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Green approach for selective Cu(II) recovery from aqueous solutions: Efficient separation from Ni(II) and Co(II) with organic phase regeneration

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Abstract

The objective of this study was to achieve the selective recovery of Cu(II) from aqueous solutions in the presence of Ni(II) and Co(II) by utilising a green approach, palm kernel fatty acid distillate (PKFAD) as the organic phase. PKFAD was employed without the use of diluent, extractant, or modifier typically required in conventional solvent extraction processes. In the first stage of the procedure, Cu(II) was selectively extracted and stripped from the multi-element solution. In the second stage, Ni(II) and Co(II) were subsequently recovered. The selectivity of the extraction process was driven by the difference in *pH*-dependence equilibrium (pH_{eq}) for each metal ion. A high Cu(II) efficiency of 97% was achieved in the first stage at pH_{eq} of 4.8, while Ni(II) and Co(II) extraction efficiencies of 88% and 85%, respectively, were obtained in the subsequent extraction stage at a pH_{eq} of 5.9. Separation factor for Cu(II) over Ni(II) and Co(II) were ≥ 180, indicating effective selective separation. Additionally, the PKFAD was successfully regenerated, with the stripping process achieved 98% of Cu(II), 85% of Ni(II) and 72% of Co(II) recovery. These results highlight the efficacy of PKFAD as a sustainable, regenerable organic phase with high potential for selective metal ion recovery.

Keywords: copper, green organic solvent, palm kernel fatty acid distillate, solvent extraction, selectivity

1. Introduction

Copper (Cu) is a valuable material in many industrial applications for its distinct traits, such as malleability, ductility, and excellent electrical and thermal conductivity [1]. Blending Cu with elements like nickel (Ni) and cobalt (Co) bolsters the properties of Cu-Ni and Cu-Co alloys, enhancing strength and corrosion resistance and expanding applications in seawater piping, heat exchangers, condensers, bearing assemblies, ballasts, castings, step-soldering, and radiation shielding [2]. Consequently, the widespread use of Cu and its alloys across industries results in substantial industrial waste solutions containing Cu(II) and other metal ions like Ni(II) and Co(II). Inadequate treatment of these metal-laden waste solutions, which are discharged directly into waterways, not only harms the environment but also results in the depletion of valuable resources [3].

Numerous techniques, including chemical precipitation [4], adsorption [5,6], electrocoagulation [7], solvent extraction [8], micromotor [9], and liquid membrane [10], have been employed to recover Cu(II) selectively from aqueous solutions containing various metal ions. Among these techniques, solvent extraction, involving extraction based on the polarity and solubility of a solute in a liquid phase, typically an organic solvent, is one of the most widely used techniques by the industry [11]. This technique finds extensive application in industries due to its simple operation, cost-effective equipment, applicability across a wide solute concentration range, high throughput, selectivity, and recovery rates [12]. Nevertheless, the typical solvents used for organic extraction primarily consist of volatile organic compounds derived from non-renewable sources, predominantly petroleum-based. Examples of such solvents include hexane, heptane, benzene, toluene, kerosene, and chloroform. It is important to note that these solvents are consistently associated with toxicity and pose significant risks to both human health and the environment [13]. Furthermore, effectively separating metal ions with equivalent valence and comparable sizes using classical extraction solvents remains a significant challenge [14]. Several recent studies have showcased encouraging outcomes in the selective recovery of Cu(II) from aqueous solutions with mixed metal ions, including Ni(II) and Co(II). For instance, [15] studied the synergistic extraction of Cu(II), Ni(II), Co(II), Zn(II), and Cd(II) using a mixture of Versatic 10 acid and Mextral 984H, diluted with Mextral DT100. A different formulation of LIX63, Versatic 10, and TBP in Shellsol D70 for the recovery of Cu(II), Ni(II), Co(II), and Zn(II) from strong chloride solutions was investigated by Zhu et al. [16], who reported more than 95% Cu(II) extraction at pH_{eq} 0.5, A/O 1:2, and 40 °C using 0.3 M LIX63, 0.3 M Versatic 10, and 0.7 M TBP. Meanwhile, Sridhar and Verma [17] reported the synergistic extraction of Cu(II), Ni(II), and Co(II) using the combination of LIX 984N and ACORGA M5640 diluted in kerosene solvent. Nevertheless, most of these studies employed intricate extraction solvents derived mainly from petroleum [18] alongside alternatives such as vegetable oils [19], ionic liquids [20], and eutectic solvents [21], all composed of multiple components like extractants, diluents, and/or modifiers.

The regeneration of the organic phase in solvent extraction is essential for maintaining the long-term viability of metal recovery processes. Stripping, typically achieved using an acid, base, or salt solution as a stripping agent, often involves petroleum-based solvents or other chemical sources [13]. It is crucial to focus on the concentration of the solute and the regeneration of these stripping agents to enhance valuable solute recovery and support environmental sustainability. However, the effectiveness of organic solvent regeneration can be compromised by solvent degradation, which may result from exposure to stripping agents, high temperatures, or other operational conditions. Additionally, solvent volume loss can occur due to the volatility of organic solvents. Changes in the physical properties of the solvent, such as increased viscosity, can also affect mass transfer efficiency. Therefore, the selection of an effective, regenerable organic solvent is critical for ensuring process efficiency.

Palm kernel fatty acid distillate (PKFAD), a byproduct of palm kernel oil refining containing ~92 wt.% free fatty acids (FFA) and ~8 wt.% triglycerides, has emerged as a sustainable organic solvent for Cu(II) extraction from aqueous solutions. Rich in palmitic (49.1 wt.%), myristic (17.0 wt.%), and oleic (11.0 wt.%) acids, PKFAD exhibits moderate viscosity (23.0 mPa·s at 50 °C) and a low unsaturated-to-saturated fatty acid ratio (1:7), providing hydrophobicity and stability for metal extraction [22]. Remarkably, this approach involves the application of PKFAD, in the absence of other components like diluents and modifiers, as demonstrated by our previous research [22–24]. In our earlier investigations, we ascertained that the FFAs within PKFAD served as the active component, effectively extracting 98% of Cu(II) from single-metal aqueous solutions containing Cu(II). This extraction occurred through a cation exchange mechanism at pH_{eq} of 4.7, followed by stripping of Cu(II) from Cu(II)-loaded PKFAD using formic acid [22]. Additionally, PKFAD was also employed as a nanocomposite adsorbent for selective extraction from binary-metal aqueous solutions consists of Cu(II) and Au(III) [25]. Nevertheless, the selective recovery of Cu(II) from aqueous solutions containing metal ions with identical valence and similar sizes using PKFAD remains an unexplored realm of study. This uncharted domain presents an exciting opportunity to delve further into the capabilities of PKFAD as a sustainable and selective extraction solvent.

Herein, selective recovery of Cu(II) from aqueous solutions containing Cu(II), Ni(II), and Co(II) was performed. In the first stage, Cu(II) was selectively extracted and stripped from the mixed solution. Subsequently, in the second stage, Ni(II) and Co(II) were recovered. The extraction process employed PKFAD as a green organic solvent for metal extraction, while the stripping process utilized formic acid and sulfuric acid as stripping agents to recover metals from the metal-loaded PKFAD. Additionally, the PKFAD organic phase was successfully regenerated after the first and second stage of extraction and stripping process, enhancing its sustainability in the metal recovery process.

2. Materials and methods

2.1 Materials and Equipment

The PKFAD was purchased locally. Copper sulfate pentahydrate ($CuSO_4·5H_2O$) (ChemAR ≥ 99.5% purity), cobalt sulfate-heptahydrate ($CoSO_4·7H_2O_0$) (HmbG ≥ 99% purity), nickel sulfate hexahydrate ($NiSO_4·6H_2O$) (EMSURE ACS, 99% ≥ purity), sodium sulfate anhydrous (Na_2SO_4) (ChemAR, 99.5% ≥ purity), sodium hydroxide (NaOH) (R&M Chemicals, 99% ≥ purity), sulfuric acid (H_2SO_4) (QReC, 95-97% ≥ purity), formic acid (CH_2O_2) (R&M Chemicals, 88% ≥ purity), were used as per received. The aqueous and organic phases were mixed using an incubator shaker (Lab Companion, SI-300). The *pH* of the aqueous phase was measured using a *pH* meter (Hanna Instruments, HI11310) both before and after the extraction process. The flame atomic absorption spectrophotometer (FAAS) (Shimadzu, AA7000) was used to determine the concentration of Cu(II), Ni(II), and Co(II) in aqueous phases after extraction.

2.2 Preparation of Organic and Aqueous Phase

Aqueous phases containing single- or multi-element solutions of Cu(II), Ni(II), and Co(II) were prepared by dissolving $CuSO_4\cdot5H_2O$, $NiSO_4\cdot6H_2O$, and $CoSO_4\cdot7H_2O$ in distilled water, followed by the addition of 200 mM Na_2SO_4 as an impurity. Extractions were conducted at 25 ± 2 °C with an organic-to-aqueous (O:A) phase ratio of 1:1, an initial metal concentration of 100 mg/L, and an equilibrium pH (pH_{eq}) of 3.5–6.5, adjusted using 1.0 M NaOH or 1.0 M H_2SO_4. The organic phase, comprising PKFAD, was used directly without pre-treatment or the addition of extractants, diluents, or modifiers.

Stripping solutions comprised either 1.0 M formic acid or 1.0 M sulfuric acid and were applied at a 1:1 extract-to-strip phase ratio under the same temperature and contact time as the extraction step. Cu-loaded PKFAD and Ni–Co-loaded PKFAD, obtained from the first- and second-stage raffinate phases, respectively, were used as the organic phase in stripping experiments.

2.3 Experimental Setup and Procedures

Figure 1 illustrates the solvent extraction and stripping systems employed in this study. All extraction and stripping experiments were conducted in a conical flask. An incubator shaker was employed to mix and agitate the organic and aqueous phase. Subsequently, the settling process was carried out by using a separating funnel to separate the organic and aqueous phases following the mixing process. Cu(II) was selectively extracted and recovered during the first extraction–stripping stage (Extracted 1 → Raffinate 2), while Ni(II) and Co(II) were extracted and recovered in the second stage (Extracted 3 → Raffinate 4).

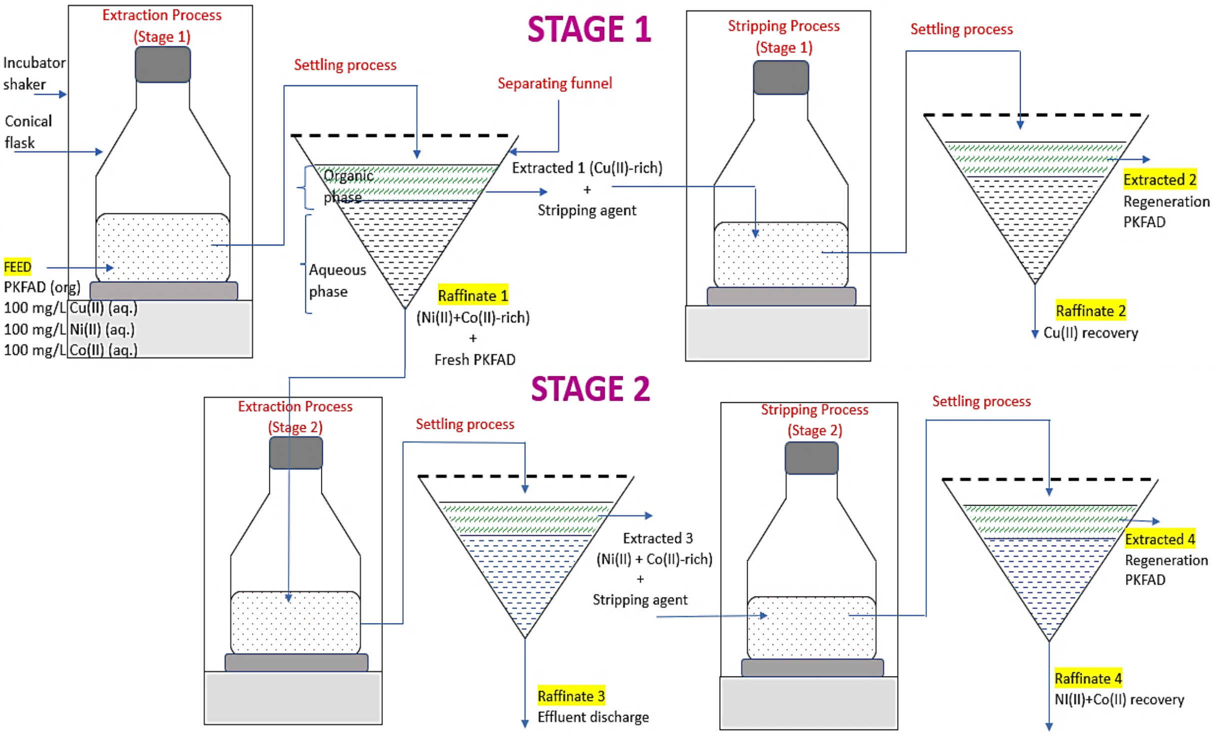

Figure 1 Experimental configuration for the extraction and stripping process.

2.3.1 Determination of pH-extraction isotherm for single-metal solution

Experiments initially utilized single-metal aqueous solutions in order to obtain the pH-extraction isotherm of each metal ion by varying the pH equilibrium (pH_{eq}) of the aqueous solution. The extraction procedure was conducted, as described in previous studies [22,24]. Approximately 15 mL of PKFAD and 15 mL of aqueous solution were transferred into a glass-stoppered conical flask and agitated in an incubator shaker at 150 rpm for 8 min. The mixture was subsequently transferred to a separating funnel and allowed to settle for 5 min. About 8 mL of the aqueous phase was then withdrawn for pH_{eq} measurement. If required, the pH_{eq} of the solution was adjusted using 1.0 M H_2SO_4 or 1.0 M NaOH and returned to the shaker for a further 8 min of equilibration.

2.3.2 Selective recovery of Cu(II) from multi-element solution (Stage 1)

Selective extraction of Cu(II) from a multi-element solution containing Cu(II), Ni(II) and Co(II) was carried out at the optimum pH_{eq} obtained from the Cu(II) pH-extraction isotherm (Section 2.3.1). The extraction was performed using the same procedure described for single-metal systems. After phase separation, the organic layer (Extracted 1 in Figure 1) was stripped with either sulfuric acid or formic acid to recover Cu(II), resulting in Raffinate 2 and regenerated PKFAD (Extracted 2). The remaining aqueous phase from the extraction step (Raffinate 1 in Figure 1), containing Ni(II) and Co(II), served as feed for the second-stage extraction.

2.3.3 Regeneration of PKFAD and recovery of Ni(II) and Co(II) (Stage 2)

The aqueous phase from Stage 1 (Raffinate 1 in Figure 1), containing Ni(II) and Co(II), was re-extracted using fresh PKFAD at the respective optimum pH_{eq} values determined in Section 2.3.1. The extraction and stripping procedures were performed similarly to Stage 1 for the purpose of regenerating PKFAD and recovering Ni(II) and Co(II), producing Extracted 4 and Raffinate 4 (Figure 1). Equations 1 and 2 were used to determine the percentage extraction (*%E*) and overall recovery (*%OR*), respectively:

$$\%E = \frac{X_{i,feed} - X_{f,feed}}{X_{i,feed}}\ X\ 100\% \tag{1}$$

$$\%OR = \frac{X_{f,strip}}{X_{i,feed}}\ x\ 100\% \tag{2}$$

where $X_{i,\, feed}$, $X_{f,\, feed}$ represent the initial and final amount of metal ion in the aqueous feed phase respectively, and $X_{f,\, strip}$ represent the final amount of metal ion in the aqueous stripping phase. Equations 3 and 4 were used to obtain the distribution ratio (*D*) and separation factors ($SF_{Cu/x}$), respectively.

$$D = \frac{[X]_{org}}{[X]_{aq}} \tag{3}$$

$$SF_{Cu/x} = \frac{D_{Cu}}{D_x} \tag{4}$$

where, $[X]_{org}$ and $[X]_{aq}$ represent the equilibrium concentrations of metal ions in the organic and aqueous phases, respectively. D_{cu} and D_x represent the distribution ratios of Cu(II) and Co(II)/Ni(II), respectively. Unless stated otherwise, all samples were run in duplicate, and the relative standard deviation between repeat samples within each experiment was determined to be below 5%.

3. Results and discussion

3.1 pH-Extraction Isotherm for Single- and Multi-Element Solutions

The effect of pH_{eq} on the individual extraction of Cu(II), Ni(II), and Co(II) from single-element solutions was investigated by altering the pH_{eq} within the range of 3.7 to 6.5. The pH_{eq} values for Cu(II), Ni(II), and Co(II) were set below 5.6, 7.9, and 8.0, respectively, in order to avoid precipitation, i.e., copper hydroxide was set at 2.2×10^{-20} [26], nickel hydroxide at 2.0×10^{-15} [27], and cobalt hydroxide at 1.3×10^{-15} [28]. The results depicted in Figure 2 (A) illustrate the notable impact of pH_{eq} on the extraction of Cu(II), Ni(II), and Co(II). In addition, all of the *pH*-isotherms that were analysed showed a sigmoid curve. The *%E* of Cu(II) was found to be less than 60% at a *pH* of 4.0. As the *pH* increased, the *%E* of Cu(II) continued to climb until it reached its maximum value at a *pH* of 4.8, after which it reached a plateau. In contrast, the *pH*-extraction isotherms of Ni(II) and Co(II) were comparable, with a *%E* < 50% at a *pH* of <5.2. The optimum *pH* for both metals was found to be 5.9.

The strong correlation between the pH_{eq} and the *%E* of PKFAD in metal extraction can be elucidated by considering the equilibrium extraction-stripping process described in Equations 5-7 [22], where the rise of pH_{eq} (decreasing the H^+) would promote the forward process (extraction) to produce more metal-FFA complexes (extracted species) while decreasing the pH_{eq} would promote the backward process (stripping) and produce fewer metal-FFA complexes (extracted species). Our previous investigation [22,24] discovered similar patterns in the extraction of Cu(II) from single-metal aqueous solutions. Overall, the pH_{eq} extraction-isotherm curve for Cu(II) was more acidic than the curves for Ni(II) and Co(II), where the latter moved further to the right side (less acidic)

(Figure 2(A)). Consequently, the difference between the Cu(II) pH_{eq} extraction-isotherm curve with Ni(II) and Co(II) curves appears to offer the possibility of selective separation of Cu(II) over Ni(II) and Co(II).

$$Cu^{2+}_{(aq)} + 3(RCOOH)_{2(org)} \leftrightarrow Cu[(RCOO)_2\,(RCOOH)_4]_{(org)} + 2H^{+}_{(aq)} \quad (5)$$

$$Ni^{2+}_{(aq)} + 3(RCOOH)_{2(org)} \leftrightarrow Ni[(RCOO)_2\,(RCOOH)_4]_{(org)} + 2H^{+}_{(aq)} \quad (6)$$

$$Co^{2+}_{(aq)} + 3(RCOOH)_{2(org)} \leftrightarrow Co[(RCOO)_2\,(RCOOH)_4]_{(org)} + 2H^{+}_{(aq)} \quad (7)$$

Where $(RCOOH)_2$ is a dimeric fatty acid, while $Cu(RCOO)_2(RCOOH)_4$, $Ni(RCOO)_2(RCOOH)_4$, $Co(RCOO)_2(RCOOH)_4$ are the metal-FFA complexes for Cu(II), Ni(II), and Co(II), respectively.

Based on the results obtained in Figure 2 (A), the influence on pH_{eq} extraction-isoherm of Cu(II), Ni(II), and Co(II) ions in multi-element solution was investigated for the attainability of selective extraction of Cu(II) over Ni(II) and Co(II). Figure 2 (B) presents the pH_{eq} extraction-isotherm of Cu(II), Ni(II), and Co(II) at various pH_{eq} of 2.0 to 4.8 from a multi-element solution. The results demonstrated that a high Cu(II) extraction of 97% was achieved at an optimum pH_{eq} of 4.8, while $\%E$ for other metals, Ni(II) and Co(II), were <15% at all ranges of pH_{eq} studied (2.0-4.8). These results are well in agreement with the previous finding in pH_{eq} extraction-isotherm for single metal ions (Figure 2 (A)). In addition, the pH_{eq}-extraction isotherms showed that Cu(II) had the lowest pH_{50} value (defined as the pH_{eq} at which 50 % extraction occurs) of 4.0, whereas, pH_{50} >> 4.8 was found for Ni(II) and Co(II). The low pH_{50} of cationic extractants (FFA from PKFAD) indicates their strong ability and tendency to extract solutes from very acidic aqueous conditions [29]. This is the characteristic of acidic extractants which are dependent on the pH_{eq}. Thus, the metals can be separated at different optimum pH_{eq} based on the molecular weight, size, and coordination of the molecules [29].

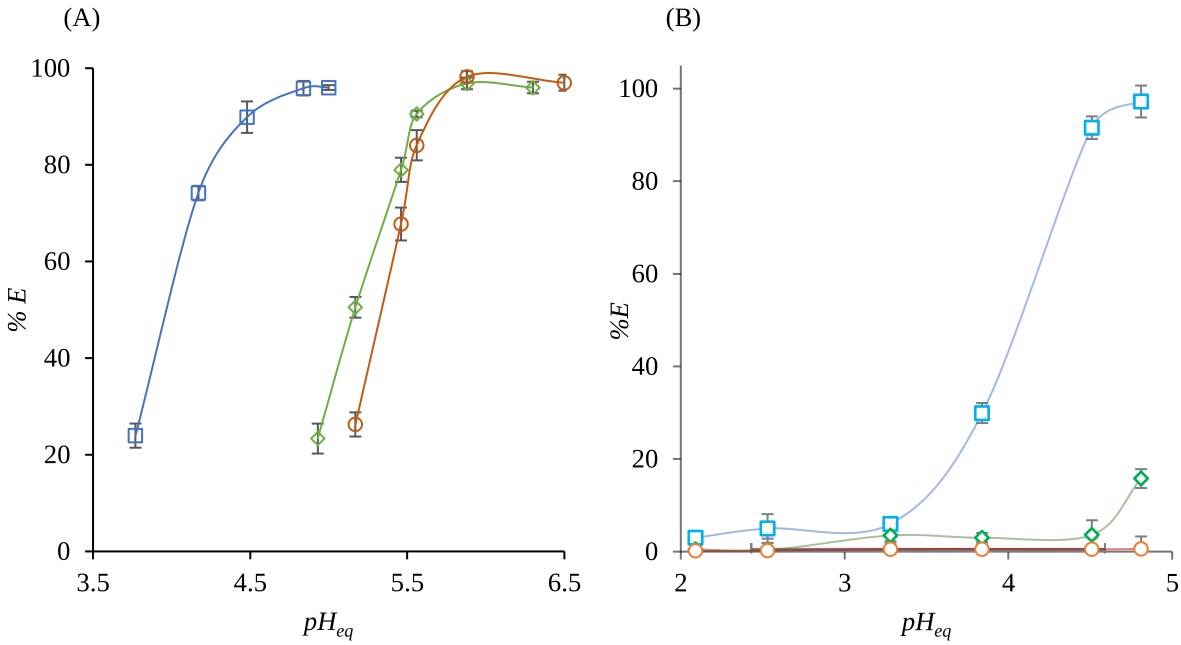

Figure 2 (A) pH_{eq}-isotherms of Cu(II) (⊟), Ni(II) (◇) and Co(II)(⊖) (experimental conditions: single element solution, (B**)** $\%E$ of Cu(II)-(⊟), Ni(II)-(◇) and Co(II)-(⊖) at various pH_{eq} (experimental conditions: multi-element solutions) (metal concentration = 100 ppm Cu(II), 100 ppm Ni(II) and 100 ppm Co(II), organic to aqueous volume ratio = 1:1, temperature = 25 °C).

The excellent selectivity of PKFAD for separating Cu(II) from other metals is evidenced by the lower pH_{50} obtained. Hence, suggested that Cu(II) has a greater ability to form more stable Cu(II)-FFA complexes compared to Ni- and Co-FFA complexes at a pH_{eq} of 4.8. This enhanced stability could be attributed to the higher charge density of Cu^{2+}, which results from its smaller ionic radius relative to Ni^{2+} and Co^{2+}. Consequently, the stronger electrostatic attraction between Cu^{2+} and the FFA (extractant) leads to the formation of more stable Cu(II)-FFA complexes at pH_{eq} of 4.8 [30]. The extraction reaction between the metal ion with FFA from PKFAD involved, two moles of H^+ being deprotonated to form a free hydroxyl, and then reacted with one mol metal ion through a cation exchange process to generate metal-FFA complexes [23]. The remaining one mol dimeric FFA attached to the metal ion to form a complex with one coordinated covalent bond (Equations 5-7) [31].

3.2 Selective recovery of Cu(II) from multi-element solution and regeneration of PKFAD

The selectivity of Cu(II) from a multi-element solution using a PKFAD system was studied. The selective extraction of Cu(II) ions over Ni(II) and Co(II) solution was run at the first stage of the extraction process at the optimum pH_{eq} of 4.8 obtained from the previous studies (Figure 2 (A) and (B)). Meanwhile, both Ni(II) and Co(II) extractions were carried out at the second stage of the extraction process at the optimum pH_{eq} of 5.9 attained from earlier studies (Figure 2 (A)). Furthermore, the Cu(II) ions were stripped from the Extracted 1 stream (Figure 1, Section 2.3), whereas the Ni(II) and Co(II) ions were stripped from the Extracted 3 stream (Figure 1, Section 2.3) for regeneration of PKFAD. Two types of stripping agents i.e., sulfuric acid or formic acid were investigated as stripping agents.

Figure 3 depicts the *%E* and *%OR* values of each element during the first and second stage extraction and stripping process. The results show a high *%E* (97%) of Cu(II) was achieved in the first stage of the extraction process while the *%E* of other elements, Ni(II) and Co(II) were less than 16%. This is in good agreement with the results obtained in Section 3.1 (Figure 2(B)). Next, the raffinate from the first stage of extraction which was rich in Ni(II) and Co(II) (Raffinate 1 stream- Figure 1, Section 2.3) was extracted in the second stage of the extraction process using a fresh PKFAD at an optimum pH_{eq} of 5.9. The result shows a high *%E* of 88% and 85% for Ni(II) and Co(II) respectively were obtained (Figure 3).

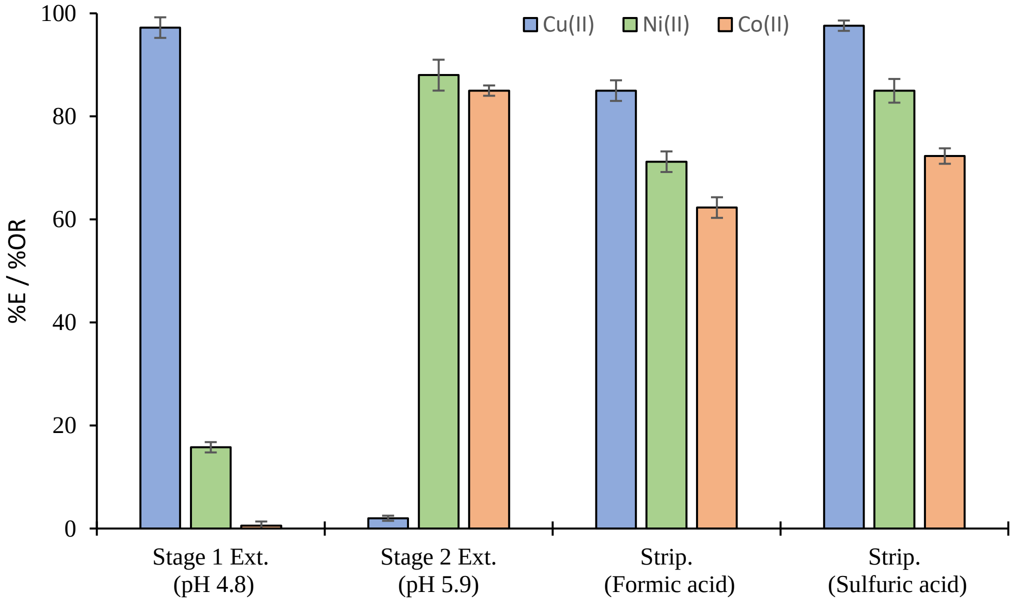

Figure 3 *%E* and *%OR* of Cu(II), Ni(II), and Co(II) from the first stage extraction (pH_{eq} 4.8), second stage extraction (pH_{eq} 5.9), and stripping process (formic and sulfuric acid.

Meanwhile, for the stripping process, the highest *%OR* (98%) for Cu(II) was obtained using sulfuric acid. Overall, a greater *%OR* was observed when employing sulfuric acid as a stripping agent for all elements, compared to formic acid. One possible explanation for this phenomenon is that formic acid, being a weak acid with a k_a value of 1.77 x 10^{-4}, exhibits partial dissociation in aqueous solution. Conversely, sulfuric acid, a strong acid with a k_a greater than 1.0, demonstrates complete dissociation in an aqueous solution, providing higher concentration of H^+ ions in the aqueous phase [26]. Furthermore, the chemical structure of sulfuric acid has a more complex structure with two acidic hydrogen per molecule (Figure 4(A)), while formic acid has one acidic hydrogen and a simpler structure (Figure 4(B)). The greater number of H^+ ions released by sulfuric acid would enhance the driving force and thus elevate the stripping process. The stripping reaction between the metal-FFA complexes ($M(RCOO)_2(RCOOH)_4$) with sulfuric acid and formic acid is illustrated in Figure 4(A) and (B), respectively. As shown in the figure, two moles of H^+ were deprotonated from one mol of sulfuric acid (Figure 4 (A)) and reacted with one mol of metal-FFA complexes, while two moles of H^+ released from two moles of formic acid (Figure 4 (B)) and bind with one mole of metal-FFA complexes.

Both sulfuric and formic acids are hydrophilic, but their partitioning is strongly influenced by polarity, ionization state, and the composition of PKFAD. Under our experimental conditions, sulfuric acid exists almost entirely in its dissociated form in the aqueous phase, making its solubility in the hydrophobic PKFAD phase negligible. Formic acid, although less ionized at low pH, still strongly favors the aqueous phase due to its high polarity and hydrogen bonding with water. Since PKFAD is primarily composed of long-chain fatty acids and esters, it forms a bulk nonpolar environment where the partitioning of these highly hydrophilic acids is thermodynamically unfavorable. Consequently, any transfer would be minimal and insufficient to affect the stripping process or compromise our results. Although both acids are expected to remain predominantly in the aqueous phase, their distribution could be experimentally confirmed, for example, by titration or ion chromatography, in future studies.

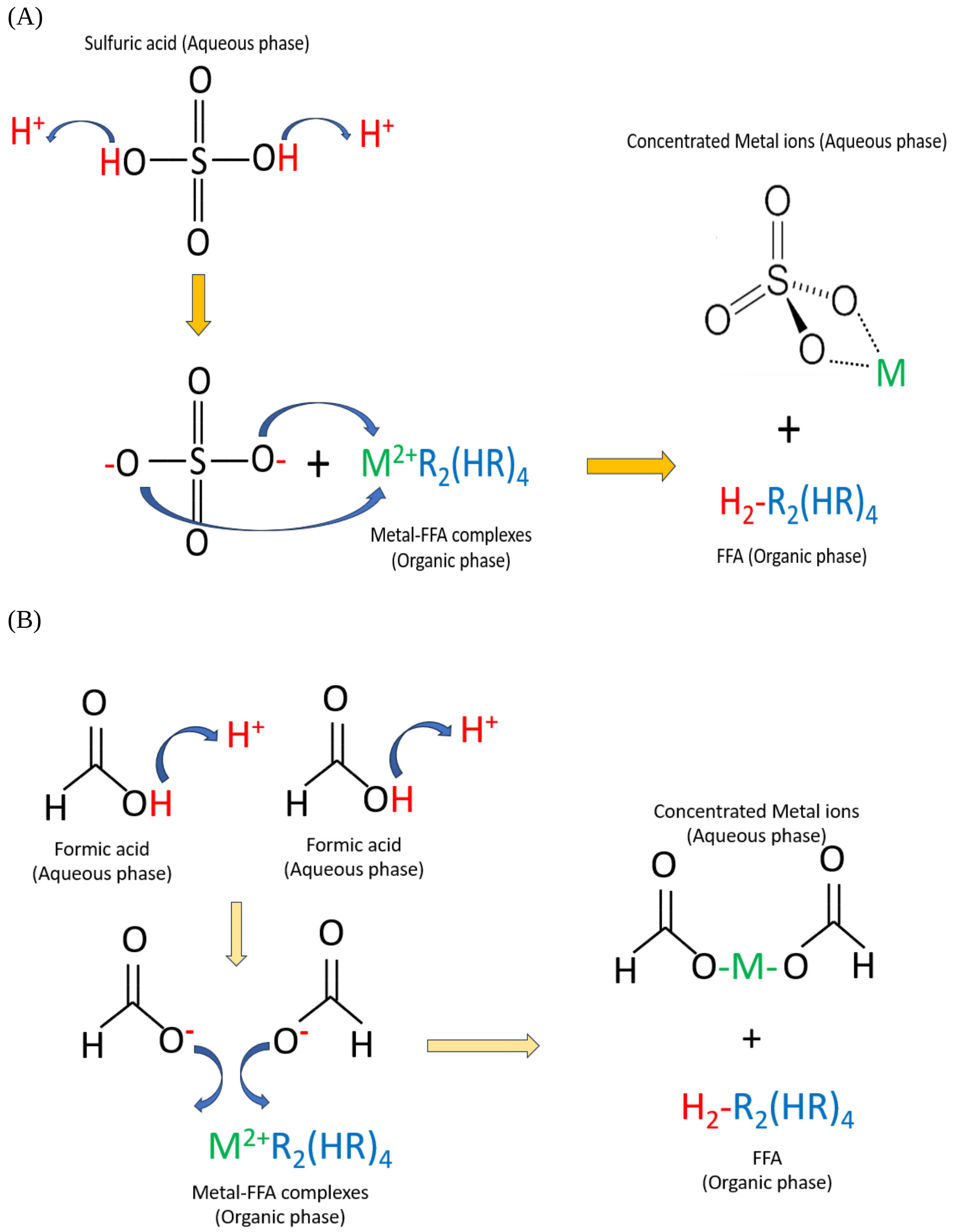

Figure 4 Stripping reaction between metal-organic complexes with (A) sulfuric acid and (B) formic acid.

A high percentage of *%OR* was achieved for all metals, ranging from 62% to 98%, demonstrating the effectiveness of PKFAD as the organic solvent for metal recovery and the potential for efficient regeneration of the PKFAD. In addition to the performance of the stripping agent i.e. sulfuric acid and formic acid, the properties of the organic solvent also impact the stripping process. The low volatility of PKFAD and the moderate operating conditions (25°C), which prevent the degradation of the organic phase, further contribute to the efficiency of the back-extraction process. Moreover, the hydrophobic nature and variation of functional groups present in PKFAD could enhance the stripping of Cu-FFA complexes from the organic phase into the aqueous phase

To further elucidate the distribution of metals concentration during the process, a mass balance calculation was performed based on the extraction and stripping efficiencies, and the distribution of Cu(II), Ni(II), and Co(II) across all process streams (Feed, Raffinate 1, Raffinate 2, Raffinate 3, Raffinate 4, Extracted 2 and Extracted 4) is summarised in Table 1. The result shows that the majority of Cu(II) (1.424 mg from an initial 1.50 mg) was transferred into the Raffinate 2, confirming the effective recovery of Cu(II) and demonstrating that only a small amount (0.035 mg) remained in the regenerated PKFAD (Extracted 2). Due to the low extraction of Ni(II) and Co(II) in Stage 1, most of their mass (1.263 mg (II) and 1.491 mg Co(II)) proceeded to Raffinate 1 and subsequently to Stage 2. In Stage 2, appreciable recovery of Ni(II) and Co(II) was obtained, with 0.944 mg Ni(II) and 0.913 mg Co(II) appearing in the strip aqueous phase (Raffinate 4). Small residual amounts of Ni(II) (0.167 mg) and Co(II) (0.355 mg) were detected in the regenerated PKFAD (Extracted 4). Overall, the results demonstrate that a two-stage PKFAD-based extraction–stripping system enables sequential recovery of Cu(II), Ni(II), and Co(II), while allowing the organic phase to be regenerated with only minimal residual metal contamination.

Table 1 Mass Balance of Cu(II), Ni(II), and Co(II) in two-stage extraction using sulfuric acid as stripping agents.

Stream (Figure 1)	Cu (mg/L)	Ni (mg/L)	Co (mg/L)
Stage 1			
Feed	1.5	1.5	1.5
Raffinate 2 (Cu(II) recovery)	1.423	-	-
Extracted 2 (Regenerated PKFAD)	0.035	0.237	0.009
Stage 2			
Raffinate 1	0.042	1.263	1.491
Raffinate 4 (Ni(II), Co(II) recovery)	-	0.944	0.913
Extracted 4 (Regenerated PKFAD)	-	0.167	0.355
Raffinate 3 (Effluent discharge)	0.042	0.152	0.223

On the other hand, the quantitative analysis of Cu(II) selectivity over Ni(II) and Co(II) can be determined by Equation 4. The values of $SF_{Cu/x} \geq 180$ achieved at an optimum pH_{eq} of 4.8, as shown in Figure 5 suggest a high level of selectivity in separating Cu(II) from multi-element solutions containing Co(II) and Ni(II). In general, the $SF_{cu/x}$ value exhibited an upward trend as the pH_{eq} increased. This finding is in line with results obtained previously in Figure 2(B) and 3. However, the $SF_{Cu/Ni}$ was found to decrease at pH_{eq} *4.8* which was attributed to increment Ni(II) extraction after pH_{eq} of 4.5 (Figure 2(B)).

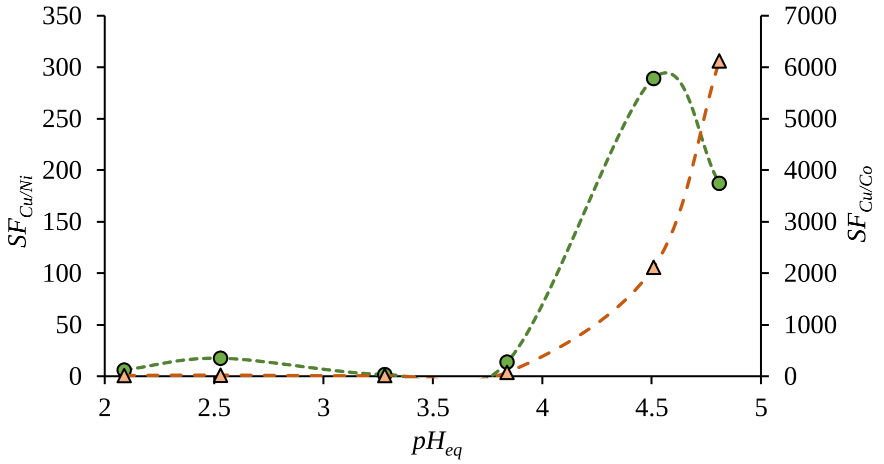

Figure 5 Selectivity factor of $SF_{Cu/Ni}$ (⊖) and $SF_{Cu/Co}$ (△) at various pH_{eq} (multi-element solution).

3.3 Determination of Cu-FFA complexes (extracted species) using FTIR analysis.

FTIR analysis was conducted on PKFAD samples before and after extraction to verify the formation of Cu(II)-FFA complexes within the PKFAD. The corresponding spectra are presented in Figure 6. The FFA component of PKFAD consists of long hydrocarbon chains with carboxylic acid groups at the end. As depicted in Figure 6 the carbon double bond (C=) and hydroxyl group (OH) stretching bands appear in the ranges of 1650-1790 cm^{-1} and 2800-3000 cm^{-1}, respectively [32]. The amplitude of the %transmittance for both the C= and OH bands was lower in PKFAD after extraction compared to before extraction. This could be attributed to the cleavage of the OH bond, releasing H^+ ions that bond with Cu(II) ions to form Cu(II)-FFA complexes (observed in PKFAD after extraction), which results in reduction of the %transmittance amplitude as shown in Figure 6.

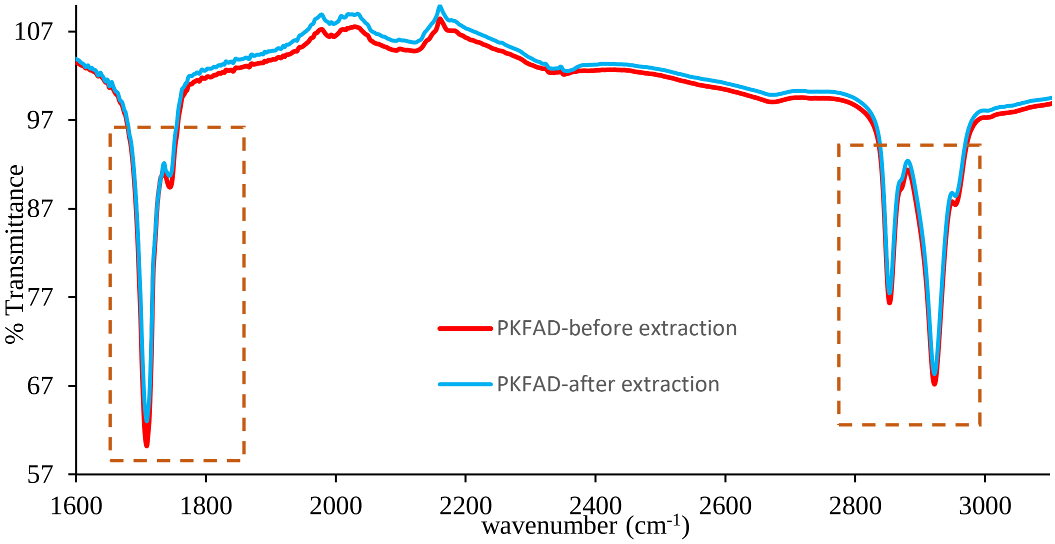

Figure 6 FTIR spectra for PKFAD before and after extraction.

4. Conclusions

The use of PKFAD as a green extractant has demonstrated high efficiency in selectively recovering Cu(II) in the presence of Ni(II) and Co(II). Optimal extraction of Cu(II) was achieved at pH_{eq} 4.8, while Ni(II) and Co(II) were extracted at pH_{eq} 5.9. PKFAD showed strong selectivity toward Cu(II) in multi-element systems, with $SF_{Cu/x}$ values exceeding 180. Stripping efficiencies of 62–98 % were achieved for all metals tested. While selective separation between Ni(II) and Co(II) needs further investigation to enable complete recovery of all metals present, the PKFAD-based method offers excellent selectivity and promotes sustainability through its regenerable organic phase. Future work will evaluate its long-term recyclability to further confirm process robustness.

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