text{L}^{-1}$) Cu 2.0, Ni 0.5, Co 0.5, Zn 5.0, Cd 0.7, Mg 10, and Ca 0.2, was prepared by dissolving analytical grade metal sulfate salts in de-ionized water including $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. The typical hydrometallurgical wastewaters data were acquired by statistic treatment and got average value from the wastewater samples, which were collected and analyzed in the onsite hydrometallurgical plants distributed around some main metallurgical and mining companies in China.

2.2. Organic solution

The organic solvents Mextral 984H and Mextral DT100 were supplied by Kopperchem of China. Versatic 10 acid was supplied by Shell Chemicals. The components of the extractant are provided by the original company. Mextral 984H is a mixture of 2-hydroxy-5-nonylacetophenone oxime and 5-nonylsalicylaloxime in a high flash point hydrocarbon diluent, and reportedly contained no more than 50% active extractant component, the ratio of ketoxime to aldoxime is 1:1. Mextral DT100 (containing >99% aliphatics and <0.5% aromatics) was used as the diluent for all organic systems tested and kept as diluent in all our extraction system experiment. All reagents were used as received.

2.3. Experimental procedure

All batch experiments were carried out in glass bottles with stoppers. The pH of the solution in all experiment, adjusted to the desired value by adding drops of $5 \text{ mol} \cdot \text{L}^{-1}$ NaOH or $0.5 \text{ mol} \cdot \text{L}^{-1}$ diluted sulfuric acid, was measured by a special provided on-line pH monitor (Thermo Scientific A211 Benchtop pH Meter). The electrode probe was held and placed into the sample mixture and the pH value could be read on the screen in any time intervals instantly. The volume of the aqueous sample was 40 ml and the ratio of the two phases (A/O) was 1:1 each time. The two phases were mixed for enough time with 20 min to ensure that equilibrium was reached. After phase separation, the metal concentrations in the raffinate were detected by inductively coupled plasma atomic emission spectroscopy (ICP-AES), and the metal concentrations in the organic phase were calculated by mass balance. All shakeouts were run at 40 °C.

To determine the extraction kinetics of the metals, the organic solutions were saponified with sodium hydroxide solution to reach the required pH equilibration. The 40 ml synthetic wastewater and the pre-equilibrated organic solution were mixed at an A/O ratio of 1:1 and 40 °C. Samples of the solution mixture were taken at 0.5, 1.0, 2.0, 3.0, 5.0, 7.0, 10.0, and 20.0 min, using a sampling syringe. Likewise, to determine the stripping kinetics, a loaded organic solution prepared by the extraction of metals at selected pH values was mixed with the acidic stripping solution at an A/O ratio of 1:1 and 40 °C. Samples of the solution mixture were taken at different times as previously described for the determination of extraction kinetics.

To study the effect of Mextral 984H concentration, organic phases containing Mextral 984H in concentrations ranging from 0.1 to $0.5 \text{ mol} \cdot \text{L}^{-1}$ were prepared with a constant concentration of Versatic 10 acid ($0.5 \text{ mol} \cdot \text{L}^{-1}$). With this constant extractant concentration, we then investigated the effect of varying the pH in steps of 0.5, between 1.0 and 7.0. After phase separation, the concentration of ions in the aqueous phase was again determined by ICP-AES, and the concentration of metal ions in the organic phase was determined by mass balance. The concentrations were used to obtain the distribution ratio *D*, which was taken as the ratio of the concentration of metal ions in the organic phase to that present in the aqueous phase. The similar process was used when we studied the effect of Versatic 10 acid concentration. As for the slope analysis experiments, the experimental condition was selected so that the percent extraction of the metals was found to be in the 20%–90% ranges. Solutions of $10 \mu\text{g} \cdot \text{g}^{-1}$ of each metal were prepared by weighing the quantity of the corresponding salts. Equal volumes of the aqueous and organic phases were shaken long enough for 20 min to ensure that equilibrium was reached. This time was previously determined by measuring the kinetics of the SSX system.

3. Results and Discussion

3.1. Extraction pH isotherms of a Versatic10 and Mextral 984H system

The synergism happens when two extractants cooperate to increase the extraction, which is greater than the sum values obtained with each extractant operating independently [30]. Except for the variation in the distribution ratios of a metal ion with mixture of extractants, it is usually seen with large shifts of the curves drawn in the extraction pH isotherms. The method which presents ΔpH_{50} to compare the effect of each solvent extractant was commonly used in the works by Cheng *et al.* [21,31] and Preston [16,18].

The divalent metals in the simulated typical wastewater, including copper, nickel, cobalt, zinc, and cadmium, are desirable substances to extract and recycle. Fig. 1 shows the metal extraction pH isotherms with the organic system consisting of $0.5 \text{ mol} \cdot \text{L}^{-1}$ Mextral 984H, in our experiment the extraction percentage of metals varied with increasing pH of the aqueous solution. The metal extraction order was found to be $\text{Cu} \gg \text{Ni} > \text{Co} \approx \text{Zn} > \text{Cd} > \text{Ca} \approx \text{Mg}$ (Table 1). The results showed that

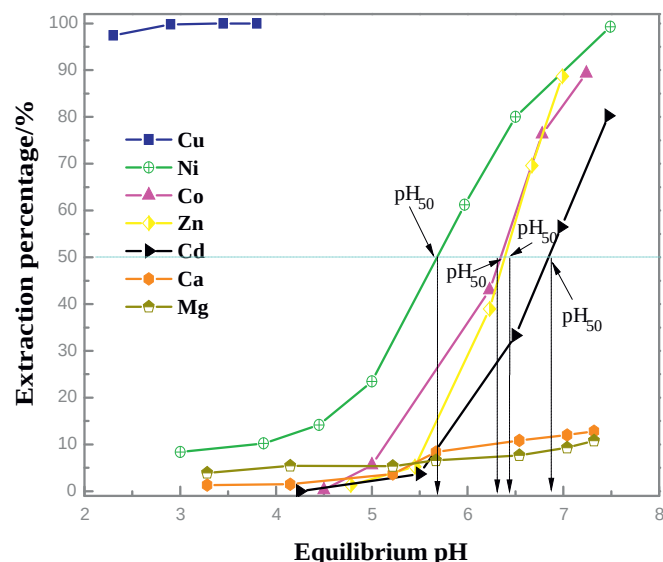


Fig. 1. Extraction pH isotherms of metals with 0.5 mol·L⁻¹ Mextral 984H in Mextral DT100 and the synthetic solution at an A/O ratio of 1:1 and 40 °C.

Table 1

pH₅₀ and ΔpH₅₀ values of metals with the organic systems containing Versatic 10 or Mextral 984H alone, and both Versatic 10 and Mextral 984H^①

System	Metal values							
	pH	Ni	Co	Cu	Zn	Cd	Mg	Ca
0.5 mol·L ⁻¹ Versatic 10	pH ₅₀	6.4	6.6	4	5.7	6.12	7.85	7.36
0.5 mol·L ⁻¹ Mextral 984H	pH ₅₀	5.66	6.4	1.8	6.5	6.9	–	>
0.5 mol·L ⁻¹ Versatic 10/ 0.1 mol·L ⁻¹ Mextral 984H	pH ₅₀	3.9	4.6	<2	5.3	5.1	–	7.39
	ΔpH ₅₀	2.5	2	>2	0.4	1.02	–	–0.03
0.5 mol·L ⁻¹ Versatic 10/ 0.3 mol·L ⁻¹ Mextral 984H	pH ₅₀	3.47	3.85	<2	5.2	5.05	–	7.56
	ΔpH ₅₀	2.78	2.75	>2	0.55	1.07	–	–0.2
0.5 mol·L ⁻¹ Versatic 10/ 0.5 mol·L ⁻¹ Mextral 984H	pH ₅₀	3.10	3.75	<2	4.75	4.8	8.02	7
	ΔpH ₅₀	3.30	2.85	>2	0.95	1.32	–0.17	0.36

^① An aqueous solution containing simultaneously all the metal cations, Versatic 10 denotes Versatic 10 acid.

pH₅₀^{Ni} = 5.66, pH₅₀^{Co} = 6.4, pH₅₀^{Zn} = 6.5, and pH₅₀^{Cd} = 6.9. Cu was well extracted at low pH values by Mextral 984H, while Ni, Co, Zn, and Cd extraction required high pH values. The pH₅₀ values between these metals are very close and therefore, it was difficult to separate nickel, zinc, and cadmium by using Mextral 984H.

Fig. 2 shows the metal extraction pH isotherms with the organic system consisting of 0.5 mol·L⁻¹ Versatic 10 acid. It can be seen that the metal extraction order is Cu > Zn > Cd > Ni > Co > Ca > Mg, and the heavy metal ions were usually extracted within the range of high pH values, where metal hydrolysis occurred. The separation factors between the desirable metals with calcite are small which could introduce the generation of gypsum in aqueous solution if operated under this condition. It would thus be difficult to separate the valuable metals from others with only a few steps, and using the cascade process to extract these metals would be costly [32]. As discussed earlier [33–36], Versatic 10 acid alone showed poor selectivity for metal values, and the pH₅₀ values were relatively close. However, with the mixed extractant systems, metal extraction could be carried out over a wide range of pH values.

The metal extraction pH isotherms with the organic system consisting of 0.5 mol·L⁻¹ Versatic 10 acid and 0.5 mol·L⁻¹ Mextral 984H are shown in Fig. 3. It can be seen that the metal extraction order changed to Cu > Ni > Co > Cd > Zn > Ca > Mg and the metal pH₅₀ values were 3.10, 3.75, 4.75 and 4.80 for Ni, Co, Zn and Cd,

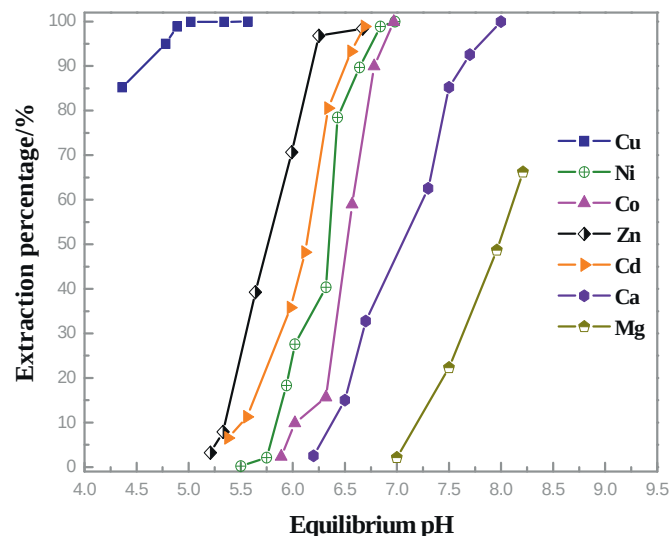


Fig. 2. Extraction pH isotherms of metals with 0.5 mol·L⁻¹ Versatic 10 in Mextral DT100 and the synthetic solution at an A/O ratio of 1:1 and 40 °C.

respectively, resulting in ΔpH₅₀ values of 3.30, 2.85, 0.95 and 1.32 for these metals, respectively (Table 1). The synergistic effect by mixing Mextral 984H with Versatic 10 acid on the extraction of the heavy metals is very significant. This is especially true for nickel and cobalt with pH₅₀ shift of massive 3.30 and 2.85, respectively. The ΔpH₅₀ value of zinc and calcium was found to be 2.25 (Table 2), indicating that it is very easy to separate the heavy metal group from calcium and magnesium using the mixed Versatic 10 acid and Mextral 984H sys-

Table 2

ΔpH₅₀ values between different metals while the organic systems containing Versatic 10 alone, and both Versatic 10 and Mextral 984H

Selective extraction	Synergistic extraction system (Extractant/synergist)			
	0.5 mol·L ⁻¹ Versatic 10	0.5 mol·L ⁻¹ Versatic 10/ 0.1 mol·L ⁻¹ Mextral 984H	0.5 mol·L ⁻¹ Versatic 10/ 0.3 mol·L ⁻¹ Mextral 984H	0.5 mol·L ⁻¹ Versatic 10/ 0.5 mol·L ⁻¹ Mextral 984H
ΔpH ₅₀ (Zn-Mg)	2.15	–	–	3.27
ΔpH ₅₀ (Zn-Ca)	1.66	2.09	2.36	2.25

tem. As copper was extracted at very low pH, the metals of concern can be separated to three groups as shown in Fig. 3. Copper, nickel, cobalt, zinc and cadmium can be separated from calcium and magnesium by extraction with the mixed Versatic 10 acid/Mextral 984H system at pH 5.5 and nickel, cobalt, zinc and cadmium can be selectively stripped at pH 2, leaving only copper in the organic solution. The copper in the organic solution can be stripped using very acidic solution, for example, 100 g·L⁻¹ H₂SO₄. The heavy metals except copper were extracted in the pH range of 3.0–5.5, where no heavy metal hydrolysis would occur. This means that with the mixed Versatic 10 acid/Mextral 984H system, not only the heavy metals can be readily recovered and separated from calcium and magnesium, but also avoiding heavy metal hydrolysis.

3.2. Effect of Mextral 984H concentration on metal extraction

Adding five different concentrations of Mextral 984H (0.1 mol·L⁻¹, 0.2 mol·L⁻¹, 0.3 mol·L⁻¹, 0.4 mol·L⁻¹, and 0.5 mol·L⁻¹) to 0.5 mol·L⁻¹ Versatic 10 acid caused the metal extraction pH isotherm shift to lower pH values and the shifts increased with the increasing Mextral 984H concentration. The similar synergistic effect trend was observed by Cheng [19] during solvent extraction of nickel and cobalt

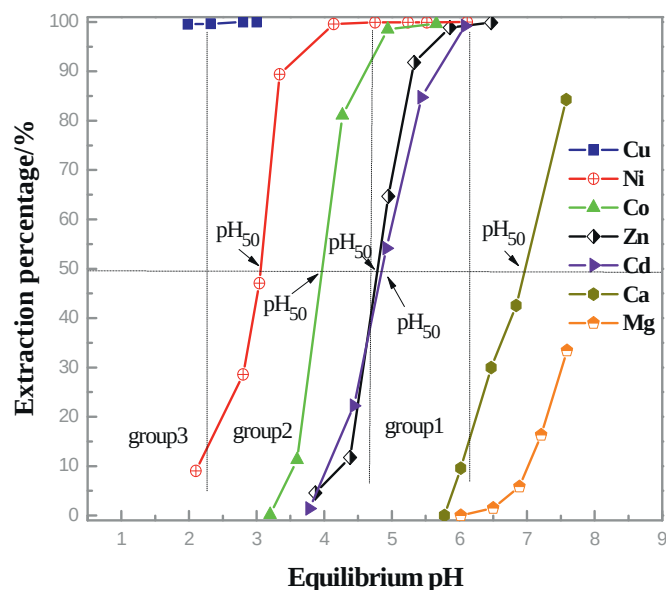


Fig. 3. Extraction pH isotherms of metals with 0.5 mol·L⁻¹ Versatic 10 acid/0.5 mol·L⁻¹ Mextral 984H in Mextral DT100 and the synthetic wastewater solution at an A/O ratio of 1:1 and 40 °C.

from sulfate solutions with carboxylic acid and aliphatic hydroxyoxime mixture. Fig. 4 shows the nickel pH isotherms with the 0.5 mol·L⁻¹ Versatic 10 acid alone and the five mixed organic systems and how increasing concentrations of Mextral 984H in 0.5 mol·L⁻¹ Versatic 10 acid affected the pH₅₀ values for nickel. The ΔpH₅₀ value changed by 0.8 units between the maximum concentration, with 0.5 mol·L⁻¹ Mextral 984H, and the lowest concentration, with 0.1 mol·L⁻¹ Mextral 984H. The effect of Mextral concentration on the extraction isotherms of cobalt, zinc and cadmium was found similar. "The pH₅₀ and ΔpH₅₀ values of cobalt, zinc and cadmium with the Versatic 10 acid alone and the three mixed Versatic 10 acid/Mextral 984H systems are also listed in Table 1." It was noted that the effect of Mextral 984H on the nickel and cobalt extraction pH isotherms is much more significant than that on zinc and cadmium extraction pH isotherms. For example, by adding 0.1 mol·L⁻¹ Mextral 984H in 0.5 mol·L⁻¹ Versatic 10 acid system, the nickel pH₅₀ decreased from 6.4 to 3.9, resulting in a ΔpH₅₀ value of 2.5

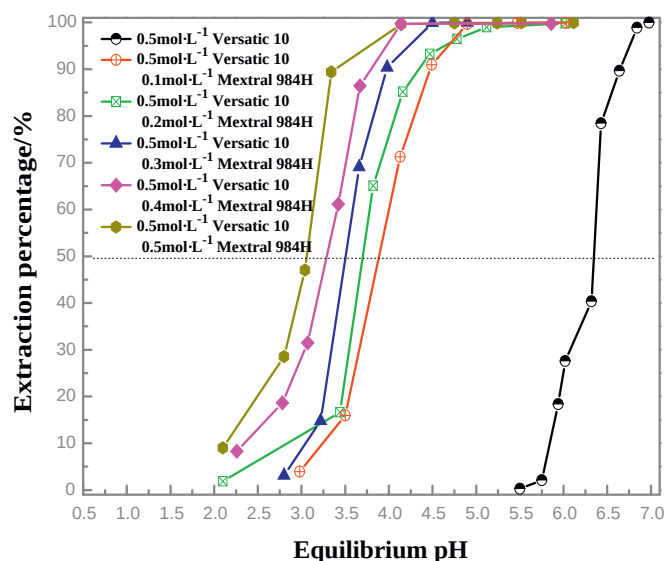


Fig. 4. Effect of addition of Mextral 984H on extraction of nickel with 0.5 mol·L⁻¹ Versatic 10 and Mextral 984H in Mextral DT100 diluent at an A/O ratio of 1:1 and 40 °C.

and the zinc pH₅₀ decreased from 5.7 to 5.3, resulting in a ΔpH₅₀ value of 0.4 (Table 1).

The addition of the Mextral 984H to a zinc and cadmium system brought about a slight but still substantial increase in the pH₅₀ value. The effects for nickel, cobalt, zinc, and cadmium increased the separation factor between the desirable metal values and the values for undesirable metals like magnesium and calcium. Among the desirable metals, pH₅₀ values for Cu, Ni/Co, and Zn/Cd fell into three groups, with large pH₅₀ intervals between them, showing that it is possible for the synergistic system to separate different metal values with appropriate concentration ratios.

3.3. Effect of temperature on metal extraction by a Versatic 10 acid/Mextral 984H mixture

The effect of temperature on the extraction of metal ions by a mixture of 0.5 mol·L⁻¹ Versatic 10 acid and 0.3 mol·L⁻¹ Mextral 984H was investigated at 20 and 40 °C. Generally, the higher temperature increased the extraction percents of metal values for a given pH value. The effect of temperature on the nickel extraction pH isotherms is shown in Fig. 5 and that on cobalt, zinc and cadmium is similar. As the figure shows, the extraction isotherm is shifted to a lower pH value at the higher temperature, facilitating the extraction and separation of valuable metals from undesirable metals. A pronounced influence of temperature was observed in the extraction of nickel, cobalt, zinc, and cadmium, but not in the extraction of magnesium and calcium. It is indicated that the separation of heavy metals from magnesium and calcium can be slightly enhanced at higher temperature, for example 40 °C, with the mixed Versatic 10 acid/Mextral 984H system.

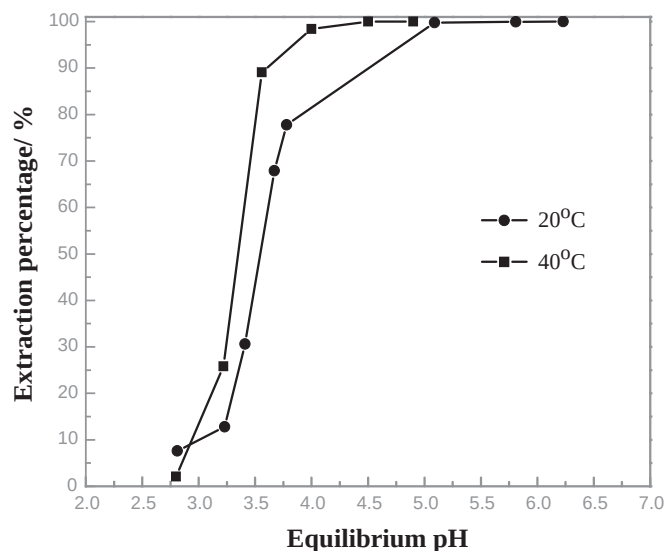


Fig. 5. Effect of temperature on extraction of nickel with 0.5 mol·L⁻¹ Versatic 10 and 0.3 mol·L⁻¹ Mextral 984H in Mextral DT100 at an A/O ratio of 1:1.

3.4. Metal extraction kinetics with the mixed Versatic 10 acid/Mextral 984H system

The extraction kinetics of copper, nickel, cobalt, zinc, and cadmium using the 0.5 mol·L⁻¹ Versatic 10 acid/0.5 mol·L⁻¹ Mextral 984H system are shown in Fig. 6. The extraction rates of Cu, Ni, Co were fast, and the extraction rates of zinc and cadmium were relatively slow. Within 2 min, all of the nickel and copper, as well as almost all of the cobalt, was extracted. However, only 60% of the zinc was extracted. The

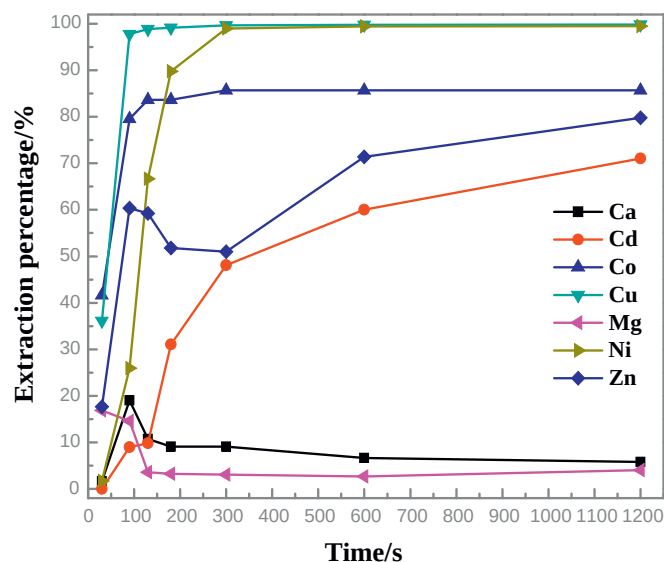


Fig. 6. Extraction kinetics of metals with $0.5 \text{ mol} \cdot \text{L}^{-1}$ Versatic 10 and $0.5 \text{ mol} \cdot \text{L}^{-1}$ Mextral 984H in Mextral DT100 and the synthetic solution at an A/O ratio of 1:1 and 40°C .

extraction efficiency for zinc and cadmium slowly increased with time, reaching 70% after 10 min.

3.5. Metal stripping kinetics with the mixed Versatic 10 acid/Mextral 984H system

The extraction curves indicate that by varying the acidity, the desirable metals can be readily stripped from the organic phase in separate groups. Fig. 7 shows the stripping kinetics of copper, nickel, cobalt, zinc, and cadmium with the loaded $0.5 \text{ mol} \cdot \text{L}^{-1}$ Versatic 10 acid and

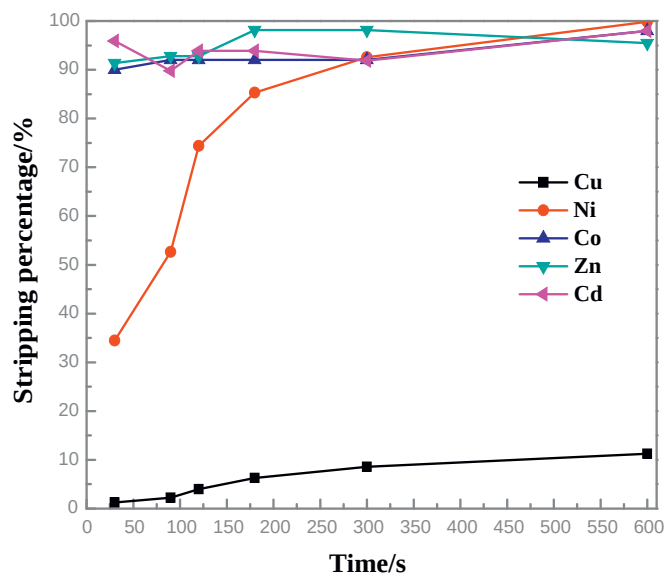


Fig. 7. Stripping kinetics of metals using the loaded organic solution and the strip solution containing $20 \text{ g} \cdot \text{L}^{-1}$ H_2SO_4 at an A/O ratio of 1:1 and 40°C .

$0.5 \text{ mol} \cdot \text{L}^{-1}$ Mextral 984H mixture using a stripping solution containing $20 \text{ g} \cdot \text{L}^{-1}$ sulfuric acid at 40°C . The stripping of cobalt, zinc, and cadmium was fast. Within 30 s, 90% of the Co, 91% of the Zn, and 94% of the Cd were stripped. The stripping kinetics of nickel were very slow, reaching only 35% in 2 min and 87% in 5 min.

3.6. Effect of strip solution acidity on metal stripping

The effect of strip solution acidity on metal stripping was obtained with the loaded $0.5 \text{ mol} \cdot \text{L}^{-1}$ Versatic 10 acid and $0.5 \text{ mol} \cdot \text{L}^{-1}$ Mextral 984H mixture and using a strip solution in the acidity range of $5\text{--}100 \text{ g} \cdot \text{L}^{-1}$ sulfuric acid at 40°C (Fig. 8). 90%–95% Ni, Co, Zn and Cd

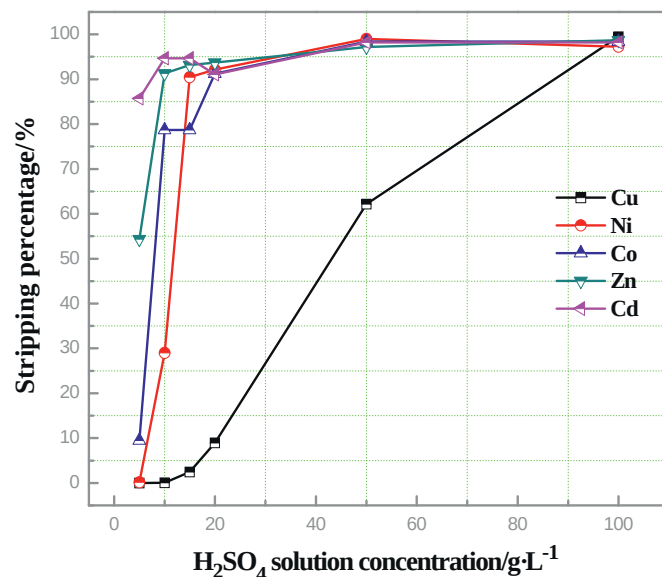


Fig. 8. Stripping percentage of metals with different sulfuric acid solution concentration among $0\text{--}100 \text{ g} \cdot \text{L}^{-1}$ and the loaded organic solution at an A/O ratio of 1:1 and 40°C .

were stripped using $20 \text{ g} \cdot \text{L}^{-1}$ sulfuric acid while only 8% Cu was stripping at this acidity. To strip over 95% Cu, a strip solution acidity of $100 \text{ g} \cdot \text{L}^{-1}$ sulfuric acid was used, as higher concentration of acid is required for copper stripping.

As shown in Fig. 9, an enlargement of part of Fig. 8, a low acid stripping liquor concentration of around $4\text{--}7 \text{ g} \cdot \text{L}^{-1}$ achieves a higher stripping percentage of zinc and cadmium. When the concentration of acid

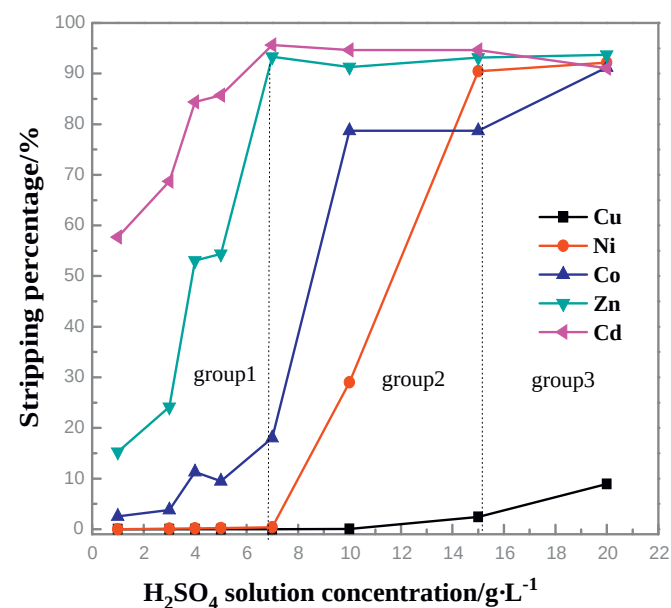


Fig. 9. Stripping percentage of metals with different sulfuric acid solution concentration among $0\text{--}20 \text{ g} \cdot \text{L}^{-1}$ and the loaded organic solution at an A/O ratio of 1:1 and 40°C .

increases to around $15\text{--}20\text{ g}\cdot\text{L}^{-1}$, the nickel and cobalt are stripped out. Finally, as the acid concentration increases to around $100\text{ g}\cdot\text{L}^{-1}$, copper is finally stripped out. The tests were conducted under these conditions to validate the effectiveness of the extraction process (Table 3).

Table 3

The extraction percentage of desirable metals at different selective stripping steps^①

Stage	Content	Metal concentration/ $\text{g}\cdot\text{L}^{-1}$				
		Cu	Ni	Co	Zn	Cd
Loaded O	In feed(A)	2.17	0.529	0.53	3.4	0.2143
Stripping(I), $5\text{ g}\cdot\text{L}^{-1}$	Stripping(I)/%	<0.0001	0.698	18.2	88.2	99.2
Stripping(II), $15\text{ g}\cdot\text{L}^{-1}$	Stripping(II)/%	21.77	98.36	87.65	5.19	~
Stripping(III), $100\text{ g}\cdot\text{L}^{-1}$	Stripping(III)/%	82.47	2.118	1.7	~	~

^① The values with bold in the table show the extraction percentage of some main metals in stripping solution from loaded feed organic solution in the selective stripping process. The in feed metal concentrations in the selective stripping test were different from the batch test before. The concentrations were all given out by the chemical analysis results. In the stripping process, extraction percentage of each metal was calculated by the ratio of the metal concentration in the stripping solution to the metal concentration in each step initial organic solution.

The goal of the batch selective stripping tests was to prepare a loaded stripping solution containing the metals we desire and to separate different groups of metals. With 5 min residence time and an A/O ratio of 1:1, the effects of different acid concentrations on the stripping of the loaded organic solution were investigated. Fig. 9 shows the resulting concentration distributions in the loaded stripping solution. Given this behavior, by controlling the pH value of the stripping solution, different groups of desirable metals could be stripped out in sequence.

The present work proposes a convenient extraction method for separating copper, nickel, cobalt, zinc, and cadmium in the presence of magnesium and calcium. It uses a synergistic extraction step, a scrubbing step, and three passes of a selective stripping process (Fig. 10). The technology can recover copper, nickel, cobalt, zinc, and cadmium from wastewater solutions with the optimum conditions.

3.7. Determination of the nature of the extracted complexes

The solvent extraction of nickel, cobalt, zinc, and cadmium by Versatic 10 or Mextral 984H alone was studied previously, and the extraction mechanism by Versatic 10 acid or Mextral 984H alone was cation exchange reported by a number of researchers using slope analysis

[37–40]. According to previous literature [41–44], the general equation for the extraction of divalent metal by Versatic 10 acid (HR) and Mextral 984H (HL) can be expressed (if the polymerization and the interaction between Versatic 10 acid and Mextral 984H are not considered) as follows:



where the subscript *org* denotes the species in the organic phase, *aq* denotes the species in the aqueous phase and *m* and *n* are digital numbers. Let K_{ex} be the extraction equilibrium constant. The characterization of the composition and stability of hydroxyoxime complexes with metals was studied by Jan Szymanowska *et al.* [45] and de San Miguel *et al.* [46]. By taking the logarithm of the equation and rearranging, we get the following linear equation (Eq. (2)):

$$\lg D = \lg K_{ex} + 2 \lg [H^+] + m \lg [\widehat{HR}] + n \lg [\widehat{HL}], \quad (2)$$

Where *D* defined as the distribution ratio:

$$D = \frac{[M^{2+}]_{org}}{[M^{2+}]_{aq}} = \frac{[\widehat{MR}_m \widehat{L}_n]}{[\widehat{M}^{2+}]}. \quad (3)$$

Here, for constant organic volumes, the balances of the free active Versatic 10 acid and Mextral 984H concentrations are calculated as follows:

$$\widehat{HL}_{org} = \widehat{HL}_{org}^0 - \widehat{MR}_m \widehat{L}_n_{(org)}. \quad (4)$$

If the metal complex concentration ($\widehat{MR}_m \widehat{L}_n_{(org)}$) is low enough, it can be ignored. Compared to the initial organic concentration $\widehat{HL}_{org}^0$, the $\widehat{HL}_{org}$ concentration is approximately equal to $\widehat{HL}_{org}^0$ under this condition.

As shown in Fig. 11, the plots of $\lg(D)$ vs. pH with the $0.5\text{ mol}\cdot\text{L}^{-1}$ Versatic 10 acid and $0.5\text{ mol}\cdot\text{L}^{-1}$ Mextral 984H system and single metal concentrations ($0.025\text{ g}\cdot\text{L}^{-1}$) give straight lines with slope values of 1.6–1.9 which is close to 2 for Ni, Co, Zn and Cd. This confirmed that the

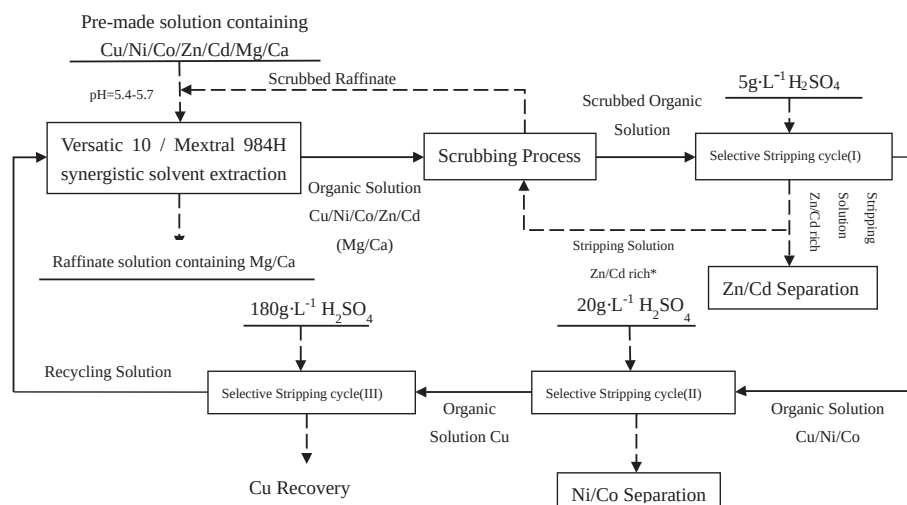


Fig. 10. A designed flow sheet for recovering Cu, Ni, Co, Zn and Cd using synthesis solution. *Scrubbing process influx: the loaded organic solution came from the previous synergistic solvent extraction test, and the aqueous scrubbing solution was typically the pH-neutral effluent of the stripping process, rich in zinc and cadmium salts.

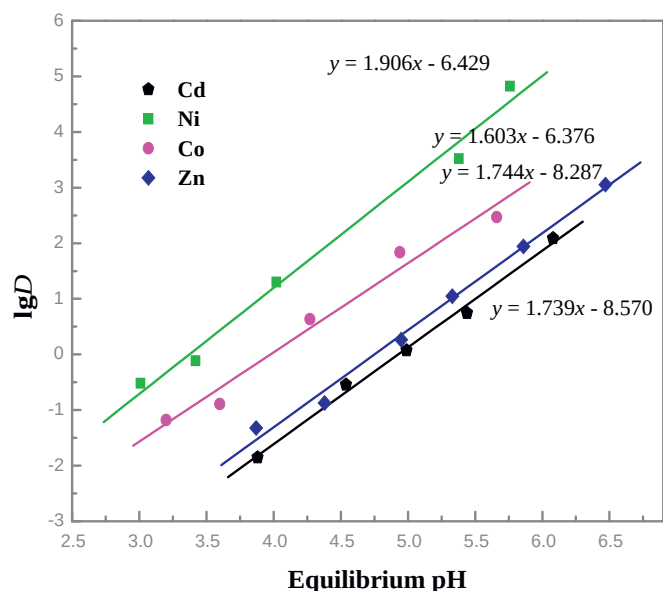


Fig. 11. Plots of lgD of nickel, cobalt, zinc and cadmium as a function of equilibrium pH with a mixture of 0.5 mol·L⁻¹ Versatic 10 and 0.5 mol·L⁻¹ Mextral 984H at an A/O ratio of 1:1 and 40 °C. A series of solutions containing only a single metal each time.

coefficient of the pH term in Eq. (1) is 2, which means that 2 mol of hydrogen ions is liberated from the cationic extractants during extraction of 1 mol of divalent heavy metal ions.

The coefficient n in Eq. (1) is determined by varying the Mextral 984H concentration while keeping the concentration of Versatic 10 acid constant. Single metal solutions containing 0.025 g·L⁻¹ Ni and 0.025 g·L⁻¹ Zn separately were used in the experiments. At constant aqueous pH of 5.5, the plot of lgD vs. lg[Mextral 984H] was found to be approximately linear with slope of about 1 for the Versatic 10 acid/Mextral 984H system (Figs. 12 and 13), indicating one Mextral 984H molecule was involved in the reactions for the extraction of nickel and zinc. In the same way, slope analysis method was applied for Versatic 10 acid with similar results (The results haven't been included here), indicating that one Versatic 10 acid molecule was involved in the

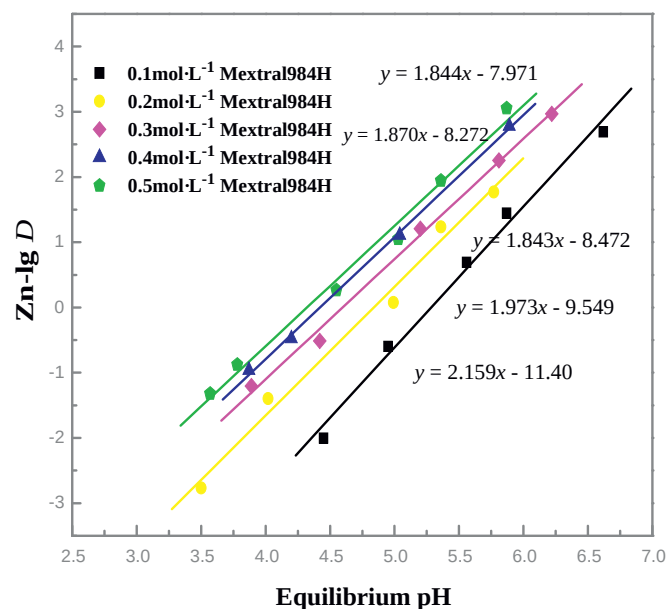


Fig. 12. Plots of lgD of zinc as a function of equilibrium pH with a mixture of 0.5 mol·L⁻¹ Versatic 10 and different Mextral 984H (0.1 mol·L⁻¹, 0.2 mol·L⁻¹, 0.3 mol·L⁻¹, 0.4 mol·L⁻¹, 0.5 mol·L⁻¹) concentrations at an A/O ratio = 1:1 and 40 °C. A series of solutions containing only a single metal each time.

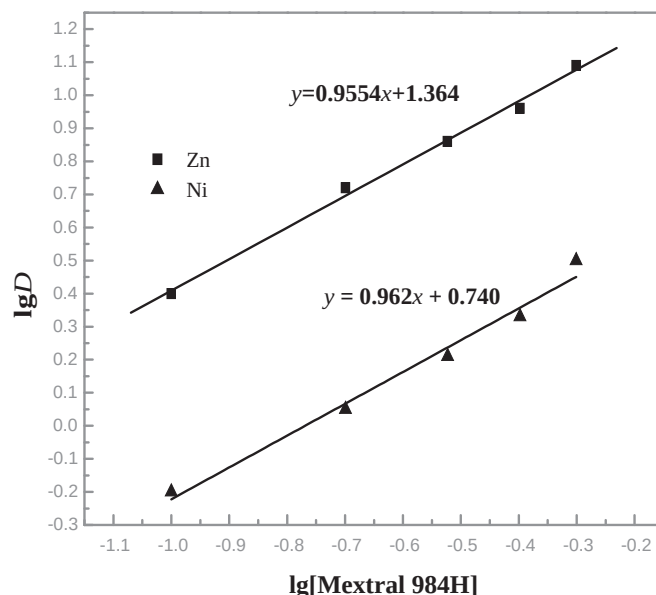
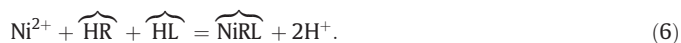
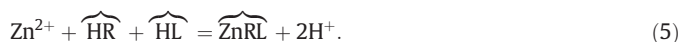


Fig. 13. lgD vs. lg[HL] for the effect of Mextral 984H concentration on the extraction of Zn(II) and Ni(II) with 0.5 mol·L⁻¹ Versatic 10 at an A/O ratio of 1:1 and 40 °C.

reactions for the extraction of nickel and zinc. Therefore, the extraction of zinc and nickel can be expressed by Eqs. (5) and (6), respectively



The equation shows that both Versatic 10 acid (HR) and Mextral 984H (HL) offered one deprotonated molecule to the metal complex when each of them was attached to the synergistic species extracted into the organic phase.

4. Conclusions

A carboxylic acid synergistic system was proposed. It was determined that the utilization of Versatic 10 or Mextral 984H alone cannot separate desirable metals from undesirable ones. Also, solvent extraction and separation of copper, nickel, cobalt, zinc, and cadmium in sulfate medium with a mixture of Versatic 10 acid and Mextral 984H were also investigated. The extraction order of metals with a mixture of Versatic 10 acid and Mextral 984H in Mextral DT100 was Cu > Ni > Co > Cd ~ Zn > Ca > Mg. The Versatic 10 acid/Mextral 984H system produced significant synergistic shifts for nickel, cobalt, zinc, and cadmium, but antagonistic shifts for magnesium and calcium. With 0.5 mol·L⁻¹ Versatic 10 acid/0.5 mol·L⁻¹ Mextral 984H, for an A/O ratio of 1:1 at 40 °C, the $\Delta\text{pH}_{50(\text{Zn-Mg})}$ value was found to be 3.27 pH units and the $\Delta\text{pH}_{50(\text{Zn-Ca})}$ value was 2.25 pH units, indicating easy separation of desirable metals from calcium and magnesium. The extraction kinetics of copper, cobalt, and zinc were fast, and the extraction kinetics of zinc and cadmium were slow. The stripping kinetics of cobalt, copper, zinc, and cadmium were fast, and the stripping kinetics of nickel were slow. The extraction mechanism of nickel and zinc from sulfuric acid solutions was investigated using Versatic 10 acid/Mextral 984H mixtures. The stoichiometry of the complexes extracted with the synergistic mixture revealed the following reaction equations: $\text{Zn}^{2+} + \widehat{\text{HR}} + \widehat{\text{HL}} = \widehat{\text{ZnRL}} + 2\text{H}^+$, and $\text{Ni}^{2+} + \widehat{\text{HR}} + \widehat{\text{HL}} = \widehat{\text{NiRL}} + 2\text{H}^+$. Metal extraction pH isotherms and extraction and stripping kinetics sufficiently proved that a mixture of Versatic 10 acid and Mextral 984H is a promising

solvent extraction system for the separation, purification, and recovery of desirable metals from sulfated wastewater solutions.

Acknowledgments

The authors thank Professor James Ballard (Washington University in St. Louis), for reading the manuscript and offering numerous suggestions.

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