Solvent extraction of copper from an industrial sulfate liquor using Chemorex CP-150

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Abstract

The extraction behavior of Cu(II) ions from a real sulfate liquor obtained from the heap leaching stage of a copper oxide ore was investigated using a chelating reagent, Chemorex CP-150 in kerosene. A comparative study was also carried out on the extraction capability of Cu(II) ions using other solvents including D2EHPA and Cyanex 272. Chemorex CP-150 demonstrated an effective and selective extraction performance of copper with the amount of extracted Fe less than 15%. Also the results obtained indicated that more than 66.4% and 96.99% of Cu were transferred to the organic phase in a single extraction stage using 15% (v/v) Chemorex CP-150 at the A:O phase ratios of 1:1 and 1:4, respectively. In addition, the McCabe-Thiele diagram exhibited that two extraction stages were required to achieve the maximum amount of Cu at a 1:1 phase ratio under the optimal conditions (25 °C, pH 2.5, and 20 min contact time). Also, thermodynamic data proved that the extraction process was slightly endothermic (ΔH = 7.62 kJ/mol), indicating the relatively smaller heat effects on the formation of a single complex species (CuR_2). Stripping of copper from the loaded organic phase was also conducted, and it was found that ~99.38% copper could be recovered using 165 g/L H_2SO_4 at a 2:1 A:O phase ratio after 5 minutes stripping.

Keywords: *Copper Extraction, Pregnant Leach Solution, Solvent Extraction, Stripping, Chemorex CP-150.*

1. Introduction

Due to the technological important applications of copper in different industries such as use in electrical materials and construction, power generation, telecommunications, transportation, petroleum refining, brass manufacture, electroplating industries, and industrial machinery parts [1-3], the world demand and production of this metal has drastically increased and its quality has become a significant criterion for proper marketing. Consequently, the production of high purity copper and development of the new technologies have attracted a lot of attention. It is known that about 80% of copper production from ores is obtained by flotation, smelting, and refining. The other 20% is obtained by hydrometallurgical techniques (leaching followed by the solvent extraction–electrowinning, SX-EW, process) [4].

It has been proved that solvent extraction (SX) is one of the most effective, simple, intensive, and applicable methods used for extraction of copper from a pregnant leach solution in hydrometallurgical industry, and it has a great influence on the electro-winning (EW) efficiency [5-11]. Nowadays, more than 20% of the world's total copper production is through SX as a desirable process for metal winning from the viewpoints of natural resources and energy conservation [12, 13].

Thus considering the industrial and economic importance of copper, the selection of extractants with high efficiency is an important issue in the separation and recovery of copper. The choice of a suitable extractant depends upon its availability, physical performance, overall complexing ability, and chemical properties [14]. A great deal of research works have been published based on the use of various organic compounds as extractants for SX of copper; a number of the most important research works published in the recent years are shown in Table 1.

Table 1. A number of the most important chemical reagent used as extractant in solvent extraction system of copper.

References	Extractant	Leach liquor	Results
Alguacil and Alonso [15]	LIX 54 in Iberfluid	Ammonium sulfate medium	Copper can be extracted only at pH above 3, and the highest extraction percentage is obtained in the pH range of 7–9
Alguacil et al. [16]	Acorga M5640 in Iberfluid	Nitrate/nitric acid aqueous solutions	The maximum extraction percentage of copper obtained at pH 2 using 0.5% (v/v) Acorga M5640 in Iberfluid.
Z. Lazarova and M. Lazarova [17]	LIX (LIX 984N-I, LIX 860N, LIX 84-I and LIX 65N) in undecane	Aqueous nitrate solutions	The extraction capacity was in the order: LIX 65N < LIX 84N < LIX 984N < LIX 860N-I.
El-Hefny and Daoud [18]	Cyanex 302 in kerosene	Different liquor including sulfate, chloride, and nitrate media	Cyanex 302 was a potential extractant for the extraction of copper from aqueous solutions. The endothermic nature of the extraction process for the three studied systems was in the order chloride > nitrate > sulfate medium.
Ren et al. [19]	D2EHPA in Kerosene	Acetate buffer media	Results indicated that the acetate ions could greatly improve the extraction of copper. When the initial pH value was 4.44 and the acetate ion concentration was 0.18 mol/L, the single stage extraction efficiency was >99.5%.
Reddy et al. [20]	LIX 84 and LIX 973N in kerosene	Sulfate leach liquors of synthetic Cu–Ni–Co–Fe matte	Comparison of the extraction behavior of extractants for copper at 40 vol% concentrations showed 10% more extraction with LIX 973N. Also the results indicated 3 extraction stages with LIX 84 and 2 extraction stages with LIX 973N to achieve above 95–99% copper extraction.
Panigrahi et al. [21]	LIX84-I and LIX622N in kerosene	Mn nodule bulk sulfide leach liquor	The quantitative extraction of copper with LIX 84-I was obtained in 4 stages at an A/O ratio of 3:4 but with LIX 622N, it was obtained in 3 stages at a 1:1 phase ratio.
Fouad [22]	Cyanex 301, LIX® 984N and their mixture	Sulfate leach solution	Mixture of Cyanex 301 and LIX® 984N demonstrated evident synergistic effects to extract copper. The maximal synergistic enhancement was achieved at a ratio of Cyanex 301 to LIX® 984N of 1 to 1.
Agarwal at al. [23]	Acorga M5640 and ShellSol D70 (aliphatic diluent)	Zinc ferric sulfate leach solution	It was found that pH 1.35 was the most adequate to perform the separation of copper from leach solution.
Mishra and Devi [24]	Cyanex 921 in kerosene	Chloride leach solution	Extraction of Cu(II) is quantitative using 0.5 mol/L Cyanex 921 and 5 mol/L HCl. Also around 99.7% copper was recovered from the loaded organic phase using 0.2 M H_2SO_4 or 0.5 M HCl.
Staszak et al. [25]	Cyanex 272 and its sodium salt in kerosene	Sulphate leach solution	Solvent extraction of Cu(II) with Na-Cyanex 272 was more efficient than its acidic form.
Panda et al. [26]	LIX 984N-C	Bacterial leach liquor of Low grade Chalcopyrite Test Heap	The extraction of copper was quantitative in 2 stages using 1.5% (v/v) LIX 984N-C at an A/O ratio of 1:2 and pH_e 1.85.
Devi and Mishra [27]	Cyanex 923 in kerosene	Chloride leach solution	97.5% of copper was extracted with 1 M Cyanex 923 from 5 M HCl solution.
Barik et al. [28]	LIX 84I and LIX 622N in kerosene	Waste heat boiler dust leach liquor	The counter-current extraction study showed 0.21 kg/m³ and 6.77 g/m³ copper in the third stage raffinates of LIX 84I and LIX 622N indicating 98.64% and 99.95% extractions, respectively.
Lu and Dreisinger [29]	LIX84-I, LIX612N-LV, XI-04003 and LIX984N	Chloride leach solution	The loading capacity order of copper for four extractants was: LIX984N > LIX612N-LV, XI04003 > LIX84-I. At a pH below 0.5, the copper extraction increased quickly with increasing pH, while at a pH above 0.5, it increased only slightly with pH.
Ochromowicz et al. [30]	LIX 84-I, LIX 984N and LIX 54-100	Ammonia leach solution	In the case of systems using hydroxyoximes, extraction efficiency was much better than for β-diketone reagent.
Cheng et al. [31]	LIX 63 and Versatic 10	Chloride leach solution	Over 95% Cu was extracted using the mixture of 0.3 mol/L LIX 63 and 0.33 mol/L Versatic 10 in Shellsol D70.
Sadat et al. [32]	Chemorex CP-150 in kerosene	Real bioleaching solutions obtained from a complex Cu–Ni–Co bearing tailing	More than 99.9% Cu can be transferred with a single stage for each of the extraction and stripping steps.
Sombhatla el al. [33]	LIX-54, cinnamate and β diketone	Ammoniacal carbonate solution	Solvents cinnamate and mixture of β diketone can efficiently replace LIX 54. About 97.3%, 99.7%, and 99.6% of copper can be extracted using LIX 54, cinnamate, and β diketone, respectively.
Tanda et al. [34]	Mextral 84H and Mextral 54-100 in kerosene	Alkaline glycine leach solution	Over 99.9% Cu was extracted with 5% Mextral 84H at room temperature at an A/O ratio of 2:1. Under similar conditions, the extraction efficiency of Cu was 95.87% by 10% Mextral 54-100.

As it can be seen in this table, generally, the previous studies demonstrate that the followings: 1) There are two classes of main extractants for SX of copper [4, 14, 35]: a) chelating extractants including ketoximes (such as LIX 84I and LIX 63) and aldoximes (LIX 622 and Acorga M5640) and b) acidic and solvating extractants such as Cyanex 272, Cyanex 302, Cyanex 301; Cyanex 921 and Cyanex 923, and E2EHPA; 2) The chelating type extractants (ketoximes and aldoximes) have proved to be the most effective for the extraction of copper, and to be the most widely used Cu extractants on commercial levels; 3) Ketoxime properties are moderate strength, excellent phase separation, low entrainment losses to the raffinate, useful above a pH of 1.6–1.8 with a good physical performance, and not promoting excessive crud [17]; 4) Aldoximes have a better extraction ability, especially in a highly acidic leachate, and also have a good selectivity over iron. Salicylaldoximes are very strong copper extractants, developed to overcome the perceived shortcomings of the ketoximes. Their outstanding characteristics include rapid copper transfer kinetics and high extractive strength. However, their Cu content can be stripped by contact with a high value of H_2SO_4; a high level of acid is too corrosive for industrial EW and also may tend to degrade the extractant. For these reasons, aldoximes are only used when mixed with ketoximes or modifiers, e.g. highly branched alcohols or esters.

In addition, the above literature reveals that the choice of extractants and subsequently the selective extraction of copper from pregnant leach solutions (PLSs) containing other metals especially iron are a particular stimulus and an important step for the successful use of SX in both the technical and economic aspects. However, many studies have been performed to develop reagents for the selective extraction of copper from leachates, although there is still the concern for Cu selective extraction, keeping the other elements in the PLS solution. Thus this work focused on finding an efficient extraction system for recovery of copper from a real PLS solution. Since modified aldoximes have faster reaction kinetics today, a greater selectivity for copper over impurities, and a better extraction performance [35], Chemorex CP-150, which is a blend of 5-nonylsalicylaldoxime and a branched chain di-isobutyrate modifier together with a high flash point diluent and have been industrially used in several hydrometallurgical plants, was employed as an alternative selective extractant for copper in this work. A comparative study was also carried out on the extractive ability of Chemorex CP-150 with organophosphorus acid extractants such as di-(2-ethylhexyl) phosphoric acid (D2EHPA) and bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272) and their synergistic effects. Moreover, a few works relevant to the use of Chemorex CP-150 for extraction of copper have been reported [32], and thus it has become important to focus our research work on the extraction behavior of copper using Chemorex CP-150. In this work, we studied the extraction behavior of copper from a real leaching solution and process mechanism with CP-150 in detail. Also we investigated the stripping of copper from the loaded organic phase using response surface modeling.

2. Experimental
2.1. Reagents and solutions
The real pregnant leach solution (PLS) used in this work was obtained from the heap leaching stage of Chahmousa copper oxide ore in the Semnan Province (Iran), and was employed as the aqueous phase. This solution, analyzed for copper and iron content by an atomic absorption spectrophotometer, contained 0.727 g/L Fe and 2.14 g/L Cu.

Chemorex CP-150 provided was of commercial grade, and was originally procured from the Longlight International Company (United Kingdom). The other organic solvents used in the present work were industrial-grade reagents including Cyanex 272 ($C_{16}H_{35}O_2P$, 90% pure) and D2EHPA ($C_{16}H_{35}O_4P$, 95% pure). Cyanex 272 was supplied from Aldrich Chemistry Co., and D2EHPA was obtained from Merck, Germany. These solvents were used without further purification and diluted in kerosene to achieve the required concentration.

Sodium hydroxide pellets, obtained from the Merck, were used to adjust the pH, wherever necessary. In addition, the analytical grade H_2SO_4 (96-98%), supplied from Merck, was used to strip copper from the organic phase to the aqueous phase.

2.2. Extraction experiments
Solvent extraction experiments were performed in a beaker with equal volumes (10 mL) of the aqueous and organic phases (A/O = 1) (except for the McCabe Thiele diagram construction). The mixture (aqueous and organic) was stirred thoroughly using a magnetic stirrer (520 rpm) at room temperature (25 ± 2 °C) for about 20 min to ensure the maximum mass transfer. When mixing

was completed, the mixture was transferred to a separatory funnel for separation of the two phases. After separation, the metal ion concentrations in the aqueous phase were determined by atomic absorption spectroscopy (AAS) after the necessary dilution. The Cu contents in the organic phase were also obtained by mass balance. The distribution coefficient (D) and extraction efficiency (E) were computed by the following equations:

$$D = \frac{[Cu]_t - [Cu]_a}{[Cu]_a} \tag{1}$$

$$\%E = \frac{D}{D + \left(\dfrac{V_{aq}}{V_{org}}\right)} \times 100 \tag{2}$$

where $[Cu]_t$ and $[Cu]_a$ represent the initial and final concentrations of copper in the aqueous phase, and V_{aq} and V_{org} are the volumes of the aqueous and organic phases of the extraction process.
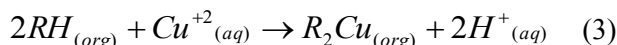
2.3. Stripping experiments

The loaded organic phase was obtained from the extraction experiments at the determined optimum conditions. Then the stripping experiments were conducted on the loaded organic phase using H_2SO_4 at certain concentrations with the desired organic to aqueous phase ratio and with the same procedures and conditions described for the solvent extraction stage.

3. Results and discussion
3.1. Effect of solution pH

To determine the effect of solution pH on the extraction of copper from the leach liquor, the extraction experiments were carried out using 10% (v/v) Chemorex CP-150, 10% (v/v) D2EHPA, and 0.025 mol/L Cyanex 272 in kerosene within the initial pH range of 0.5-3.5 at 25 °C, 1:1 phase ratio, and contact time of 20 min. Figure 1 displays the extraction behavior of Cu from real pregnant sulfate leach solution (PLS) based on the solution pH. It was seen that Chemorex CP-150 solvent had a higher extraction percentage than the other extractants (D2EHPA and Cyanex 272). However, the extraction percentage using D2EHPA and Cyanex 272 enhanced with increase in the pH in the range studied; this behavior is characteristic of most cationic acidic and solvating extractants. From this plot (Figure 1), it was also observed that Cu extraction using Chemorex CP-150 increased dramatically with rise in pH, reached a maximum

at pH 2.5, and then remained relatively constant. According to the reaction presented in Eq. 3, this behavior is attributed to the fact that with increase in the pH, the extraction reaction shifts towards the right to chelate Cu(II), and consequently, the extraction efficiency initially increases with pH and reaches a plateau at pH 2.5. However, at a high pH, Cu(II) presents a solid or colloidal particle form, which may interfere with its extraction [36, 37], and therefore, the extraction value remained relatively unchanged.

$$2RH_{(org)} + Cu^{+2}{}_{(aq)} \rightarrow R_2Cu_{(org)} + 2H^+{}_{(aq)} \tag{3}$$

where RH is a salicylaldoxime-based extractant, R_2Cu is the complex formed in the loaded organic solution and the subscripts *aq* and *org* refer to the aqueous and organic phases, respectively [12].

In addition, final solution pH was measured after each experiment, and it was observed that at initial pH 2.5, difference between the initial and final pH values was much less than the other cases and was about 0.2 (final pH 2.7) for Chemorex CP-150. Therefore, the pH of 2.5 was selected as a suitable pH for further studies. This conclusion is in good agreement with those reported in previous works for oxime-based extractants [13, 26, 32, 37]. It should be pointed out that Fe ions were not significantly extracted into the organic phase at initial pH 2.5 when Chemorex CP-150 was used as the reagent (as seen in Figures 3-5).

3.2. Effect of extractant concentration

In order to study the extraction behavior of Cu(II) ions as a function of extractant concentration, the concentrations of Chemorex CP-150 and D2EHPA were varied within 5-20 vol% (0.15 to 0.6 mol/L), and the experiments were conducted at 25 °C, pH 2.5, stirring rate of 520 rpm, 1:1 phase ratio, and contact time of 20 min (Figure 2). Extraction experiments using 0.015, 0.025, and 0.035 mol/L Cyanex 272 were also carried out in the above-mentioned conditions and the extraction efficiencies were obtained to be 44.37%, 39.77%, and 43.47%, respectively.

As expected and considered from the results, the extraction percentage of copper using D2EHPA and Cyanex 272 from leach liquor was not effective (it was about 40%). As shown in Figure 2, the percentage extraction of copper with Chemorex CP-150 increased with increase in the extractant concentration. Considering the results, it was found that economically, 15% (v/v) Chemorex CP-150 was sufficient to extract Cu from PLS in a single contact of the aqueous and organic phases.
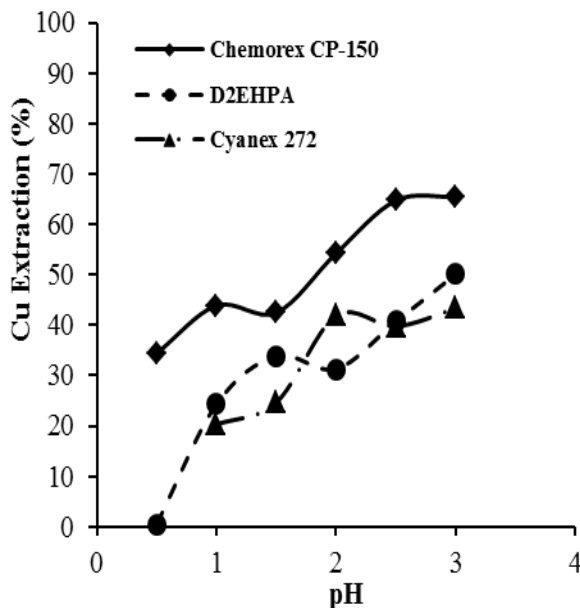
Figure 1. Effect of solution pH on the extraction of copper from PLS using 10% (v/v) Chemorex CP-150, 10% (v/v) D2EHPA, and 0.025 mol/L Cyanex 272 in kerosene.
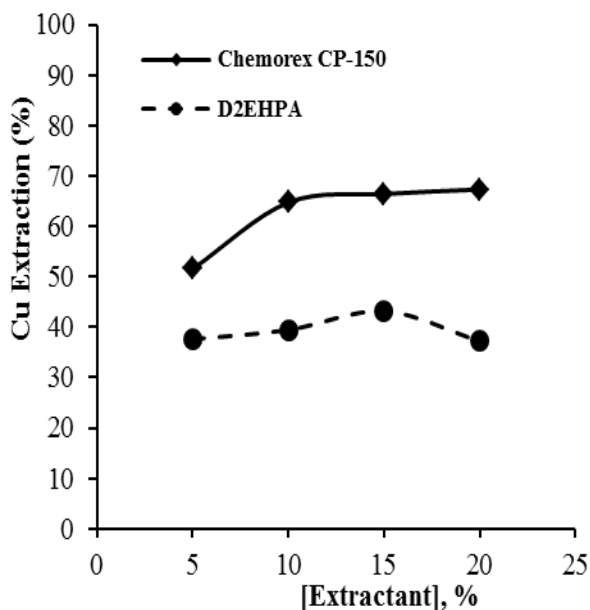

Figure 2. Effect of extractant concentration on the extraction of copper from PLS.

3.3. Effect of mixture of extractants

Cyanex 272 and D2EHPA mixed with Chemorex CP-150 and Cyanex 272 mixed with D2EHPA were applied in the extraction of Cu. The extraction experiments were performed with 0.025 mol/L Cyanex 272, 15% (v/v) D2EHPA, and 15% (v/v) Chemorex CP-150 at 25 °C, pH 2.5, an organic/aqueous phase ratio of 1, agitation of 520 rpm, and a contact time of 20 minutes. Figures 3 to 5 show the change in the extraction rate of copper and iron with mixture of extractants. It can be deduced that Cyanex 272 and D2EHPA have a high extraction capability toward Fe from the sulfate pregnant leach solution (PLS) studied, and also these reagents cannot extract copper selectively and effectively. Also the mixture of solvents has no positive effect on the extraction of Cu, whereas Chemorex CP-150 displayed a very good and selective extraction performance for copper from PLS with the extraction value of Fe less than 15%, which can be attributed to 5-nonylsalicylaldoxime ($C_{16}H_{25}NO_2$) as a main constituent of Chemorex CP-150. Therefore, Chemorex CP-150 was investigated to continue the work.
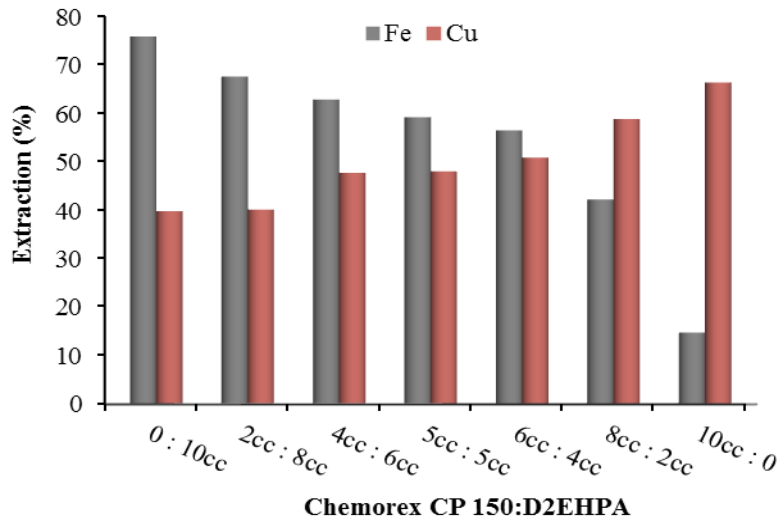
Figure 3. Effect of mixture of D2EHPA with Chemorex CP-150 on the extraction of copper and iron from PLS at various proportions.
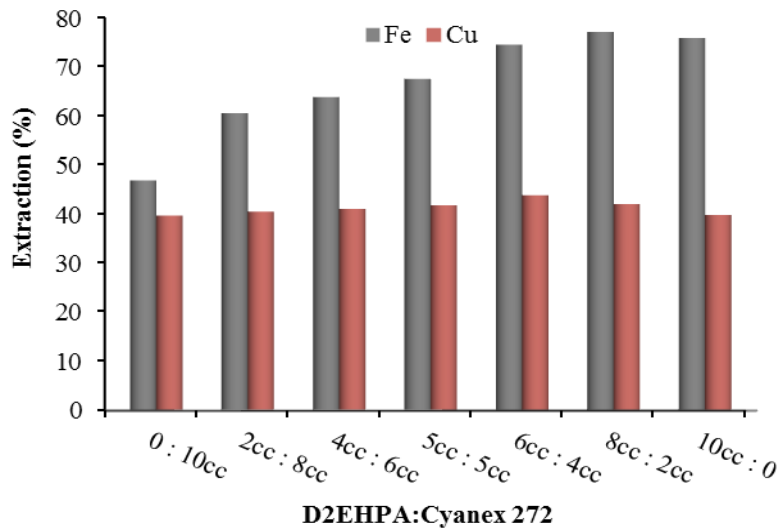

Figure 4. Effect of mixture of D2EHPA with Cyanex 272 on the extraction of copper and iron from PLS at various proportions.
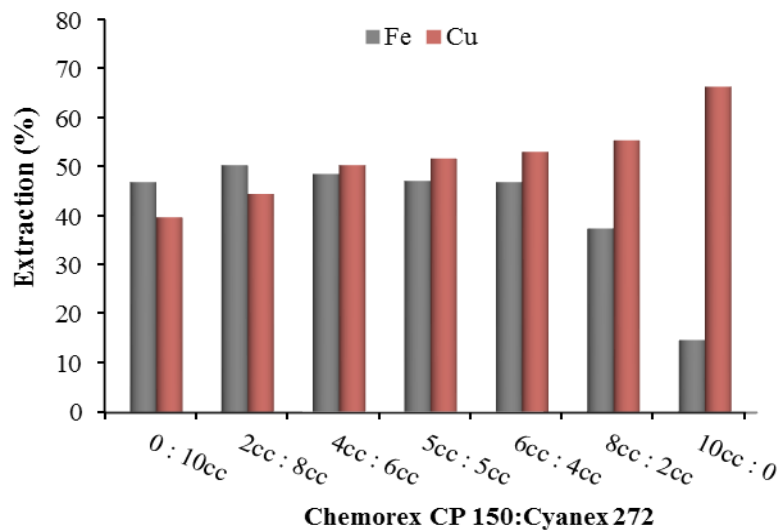

Figure 5. Effect of mixture of Cyanex 272 with Chemorex CP-150 on the extraction of copper and iron from PLS at various proportions.

3.4. Effect of temperature and extraction mechanism

In order to investigate the impact of temperature, the extraction experiments were performed with 15% (v/v) Chemorex CP-150 in kerosene at the temperatures 298, 308, and 318 K (25, 35, and 45 °C), pH 2.5, stirring rate of 520 rpm, 1:1 phase ratio, and contact time of 20 min. Under these conditions, the extraction efficiencies were measured to be 66.4%, 66.86%, and 70.61% at 298, 308, and 318 K, respectively. It was observed that the extraction efficiency increased slightly with increase in the temperature throughout the investigated temperature range. Therefore, the ambient temperature (298 K) was chosen to continue the work.

Furthermore, in order to understand the mechanism and feasibility of the extraction process, the extraction equilibrium constant and the thermodynamic parameters including the enthalpy change (ΔH), Gibbs free energy (ΔG), and entropy (ΔS) were measured. The equilibrium constant, *K*, was obtained by taking the logarithm of Eq. (4) and rearrangement (Eq. (5)). The thermodynamic parameters involved were calculated using the Van't Hoff equation (Eqs. (6)-(8)).

$$K = \frac{[R_2Cu]_{(org)}[H^+]_{(aq)}^2}{[Cu^{+2}]_{(aq)}[RH]_{(org)}^2} \tag{4}$$

$$\log(K) = \log(D) - 2\log[RH]_{(org)} + 2\log[H^+]_{(aq)} \tag{5}$$

where the distribution ratio (D) is defined as:

$$D = \frac{[Cu^{+2}]_{(org)}}{[Cu^{+2}]_{(aq)}} = \frac{[R_2Cu]_{(org)}}{[Cu^{+2}]_{(aq)}}$$

$$\log D = \frac{-\Delta H}{2.303R}\frac{1}{T} + C \tag{6}$$

$$\Delta G = -RT \ln K \tag{7}$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \tag{8}$$

where *R* is the universal gas constant (8.314 J mol^{-1}K^{-1}), C is a constant for a solution, and *T* is the absolute temperature [22, 38].

In order to study the thermodynamic of the extraction process, firstly, different values of the extraction constant were evaluated at different Chemorex CP-150 and hydrogen ion [H$^+$] concentrations [38], and the average value of log *K* was calculated to be -3.195. Then in the second stage, the van't Hoff relationship was plotted in the form of log D versus 1/T. The plot (Figure 6) gives a straight line with the corresponding slope of $\frac{-\Delta H}{2.303R}$, indicating the formation of a single complex species (CuR$_2$) [16, 23]. According to Eq. (6), ΔH was calculated to be 7.62 kJ/mol. This value indicates that the extraction process with Chemorex CP-150 is slightly endothermic, and also it is indicative of the relatively lower heat effects involved in the formation of the extracted complex, which can be beneficial to this hydrometallurgical process. Similar values were obtained by Alguacil and Alonso [15] (ΔH = 6.9 kJ/mol) for the system Cu/ammonium sulfate medium/LIX54 and Barik et al. [28] for system Cu/waste heat boiler dust leach liquor/LIX 622N (ΔH = 7.2 kJ/mol). The values for ΔG and ΔS were also found to be 18.23 kJ/mol and -35.58 J mol^{-1}K^{-1} at the ambient temperature (298 K).
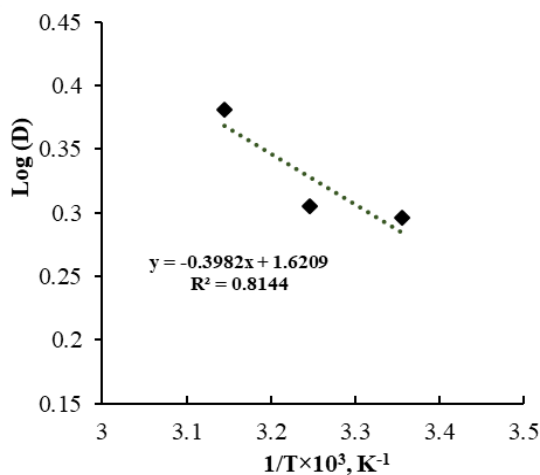

Figure 6. Plot of log D against 1/T (Conditions: 15% (v/v) Chemorex CP-150, pH 2.5, 1:1 phase ratio, and contact time = 20 min).

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3.5. Effect of organic/aqueous (O/A) ratio

Effect of the organic to aqueous volume ratio, ranging from 1:4 to 4:1, on the recovery of Cu(II) ions using CP-150 is shown in Table 2. It is clear that the percentage Cu extraction increases with increase in the O/A ratio. The variation in the O/A phase ratio from 1:4 to 4:1 led to an increase in the extraction percentage from 49.47% to 96.998%.

Table 2. Effect of organic/aqueous phase ratio on the extraction efficiency of Cu from PLS using 15% (v/v) Chemorex CP-150.

Organic:aqueous phase volume ratio (O:A)	Extraction efficiency (%)
1:4	49.47
1:2	59.32
1:1	66.4
2:1	90.93
4:1	96.998

3.6. Extraction isotherm

The extraction isotherm determines the maximum copper extracted from PLS for each organic to aqueous volumetric ratio (A/O). Hence, in order to estimate the number of theoretical stages required to obtain the maximum copper extraction, the McCabe-Thiele diagram was constructed by contacting the aqueous solution with the organic phase at different O/A phase ratios varying from 1:4 to 4:1. From the results shown in Figure 7, it can be observed that at a O/A ratio of 1, a two-stage sequential extraction is required to achieve the maximum Cu recovery. Thus for this purpose, a two-stage counter-current batch simulation experiment was carried out with 15% (v/v) Chemorex CP-150 at 25 °C, pH of 2.5, O/A ratio of 1/1, stirring rate of 520 rpm, and contact time of 20 min. It was found that in two stages, approximately 89.71% of copper could be extracted.
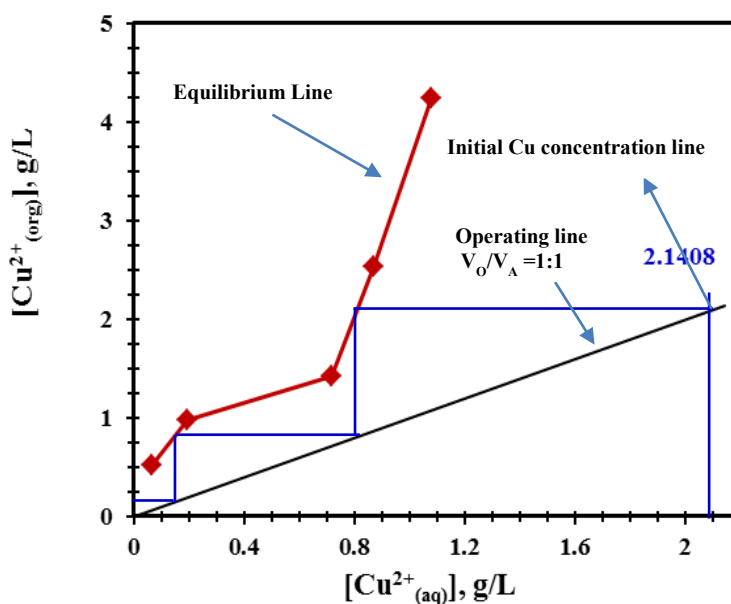

Figure 7. McCabe–Thiele diagram for the extraction of Cu from real PLS by 15% (v/v) Chemorex CP-150 at pH 2.5, temperature 25 ± 2 °C, and contact time = 20 min.

3.7. Stripping study of loaded organic phase

The stripping of copper from the loaded organic phase obtained from the solvent extraction stage was carried out using different concentrations of H_2SO_4 (5%, 10%, 15%, and 20%) at 25 °C, contact times ranging from 2.5 to 20 minutes, and O/A phase ratios of 1:4 to 4:1 with agitation rate of 520 rpm. The results obtained are given in Table 3.

Table 3. Effect of H$_2$SO$_4$ concentration, organic/aqueous phase ratio (A/O), and contact time on the stripping efficiency of Cu.

Run	H$_2$SO$_4$ concentration (g/L)	A/O phase ratio	Contact time (min)	Cu stripping efficiency (%)
1	50	1:1	20	34.14
2	100	1:1	20	44.08
3	165	1:1	20	49.94
4	220	1:1	20	51.81
5	165	1:1	2.5	41.93
6	165	1:1	5	44.45
7	165	1:1	10	45.07
8	165	1:1	15	47.53
9	165	1:4	5	16.73
10	165	1:2	5	29.71
11	165	2:1	5	99.38
12	165	4:1	5	100

In order to describe the behavior of the factors involved in the stripping rate of copper, it is first necessary to choose a suitable model. Therefore, the data in Table 3 was fitted to a quadratic model (Eq. 9); the results obtained from the statistical analysis (analysis of variance (ANOVA)) after removing the insignificant terms are summarized in Table 4.

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{1\langle i \langle j}^{k} \beta_{ij} x_i x_j + \sum_{1\langle i \langle j}^{k} \beta_{ii} x_i^2 + \varepsilon \quad (9)$$

where Y is the estimated response value; x_i and x_j are the experimental factor codes; β_0 is the constant term; k is the number of factors studied; βi, βij, and βii are the linear, interaction, and squared coefficients, respectively; and ε is the residual corresponding to the experiments [39, 40].

ANOVA was used to determine the adequacy of the model and its significance, and also to determine the effects of the factors involved. ANOVA demonstrated that the stripping of copper was most suitably described with a quadratic polynomial model. Table 4 shows that the degree of influence of the factors involved is in the order of phase ratio > H$_2$SO$_4$ concentration > contact time. The F value of 30.09 implies that the model was significant. Also it indicates that 94.5% of the experimental data and predicted data can be explained by the model. In addition, in the present work, the distinction amongst the R^2 and R^2-adjust values is under 0.0314 (Table 4), which proves that the model does not contain irrelevant terms. The final equation representing the stripping rate (R) of copper based on the actual values was achieved as functions of the H$_2$SO$_4$ concentration (A), phase ratio (B), and contact time (C):

$$-20.4983 + 0.09984 \times A + 65.41355 \times B - 0.19125 \times C - 9.6761 \times B^2 \quad (10)$$

In addition, in order to gain a better understanding of the effects of the parameters involved, a series of 16 tests were designed, performed, and analysed according to the response surface methodology (D-optimal design) using Design Expert Software (DX7), in which only 3D surface plots simulated by DX7 were displayed in Figure 8, in which two parameters were varied within the experimental range, while another factor was fixed at the centre level (contact time = 11 min, A/O phase ratio = 2.15:1, and H$_2$SO$_4$ concentration = 135 g/L). According to Table 3, by increasing the acid concentration, the Cu stripping efficiency was increased from 34.14% to 51.81% at a phase ratio of 1. This can be attributed to the reduction of pH due to increase in the H$_2$SO$_4$ concentration, which results in a further dissociation of Cu-extractant complexes in the organic phase. From the stripping results, it can also be concluded that 165 g/L of H$_2$SO$_4$ is a suitable concentration for the stripping of Cu from the loaded organic phase, and therefore, this concentration was fixed for further investigations. According to Tables 3 and 4 and Figure 8, the impact of contact time between the aqueous and organic phases on the stripping efficiency indicates that a mixing time of 5 min is sufficient for the stripping of Cu from the loaded organic phase. Moreover, it was found that copper could be completely stripped using 165 g/L H$_2$SO$_4$ at an A/O phase ratio of 4:1 but from an economical viewpoint, the 2:1 A/O ratio was better because it gave 99.38% copper recovery in a one stage stripping under the experimental conditions studied.

Table 4. ANOVA for response surface reduced quadratic model to predict the stripping rate of copper.

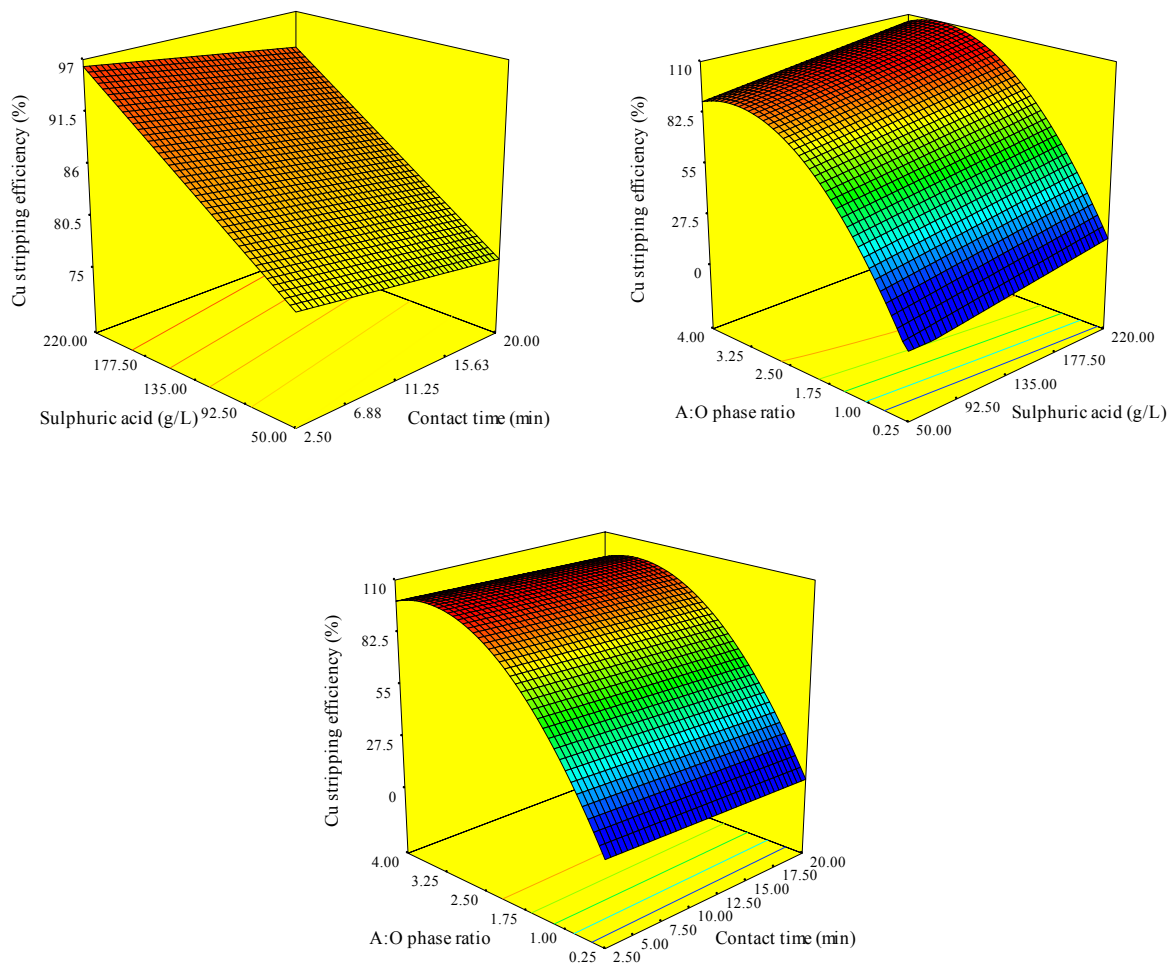| Source	Sum of squares	DF	Mean square	F-Value	p-value Prob > F	
Model	6493.66	4	1623.41	30.09	0.0002	significant
A- Sulfuric acid (g/L)	170.01	1	170.01	3.15	0.1191	
B- A/O phase ratio	5640.34	1	5640.34	104.56	< 0.0001	
C- Contact time (min)	16.9	1	16.9	0.31	0.5931	
B^2	965.21	1	965.21	17.89	0.0039	
Residual	377.61	7	53.94			
Cor Total	6871.26	11				
R-Squared	0.945					
Adj R-Squared	0.9136					
Std. Dev.	7.34					
Adeq. Precision	19.213					

Figure 8. 3D response surface plot showing effect of H_2SO_4 concentration and contact time (a); H_2SO_4 concentration and phase ratio (b); and phase ratio and contact time (c) on the stripping efficiency of copper when another factor kept at its centre level.

4. Conclusions

A comprehensive study was carried out on the extraction behavior of copper from a real pregnant sulfate leach solution (PLS) using Chemorex CP-150 in kerosene, and its extraction ability for Cu was compared with the acidic and solvating extractants including di-(2-ethylhexyl)phosphoric acid (D2EHPA) and bis-(2,4,4-trimethylpentyl)phosphinic acid (Cyanex272). The results obtained showed that D2EHPA and Cyanex 272 and their mixture with Chemorex CP-150 were not efficient for a selective extraction of

Cu due to the high extraction of Fe. The sole Chemorex CP-150 diluted in kerosene showed the selective and effective extraction capability of copper from the PLS studied. The effective Chemorex CP-150 concentration, suitable temperature, and optimal PLS pH were found to be 1.5 mol/L, 25 °C, and 2.5, respectively. Under these conditions, almost 66.4% and 97% of Cu could be extracted at A/O phase ratios of 1:1 and 1:2, respectively. A two-stage sequential extraction was determined on the basis of the McCabe-Thiele diagram to obtain the maximum extraction efficiency, and it was found that more that 89.71% of Cu could be extracted. The thermodynamic parameters involved were also calculated, and the findings showed that the extraction process was endothermic with ΔH of 7.62. The values for ΔG and ΔS were also measured to be 18.23 kJ/mol and -35.58 J mol^{-1} K^{-1} at the ambient temperature. The stripping of loaded organic phase was performed using different concentrations of sulfuric acid. The highest stripping percentage of copper (~99.4%) was obtained using 165 g/L H_2SO_4 at an A/O phase ratio of 2:1 after 5 minutes stripping.

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استخراج حلالی مس از یک محلول فروشویی سولفاته صنعتی با استفاده از چمورکس CP-150

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چکیده:

رفتار استخراجی مس از محلول فروشویی سولفاته‌ی واقعی به دست آمده از مرحله‌ی هیپ لیچینگ یک کانه مس اکسیدی بـه وسـیله‌ی یـک عامـل کیلیـت‌سـاز، چمورکس CP-۱۵۰ در کروزین مورد بررسی قرار گرفت. یک مطالعه‌ی مقایسه‌ای نیز با استفاده از حلال‌های دیگـر شـامل دپـا و سـیانکس ۲۷۲ بـر روی قابلیـت استخراجی یون‌های (II)Cu انجام شد. چمورکس CP-۱۵۰ عملکرد استخراجی مؤثر و انتخابی را برای مس با مقدار آهـن اسـتخراج شـده‌ی کمتـر از ۱۵ درصد نشان داد. همچنین نتایج به دست آمده نشان داد که بیش از ۶۶/۴ و ۹۶/۹۹ درصد مس در استخراج تک مرحله‌ای با استفاده از چمـورکس CP-۱۵۰ ۱۵ درصد تحت شرایط دمای ۲۵ درجه سانتی‌گراد، ۲/۵ pH و زمان تماس ۲۰ دقیقه به ترتیب در نسبت‌های فاز آبی به آلی ۱:۱ و ۱:۴ به فاز آلی منتقـل مـی‌شـود. بعـلاوه دیاگرام مک کیپ- تیل نشان داد که دو مرحله استخراج برای بـه دست آوردن مـاکزیمم مقـدار مـس در نسـبت فـاز ۱ بـه ۱ تحـت شـرایط اپتیـمم (۲۵ درجـه سانتی‌گراد، ۲/۵ pH و زمان تماس ۲۰ دقیقه) نیاز است. داده‌های ترمودینامیکی هم ثابت کرد که فرآیند اسـتخراج نسـبتاً گرمـاگیر (ΔH=7.62 kJ/mol) بـود که نشان‌دهنده‌ی اثرات نسبتاً پایین دما در تشکیل گونه‌های CuR_2 است. استریپینگ مس از فاز آلی به دست آمده با اسـتفاده از اسـید سـولفوریک انجـام شـد و نتایج نشان داد که ۹۹/۳۸ درصد مس می‌تواند با استفاده از ۱۶۵ گرم بر لیتر H_2SO_4 در نسبت فاز آبی به آلـی ۱:۲ پـس از ۵ دقیقـه زمـان اسـتریپینگ بازیـابی شود.

کلمات کلیدی: استخراج مس، محلول لیچینگ باردار، استخراج با حلال، استریپینگ، چمورکس CP-150.