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Separation and Recovery of Copper and Nickel in the Leachate of a Waste IC Lead Frame through Synergistic Solvent Extraction Using a Binary Extractant Containing LIX984N and Cyanex302 Followed by Selective Stripping

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Abstract: The IC lead frame is an essential component in semiconductor packaging, primarily composed of a nickel (Ni)–copper (Cu) alloy in which Ni is electroplated onto a Cu substrate. In this study, synergistic solvent extraction using a binary extractant containing LIX984N and Cyanex302, followed by two-stage selective stripping using sulfuric acid (H_2SO_4) and nitric acid (HNO_3) as the stripping agent, was employed to separate and recover Cu and Ni from the leachate of an IC lead frame. The results indicated that under the optimal conditions of synergistic solvent extraction with an extraction pH value of 1, an extractant concentration of 0.015 M LIX984N + 0.0375 M Cyanex302, an extraction aqueous/organic (A/O) ratio of 1:1, and an extraction time of 5 min, the extraction efficiencies for Cu and Ni were 99.8% and 1.17%, respectively. The distribution ratios were D_{Cu} 999 and D_{Ni} 0.012, resulting in a separation factor of 83,250. In addition, the separation factor was much higher than that of using individual extractant of LIX984N (6208.3) or Cyanex302 (22,185.2). Subsequently, under optimal first-stage stripping conditions, using 0.05 M H_2SO_4 at a stripping organic/aqueous (O/A) ratio of 1:1, and with a stripping time of 3 min, a stripping efficiency of 99.9% for Ni was achieved. Next, under optimal second-stage stripping conditions, using 5 M HNO_3 at a stripping O/A ratio of 2:1, and with a striping time of 3 min, a stripping efficiency of 99.9% for Cu was achieved. Finally, sodium hydroxide (NaOH) was added to the respective stripping solutions to precipitate Ni and Cu ions, followed by calcination treatment for the precipitates to obtain NiO and CuO, respectively. The purity of the former was 99.74% and that of the latter was 99.82%. The results demonstrate that synergistic solvent extraction using a binary extractant containing LIX984N and Cyanex302 can almost entirely extract Cu in the leachate of an IC lead frame at a lower extraction pH and a lower extractant concentration, thus reducing the co-extraction of Ni. In addition, less co-extracted Ni in the organic phase can be selectively stripped using dilute H_2SO_4, thus reducing the co-stripping of Cu. Hence, the effective separation and recovery of Cu and Ni in IC lead frame leachate can be achieved, which contributes to improving the sustainability of natural resources.

Keywords: IC lead frame; copper; nickel; synergistic solvent extraction; binary extractant; LIX984N; Cyanex302; selective stripping

1. Introduction

Many semiconductors and semiconductor devices, such as transistors and integrated circuits (ICs), are widely applied in modern computing, communications, and manufacturing systems [1,2]. The IC lead frame is an important component used in semiconductor packaging, serving as a connecting medium between the IC chip and printed circuit board (PCB) [3]. The functions of the IC lead frame include to support and fix the IC chip on the PCB and to transmit signals in ICs. Most IC lead frames consist of a copper (Cu) substrate plating with a thin layer of nickel (Ni). In recent years, the semiconductor industry in Taiwan has made dramatic developments, including in the design and fabrication of semiconductors and semiconductor devices. Much IC lead frame waste, including scraps and off-specifications, is produced during the fabrication of semiconductor devices. Nowadays, most wasted IC lead frames are not well recycled but disposed of via landfill, which leads to the pollution of soil and groundwater as well as the wastage of Ni and Cu metal resources. There are no mineral resources of Ni or Cu in Taiwan. If the Ni and Cu in waste IC lead frames can be recovered, they can act as a secondary resource of Ni and Cu, and therefore, the goals of waste reduction and circular economy can be achieved simultaneously.

In order to separate and recover Ni and Cu from waste IC lead frames, acid leaching is often applied initially. While Ni plating on the surface is leached out, a portion of Cu substrate is also leached out simultaneously. Therefore, the leachate contains both Ni and Cu. Chemical precipitation is an effective method for separating and recovering heavy metals from aqueous solution. Giannopoulou et al. [4] employed chemical precipitation to recover Ni and Cu from an acidic aqueous solution containing multiple metals. The pH of the acidic solution was initially 0.25, and it was adjusted using 2 N sodium hydroxide (NaOH). When the pH was adjusted to 6.7 and 9.8, approximately 99.7% of Cu and 99.7% of Ni was precipitated and recovered, respectively. However, due to the fact that Ni begins to precipitate at pH values above 6, it will thus co-precipitate with Cu, which leads to lower the purity of the recovered Cu. In contrast, starting Ni recovery after complete Cu precipitation at pH values above 6.7 can result in recovering Ni of a higher purity. However, this leads to a reduction in the recovery of Ni. To avoid the co-precipitation of Ni and Cu during the subsequent metal recovery process, which affects the effectiveness of separation and recovery, it is necessary to first separate and concentrate the Ni and Cu in the leachate of IC lead frames.

Several studies have demonstrated the solvent extraction method, utilizing various extractants to extract Cu or Ni ions from different wastewaters or leachates. Sridhar et al. [5] utilized LIX984N as the extractant to simultaneously extract Cu and Ni from an ammonia (NH_3)/ammonium carbonate $(NH_4)_2CO_3$ medium and employed three stripping stages to selectively strip NH_3, Ni, and Cu from the organic phase into the aqueous phase to separate them. The maximum Cu loading capacity was 5.1 g/dm^3 when LIX984N of 10 vol.% was added. Li et al. [6] also employed LIX984N as the extractant to extract and separate Cu and Ni from an electroplating wastewater with a H_2SO_4 medium. With the addition of 15 vol.% LIX984N and an aqueous/organic (A/O) ratio of 1:1, adjusting the pH to 5 yielded a Cu extraction efficiency of 92.9%, while adjusting the pH to 10.5 resulted in a Ni extraction efficiency of 93%. Soeezi et al. [7] extracted Cu and Ni from a Cu mining industrial wastewater using LIX984N as the extractant. Cu was effectively extracted under optimal conditions of pH 2.5, a LIX984N concentration of 10 vol.%, an A/O ratio of 1:1, and an extraction time of 3 min, achieving a Cu extraction efficiency of 99.5% and a Ni extraction efficiency of 71.0%. Sole et al. [8] and Tait [9] used Cyanex302 as the extractant to extract Cu and Ni from a H_2SO_4 solution, respectively. In these studies, Cu could be fully extracted even at low pH (<1). The extraction efficiency for Ni increased with increasing pH but remained below 10% at pH 6. Padhan et al. [10] used H_2SO_4 to leach manganese (Mn), Cu, Ni, and other metals from deep-sea manganese nodules and then employed LIX84I as the extractant for Cu extraction. Initially, a small amount of calcium hydroxide Ca(OH)$_2$ was added to adjust the pH of the leachate, causing iron (Fe) precipitation. Subsequently, the pH was adjusted to 3.8 and 5 vol.% LIX84I was employed to extract Cu using an A/O ratio

of 1:1, achieving a Cu extraction efficiency of approximately 99.9%. Chen et al. [11] applied Mextral@5640 as the extractant to extract Cu from the leachate of a spent lithium (Li) ion battery containing Cu, Mn, Ni, and Li. Cu was extracted into the organic phase under optimal conditions of pH 1.94, with an A/O ratio of 2:1 and an Mextral@5640 concentration of 10 vol.%, achieving a Cu extraction efficiency of approximately 100%. Shi et al. [12] employed N902 as the extractant to simultaneously extract Cu and Ni from a $(NH_4)_2CO_3$ leachate of metal electroplating sludge, followed by selective stripping to separate Cu and Ni from the extraction solution. The optimal conditions were determined to be pH 9, an A/O ratio of 1:1, 20 vol.% N902 addition, and an extraction time of 4 min. The extraction efficiencies of both Cu and Ni exceeded 97%. Using H_2SO_4 of 1 M as the stripping agent, Ni and Cu were stripped into the aqueous phase, achieving extraction efficiencies of 99.8% and 1.23%, respectively.

On another note, synergistic solvent extraction involves using a binary extractant of two kinds of extractants to extract a specific metal ion or compound. Zhang et al. [13] utilized a binary extractant composed of D2EHPA and LIX860 to separate cobalt (Co) and Ni from an H_2SO_4 wastewater. This study demonstrated that the binary extractant could extract Ni at lower pH values compared to a single extractant. Additionally, the stripping of Ni was also more effective and faster in the stripping stage. Fouad [14] investigated the synergistic extraction reaction of two extractants, Cyanex301 and LIX984N, on Cu extraction from an H_2SO_4 solution. The optimal ratio of Cyanex301 to LIX984N was found to be 1:5, exhibiting the maximum synergistic effect on Cu extraction. Sulaiman et al. [15] found that at pH 4.8, the extraction efficiency for Ni using D2EHPA was 60% and that extraction using octanol exhibited 0% efficiency. However, when D2EHPA was mixed with octanol, the extraction efficiency increased to 80%, demonstrating a synergistic effect. Sun et al. [16] pointed out that the Mextral 84H and P204 extractants exhibited a synergistic effect in the extraction of Ni ions. These studies highlighted the applications of synergistic solvent extraction in enhancing the efficiency of metal ion extraction and separation using a mixture of distinct extractants. The mechanism of synergistic solvent extraction is commonly believed that the extracted species containing two ligands and two extractants are more stable and more hydrophobic, and thus easier to be extracted into the organic phase to increase the distribution ratio [17].

From the aforementioned studies, it is evident that LIX984 and Cyanex302 are feasible extractants for extracting Cu or Ni from various wastewaters or leachates. In addition, employing a binary extractant composed of a mixture of extractants can enhance the extraction efficiency for extracting Cu or Ni. However, there is currently limited research investigating the use of a binary extractant involving LIX984N and Cyanex302 for selectively separating Cu and Ni when the two are present simultaneously in aqueous solutions. In addition, there is also a lack of research on the utilization of selective stripping to separate Cu and Ni when the two have been co-extracted. Furthermore, there has been limited exploration into the separation and recovery of Cu and Ni from the leachate of an IC lead frame. These indicate that there is a research gap when it comes to addressing the specific challenges and complexities associated with the selective separation and recovery of Cu and Ni ions from such leachates.

This study applied synergistic solvent extraction using a binary extractant containing LIX984N and Cyanex302, followed by employing two-stage selective stripping to separate and recover Cu and Ni from the leachate of an IC lead frame. Firstly, the effects of extraction parameters, including extraction pH, extractant concentration, extraction A/O ratio, and extraction time, on extraction efficiency for Cu and Ni using the extractants LIX984N and Cyanex302 individually and a mixture of them were investigated and compared. Secondly, the effects of stripping agents and their concentrations, stripping organic/aqueous (O/A) ratio, and stripping time on stripping efficiency for Cu and Ni were explored. Finally, chemical precipitation using NaOH as the precipitating agent was employed to precipitate and recover Cu and Ni from the respective stripping solutions.

2. Materials and Methods

2.1. Materials

The IC lead frame used in this study was provided by a semiconductor manufacturing company in Taiwan, as shown in Figure 1. The IC lead frame was a Ni–Cu alloy in which a thin layer of Ni was electroplated on the Cu substrate. The leachate of the IC lead frame used in this study was obtained from UWin Nanotech. Co., Ltd., Taiwan, and it was produced by conducting H_2SO_4 leaching with hydrogen peroxide (H_2O_2) on the IC lead frame. The concentrations of Ni and Cu ions in the leachate were 3000 mg/L and 300 mg/L, respectively. The purpose of H_2SO_4 leaching was to fully leach out the Ni metal plating on the surface of the IC lead frame rather than to fully dissolve the IC lead frame. Hence, the concentration of Ni in the leachate was higher than that of Cu. In addition, the H_2SO_4 leaching residue, i.e., the Cu metal, could be used as a secondary resource of Cu for the manufacture of related products. LIX984N (a mixture of 5-nonyl salicylaldoxime ($C_{16}H_{25}NO_2$) and 2-hydroxy-5-nonyl acetophenone ($C_{14}H_{13}NO_2$) at the same volume) (Zhengzhou Dezhong Chemical Reagent Factory, Zhengzhou, China) and Cyanex302 (bis-(2,4,4-trimethylpentyl) monothiophosphinic acid) (Sigma-Aldrich Co., St Louis, MO, USA) were used as the extractants in the extraction experiments. Kerosene (Sigma-Aldrich) was used as both the organic phase and the diluent of the extractants in the extraction experiments. Sulfonation treatment was carried out to remove the impurities that existed in the kerosene. During the sulfonation procedure, H_2SO_4 (concentration: 98%) (J.T.Baker, Inc., Phillipsburg, NJ, USA) was added to the kerosene. After the kerosene was sulfonated, NaOH solution (purity: 99%) (Avantor, Inc., Radnor, PA, USA) and deionized water (18.0 MΩ·cm) (Honeywell, Inc., Charlotte, NC, USA) were applied to conduct acid–base neutralization and to remove the impurities. In addition, NaOH (Avantor) was also used to adjust the pH value of the leachate and used as the precipitating agent for metal ion precipitation. H_2SO_4 (J.T.Baker), nitric acid (HNO_3) (concentration: 68%) (Honeywell), and hydrochloric acid (HCl) (concentration: 36.5%) (Honeywell) were used as the stripping agents in the stripping experiments. ICP standard solutions of Cu and Ni (High-Purity Standards, Inc., North Charleston, SC, USA) were used for the analysis of Cu and Ni concentrations, respectively.
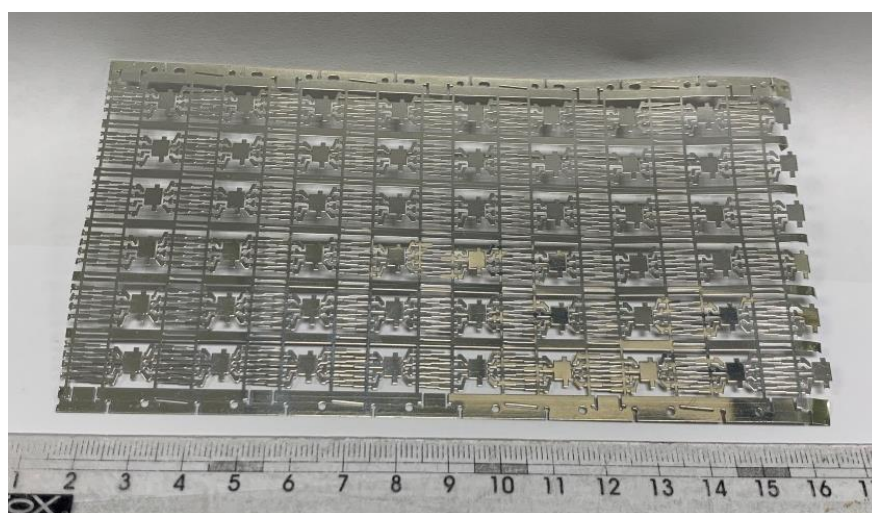

Figure 1. Photograph of the IC lead frame used in this study.

2.2. Methods

The experimental setup of this study is shown in Figure 2, including the extraction experiments, stripping experiments, and metal precipitation experiments. The details are as follows.
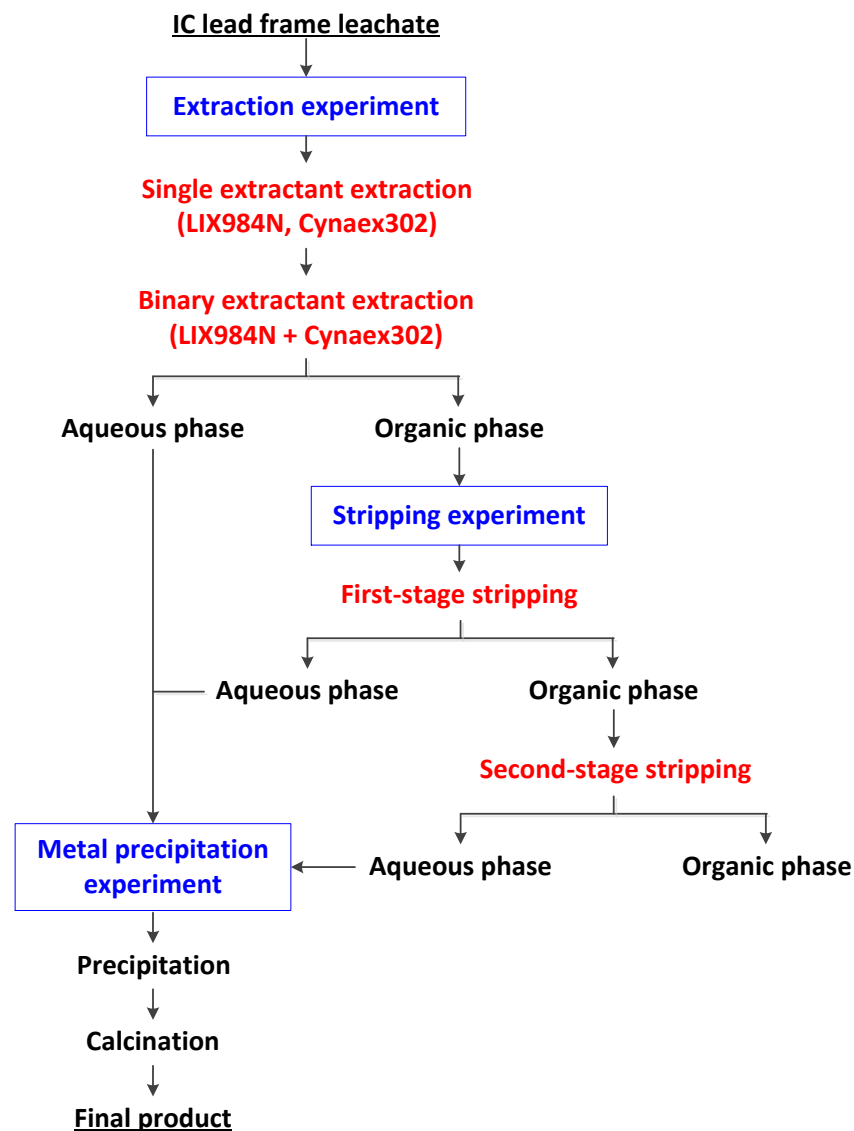
IC lead frame leachate

↓

Extraction experiment

↓

**Single extractant extraction
(LIX984N, Cynaex302)**

↓

**Binary extractant extraction
(LIX984N + Cynaex302)**

Aqueous phase   **Organic phase**

↓

Stripping experiment

↓

First-stage stripping

Aqueous phase   **Organic phase**

↓

Second-stage stripping

**Metal precipitation
experiment** ← **Aqueous phase**   **Organic phase**

↓

Precipitation

↓

Calcination

↓

Final product

Figure 2. Experimental setup of this study.

2.2.1. Extraction Experiments

The extraction experiments focused on parameters that included extraction pH, extractant concentration, extraction A/O ratio, and extraction time. Unless otherwise specified, the pH values mentioned below refer to the initial pH values. To conduct the experiments, 20 mL of the leachate of the IC lead frame was taken and adjusted to the decided pH. This solution was then poured into a 150 mL separatory funnel. A selected volume of kerosene containing a fixed concentration of the extractant was added. The separatory funnel was placed on a shaker and mixed uniformly at a frequency of 3000 rpm. After a designated period of time, the mixture was allowed to settle, forming distinct organic and aqueous phases. The aqueous phase was then collected from the bottom of the separatory funnel. The concentrations of Cu and Ni in the aqueous phase were determined using an inductively coupled plasma optical emission spectrometer (ICP-OES) (Optima 8000, PerkinElmer, Inc., Waltham, MA, USA). The distribution ratio (D), extraction efficiency (E_{ex}), and separation factor ($\beta_{Cu/Ni}$) were calculated as follows:

$$\text{Distribution ratio (D)} = \frac{M_{org}}{M_{aq}} = \frac{C_i - C_f}{C_f} \times \frac{V_{aq}}{V_{org}}$$

$$\text{Extraction efficiency} \; (E_{ex})(\%) = \frac{D}{D + V_{aq}/V_{org}} \times 100\%$$

$$\text{Separation factor} \; (\beta_{Cu/Ni}) = \frac{D_{Cu}}{D_{Ni}} = \frac{[M_{Cu}]_{org} \times [M_{Ni}]_{aq}}{[M_{Cu}]_{aq} \times [M_{Ni}]_{org}}$$

C_i and C_f are the initial and equilibrium metal concentrations in the aqueous phase, respectively. V_{aq} and V_{org} are the volumes of the aqueous and organic phase, respectively. The distribution ratio (D) is the ratio of metal concentration in the organic phase to that in the aqueous phase at equilibrium. The extraction efficiency (E_{ex}) can be represented by D, showing the extraction ability of the extractant. The separation factor ($\beta_{Cu/Ni}$) is the ratio of the distribution ratios of Cu (D_{Cu}) and Ni (D_{Ni}), indicating the relative difference in the extraction capabilities for these two metals. A higher separation factor implies a greater difference in the extraction abilities of the extractant for these two metals, thus indicating better separation performance between them. In Section 3, the extraction efficiency is presented more prominently.

2.2.2. Stripping Experiments

The stripping experiments focused on parameters that included stripping agent type, stripping agent concentration, stripping O/A ratio, and stripping time. Under the optimal conditions determined in the extraction experiments that used a binary extractant containing LIX984N and Cynaex302, the aqueous phase of the extraction solution was removed. Then, the organic phase in the separatory funnel was mixed with a stripping agent of specified concentration and volume. This mixture was placed on a shaker and mixed uniformly at a frequency of 3000 rpm. After a designated period of time, the mixture was allowed to settle, forming distinct aqueous and organic phases. The aqueous phase was then collected from the bottom of the separatory funnel. The Cu and Ni ion concentrations in the aqueous phase were subsequently analyzed using an ICP-OES (Optima 8000, PerkinElmer, Inc.). The stripping efficiency (E_{st}) was calculated as follows:

$$\text{Stripping efficiency} \; (E_{st})(\%) = \frac{M_{aq}}{M_{org}} \times 100\%$$

M_{aq} is the mass of metal in the aqueous phase after stripping, whereas M_{org} is that in the organic phase before stripping.

2.2.3. Metal Precipitation Experiments

The aqueous solutions containing Cu and Ni ions obtained from the extraction and stripping experiments were subjected to pH adjustment using NaOH to achieve pH values ranging from 1 to 12. This adjustment led to the precipitation of Cu ions as copper hydroxide ($Cu(OH)_2$) and that of Ni ions as nickel hydroxide ($Ni(OH)_2$). The concentrations of Cu or Ni ions in the aqueous solutions at different pH levels were analyzed using ICP-OES (Optima 8000, PerkinElmer, Inc.). The precipitation efficiency (P) at each pH was calculated as follows:

$$\text{Precipitation efficiency} \; (P) \; (\%) = \frac{Mo - M}{Mo} \times 100\% = \frac{C_o \times V_o - C \times V}{C_o \times V_o} \times 100\%$$

Mo and Co represent the initial mass and concentration of metal in the aqueous solution, respectively, and Vo indicates the initial volume of the aqueous solution, whereas M, C, and V represent each of these after precipitation at each pH.

The precipitates of $Ni(OH)_2$ and $Cu(OH)_2$ obtained at the optimal precipitation pH for each metal ion were subjected to calcination to obtain the final products of NiO and CuO. Qualitative and quantitative analyses of the obtained final products were conducted as follows. Crystal phases were analyzed using X-ray diffraction (XRD) (BRUKER-D2 Phaser, Germany). The results were compared with the crystal phase data from the International

Centre for Diffraction Data (ICDD) database (PDF-2, 2016) using the MDI Jade 6.0 software developed by Materials Data, Inc., Livermore, CA, USA. Element composition was analyzed using X-ray fluorescence (XRF) (SEA6000VX, TechMax, HITACHI, Tokyo, Japan). The purity of the final products was analyzed using ICP-OES (Optima 8000, PerkinElmer, Inc.).

3. Results and Discussion

3.1. Extraction Experiments

3.1.1. Extraction Using a Single Extractant of LIX984

Different extractants exhibit varying extraction abilities for distinct metals. To avoid the co-extraction of Cu and Ni when using a binary extractant containing LIX984N and Cynaex302, it is necessary to investigate the individual extraction behavior of each extractant for Cu and Ni. The effects of extraction pH, extractant concentration, extraction A/O ratio, and extraction time on extraction efficiency for Cu and Ni using a single extractant of LIX984N are illustrated in Figure 3a–d, respectively. Regarding the effect of extraction pH (Figure 3a), the tested initial pHs were 0.5, 1, 1.5, 2, 3, and 4. The LIX984N concentration was 0.05 M, the extraction A/O ratio was 1:1, and the extraction time was 10 min. The extraction efficiency for both Cu and Ni increased gradually with the increase in extraction pH. The extraction efficiency for Cu was 73.3% at pH 1, and it reached 99.2% at pH 2, remaining relatively constant thereafter. In contrast, the extraction efficiency for Ni was only 2.3% at pH 2 and increased to 12.8% at pH 4.

LIX984N is a cationic chelating extractant consisting of a mixture of 5-nonyl salicylaldoxime and 2-hydroxy-5-nonyl acetophenone, each at the same volume [18,19]. Its extraction reaction for divalent metal ion is as follows:
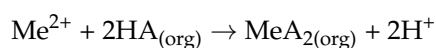
$$Me^{2+} + 2HA_{(org)} \rightarrow MeA_{2(org)} + 2H^+$$

As the pH value increases, the concentration of hydrogen ions in the solution decreases, driving the extraction reaction to the right and resulting in higher extraction efficiency. Hence, the extraction ability of LIX984N for Cu and Ni increases with elevated pH. Above pH 2, the extraction efficiency for Cu was higher than 99%; however, that for Ni also increased. To avoid co-extraction, pH 2 was chosen as the optimal extraction pH. On the other hand, this result also suggested that LIX984N possessed little extraction ability for Ni at pH 2. Higher LIX984N concentration drives the aforementioned extraction reaction to the right, which also causes co-extraction and lowers separation performance. Hence, the following investigation focused on the feasibility of reducing the LIX984N concentration.

To test the effect of LIX984N concentration (Figure 3b), the tested LIX984N concentrations were 0.0075 M, 0.015 M, 0.03 M, and 0.05 M. The extraction pH was 2, the extraction A/O ratio was 1:1, and the extraction time was 10 min. The extraction efficiency for Cu increased with LIX984N concentration. The extraction efficiency for Cu was 99.2% when the concentration of LIX984N was 0.05 M. When the LIX984N concentration decreased to 0.03 M and 0.015 M, the efficiency reduced to 90.0% and 79.0%, respectively. In contrast, the decrease in LIX984N concentration had no substantial influence on the extraction efficiency for Ni, which was ca. 2%. Hence, the optimal LIX984N concentration was chosen as 0.05 M.

To test the effect of extraction A/O ratio (Figure 3c), the tested extraction A/O ratios were 0.5:1, 1:1, 1.5:1, 2:1, and 3:1. The extraction pH was 2, the LIX984N concentration was 0.05 M, and the extraction time was 10 min. The extraction efficiency for Cu decreased with the increase in extraction A/O ratio (i.e., more aqueous phase and less organic phase). The extraction efficiency for Cu was higher than 99% when the extraction A/O ratio was 0.5:1 and 1:1. When the extraction A/O ratio was 1.5:1, 2:1, and 3:1, the efficiency reduced to 92%, 87%, and 74%, respectively. This is because as the extraction A/O ratio increases, the volume of organic phase decreases. At the fixed LIX984N concentration, the amount of LIX984N also decreases, which leads to a lower extraction efficiency for Cu. In contrast, the extraction efficiency for Ni was its highest, at 4.8%, when the extraction A/O ratio was 0.5:1. As the extraction A/O ratio increased, it caused no substantial change from ca. 2.3%.

In order to reduce the usage of extractant and diluent (i.e., less organic phase), the optimal extraction A/O ratio was selected as 1:1.
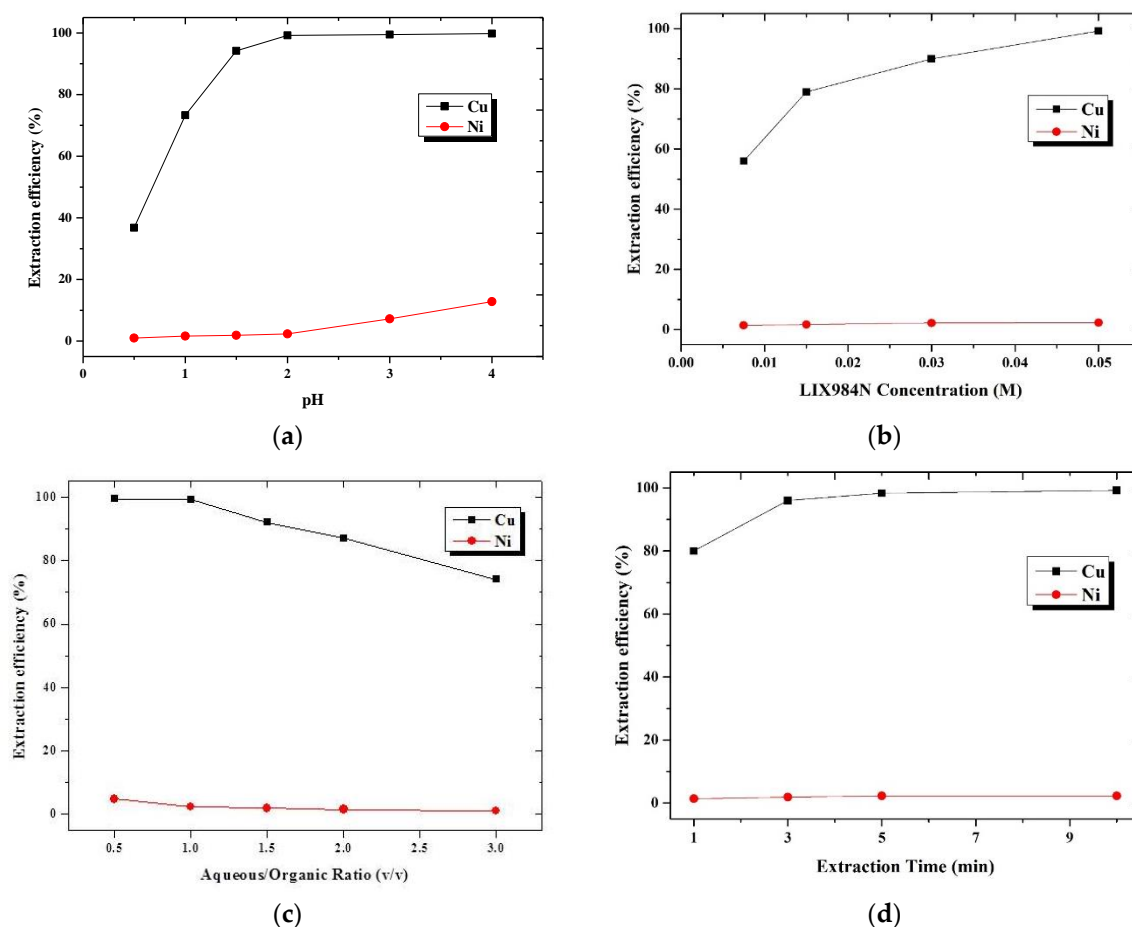

(**a**)

(**b**)

(**c**)

(**d**)

Figure 3. Effects of extraction pH (**a**), LIX984N concentration (**b**), extraction A/O ratio (**c**), and extraction time (**d**) on Cu and Ni extraction efficiency using a single extractant of LIX984. Experimental conditions: (**a**) LIX984N concentration 0.05 M, extraction A/O ratio 1:1, extraction time 10 min; (**b**) extraction pH 2, extraction A/O ratio 1:1, extraction time 10 min; (**c**) extraction pH 2, LIX984N concentration 0.05 M, extraction time 10 min; (**d**) extraction pH 2, LIX984N concentration 0.05 M, extraction A/O ratio 1:1.

To test the effect of extraction time (Figure 3d), the tested extraction times were 1 min, 3 min, 5 min, and 10 min. The extraction pH was 2, the LIX984N concentration was 0.05 M, and the extraction A/O ratio was 1:1. The extraction efficiency for Cu increased with the increase in extraction time. At 1 min of extraction time, the Cu extraction efficiency was 80%. As the extraction time exceeded 5 min, this extraction efficiency reached over 99.2%, and the extraction reaction tended to reach equilibrium. In contrast, the extraction efficiency for Ni showed no significant change with time from ca. 2%. Hence, the optimal extraction was selected as 5 min.

Li et al. [6] used LIX984N as the extractant to extract Cu and Ni from an electroplating wastewater of sulfate medium. At pH 5, the extraction efficiency for Cu was 92.9%; when the pH was adjusted to 10.5, the extraction efficiency for Ni was 93.0%. Soeezi et al. [7] extracted Cu and Ni from Cu mining industrial wastewater using LIX984N as the extractant. At pH 2.5, the extraction efficiency for Cu was 99.5% and that for Ni was 71.0%. These findings suggest that LIX984N exhibits higher extraction ability for Cu than for Ni in low pH environments, whereas effective Ni extraction occurs at higher pH levels, aligning with the results of this study.

3.1.2. Extraction Using a Single Extractant of Cyanex302

The effects of extraction pH, extractant concentration, extraction O/A ratio, and extraction time, on the extraction efficiency for Cu and Ni using a single extractant of Cyanex302 are illustrated in Figure 4a–d. To test the effect of extraction pH (Figure 4a), the initial pHs were 0.5, 1, 1.5, 2, 3, and 4. The Cyanex302 concentration was 0.05 M, the A/O ratio was 1:1, and the extraction time was 10 min. The extraction efficiency for Cu gradually increased from 92.0% to 99.5% when the pH value increased from 0.5 to 1 and remained relatively constant when the pH value was above pH 1. In contrast, the extraction efficiency for Ni was only 2.5% at pH 1 and increased to nearly 20% at pH 4. Hence, pH 1 was chosen as the optimal extraction pH.
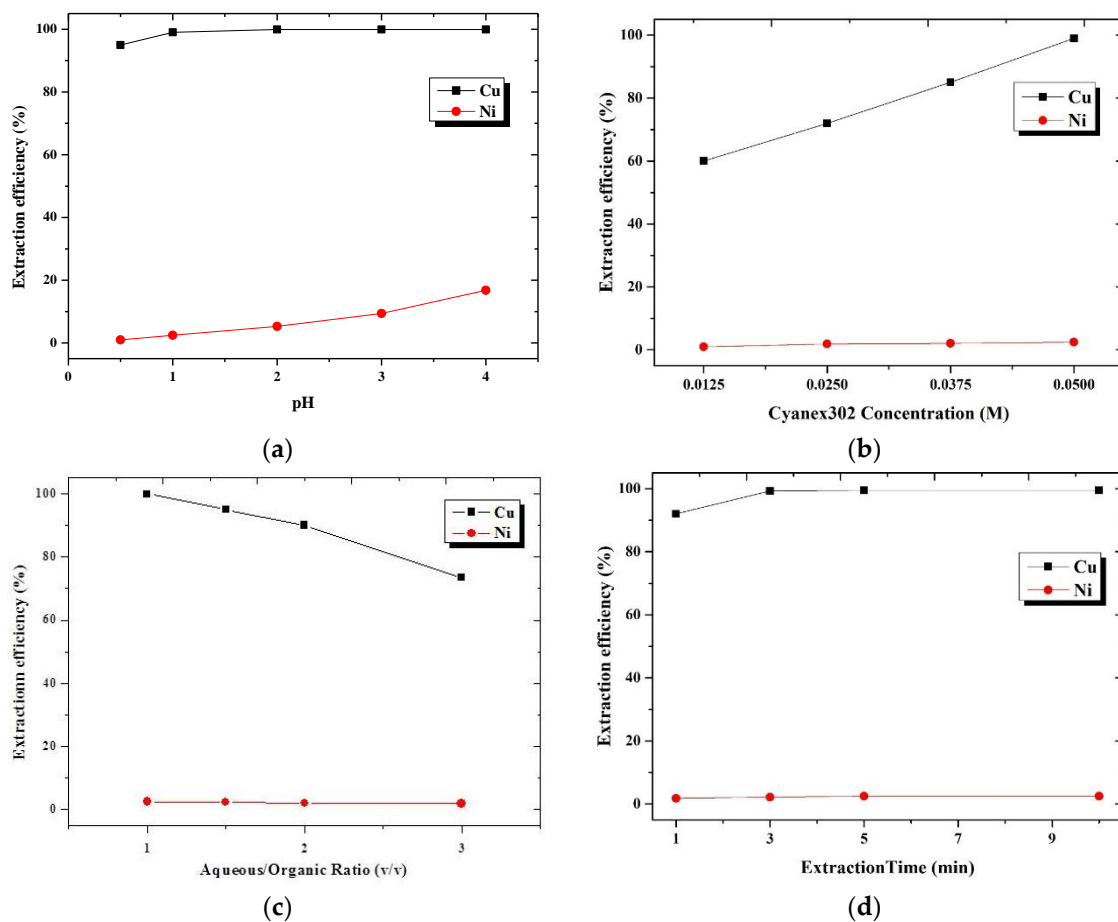

Figure 4. Effects of extraction pH (**a**), Cyanex302 concentration (**b**), extraction A/O ratio (**c**), and extraction time (**d**) on Cu and Ni extraction efficiency using a single extractant of Cyanex302. Experimental conditions: (**a**) Cyanex302 concentration 0.05 M, extraction A/O ratio 1:1, extraction time 10 min; (**b**) extraction pH 1, extraction A/O ratio 1:1, extraction time 10 min; (**c**) extraction pH 1, Cyanex302 concentration 0.05 M, extraction time 10 min; (**d**) extraction pH 1, Cyanex302 concentration 0.05 M, extraction A/O ratio 1:1.

Cyanex302 is a cationic organophosphorus extractant that has a dimer structure. Its extraction reaction for divalent metal ion is as follows:
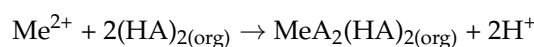
$$Me^{2+} + 2(HA)_{2(org)} \rightarrow MeA_2(HA)_{2(org)} + 2H^+$$

As the pH value increases, the concentration of hydrogen ions in the solution decreases, driving the extraction reaction to the right and resulting in higher extraction efficiency. Similar to LIX984N, the extraction ability of Cyanex302 for Cu and Ni increases with the elevated pH. Above pH 1, the extraction efficiency for Cu was higher than 99%; however,

that for Ni also increased. To avoid co-extraction, pH 1 was chosen as the optimal extraction pH. On the other hand, this result also suggested that Cyanex302 had little extraction ability for Ni at pH 1. Higher Cyanex302 concentration drives the foregoing extraction reaction to the right, which also causes co-extraction and lowers separation performance. Hence, the following investigation focused on the feasibility of reducing the Cyanex302 concentration.

To test the effect of Cyanex302 concentration (Figure 4b), the tested Cyanex302 concentrations were 0.0125 M, 0.025 M, 0.0375 M, and 0.05 M. The extraction pH was 1, the extraction A/O ratio was 1:1, and the extraction time was 10 min. The extraction efficiency for Cu increased with the increase in Cyanex302 concentration. The extraction efficiency for Cu was 99.5% when the concentration of Cyanex302 was 0.05 M. When the Cyanex302 concentration decreased to 0.0375 M and 0.025 M, this extraction efficiency reduced to 82.0% and 65.0%, respectively. In contrast, the extraction efficiency for Ni showed no substantial variation with the decrease in Cyanex302 concentration from ca. 2.5%. Hence, the optimal Cyanex302 concentration was chosen as 0.05 M.

To test the effect of extraction A/O ratio (Figure 4c), the tested extraction A/O ratios were 1:1, 1.5:1, 2:1, and 3:1. The extraction pH was 1, the Cyanex302 concentration was 0.05 M, and the extraction time was 10 min. The extraction efficiency for Cu decreased with the increase in extraction A/O ratio (i.e., more aqueous phase and less organic phase). The extraction efficiency for Cu reached its highest value of 99.5% when the extraction A/O ratio was 1:1. When the extraction A/O ratio was 1.5:1, 2:1, and 3:1, this extraction efficiency reduced to 95.0%, 90.0%, and 73.4%, respectively. The reason for this is similar to that which applies to LIX984N. As the extraction A/O ratio increases, the volume of organic phase decreases. At the fixed Cyanex302 concentration, the amount of Cyanex302 also decreases, which leads to a lower extraction efficiency for Cu. In contrast, the extraction efficiency for Ni showed no substantial change with the increase in extraction A/O ratio from ca. 2.3%. In order to reduce the usage of extractant and diluent (i.e., less organic phase), the optimal extraction A/O ratio was selected as 1:1.

To test the effect of extraction time (Figure 4d), the tested extraction times were 1 min, 3 min, 5 min, and 10 min. The extraction pH was 1, the Cyanex302 concentration was 0.05 M, and the extraction A/O ratio was 1:1. The extraction efficiency for Cu increased with the increase in extraction time. At 1 min of extraction time, the Cu extraction efficiency was 92%. As the extraction time exceeded 5 min, this extraction efficiency reached over 99.5%, and the extraction reaction tended to reach equilibrium. In contrast, the extraction efficiency for Ni showed no significant change with time from ca. 2.5%. Hence, the optimal extraction was selected as 5 min.

Sole et al. [8] observed that when using Cyanex302 as the extractant to extract Cu from H_2SO_4 solution, Cu could be fully extracted even at low pH (<1). Similarly, Tait [9] employed Cyanex302 to extract and separate Ni and Co from H_2SO_4 solution. He observed that Co could be fully extracted above pH 6. The extraction efficiency for Ni also increased with increasing pH but remained below 10% at pH 6. These findings suggest that Cyanex302 exhibits higher extraction ability for Cu than for Ni at low pH environments, whereas effective Ni extraction occurs at higher pH levels, aligning with the results of this study.

3.1.3. Extraction Using a Binary Extractant Containing LIX984 and Cyanex302

According to the results of the above extraction experiments using individual extractants, both LIX984N and Cyanex302 exhibited varying extraction efficiencies for Cu and Ni below pH 4. However, LIX984N required pH 2 or above to achieve nearly complete Cu extraction, while Cyanex302 achieved nearly complete Cu extraction above pH 1. Considering that the initial pH of the leachate of the IC lead frame was 0.5 and with the aim of minimizing the co-extraction of Ni and reducing the usage of pH adjustment reagent, pH 1 was chosen as the optimal extraction pH for the subsequent synergistic solvent extraction experiments. The effects of binary extractant concentration, extraction O/A ratio, and extraction time on the extraction efficiency for Cu and Ni using a binary extractant containing LIX984 and Cyanex302 are illustrated in Figure 5a–d. To test the effect of binary extractant

concentration, the extraction pH was set at 1, A/O ratio at 1:1, and extraction time at 10 min. Firstly, Cyanex302 concentration was fixed at 0.02 M and LIX984N concentration was varied at 0 M, 0.0075 M, 0.015 M, and 0.03 M. When no LIX984N was added, the Cu extraction efficiency was 72.0%. Upon adding 0.015 M and 0.03 M LIX984N, this extraction efficiency increased to 92.0% and 95.0%, respectively. However, the Ni extraction efficiency showed no significant change and remained around 1.15% (Figure 5a). Subsequently, Cyanex302 concentration was increased to a fixed 0.0375 M and LIX984N concentration was varied at 0 M, 0.0075 M, 0.015 M, 0.03 M, and 0.05 M. Without adding LIX984N, the Cu extraction efficiency was 83.5%. Upon adding 0.015 M and 0.03 M LIX984N, this extraction efficiency increased to 99.8%. Similar to the previous case, the Ni extraction efficiency remained relatively constant at around 1.17% (Figure 5b). Thus, the optimal binary extractant concentration for the synergistic solvent extraction experiment was determined as 0.015 M LIX984N + 0.0375 M Cyanex302.
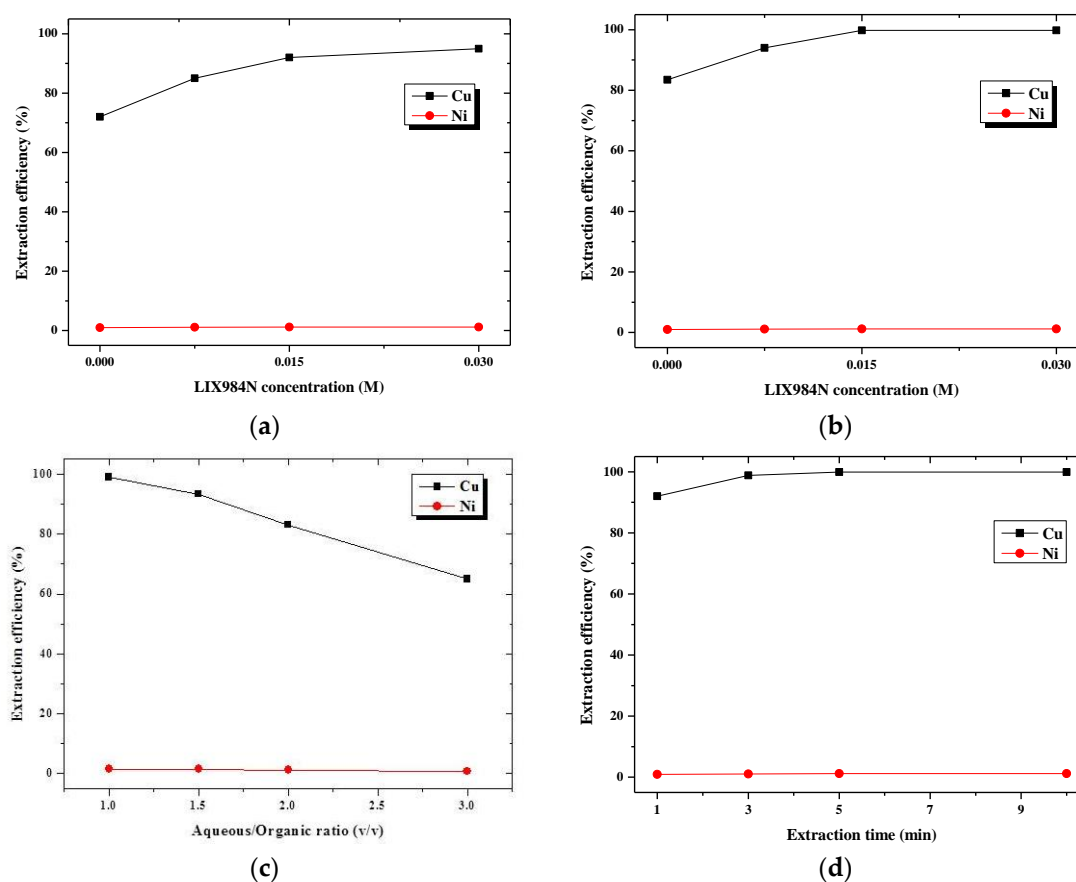

Figure 5. Effects of binary extractant concentration (Cyanex302 concentration was fixed at 0.02 M while varying the LIX984N concentration (**a**), Cyanex302 concentration was fixed at 0.0375 M while varying the LIX984N concentration (**b**)), extraction A/O ratio (**c**), and extraction time (**d**) on Cu and Ni extraction efficiency using a binary extractant containing LIX984N and Cyanex302. Experimental conditions: (**a**,**b**) extraction pH 1, extraction A/O ratio 1:1, extraction time 10 min; (**c**) extraction pH 1, 0.015 M LIX984N + 0.0375 M Cyanex302, extraction time 10 min; (**d**) extraction pH 1, 0.015 M LIX984N + 0.0375 M Cyanex302, extraction A/O ratio 1:1.

To test the effect of extraction A/O ratio (Figure 5c), the tested extraction A/O ratios were 1:1, 1.5:1, 2:1, and 3:1, with an extraction pH of 1, a concentration of 0.015 M LIX984N + 0.0375 M Cyanex302, and an extraction time of 10 min. As the A/O ratio increased (i.e., the aqueous phase increased while the organic phase decreased), the Cu extraction efficiency gradually decreased. The reason for this is similar to that which applies when using a single extractant of LIX984N and Cyanex302. As the extraction A/O ratio increases, the volume

of organic phase decreases. At the fixed binary extractant concentration, the amount of binary extractant also decreases, which leads to a lower extraction efficiency for Cu. The optimal extraction efficiency for Cu was achieved at an A/O ratio of 1:1, with an extraction efficiency of 99.8%. At A/O ratios of 1.5:1, 2:1, and 3:1, the Cu extraction efficiency was 92.0%, 83.1%, and 62.2%, respectively, while the Ni extraction efficiency remained relatively low with a slight variation of around 1.12%. Hence, an A/O ratio of 1:1 was chosen as the optimal ratio for synergistic solvent extraction experiments.

To test the effect of extraction time (Figure 5d), the tested extraction times were 1 min, 3 min, 5 min, and 10 min, with an extraction pH of 1, a concentration of 0.015 M LIX984N + 0.0375 M Cyanex302, and an A/O ratio of 1:1. Cu extraction efficiency increased with the increase in extraction time. At 1 min of extraction time, the Cu extraction efficiency was 92%. As the extraction time exceeded 5 min, the extraction efficiency reached over 99.8%, and the extraction reaction tended to reach equilibrium. On the other hand, the Ni extraction efficiency remained relatively low at about 1.17%. Thus, a 5 min extraction time was considered the optimal duration for the synergistic solvent extraction experiment.

3.1.4. Summarization and Comparison of Solvent Extraction Using Single and Binary Extractant Containing LIX984 and Cyanex302

The optimal extraction conditions, extraction efficiencies, distribution ratios, and separation factors of solvent extraction using single and binary extractant containing LIX984 and Cyanex302 obtained from the above solvent extraction experiments are summarized in Table 1. When using a single extractant of LIX984N under the optimal extraction pH of 2, LIX984N concentration of 0.05 M, extraction A/O ratio of 1:1, and extraction time of 5 min, the optimal extraction efficiencies were 99.2% for Cu and 2.3% for Ni. The optimal distribution ratio of Cu (D_{Cu}) was 149 and that of Ni (D_{Ni}) was 0.024. The optimal separation factor ($\beta_{Cu/Ni}$) was 6208.3. When using a single extractant of Cyanex302 under the optimal extraction pH of 1, Cyanex302 concentration of 0.05 M, extraction A/O ratio of 1:1, and extraction time of 5 min, the optimal extraction efficiencies were 99.5% for Cu and 2.5% for Ni. The optimal distribution ratio of Cu (D_{Cu}) was 599 and that of Ni (D_{Ni}) was 0.027. The optimal separation factor ($\beta_{Cu/Ni}$) was 22,185.2. In contrast, when using a binary extractant containing LIX984N and Cyanex302 under the optimal extraction pH of 2, binary extractant concentration of 0.015 M LIX984N + 0.0375 M Cyanex302, extraction A/O ratio of 1:1, and extraction time of 5 min, the optimal extraction efficiencies were 99.8% for Cu and 1.17% for Ni. The optimal distribution ratio of Cu (D_{Cu}) was 999 and that of Ni (D_{Ni}) was 0.012. The optimal separation factor ($\beta_{Cu/Ni}$) was 83,250.

Table 1. Summarization of the optimal conditions, extraction efficiencies, distribution ratios, and separation factors of solvent extraction using single and binary extractant containing LIX984 and Cyanex302.

Extractant	LIX984N	Cyanex302	LIX984N + Cyanex302
Initial extraction pH value	2	1	1
Extractant concentration	0.05 M	0.05 M	0.015 M + 0.0375 M
Extraction A/O ratio	1 (*v/v*)	1 (*v/v*)	1 (*v/v*)
Extraction time	5 min	5 min	5 min
Extraction efficiency for Cu	99.2%	99.5%	99.8%
Extraction efficiency for Ni	2.3%	2.5%	1.17%
Distribution ratio of Cu (D_{Cu})	149	559	999
Distribution ratio of Ni (D_{Ni})	0.024	0.027	0.012
Separation factor of Cn and Ni ($\beta_{Cu/Ni}$)	6208.3	22,185.2	83,250

According to the above results, Cynaex302 could almost entirely extract Cu from the leachate of IC lead frames at a lower pH of 1, whereas LIX984N could at pH 2. However,

Cynaex302 also possessed higher extraction ability for Ni than LIX984N. Because LIX984N and Cyanex302 are both cationic extractants, their extraction ability for both Cu and Ni increase with pH. In addition, their extraction ability for both Cu and Ni also increase with extractant concentration. Hence, extraction carried out at a lower pH and a lower extractant concentration is beneficial for the separation of Cu and Ni. When a binary extractant containing LIX984N and Cyanex302 is used, the required concentration of each extractant to completely extract Cu reduces compared to using individual extractant. In addition, the almost complete extraction of Cu is achieved at a lower pH of 1. These both reduce the co-extraction of Ni, and thus, the separation of Cu and Ni is improved. On another note, both LIX984N and Cyanex302 had high extraction selectivity of Cu over Ni. It has been reported that the selective extraction of metal ions often follows the order of stability below olation in the aqueous phase [20,21]. The hydrolysis constant (pKa value) follows the order $Cu^{2+} > Ni^{2+}$, which indicates the preferential extraction of Cu over Ni. The results suggest that compared to using individual extractant, using a binary extractant containing LIX984N and Cyanex302 could obtain a higher extraction efficiency for Cu and a lower extraction efficiency for Ni and achieve higher separation performance for Cu and Ni in the leachate of IC lead frames at a lower extraction pH and a lower extractant concentration.

3.2. Stripping Experiments

3.2.1. Effect of the Type of Stripping Agent

The effects of three inorganic acids used as the stripping agent—namely, HCl, HNO_3, and H_2SO_4—on the stripping of Cu and Ni after synergistic solvent extraction are shown in Table 2. The stripping agent concentration was 5 M, the stripping O/A ratio was 1:1, and the stripping time was 15 min. All three inorganic acids exhibited a stripping efficiency of over 98% for Ni, with H_2SO_4 having the highest stripping efficiency of 99.9% compared to HCl and HNO_3. On the other hand, HNO_3 exhibited a stripping efficiency of 99.9% for Cu; for HCl this was 48.2%, and for H_2SO_4 this was only 0.01%. Chen et al. [22] noted that when using LIX984N as an extractant, HCl had better stripping efficiency for Cu compared to H_2SO_4. Similarly, Tait et al. [9] reported that using Cyanex302 as an extractant and H_2SO_4 as a stripping agent required a H_2SO_4 concentration of at least 10 M to achieve effective stripping of Cu ions from the organic phase. Sole et al. [8] also observed that the complete stripping of Cu from H_2SO_4 solution when using Cyanex302 as an extractant required a H_2SO_4 concentration of 12 M or higher. Therefore, considering the selectivity of stripping and with the aim of promoting the separation of Cu and Ni while reducing the usage of stripping agents, this study employed a two-stage stripping procedure in which H_2SO_4 was used as the first-stage stripping agent for Ni stripping and HNO_3 was used as the second-stage stripping agent for Cu stripping.

Table 2. Effects of using HCl, HNO_3, and H_2SO_4 as the stripping agent on the stripping efficiency for Cu and Ni. Experimental conditions: stripping agent concentration of 5 M, stripping O/A ratio of 1:1, and stripping time of 15 min.

Stripping Efficiency	HCl	HNO_3	H_2SO_4
Ni	98.5%	98.2%	99.9%
Cu	48.2%	99.9%	0.01%

3.2.2. First-Stage Stripping Using H_2SO_4 as the Stripping Agent

The effects of H_2SO_4 concentration, stripping O/A ratio, and stripping time on the stripping efficiency for Cu and Ni in the first stage of stripping are shown in Figure 6. To test the effect of H_2SO_4 concentration, the tested H_2SO_4 concentrations were 0.01 M, 0.025 M, 0.05 M, 0.1 M, 1 M, 3 M, and 5 M, with a stripping O/A ratio of 1:1 and a stripping time of 10 min. A stripping efficiency of 99.9% for Ni was obtained at a H_2SO_4 concentration of 0.05 M, followed by a plateau. On the other hand, the stripping efficiency for Cu remained

relatively low at around 0.01% across all H_2SO_4 concentration conditions. Therefore, 0.05 M was chosen as the optimal H_2SO_4 concentration for the first stage of stripping.
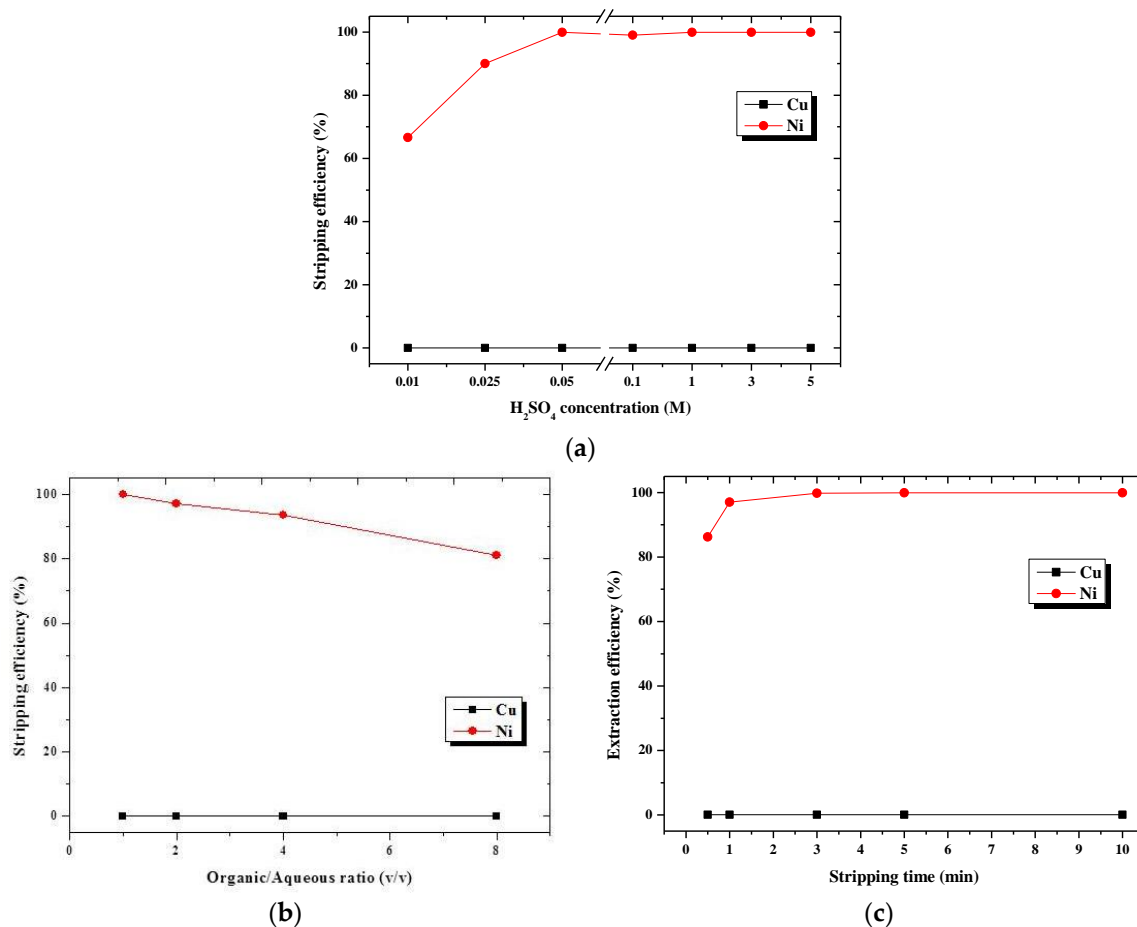

Figure 6. Effects of H_2SO_4 concentration (**a**), stripping O/A ratio (**b**), and stripping time (**c**) on the stripping efficiency for Cu and Ni in the first stage of stripping. Experimental conditions: (**a**) stripping O/A ratio of 1:1, stripping time of 10 min; (**b**) H_2SO_4 concentration of 0.05 M, stripping time of 10 min; (**c**) H_2SO_4 concentration of 0.05 M, stripping O/A ratio of 1:1.

To test the effect of stripping O/A ratio, the tested stripping O/A ratios were 1:1, 2:1, 4:1, and 8:1, with a H_2SO_4 concentration of 0.05 M and a stripping time of 10 min. The stripping efficiency for Ni decreased with an increase in stripping O/A ratio. When the stripping O/A ratio was 1:1, the stripping efficiency for Ni reached 99.9%. However, when the stripping O/A ratio was increased to 8:1, the stripping efficiency decreased to 81.0%. This is because as the stripping O/A ratio increases, the volume of aqueous phase decreases. At the fixed H_2SO_4 concentration, the amount of H_2SO_4 also decreases, which leads to a lower stripping efficiency for Cu. In contrast, the stripping efficiency for Cu showed no significant change with the increase in stripping O/A ratio, remaining at around 0.1%. Therefore, the optimal stripping O/A ratio for the first stage of stripping was determined to be 1:1.

To test the effect of stripping time, the tested stripping times were 0.5 min, 1 min, 3 min, 5 min, and 10 min, with a H_2SO_4 concentration of 0.05 M and a stripping O/A ratio of 1:1. As the stripping time increased from 0.5 min to 3 min, the stripping efficiency for Ni increased from 86.2% to 99.9%. Beyond 3 min no substantial change was noted, and the stripping was completed. In contrast, the stripping efficiency for Cu showed no significant change with an increase in stripping time, remaining at approximately 0.1%. Therefore, the optimal stripping time for the first stage of stripping was determined to be 3 min.

3.2.3. Second-Stage Stripping Using HNO_3 as the Stripping Agent

After the first stage of stripping, where Ni was stripped into the aqueous phase using 0.05 M H_2SO_4, the Cu present in the organic phase underwent a second stage of stripping using HNO_3 as the stripping agent. The effects of HNO_3 concentration, stripping O/A ratio, and stripping time on the stripping efficiency for Cu in the second stage of stripping are depicted in Figure 7. Because Ni had been nearly entirely stripped in the first stage of stripping, only the stripping efficiency for Cu is presented. To test the effect of HNO_3 concentration, the tested HNO_3 concentrations were 0.5 M, 1 M, 3 M, 3.5 M, 4 M, and 5 M, with a stripping O/A ratio of 1:1 and a stripping time of 10 min. As the HNO_3 concentration increased, the stripping efficiency for Cu also increased. The Cu stripping efficiency showed a significant increase when the HNO_3 concentration exceeded 4 M. At a HNO_3 concentration of 5 M, the Cu stripping efficiency reached 99.9% and remained stable thereafter. Hence, 5 M was determined as the optimal HNO_3 concentration for the second stage of stripping.
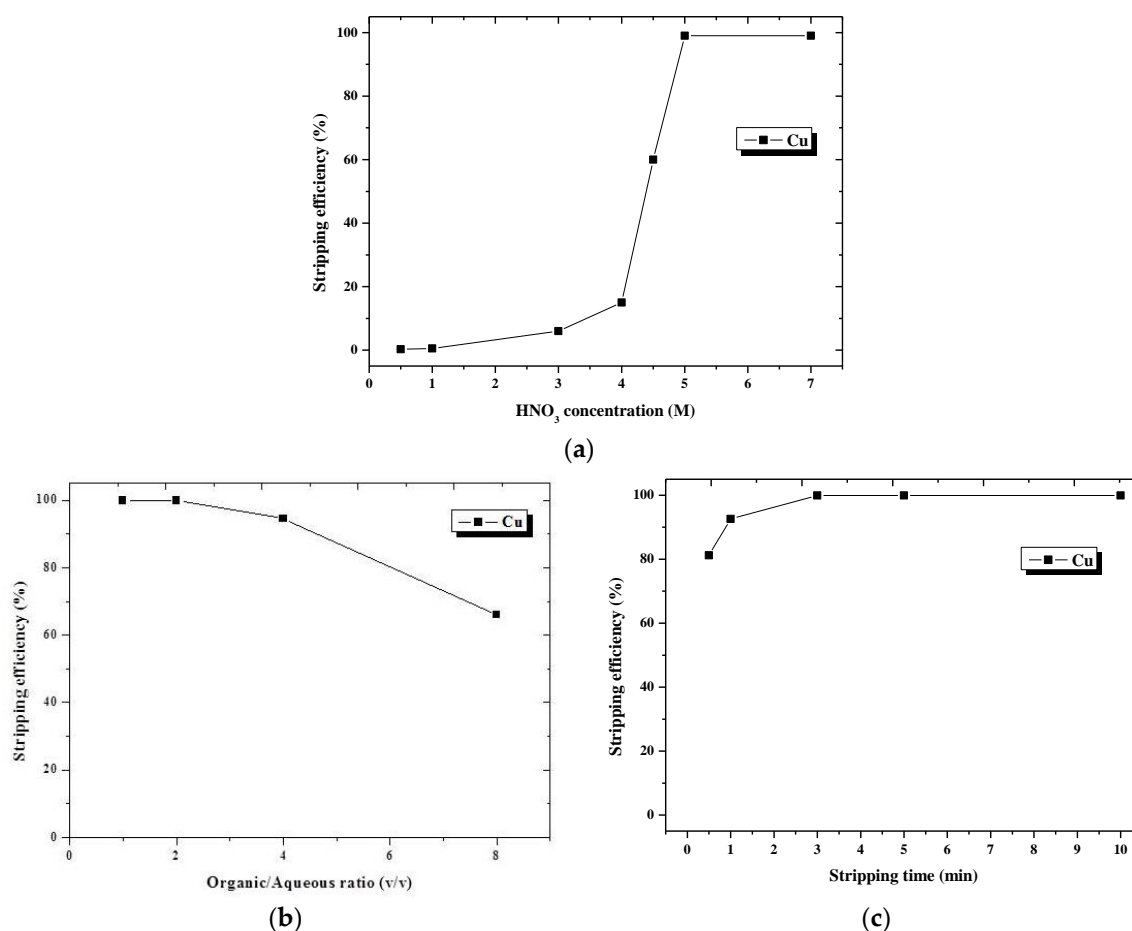

(**a**)

(**b**)　　　　　　　　　　　　　　　　　　　(**c**)

Figure 7. Effects of HNO_3 concentration (**a**), stripping O/A ratio (**b**), and stripping time (**c**) on the stripping efficiency for Cu in the second stage of stripping. Experimental conditions: (**a**) stripping O/A ratio of 1:1, stripping time of 10 min; (**b**) HNO_3 concentration of 5 M, stripping time of 10 min; (**c**) HNO_3 concentration of 5 M, stripping O/A ratio of 2:1.

To test the effect of stripping O/A ratio, the tested stripping O/A ratios were 1:1, 2:1, 4:1, and 8:1, with a HNO_3 concentration of 5 M and a stripping time of 10 min. As the stripping O/A ratio increased from 1:1 to 2:1, the Cu stripping efficiency remained at 99.9%. However, when the stripping O/A ratio exceeded 2:1, the Cu stripping efficiency decreased with an escalating stripping O/A ratio. At a stripping O/A ratio of 8:1, the Cu stripping efficiency decreased to 66.0%. The reason for this is similar to that which applies

to the first stage of stripping. As the stripping O/A ratio increases, the volume of aqueous phase decreases. At the fixed HNO_3 concentration, the amount of HNO_3 also decreases, which leads to a lower stripping efficiency for Cu. Therefore, a 2:1 stripping O/A ratio was identified as the optimal condition for the second stage of stripping.

To test the effect of stripping time, the tested stripping times were 0.5 min, 1 min, 3 min, 5 min, and 10 min, with a HNO_3 concentration of 5 M and a stripping O/A ratio of 2:1. As the stripping time increased from 0.5 min to 3 min, the Cu stripping efficiency escalated from 81.2% to 99.9%. Beyond 3 min, the reaction reached equilibrium. Therefore, a stripping time of 3 min was determined as the optimal condition for the second stage of stripping.

The optimal conditions and stripping efficiencies obtained from the above stripping experiments are summarized in Table 3. In the first stage of stripping, 0.05 M H_2SO_4 was employed as the stripping agent with a stripping O/A ratio of 1:1 and a stripping time of 3 min, resulting in a Ni stripping efficiency of 99.9% and a Cu stripping efficiency of 0.12%. The results indicate the stripping selectivity of Ni over Cu. This is because the stripping reaction is the reverse reaction of the extraction reaction. Cu is more easily extracted by the binary extractant containing LIX984N and Cynaex302 at a lower pH than Ni. Therefore, on the contrary, Ni is more easily stripped at a lower H_2SO_4 concentration than Cu. In the second stage of stripping, 5 M HNO_3 was applied as the stripping agent with a stripping O/A ratio of 2:1 and a stripping time of 3 min, leading to a Cu stripping efficiency of 99.9%. The results suggested that by applying two-stage stripping, the less co-extracted Ni in the organic phase after synergistic solvent extraction could be selectively stripped by dilute H_2SO_4 and thus reduce the co-stripping of Cu. Hence, the effective separation and recovery of Cu and Ni in IC lead frame leachate could be achieved.

Table 3. Summarization of the optimal conditions and stripping efficiencies of stripping procedure.

First-stage stripping	
$[H_2SO_4]$	0.05 M
Stripping O/A ratio	1:1
Stripping time	3 min
Stripping efficiency for Ni	99.9%
Stripping efficiency for Cu	0.12%
Second-stage stripping	
$[HNO_3]$	5 M
Stripping O/A ratio	2:1
Stripping time	3 min
Stripping efficiency for Cu	99.9%

3.3. Mass Balance of Cu and Ni in the Synergistic Solvent Extraction and Selective Stripping Procedure under Optimal Experimental Conditions

Figure 8 illustrates the mass balance of Cu and Ni in the present synergistic solvent extraction and selective stripping procedure under optimal experimental conditions. A measure of 20 mL of IC lead frame leachate was used, and the synergistic solvent extraction was carried out under the optimal conditions, which included an extraction pH of 1, extractant concentration of 0.015 M LIX984N + 0.0375 M Cyanex302, extraction A/O ratio of 1:1, and extraction time of 5 min. The aqueous phase contained 0.006 mg of Cu (with a distribution of 0.1%) and 59.3 mg of Ni (with a distribution of 98.83%), while the organic phase contained 5.994 mg of Cu and 0.7 mg of Ni. For the organic phase, two-stage stripping was performed to recover the Cu and Ni from the organic phase to the aqueous phase. In the first stage of stripping, under the optimal conditions of 0.05 M H_2SO_4, a stripping O/A ratio of 1:1, and a stripping time of 3 min, 0.007 mg of Cu (with a distribution of 0.12%) and 0.699 mg of Ni (with a distribution of 1.165%) were stripped to the aqueous phase. In the second stage of stripping, under the optimal conditions of 5 M HNO_3, a stripping O/A

ratio of 2:1, and a stripping time of 3 min, 5.987 mg of Cu (with a distribution of 99.78%) and 0.001 mg of Ni (with a distribution of 0.005%) were stripped to the aqueous phase. The distributions of Cu and Ni suggested that most of the Ni in the IC lead frame leachate was recovered from the aqueous phase after synergistic solvent extraction, and the co-extracted Ni was further recovered after first-stage stripping. In contrast, most of the Cu in the IC lead frame leachate was recovered from the aqueous phase after second-stage stripping.
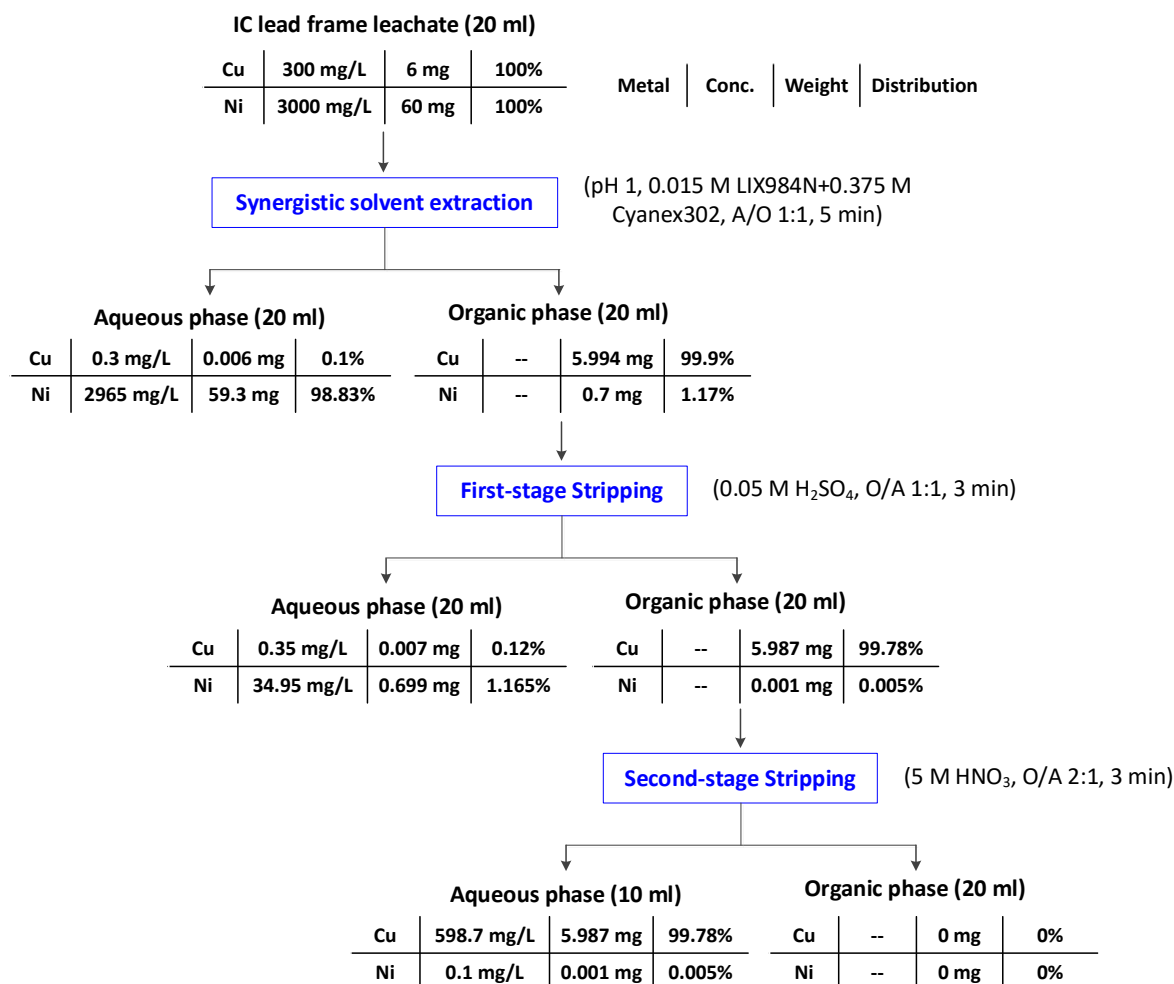
IC lead frame leachate (20 ml)

	Conc.	Weight	Distribution
Cu	300 mg/L	6 mg	100%
Ni	3000 mg/L	60 mg	100%

Metal	Conc.	Weight	Distribution

Synergistic solvent extraction (pH 1, 0.015 M LIX984N+0.375 M Cyanex302, A/O 1:1, 5 min)

Aqueous phase (20 ml)

	Conc.	Weight	Distribution
Cu	0.3 mg/L	0.006 mg	0.1%
Ni	2965 mg/L	59.3 mg	98.83%

Organic phase (20 ml)

	Conc.	Weight	Distribution
Cu	--	5.994 mg	99.9%
Ni	--	0.7 mg	1.17%

First-stage Stripping (0.05 M H_2SO_4, O/A 1:1, 3 min)

Aqueous phase (20 ml)

	Conc.	Weight	Distribution
Cu	0.35 mg/L	0.007 mg	0.12%
Ni	34.95 mg/L	0.699 mg	1.165%

Organic phase (20 ml)

	Conc.	Weight	Distribution
Cu	--	5.987 mg	99.78%
Ni	--	0.001 mg	0.005%

Second-stage Stripping (5 M HNO_3, O/A 2:1, 3 min)

Aqueous phase (10 ml)

	Conc.	Weight	Distribution
Cu	598.7 mg/L	5.987 mg	99.78%
Ni	0.1 mg/L	0.001 mg	0.005%

Organic phase (20 ml)

	Conc.	Weight	Distribution
Cu	--	0 mg	0%
Ni	--	0 mg	0%

Figure 8. Mass balance of Cu and Ni in the present synergistic solvent extraction and selective stripping procedure.

3.4. Metal Recovery from Stripping Solution

3.4.1. Precipitation pH Value

The stripping solutions containing either Cu or Ni ions obtained from the foregoing extraction and stripping processes were subjected to precipitation, using NaOH as the precipitating agent. The effect of precipitation pH on the precipitation efficiency for Cu and Ni ions is illustrated in Figure 9. The precipitation efficiency for both Cu and Ni ions increased with rising pH. Cu ions started to precipitate around pH 4, and the precipitation efficiency exceeded 99.5% at pH 7 and above. Ni ions began to precipitate at pH 5, and the precipitation efficiency reached 99.8% at pH 12. Therefore, the stripping solution containing Cu ions was adjusted to pH 7 to obtain $Cu(OH)_2$ precipitate, while the stripping solution containing Ni ions was adjusted to pH 12 to obtain $Ni(OH)_2$ precipitate.
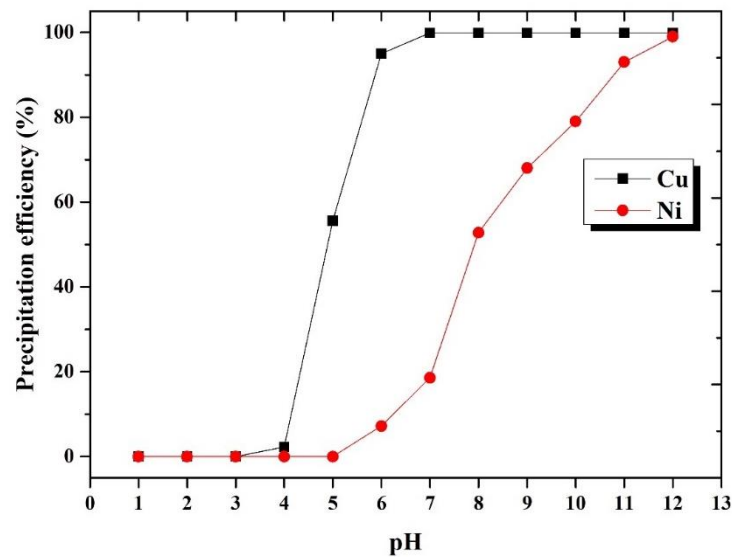
Figure 9. Effect of precipitation pH on the precipitation efficiency for Cu and Ni ions in the stripping solutions.

3.4.2. Characterization of Metal Oxide Products

To obtain the final products of metal oxides, the Cu and Ni hydroxides were subjected to calcination. X-ray diffraction (XRD) was used to conduct a crystal phase analysis of the metal oxide products after calcination, and the results are presented in Figure 10. Based on the XRD spectra, it can be confirmed that the two powders correspond to CuO (identified by the ICDD#76-0629 card) (Figure 10a) and NiO (identified by the ICDD#78-0423 card) (Figure 10b).
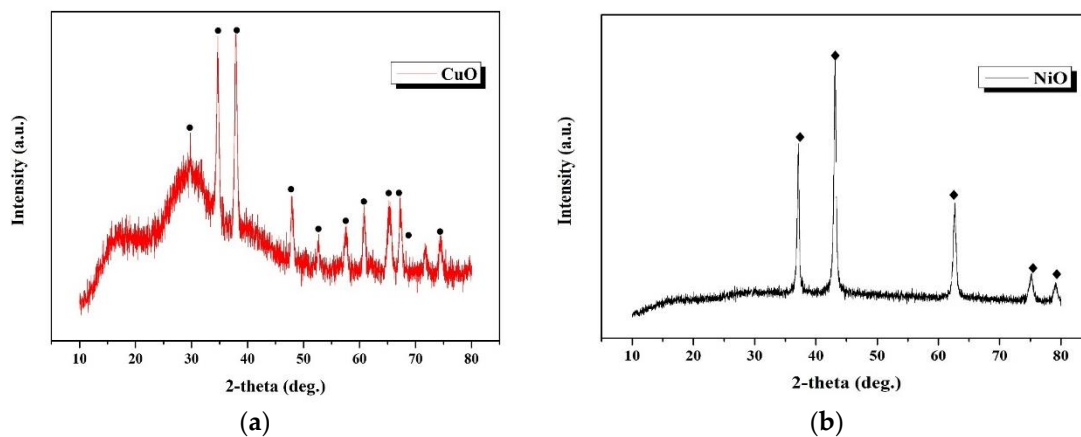
Figure 10. XRD analysis results for the metal oxide calcination products (**a**) CuO and (**b**) NiO.

To confirm the purity of the CuO and NiO products, an elemental analysis of the metal oxide products was conducted using XRF (SEA6000VX, TechMax, HITACHI). The analysis revealed the presence of various elements, including Ni, Cu, Na, and O, in both products. Subsequently, the metal oxide products were completely dissolved using aqua regia, and their contents were analyzed using ICP-OES (Optima 8000, PerkinElmer, Inc.), with the results presented in Table 4. The purity of CuO was found to be 99.82%, while that of NiO was determined to be 99.74%.

Table 4. Content analysis results for NiO and CuO.

Content	NiO	CuO
NiO	99.74%	0.05%
CuO	0.075%	99.82%
NaO	0.18%	0.12%

4. Conclusions

In this study, synergistic solvent extraction was applied using a binary extractant containing LIX984N and Cyanex302, and two-stage selective stripping was employed using H_2SO_4 and HNO_3 as the stripping agents to separate and recover Cu and Ni from the leachate of an IC lead frame. The obtained results are summarized as follows:

(1) The optimal extraction conditions using a single extractant of LIX984N included an extraction pH of 2, LIX984N concentration of 0.05 M, extraction A/O ratio of 1:1, and extraction time of 5 min. Under these conditions, the extraction efficiencies for Cu and Ni were 99.2% and 2.3%, respectively. The distribution ratios were D_{cu} = 149 and D_{Ni} = 0.024, resulting in a separation factor of 6208.3. In contrast, the optimal conditions when using a single extractant of Cyanex302 included an extraction pH of 1, Cyanex302 concentration of 0.05 M, extraction A/O ratio of 1:1, and extraction time of 5 min. Under these conditions, the extraction efficiencies for Cu and Ni were 99.5% and 2.5%, respectively. The distribution ratios were D_{cu} = 559 and D_{Ni} = 0.027, resulting in a separation factor of 22,185.2.

(2) The optimal extraction conditions for synergistic solvent extraction using a binary extractant containing LIX984N and Cyanex302 included an extraction pH of 1, extractant concentration of 0.015 M LIX984N + 0.0375 M Cyanex302, extraction A/O ratio of 1:1, and extraction time of 5 min. Under these conditions, the extraction efficiencies for Cu and Ni were 99.8% and 1.17%, respectively. The distribution ratios were D_{cu} = 999 and D_{Ni} = 0.012, resulting in a separation factor of 83,250.

(3) Compared to using an individual extractant, using a binary extractant containing LIX984N and Cyanex302 could obtain a higher extraction efficiency for Cu and a lower extraction efficiency for Ni, and achieve higher separation performance for Cu and Ni at a lower extraction pH and with a lower extractant concentration.

(4) The optimal conditions for selective stripping in the first stage of stripping included using 0.05 M H_2SO_4 as the stripping agent with a stripping O/A ratio of 1:1 and a stripping time of 3 min. As such, 99.9% of Ni could be stripped into the aqueous phase. In the second stage of stripping, 5 M HNO_3 was used as the stripping agent with a stripping O/A ratio of 2:1 and a stripping time of 3 min, and 99.9% of Cu could be stripped into the aqueous phase.

(5) The stripping solutions containing Cu or Ni ions were subjected to precipitation using NaOH as the precipitant. The precipitation efficiency for Cu ions reached above 99.5% at pH 7. The calcination of the $Cu(OH)_2$ precipitate resulted in a final product of CuO with a purity of 99.82%. In contrast, the precipitation efficiency for Ni ions reached above 99.8% at pH 12. The calcination of the $Ni(OH)_2$ precipitate resulted in a final product of NiO with a purity of 99.74%.

The results demonstrate that synergistic solvent extraction using a binary extractant containing LIX984N and Cyanex302 can almost entirely extract Cu from the leachate of an IC lead frame at a lower extraction pH and a lower extractant concentration, and thus reduce the co-extraction of Ni. In addition, the less co-extracted Ni in the organic phase can be selectively stripped using dilute H_2SO_4, thus reducing the co-stripping of Cu. Hence, the effective separation and recovery of Cu and Ni from IC lead frame leachate can be achieved while reducing the usage of pH adjusting agent, extractant, and stripping agent, which helps to reduce the consumption of raw materials and energies to produce these chemical regents. Moreover, the recovered CuO and NiO can act as a secondary resource, which helps to promote resource circulation and the sustainable utilization of Cu and Ni metals. These all contribute to improving the sustainability of natural resources.

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