

ENDOTHERMIC SOLVENT EXTRACTION OF COPPER (II) WITH FURFURYL THIOALCOHOL FROM SULFATE MEDIUM

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Abstract

A simple solvent extraction method was developed to extract copper (II) from sulfate solution. The extraction of copper (II) with furfuryl thioalcohol was investigated. The effect of variables such as aqueous phase pH, furfuryl thioalcohol concentration, temperature, stripping reagents, and diluents was investigated. The extraction data revealed that using 15% (v/v) furfuryl thioalcohol with aqueous solution containing 0.5 mol L⁻¹ Na₂SO₄, equilibrium pH 5.5, and phase ratio organic phase: aqueous phase (O:A) of 1:1 resulted in 98.20 percent extraction of copper (II) without nickel coextraction (II). Extraction isotherm results show that the extraction procedure is endothermic, with $\Delta H = 28.542 \text{ kJ mol}^{-1}$ and $\Delta S = 41.740 \text{ J K}^{-1} \text{ mol}^{-1}$. Using 2.0 M H₂SO₄, copper loaded in organic phase was stripped at a rate greater than 99 percent.

Keywords: solvent extraction, copper (II), furfuryl thioalcohol, endothermic.

1. Introduction

As significant metal, copper is extensively applied in industrial process such as electrical conductor, telecommunication, electronic circuitry [1-5]. Copper alloys are widely used in marine equipment due to their naturally occurring resistance to sea water corrosion and intrinsic befouling properties [6]. Rising requirement for copper metal is leading to rapid reduction of high grade resources. Alternative sources such as electronic waste and copper converter slag could be used to meet future demand.

Hydrometallurgical techniques such as wet chemical method [7], emulsion liquid membrane technology [8, 9], solvent extraction [10-17] etc. have been used

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significantly for the recovery of copper from various leach liquors. Among these, solvent extraction is selectively applied for the recovery of copper. Organophosphorus and organonitrogen extractants are widely used for copper extraction process applications [18-24]. *Guerdouh and Barket* [19] studied the influence of solvent on the extraction of $1.57 \times 10^{-3} \text{ mol L}^{-1}$ copper (II) from 1 mol L^{-1} NaNO_3 solution at pH 4.5 using salicylideneaniline and observed that 85.75 % extraction by using cyclohexane as diluent. *Luo et al.* [20] has been used the synergistic mixture of dinonylnaphthalene sulphonic acid (HDNNS) and 2-ethylhexyl-4-pyridinecarboxylate ester (4-PC) for extraction of copper or nickel from 0.5 mol L^{-1} Na_2SO_4 solution at pH 1.93 and suggested that as concentration of HDNNS and 4-PC increases, interfacial tension changes which leads to alteration the extraction efficiency. *Feizollahi et al.* [21] has been done comparative study between Chemorex CP 150 and mixture of D2EHPA and Cyanex 272 diluted in kerosene for the extraction of Cu (II) from sulfate liquor in presence of Fe. The quantitative extraction was achieved at pH 2.5, A:O phase ratio 1:4 within 20 minutes equilibrium time and extraction isotherm shows that $\Delta H = 7.62 \text{ kJ mol}^{-1}$, $\Delta G = 18.33 \text{ kJ mol}^{-1}$, $\Delta S = -38.58 \text{ J mol}^{-1} \text{ K}^{-1}$. *Azizi et al.* [22] findings demonstrated that 1.5 mol L^{-1} Chemorex CP-150 has greater ability and selectivity than D2EHPA for copper (II) extraction in presence of zinc(II). Extraction efficiency of copper (II) was 97.88% at pH 2.5, A:O phase ratio 1:1, equilibrium time 10 minutes and extraction isotherm suggests the extraction reaction is endothermic with the values as $\Delta H = 65.29 \text{ kJ mol}^{-1}$, $\Delta G = 9.83 \text{ kJ mol}^{-1}$, $\Delta S = 186.14 \text{ J mol}^{-1} \text{ K}^{-1}$. Recently, *Sun et al.* [23] investigated the extraction of copper (II) and silver (I) from nitrate leachate containing Cu (II), Ag (I), Ni (II), Mg (II) and Al (III) using 5,8-diethyl-7-hydroxydodecane-6-oxime (LIX63). 2.0 mol L^{-1} LIX63 successively extracted 95.52% Cu (II) over other metal ions at low nitric acid concentration, A:O phase ratio is 1:2 and 99.99 % Cu (II) was back extracted from the loaded LIX63 by using 4 mol L^{-1} HNO_3 as stripping reagent. *Wang et al.* [24] has discovered the solvent extraction equilibrium model to separate the copper (II) in presence of nickel (II) from the loaded 2-hydroxy-5-nonylacetophenoneoxime (LIX84-I) dissolved in nonpolar solvent formed by the extraction from alkaline ammonical solution. Some researchers have been added salts of organic acids in aqueous phase to form stable ion pair of metals with extractant during extraction process [25-27]. *Ren et al.* [27] investigated that single stage extraction of Cu (II) is $> 99.5 \%$ when 0.18 mol L^{-1} acetate ions were added in aqueous solution and pH was 4.44 and in the stripping process, the ability to back extract Cu(II) from the loaded D2EHPA is $6.0 \text{ mol L}^{-1} \text{ HCl} > 3.0 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4 > 2.0 \text{ mol L}^{-1} \text{ H}_3\text{PO}_4$. Some researchers have been used organosulfur compounds as extractant for effective and selective extraction of metals [28-33]. Organosulfur extractant have higher metal binding ability because presence of lone pair in high energy state and empty 3d orbitals which consequences especially in the field of metal ion complexation [34, 35]. The complexation capability of sulfur extractant with a wide range of Cu (II) selectively in presence of Zn (II) and Ni (II) ions using liquid-liquid extraction method have been reported [32, 36].

Furfuryl thioalcohol is easily obtained from agricultural byproducts like sugarcane bagasse and corn cobs, which do not, required specially designed organic synthesis route or catalysts. By taking this in mind, the present investigation efforts to study the selective separation and extraction of copper (II) by furfuryl thioalcohol from the sulfate solution. The process parameters studied include equilibrium pH, furfuryl

thioalcohol concentration, different aqueous phase medium, temperature, kinds of stripping reagents and effect of different diluents have been studied in detail to obtain the ideal conditions for maximum extraction of copper (II).

2. Experimental

2.1 Chemical reagents and apparatus

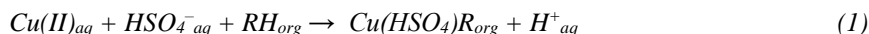
Stock solutions of copper (II) 1.000 g L⁻¹ was prepared dissolving the sulfate salts in doubly distilled water. The pH of aqueous phase was adjusted by adding of 0.1 mol L⁻¹ HClO₄ solution, not by the solution of H₂SO₄ because actual concentration of sulfate ions has been studied to check extraction efficiency of copper (II). The organic phase was prepared by dissolving furfuryl thioalcohol without purification in distilled kerosene. All the chemical reagents used were Analytical Reagent grade and purchased from commercial suppliers Alfa Aesar (Thermo Fisher Scientific Hyderabad, India) and Spectrochem (Spectrochem Pvt. Ltd. Mumbai, India). Analysis of copper and nickel was performed by A Shimadzu UV-Visible spectrophotometer (UV-1800) with 1 cm² quartz cell and pH optimization was carried out by Elico digital pH meter Model LI-120 (±0.02).

2.2 Experimental procedure

The extraction of copper (II) from aqueous phase containing sulfate ions was carried out with precise amount of furfuryl thioalcohol dissolved in kerosene at (25 ± 0.1) °C and an organic: aqueous (O:A) phase ratio of 1:1. Similar volumes of organic and aqueous solutions were contacted in separating funnel for 10 minutes. After the phase disengagement, both phases were separated and loaded organic phase samples were stripped with desired concentration of H₂SO₄ solution and finally the raffinate and strip solutions were used to analyze the extraction efficiency of copper (II) [27].

2.3 Theory of solvent extraction

The presence of copper in the aqueous solution as cation, Cu (II). The extraction procedure of copper with the extracting reagent like furfuryl thioalcohol (RH) can be illustrated in Eq. (1):



The equilibrium constant K_{ex} of the extraction reaction can be expressed as:

$$K_{ex} = [Cu(HSO_4)R]_{org} [H^+]_{aq} / [RH]_{org} [Cu(II)]_{aq} [HSO_4^-]_{aq} \quad (2)$$

or

$$K_{ex} = D [H^+]_{aq} / [HSO_4^-]_{aq} [RH]_{org} \quad (3)$$

Where, D is the distribution coefficient, on taking the logarithm of Eq. (3) and rearranging, equation can be obtained as:

$$\log D = \log K_{ex} + \log [HSO_4^-]_{aq} + \log [RH]_{org} + pH \quad (4)$$

The extractability, % E of copper ion was calculated using the Equation:

$$\% E = \frac{[M]_{org}}{[M]_{aq.init}} \times 100 \quad (5)$$

$$[M]_{org} = [M]_{aq.in} - [M]_{aq} \quad (6)$$

Where, $[M]_{org}$ is the concentration copper ions in the organic phase, $[M]_{aq.in}$ and $[M]_{aq}$ are the initial and final concentrations of copper ions, respectively, in the aqueous solution.

3. Results and discussion

3.1 Effect of equilibrium pH on copper (II) extraction:

The extraction of copper (II) ions from the aqueous solution is highly dependent on the solution pH. Therefore, the extraction efficiency of 100 mg L⁻¹ copper (II) by extracting reagent 15% (v/v) furfuryl thioalcohol was determined at different pH level which were adjusted by using perchloric acid in the range of 1.0 to 6.5 with 10 minutes of equilibrium time. The results are presented in (Fig. 1). The quantitative extraction values were observed between pH 4.5 to 6, significantly lower values were observed in low pH media. The possible reason for this may be H⁺ ions are reduced by the anionic complex formation species with metals in aqueous phase. Anionic species HSO₄⁻ is more favorable for copper (II) extraction with furfuryl thioalcohol [37, 38]. The extraction efficiency increases from pH 3 to 6 because the higher availability of the electrons pair of sulfur towards copper than pH < 2.5, which is towards the excess of H⁺ [39].

It was concluded that maximum 98.20 % of copper (II) can be extracted easily using furfuryl thioalcohol at pH 5.5. The linear plot between log D versus equilibrium pH is presented in (Fig. 2). It shows straight line (R²= 0.9990) with slope of 1.04 indicate that the one mol of H⁺ ion needed to one mol of copper (II) extraction. The resulted slope value was obtained to positive which is due to the increasing extraction tendency with increasing equilibrium pH of the solution. The slope analysis values supports the proposed extraction mechanism and can be explained as in Eq. (1). Thus, the extracted species for copper (II) with furfuryl thioalcohol diluted in kerosene is Cu(HSO₄)R.

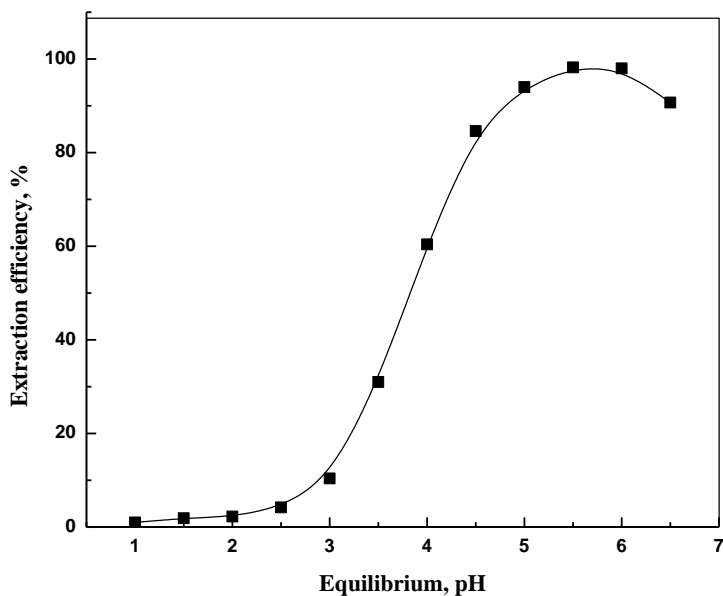


Fig. 1. Effect of pH on the extraction of copper, Conditions: 15% (v/v) furfuryl thioalcohol in kerosene, $O/A=1$, $Na_2SO_4 = 0.5 \text{ mol L}^{-1}$, equilibrium time 10 minutes.

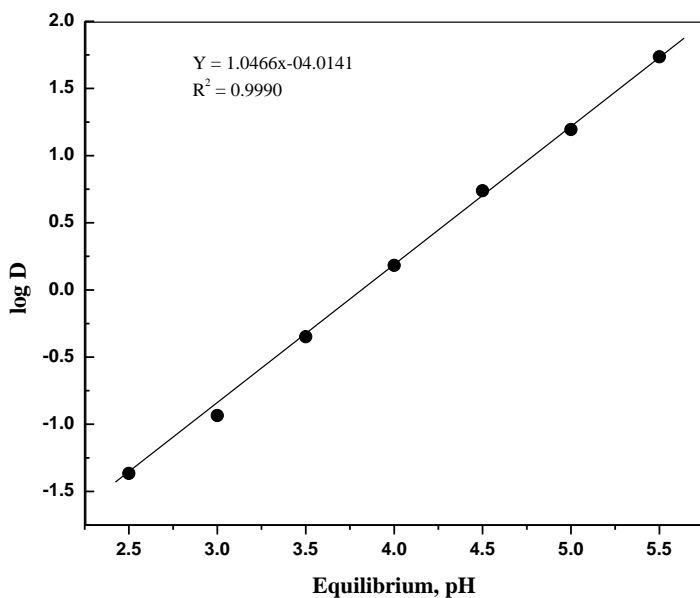


Fig. 2. Plot of log D vs equilibrium pH, Conditions: 15% (v/v) furfuryl thioalcohol in kerosene, $O/A=1$, $Na_2SO_4 = 0.5 \text{ mol L}^{-1}$, equilibrium time 10 minutes.

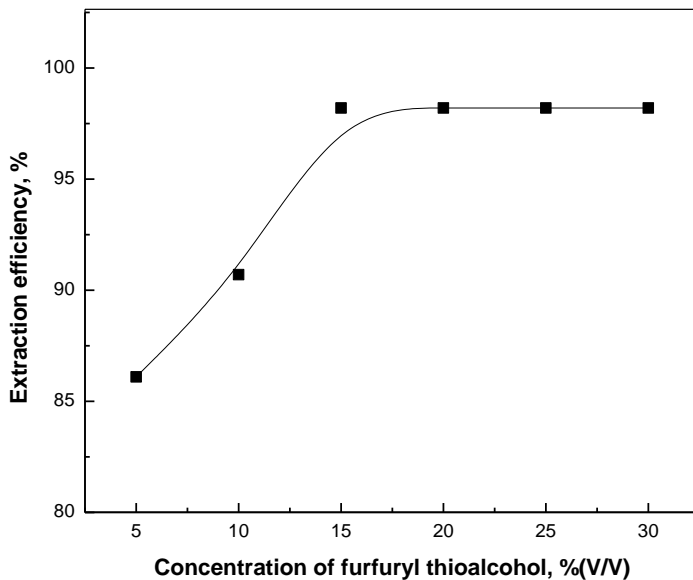


Fig. 3. Effect of furfuryl thioalcohol concentration on the extraction of copper, Conditions: pH 5.5, O/A = 1, $\text{Na}_2\text{SO}_4 = 0.5 \text{ mol L}^{-1}$, equilibrium time = 10 minutes.

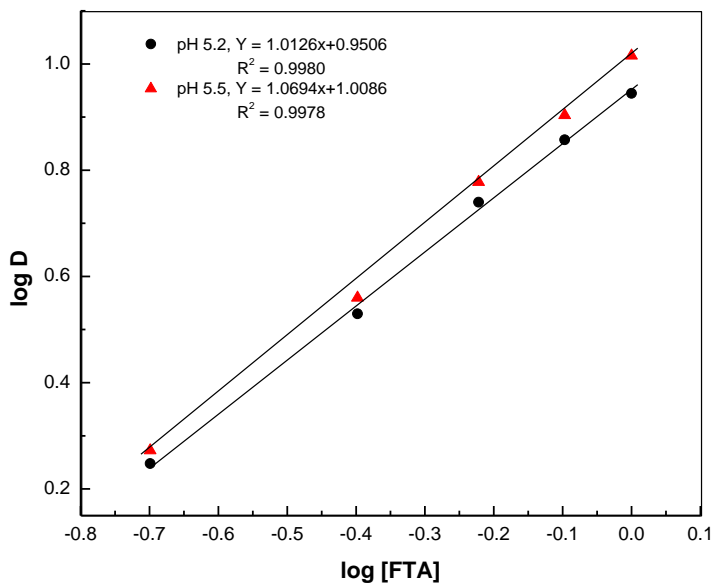


Fig. 4. Plot of log D vs log [FTA], (FTA= furfuryl thioalcohol).

3.2 Effect of furfuryl thioalcohol concentration on copper (II) extraction

The effect of furfuryl thioalcohol concentration on extraction of copper (II) was investigated by equilibrating aqueous solution containing 100 mg L⁻¹ copper (II), 0.5 mol L⁻¹ Na₂SO₄ at pH 5.5, phase ratio O/A = 1 [13] and shaking time is 10 minutes at room temperature. The results are presented in (Fig. 3), it can be seen clearly that the extraction efficiency of copper (II) has increases from 86.00 % to 98.20% by increasing furfuryl thioalcohol concentration from 5% to 15% (v/v). The extraction of copper (II) was almost kept constant by further increasing furfuryl thioalcohol concentration from 20% to 30% (v/v).

The corresponding results of log D versus log [FTA] (FTA = furfuryl thioalcohol) were plotted in (Fig. 4), the linear plot of log D versus log [FTA] shows straight line ($R^2 = 0.9980$ and $R^2 = 0.9978$) with slope of 1.01 and 1.06 at pH 5.2 and pH 5.5 respectively. These results support the proposed extraction mechanism for as given in Eq. (1), which is in good arrangement with the predicated value of 1.0, confirming the association of one mol of extractant with each of copper ion in the extracted species. The characters of the furfuryl thioalcohol and copper interactions can be specified by the softness of copper, anisotropic distribution of electron density around the sulfur atom and electrostatic potential around the sulfur has both positive and negative regions [39-41].

3.3 Effect of different media on copper (II) extraction

The liquid-liquid extraction technique depends mainly on the nature of anions present in aqueous phase solution. They have a major influence on the selection of the metal-extracting reagent used in downstream processing, which can be beneficial to form ion pair complexes of metal and extractant [38]. Keeping this in mind, the extraction of 100 mg L⁻¹ copper (II) was carried out with 15% (v/v) furfuryl thioalcohol in presence of different media such as Na₂SO₄, NaCl and NaNO₃ over the concentration range 0.1 mol L⁻¹ to 1 mol L⁻¹. The results are presented in (Table 1), showed that distribution coefficient of copper (II) increased with increase in sulfate concentration but the increase in chloride and nitrate ions concentration have negative effect. In presence of nitrate, the distribution coefficient is more than chloride medium, but decreased constantly with further increase of NaNO₃ concentration. However, the decrease is more significant with NaCl than with NaNO₃. The decrease in extraction may be due to copper (II) can form stable inner-sphere complexes of chlorides and nitrates and these complexes are not suitable to form extractable ion-pair species with furfuryl thioalcohol [42]. Therefore, 0.5 mol L⁻¹ sulfate medium is the best for the extraction of copper (II) using furfuryl thioalcohol.

Table 1. Effect of different media on extraction of copper (II).

| Concentrations of media (mol L ⁻¹) | Na ₂ SO ₄ | | NaNO ₃ | | NaCl | |
|---|---------------------------------|---------|-------------------|--------|-------|--------|
| | % E | D | % E | D | % E | D |
| 0.1 | 66.20 | 1.9585 | 65.10 | 1.8653 | 64.80 | 1.8409 |
| 0.2 | 72.66 | 2.6576 | 67.88 | 2.1133 | 62.60 | 1.6737 |
| 0.3 | 86.90 | 6.6335 | 72.44 | 2.6284 | 60.48 | 1.5303 |
| 0.4 | 90.80 | 9.8695 | 78.60 | 3.6728 | 57.10 | 1.3310 |
| 0.5 | 98.2 | 54.5555 | 77.10 | 3.3668 | 56.00 | 1.2727 |
| 0.6 | 98.00 | 49.00 | 74.90 | 2.9840 | 52.30 | 1.0964 |
| 0.7 | 98.00 | 49.00 | 70.50 | 2.3898 | 46.80 | 0.8796 |
| 0.8 | 97.40 | 37.4615 | 66.70 | 2.0030 | 41.10 | 0.6977 |
| 0.9 | 95.8 | 22.8095 | 58.25 | 1.3949 | 40.00 | 0.6666 |
| 1.0 | 94.4 | 16.8571 | 55.30 | 1.2371 | 38.90 | 0.6366 |

3.4 Effect of diluents on copper (II) extraction

The choice of solvent is significant aspect for metal extraction operation because of both physical and chemical interactions that exist between the extracting reagent and diluent. A diluent lowers the viscosity of the extractants, but, sometimes the character of diluent alters the extraction process. To examine this, the extraction of 100 mg L⁻¹ copper (II) with 15% (v/v) furfuryl thioalcohol was carried out using different diluents such as kerosene, xylene, toluene, benzene carbon tetrachloride and chloroform. The other experimental parameters were fixed at equilibrium pH 5.5, 0.5 mol L⁻¹ Na₂SO₄, O/A phase ratio 1 and the equilibrium time was 10 minutes at room temperature. The obtained results are presented in (Table 2). Carbon tetrachloride and kerosene were shown clear phase separation with good extraction efficiency 96.25% and 98.20%, respectively. It was noticed that the dielectric constant of the used diluents strongly affected copper extraction efficiency. The higher dielectric constant value of the diluent; the lower the percent extraction of copper (II). The possible reason for this is that with an increase in the dielectric constant of the diluent, the interaction between the diluent and the extractant is increased, thus decreasing availability of extractant for extraction of copper (II). The same trend was observed by *Devi and Nayak* [10] and *El-Nadi* [43] while studying the effect of diluent on extraction of copper (II) and rare earth metals.

Table 2. Effect of diluents on the extraction of copper (II).

| Diluents | Dielectric constant | Density (g/ cm ³) | % E | D |
|----------------------|---------------------|-------------------------------|-------|---------|
| Chloroform | 4.81 | 1.489 | 64.40 | 1.8089 |
| Xylene | 2.57 | 0.879 | 73.90 | 2.8314 |
| Toluene | 2.38 | 0.867 | 88.00 | 7.3330 |
| Benzene | 2.27 | 0.876 | 92.86 | 13.0056 |
| Carbon tetrachloride | 2.24 | 1.590 | 96.25 | 25.6666 |
| Kerosene | 1.8 | 0.800 | 98.20 | 54.5555 |

3.5 Effect of temperature on copper (II) extraction

Temperature is an ultimate limitation at the final extraction processing stage the reason lies in the often similar thermodynamic behavior of alloying elements that make their separation either very energy intensive or essentially impossible [44, 45]. The extraction efficiency of copper (II) by 15% furfuryl thioalcohol studied at different temperatures (298 to 328 K), the other experimental conditions were fixed at equilibrium pH 5.5, 0.5 mol L⁻¹ Na₂SO₄, O/A phase ratio 1 and equilibrium time 10 minutes. The results showed that, the extraction efficiency of copper increases as the temperature increased. The corresponding results of log D versus 1000/T, K⁻¹ are plotted in (Fig. 5) and, ΔH and ΔS were calculated and corresponding values of free energy change (ΔG) were obtained by using the Equation, (7)

$$\Delta G = -2.303 R T \log D \quad (7)$$

Where: D is the distribution coefficient, ΔH the enthalpy change, ΔS the entropy change for the extraction, R is the universal gas constant (8.314 J mol⁻¹ K⁻¹). From the plot, ΔH and ΔS were calculated and found to be 28.542 kJ mol⁻¹ and 41.740 J K⁻¹ mol⁻¹ respectively. The positive value of ΔH indicates that the extraction of copper (II) by furfuryl thioalcohol in the investigated system is an endothermic process, with randomness of system shown by the high positive value of the entropy changes (ΔS). It can be seen from (Fig. 6) that the distribution coefficient increased from 54.55 to 165.66 with increasing of temperature from 298 K to 328 K. On the other hand, the observed increase in the negative values of ΔG with elevated temperature suggests that the extraction reaction became favorable at elevated temperatures.

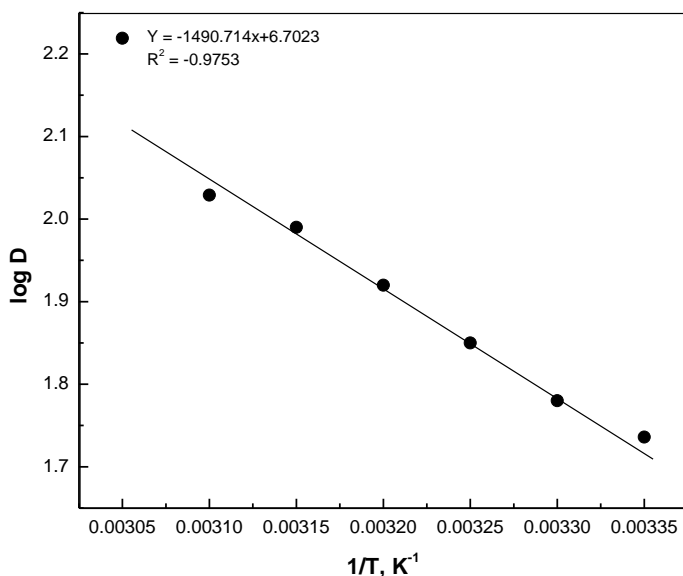


Fig. 5. Plot of log D vs 1/T for copper extraction, Conditions: 15% (v/v) furfuryl thioalcohol in kerosene, pH= 5.5, Na₂SO₄ = 0.5 mol L⁻¹, O/A = 1, equilibrium time =10 minutes.

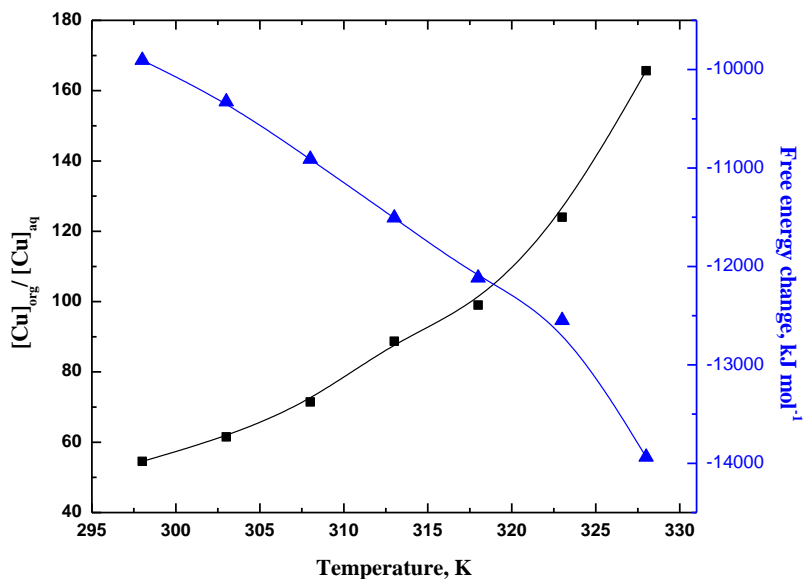


Fig. 6. Effect of temperature on free energy change (ΔG) and distribution coefficient (D).

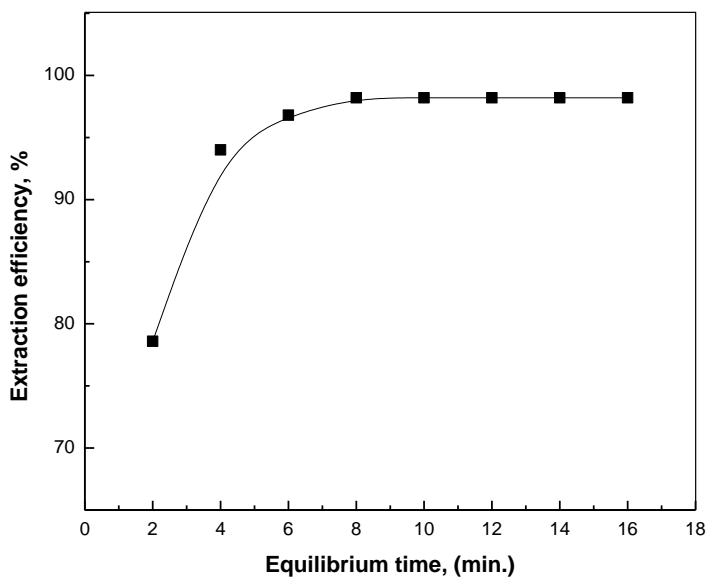


Fig. 7. Effect of equilibrium time on the extraction of copper. Conditions: pH 5.5, $O/A = 1$, $Na_2SO_4 = 0.5\ mol\ L^{-1}$, 15% (v/v) furfuryl thioalcohol in kerosene.

3.6 Effect of equilibrium time on copper (II) extraction

To study the effect of equilibrium time on 100 mg L⁻¹ copper (II) extraction using 15 % furfuryl thioalcohol, a series of experiments were performed under the conditions of pH 5.5, 0.5 mol L⁻¹ Na₂SO₄, O/A phase ratio 1 and equilibrium time varied from 5 to 30 minutes. It was observed that, an equilibrium time of 10 minutes would be sufficient to achieve quantitative extraction of copper (II), increasing the equilibrium time to 30 minutes had no effect on the extraction efficiency, (Fig. 7).

3.7 Stripping study of copper

Stripping of copper loaded organic phase was studied with different reagents such as H₂SO₄, HCl and HNO₃ with varied concentration at room temperature under controlled conditions, in which copper (II) concentration in organic phase was fixed as 98.20 mg L⁻¹, phase ratio A/O was fixed at 1 and stripping equilibrium time were 10 minutes. The results of stripping efficiency of above reagents are shown in (Fig. 8). From which, it can be seen that the stripping efficiency of copper was more effective with using 2 M H₂SO₄ and stripping reach > 99%. H₂SO₄ chosen because the presence of sulfate shows the precipitation rate of copper and results in larger precipitated particles, which is in advantage in filtering and drying the precipitate, beside H₂SO₄ is readily available and more economic.

3.8 Extraction of copper (II) in presence of nickel (II)

The leach liquor of cupronickel alloy containing 0.1 g L⁻¹ copper and 0.01 g L⁻¹ nickel was used to investigate the extraction behavior of copper (II). To study the extraction efficiency of copper (II) in presence of nickel (II), experiments were performed by the optimized experimental conditions except pH. The leached liquor by adding 0.5 mol L⁻¹ Na₂SO₄ was equilibrated with 15% (v/v) furfuryl thioalcohol, O/A phase ratio 1 and equilibrium time 10 minutes with varying pH. Results obtained are presented in (Fig. 9). Extraction efficiency of copper (II) increased from 55.60% to 98.0 % with increase in equilibrium from pH 4 to 6. On other hand, the extraction of nickel (II) decreased from 64.40% to 1.8% with increase in equilibrium pH from 1 to 4. Analysis of nickel (II) was done by glyoxime method. These results were demonstrated that copper (II) can be easily separated from nickel (II). Therefore, it can be concluded that, quantitative extraction of copper from the copper/ nickel leach liquor without co-extraction of nickel can be carried out at by proposed method.

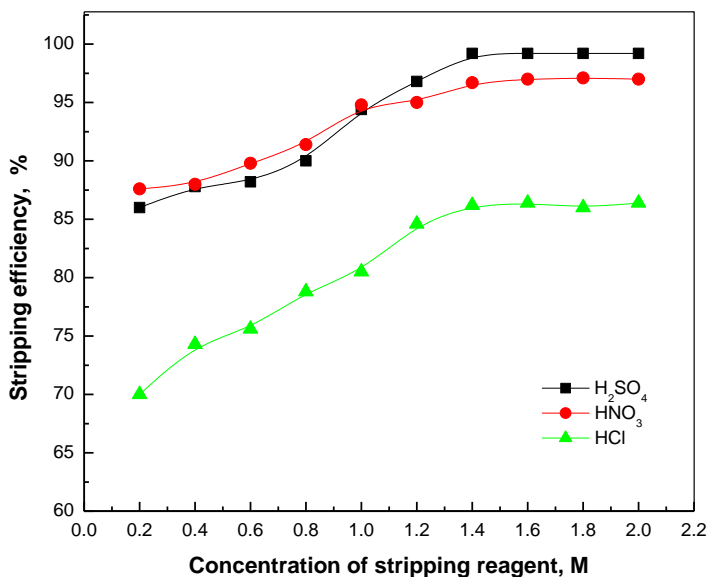


Fig. 8. Effect of reagent concentration on stripping of copper.

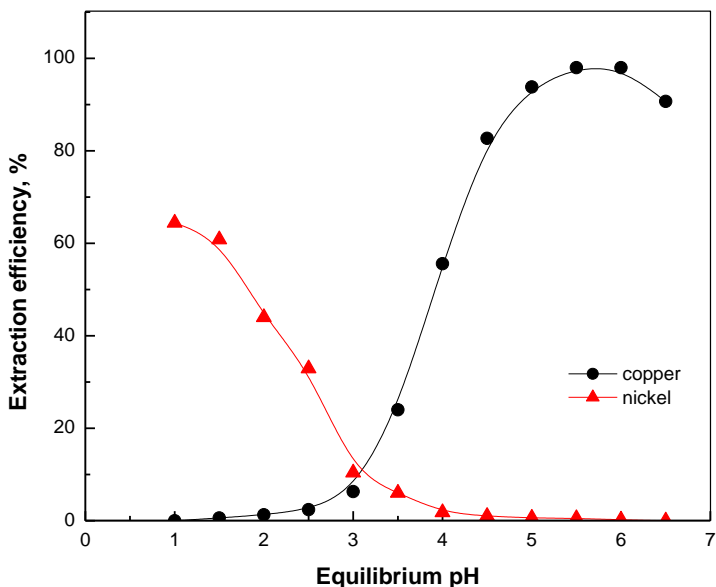


Fig. 9. Effect of equilibrium pH on extraction of copper (II) and nickel (II), Conditions: $O/A = 1$, $Na_2SO_4 = 0.5 \text{ mol L}^{-1}$, 15% (v/v) furfuryl thioalcohol in kerosene, equilibrium time 10 minutes.

Conclusions

Solvent extraction of copper (II) from sulfate solution with 15 % furfuryl thioalcohol diluted in kerosene exhibited effective performance. The extraction of copper (II) increased with increase in equilibrium pH and furfuryl thioalcohol concentration. At equilibrium pH 5.5 and using 15% (v/v) furfuryl thioalcohol the extraction efficiency of 98.20% could be achieved in single stage at phase ratio 1 without co-extraction of nickel (II). The obtained thermodynamic data for the extraction of copper (II) showed that extraction reaction is endothermic with enthalpy change 28.542 kJ mol⁻¹. Copper (II) loaded in organic phase could be stripped > 99 % by 2 M H₂SO₄ solution. The proposed method showed a remarkable high affinity and selectivity towards copper (II) in presence of nickel (II) and expected to be the new benchmark for the separation of copper.

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