



# Efficiency, stoichiometry and structural studies of Cu(II) removal from aqueous solutions using di-2-ethylhexylphosphoric acid and tributylphosphate diluted in soybean oil

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## ABSTRACT

Solvent extraction of Cu(II) from aqueous solutions by a soybean oil-based organic solvent (SOS) composed of soybean oil (diluent), di-2-ethylhexylphosphoric acid (extractant) and tributylphosphate (phase modifier) was investigated. Effects of initial Cu(II) concentration in the aqueous phase (25–500 mg/L (0.39–7.88 mM)) and temperature (298–323 K) on the percentage extraction (%E) of Cu(II) were studied. It was found that the initial Cu(II) concentration did not influence %E appreciably and high %E (>98%) was achieved throughout the experimental ranges studied. The %E at various temperatures, on the other hand, decreased consistently with temperature. The loading capacity of SOS (2400 mg/L (37.82 mM)), as well as the stoichiometry (4:1) and structure (inner sphere) of Cu(II)–organic complexes (extracted species) in SOS were also determined. Stripping of Cu(II) from the loaded SOS was investigated with various types (sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), hydrochloric acid (HCl) and nitric acid (HNO<sub>3</sub>)) and concentrations (0.05–2.00 M) of mineral acids. The decreasing order of percentage stripping (%S) of Cu(II) by various types of acids was found to be H<sub>2</sub>SO<sub>4</sub> > HCl > HNO<sub>3</sub> throughout different concentrations studied, with H<sub>2</sub>SO<sub>4</sub> attaining the highest %S (>99%) at 1.5 M.

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## 1. Introduction

Industrial effluents containing Cu(II) from numerous anthropogenic activities such as mining, electroplating, printed circuit board manufacturing, metal processing and metal finishing [1,2] are threatening the environment due to the toxicity of the Cu(II) discharged [3]. Conventional techniques used to remove Cu(II) from aqueous solutions include chemical precipitation [4], coagulation–flocculation, flotation, ion exchange, electro-oxidation, membrane filtration and biosorption [5–7]. Among all techniques, solvent extraction emerges as one of the well-established techniques applicable to Cu(II) removal from aqueous solutions [8]. The organic solvents used to remove solutes from aqueous solutions are usually composed of an extractant and a diluent. The former extracts solutes selectively while the latter controls the solvent conditions [9]. Sometimes, a phase modifier is added to overcome the emulsion formation and to improve the phase disengagement process in the aqueous–organic sys-

tem [10]. A wide variety of organic solvents have been applied to remove heavy metals from aqueous solutions, but they are mostly of petroleum-based which are not eco-friendly, non-renewable and could be inordinately expensive due to the limited resources [11]. Recently, greener solvents such as the vegetable oil-based organic solvents [12,13] were used as the alternatives to replace the classical petroleum-based organic solvents in heavy metal removal from aqueous solutions.

A soybean oil-based organic solvent (SOS) containing soybean oil (diluent), di-2-ethylhexylphosphoric acid (D2EHPA) (extractant) and tributylphosphate (TBP) (phase modifier) was found to extract Cu(II) effectively from aqueous solutions in our previous work [13]. Optimization of various process variables in Cu(II) extraction with SOS using the response surface methodology was also conducted [14]. In the present work, effects of initial Cu(II) concentration in the aqueous phase and temperature on the Cu(II) extraction with SOS were investigated under the optimized operating conditions determined earlier [14]. The loading capacity of SOS, as well as the stoichiometry and structure of Cu(II)–organic complexes (extracted species) in SOS were also determined. Lastly, stripping or back-extraction of Cu(II) from the loaded SOS using various types and concentrations of mineral acids was investigated.

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## 2. Materials, equipment and methods

### 2.1. Materials

Refined soybean oil was supplied by Soon Soon Oil Mill Sdn. Bhd., Malaysia and was used without further purification. Copper sulfate pentahydrate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) (R&M Chemicals,  $\geq 99.6\%$  purity), D2EHPA (Acros Organic,  $\geq 99\%$  purity), nitric acid ( $\text{HNO}_3$ ) (Fisher Scientific,  $\geq 65\%$  purity), as well as TBP ( $\geq 99\%$  purity), sulfuric acid ( $\text{H}_2\text{SO}_4$ ) ( $\geq 98\%$  purity), hydrochloric acid (HCl) ( $\geq 35\%$  purity), sodium hydroxide (NaOH) ( $\geq 99\%$  purity) and sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) ( $\geq 99\%$  purity) supplied by Merck were used as received.

### 2.2. Equipment

A thermostated magnetic stirrer (Cole-Parmer, StableTemp) was used to mix the aqueous and organic phases while a pH meter (Mettler Toledo, Delta 320) was used to measure the pH of aqueous phase. The concentration of Cu(II) in the aqueous phase was measured with a flame atomic absorption spectrophotometer (FAAS) (Perkin Elmer, AA-400) at a wavelength of 324.75 nm. An attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy (Thermo Scientific, Nicolet 6700) was used to examine the functional groups present in the organic phase.

### 2.3. Preparation of aqueous and organic phases

In the extraction experiments, aqueous phases containing various initial concentrations of Cu(II) (25–500 mg/L (0.39–7.88 mM)) were prepared by dissolving appropriate amounts of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  in distilled water loaded with 250 mM  $\text{Na}_2\text{SO}_4$ , while the organic phases (SOS) were prepared by loading soybean oil with 84.71 mM D2EHPA (except for those used in the equilibrium slope analysis for determining the stoichiometry of extracted species where 40–100 mM of D2EHPA were applied) and 60 mM TBP [14]. In the stripping experiments, the organic phases were Cu(II)-loaded SOS obtained from the extraction experiments, whereas the aqueous phases were prepared from various types of mineral acids ( $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$  and HCl) at different concentrations (0.05–2.0 M).

### 2.4. Extraction and stripping procedures

The extraction procedures were similar to those described in our previous works [13,14]. Initially, a volume of 10 mL of the prepared organic phase was mixed with the prepared Cu(II)-containing aqueous phase at 1:1 organic to aqueous volume ratio in a glass-stoppered bottle. The bottle was shaken by a thermostated magnetic stirrer at 100 rpm. After 3 min of mixing, the mixture was allowed to stand for 5 min for phase separation. A syringe with a small tube at the tip was used to take about 6 mL sample from the aqueous phase and its pH was measured with a pH meter. If the pH measured was different from the desired equilibrium pH ( $\text{pH}_{\text{eq}}$ ), the sample was returned to the bottle and its pH was adjusted with 1 M  $\text{H}_2\text{SO}_4$  or 1 M NaOH. The desired  $\text{pH}_{\text{eq}}$  used in this work was 4.46, which was an optimum value obtained from our previous work [14]. This  $\text{pH}_{\text{eq}}$  was applied in all the extraction experiments, except for those used in the equilibrium slope analysis for determining the stoichiometry of extracted species where  $\text{pH}_{\text{eq}}$  of 3.30–4.60 were applied. After the pH adjustment, the mixture was stirred for another 3 min and was allowed to stand for separation. The pH of the aqueous phase was then measured and adjusted again if necessary. This test was continued until the desired  $\text{pH}_{\text{eq}}$  was obtained. Next, the mixture was transferred into a separating funnel for phase disengagement, and finally, about 6 mL sample was taken from the aqueous phase for chemical analysis with an FAAS after appropri-

ate filtration and dilution. The percentage extraction (%E) of Cu(II) was calculated according to [15,16]:

$$\%E = \frac{[\text{Cu}]_{\text{o,aq}} - [\text{Cu}]_{\text{f,aq}}}{[\text{Cu}]_{\text{o,aq}}} \times 100\% \quad (1)$$

where  $[\text{Cu}]_{\text{o,aq}}$  and  $[\text{Cu}]_{\text{f,aq}}$  are the initial and final Cu(II) concentrations in the aqueous phase, respectively. The stripping experiments were conducted using the same procedures and conditions as the extraction experiments, except that the pH adjustment after mixing of two phases was omitted. The percentage of stripping (%S) of Cu(II) was given by [16]:

$$\%S = \frac{[\text{Cu}]_{\text{f,strip}}}{[\text{Cu}]_{\text{o,org}}} \times 100\% \quad (2)$$

where  $[\text{Cu}]_{\text{f,strip}}$  is the final Cu(II) concentration in the stripping phase and  $[\text{Cu}]_{\text{o,org}}$  is the initial Cu(II) concentration in the organic phase in stripping experiments (calculated by  $[\text{Cu}]_{\text{o,aq}} - [\text{Cu}]_{\text{f,aq}}$  from the extraction experiments). All the extraction and stripping experiments were carried out in duplicate or triplicate at room temperature (298 K), except for those studying the effect of temperature on %E (298–323 K) and extraction thermodynamics for determining the structure of extracted species (298–313 K), and the relative standard deviation between replicate samples within an experiment range was less than 1%.

## 3. Results and discussion

### 3.1. Effect of initial Cu(II) concentration and temperature

Effect of  $[\text{Cu}]_{\text{o,aq}}$  (25–500 mg/L (0.39–7.88 mM)) on %E using SOS was conducted at a specific temperature of 298 K, while the effect of temperature (298–323 K) was carried out at a preset  $[\text{Cu}]_{\text{o,aq}}$  of 500 mg/L (7.88 mM). It was found that  $[\text{Cu}]_{\text{o,aq}}$  did not influence %E appreciably and %E of more than 98% was achieved throughout the experimental ranges studied. This was expected since the SOS used was previously optimized for  $[\text{Cu}]_{\text{o,aq}}$  of 500 mg/L [14], which was the highest  $[\text{Cu}]_{\text{o,aq}}$  studied in this work. The %E at various temperatures, on the other hand, decreased consistently with temperature from 298 to 323 K. This finding agrees well with the results reported in Th(IV) extraction from aqueous solutions using D2EHPA diluted in toluene [17], as well as in Mn(II) extraction from aqueous solutions using Cyanex 302 dissolved in kerosene [18]. Since %E was found to decrease consistently with temperature, further studies were carried out at room temperature (298 K).

### 3.2. Loading capacity of SOS

To investigate the loading capacity of SOS, an organic phase of SOS was contacted repeatedly with a fresh aqueous phase containing  $[\text{Cu}]_{\text{o,aq}}$  of 500 mg/L (7.88 mM) until the organic phase was saturated with Cu(II). The results are presented in Fig. 1 which shows the Cu(II) concentration in the organic phase ( $[\text{Cu}]_{\text{org}}$ ) obtained at different number of contacts. It shows a linear increase of  $[\text{Cu}]_{\text{org}}$  with the number of contacts up to 6 contacts and reaches a plateau thereafter. The  $[\text{Cu}]_{\text{org}}$  of 2400 mg/L (37.82 mM) attained at the plateau signifies the loading capacity of SOS. This value is more than 2 times greater than the loading capacity of kerosene loaded with 150 mM D2EHPA attained in the Cd(II) extraction from aqueous solutions as reported by Kumar et al. [19]. This may be due to the smaller ionic radii of Cu(II) (0.073 nm) than Cd(II) (0.095 nm) [20], in addition to the mild extractability of soybean oil for Cu(II) [13] which has not been reported in any metal extraction studies with kerosene.

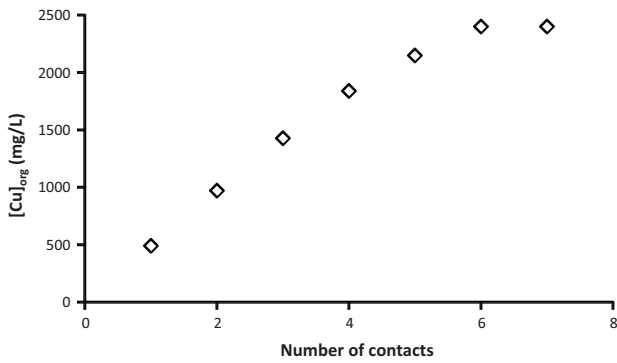


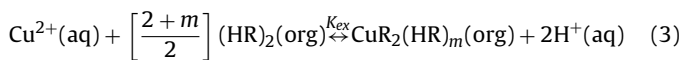
Fig. 1. [Cu]<sub>org</sub> obtained at different number of contacts.

### 3.3. Determination of stoichiometry of Cu(II)–organic complexes

The equilibrium slope [19,21–23] and numerical [24–26] analyses are two popular methods used by numerous researchers to determine the stoichiometry of various metal–organic complexes in organic solvents. Recently, a new approach has been proposed by Sainz-Diaz et al. [27] for the same purpose, i.e. quantitative analysis with FTIR. In the present work, the stoichiometry of Cu(II)–organic complexes in SOS was determined by all these methods and the results obtained were compared with each other.

#### 3.3.1. Equilibrium slope analysis

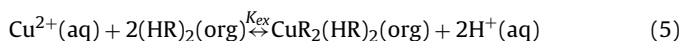
It is well known that D2EHPA exists in dimeric forms when it is dissolved in non-polar organic solvents [28–31]. Since vegetable oils are non-polar organic solvents, a dimer state of D2EHPA was presumed to be present in the soybean oil used in the present work. Thus, the extraction of Cu(II) with D2EHPA loaded in soybean oil can be expressed as:



where (HR)<sub>2</sub> is the dimeric form of D2EHPA, *m* is the number of molecules of D2EHPA engaged in the reaction and *K<sub>ex</sub>* is the equilibrium constant of the extraction reaction. Since the ionic strength of the aqueous phase was kept constant by the addition of an excess inert salt (250 mM Na<sub>2</sub>SO<sub>4</sub>) [32], the quotient of activity coefficients is effectively constant and, thus, *K<sub>ex</sub>* can be written as a concentration quotient [33]. This *K<sub>ex</sub>* is related to the distribution ratio (*D*), which is the ratio of Cu(II) concentration in the organic phase to that in the aqueous phase at reaction equilibrium [33]. By taking the logarithm of the relation between *K<sub>ex</sub>* and *D*, it follows that [33]:

$$\log D = \log K_{\text{ex}} + \left[ \frac{2+m}{2} \right] \log[(\text{HR})_2] + 2\text{pH} \quad (4)$$

A plot of log *D* versus pH<sub>eq</sub> for Cu(II) extraction from aqueous solutions containing [Cu]<sub>o,aq</sub> of 100 mg/L (1.58 mM) is given in Fig. 2. A slope value of 1.99 supports the valency of Cu(II), i.e. 2, and, thus, the compatibility of the experimental data with the empirical model (Eq. (4)). To determine the value of *m* in Eq. (4), log *D* is plotted against log[(HR)<sub>2</sub>] (Fig. 3). In this investigation, the concentration of D2EHPA was varied in the range of 40–100 mM in soybean oil loaded with 60 mM of TBP in each case and extraction studies were carried out with aqueous solutions containing [Cu]<sub>o,aq</sub> of 100 mg/L at pH<sub>eq</sub> of 4.46 [14]. The slope value of 2.07 (Fig. 3) corresponds to (2 + *m*)/2 from Eq. (4), which gives an *m* value of ~2. Hence, the extraction mechanism of Cu(II) extraction could be expressed as:



which indicates that Cu(II) is solvated with two molecules of dimeric form of D2EHPA with the formation of CuR<sub>2</sub>(HR)<sub>2</sub> com-

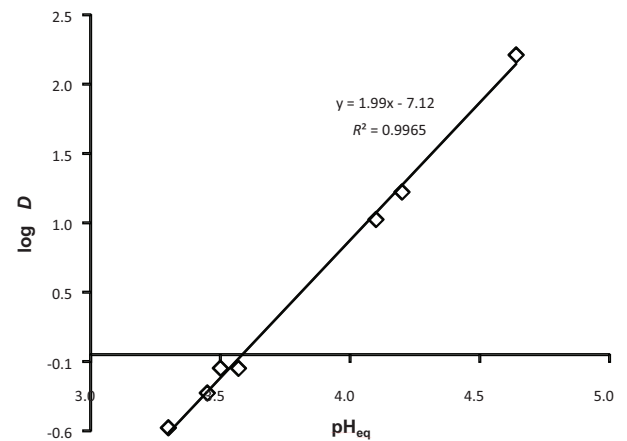


Fig. 2. Log *D* versus pH<sub>eq</sub>.

plexes in SOS, provided that the complexes were not associated with each other. This gives rise to a stoichiometric ratio of D2EHPA to Cu(II) of 4:1 in Cu(II)–organic complexes. This finding is in good agreement with that reported by Juang and Chang [34] in the extraction of Cu(II) from aqueous solutions with D2EHPA dissolved in kerosene.

#### 3.3.2. Numerical analysis

The experimental results (Figs. 2 and 3) were treated numerically by performing a multiple regression analysis which corresponds to the following first-order function:

$$y = \beta_0 + \sum_{i=1}^k \beta_i x_i + \varepsilon \quad (6)$$

where  $\beta_0$  and  $\beta_i$  are the constants for intercept and linear variables, respectively, *y* is the dependent variable, *x<sub>i</sub>* is the independent variable and  $\varepsilon$  is the error term. Estimation of the constants that caused the model to best fit a set of collected response variable data was carried out by the least squares method [35]. All analyses were performed with the Microsoft Office Excel program (Microsoft Office 2007) at 5% significance level.

Table 1 presents the estimated constants, along with the corresponding standard deviation (SD), *t*-statistics (*t*-stat) and probability (*P*) values, for the variable terms of a regression model for log *D* (Eq. (7)) obtained from the analysis. At 5% significance level, all variable terms are found to have *P* < 0.05 and, thus, are statistically significant. Hence, a first-order polynomial model that

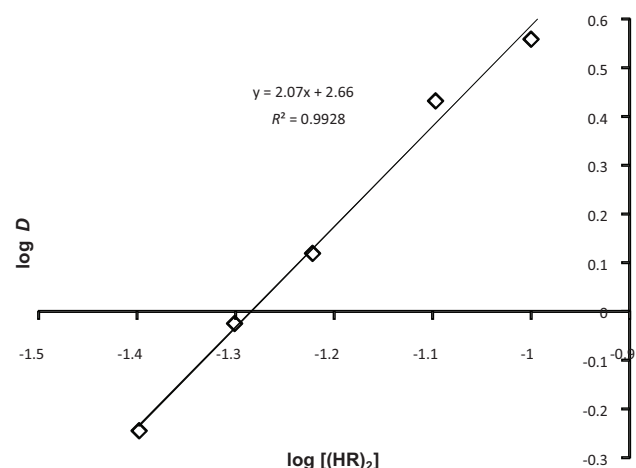
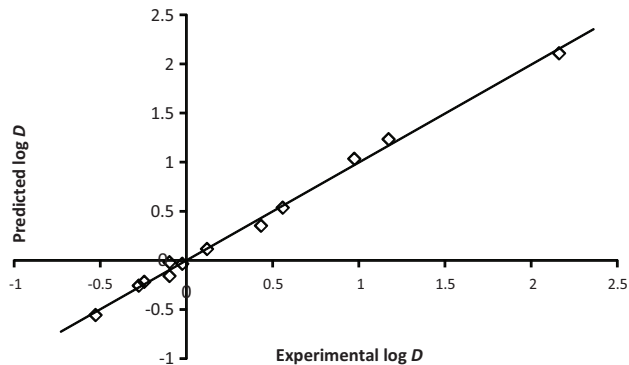


Fig. 3. Log *D* versus log[(HR)<sub>2</sub>].

**Table 1**  
Estimated constants of model for  $\log D$  (Eq. (7)).

	Constant	SD	<i>t</i> -stat	<i>P</i>
Intercept	-5.216	0.219	-23.83	0.000
$\log[(HR)_2]$	1.899	0.120	15.80	0.000
$pH_{eq}$	1.988	0.047	42.63	0.000

SD: standard deviation; *t*-stat: *t*-statistics; *P*: probability value.



**Fig. 4.** Comparison of predicted and experimental  $\log D$ .

correlates  $\log D$  with all the variable terms was developed, which is given by:

$$\log D = -5.216 + 1.899 \log[(HR)_2] + 1.988 pH_{eq} \quad (7)$$

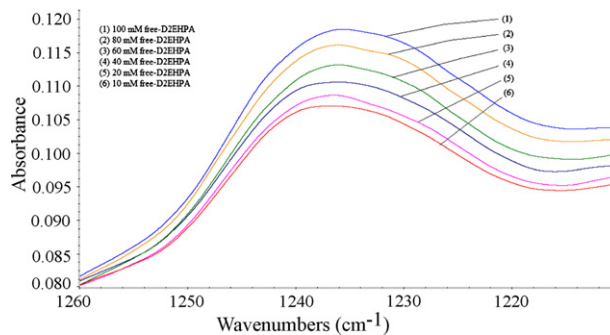
The adequacy or goodness of fit of the regression model (Eq. (7)) was analyzed by the analysis of variance (ANOVA) at 5% significance level and the results are summarized in Table 2. The *F*-critical value obtained from the literature [36] is also presented. The high *F* (*F* > *F*-critical) and low *P* (*P* < 0.05) values of the regression model indicate that it is statistically significant. To test the global fit of the model, the coefficient of determination ( $R^2$ ) was evaluated. From Table 2, the  $R^2$  value of the model is 0.996 (99.6%). This denotes that the sample variation of 99.6% for  $\log D$  is attributed to the regressors in the model and only 0.4% of the total variability is not explained by the model. The small deviation between the  $R^2$  and adjusted  $R^2$  ( $R^2(\text{adj})$ ) values, i.e. 0.1%, implies that there is less chance for the inclusion of any insignificant terms in the model and the model is highly significant [35]. Fig. 4 shows the comparison between the predicted  $\log D$  at 95% confidence level and the experimental  $\log D$  measured. All points on the plot are found to lie reasonably close to a straight line, lending support to that the model is able to give a reasonably good estimate of response for the system in the range studied.

Since Eqs. (4) and (7) are of the same forms, their constants for each variable term can be compared conveniently. The small deviation (0.6%) between the constants of  $pH_{eq}$  from Eqs. (4) and (7) indicates that they are highly compatible. By equalizing the constants of  $\log[(HR)_2]$  from Eq. (4), i.e.  $(2+m)/2$ , with that from Eq. (7), the *m* value of  $1.798 \sim 2$  is computed and, thus, brings about the stoichiometric ratio of D2EHPA to Cu(II) of 4:1 in Cu(II)-organic complexes (Eq. (3)). This finding is consistent with the previous conclusion made in the equilibrium slope analysis.

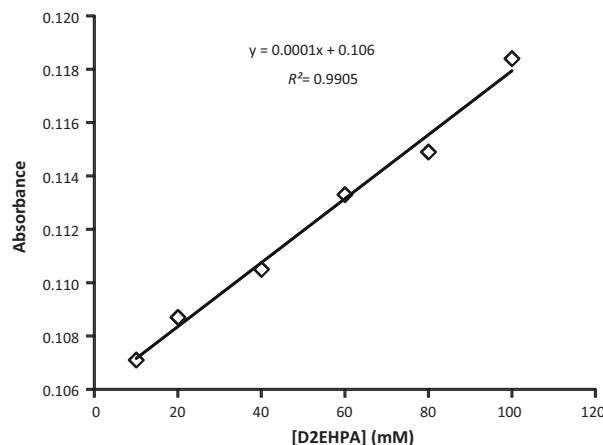
**Table 2**  
ANOVA of the regression model for  $\log D$  (Eq. (7)).

	DF	SS	MS	<i>F</i>	<i>F</i> -cr	<i>P</i>
Regression	2	6.4821	3.2410	1015.15	4.26	0.000
Residual	9	0.0287	0.0032			
Total	11	6.5108				

$SD_{reg} = 0.057$ ;  $R^2 = 0.996$ ;  $R^2(\text{adj}) = 0.995$ ;  $SD_{reg}$ : standard deviation of the regression; DF: degrees of freedom; SS: sum of squares; MS: mean sum of squares; *F*-cr: *F*-critical.



**Fig. 5.** FTIR spectra of P=O bands ( $1235 \text{ cm}^{-1}$ ) for various concentrations of D2EHPA standard solutions.



**Fig. 6.** Calibration curve for various concentrations of D2EHPA standard solutions.

### 3.3.3. Quantitative analysis with FTIR

To verify the results obtained from both the equilibrium slope and numerical analysis, a quantitative analysis with FTIR spectra was performed on the Cu(II)-loaded SOS according to the procedures described by Sainz-Diaz et al. [27]. This analysis was based on the highly polar phosphoryl bond (P=O) of D2EHPA which was susceptible to interact with Cu(II). Owing to the neat absorbance of P=O bands observed at  $1235 \text{ cm}^{-1}$  [37] for different concentrations of D2EHPA standard solutions from 10 to 100 mM (Fig. 5), a good calibration curve was obtained (Fig. 6). This calibration curve was used to determine the concentration of free-D2EHPA ([free-D2EHPA]), i.e. D2EHPA which was not associated with Cu(II), contained in the Cu(II)-loaded SOS. Fig. 7 shows the FTIR spectra of P=O bands ( $1235 \text{ cm}^{-1}$ ) for various [free-D2EHPA] in SOS loaded with different  $[Cu]_{org}$  (0–18 mM (0–1145 mg/L)). It is obvious that the relative intensity of P=O bands decreases with  $[Cu]_{org}$  from 0 to 18 mM. Based on this relative intensity of P=O bands, the [free-D2EHPA] contained in various Cu(II)-loaded SOS were determined. The concentration of Cu-D2EHPA complexes ([Cu-D2EHPA]) was then calculated by subtracting the corresponding [free-D2EHPA] from the total D2EHPA concentration used, i.e. 84.71 mM [14]. By plotting [Cu-D2EHPA] against  $[Cu]_{org}$  (Fig. 8), a slope value of 4.05 is obtained which indicates a constant stoichiometric ratio of D2EHPA

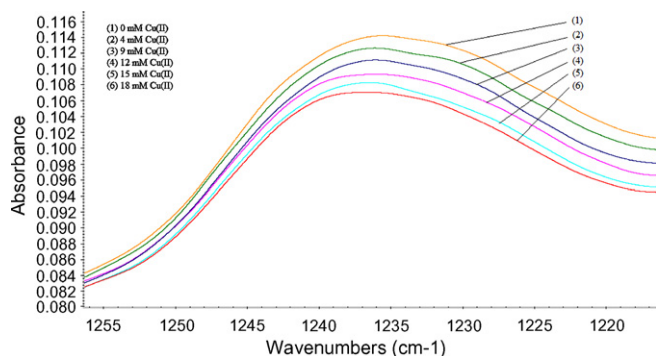


Fig. 7. FTIR spectra of P=O bands ( $1235\text{ cm}^{-1}$ ) for various [free-D2EHPA] in organic phase loaded with different  $[\text{Cu}]_{\text{org}}$ .

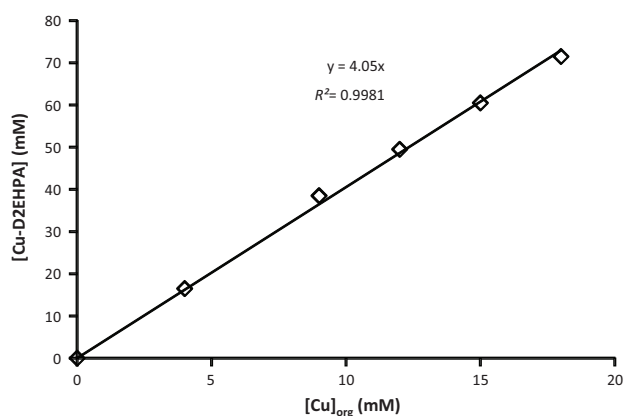


Fig. 8.  $[\text{Cu-D2EHPA}]$  versus  $[\text{Cu}]_{\text{org}}$ .

to Cu(II) of 4:1. This confirms the results obtained from both the equilibrium slope and numerical analyses.

#### 3.4. Determination of structure of Cu(II)–organic complexes

The structure of Cu(II)–organic complexes in SOS was determined from the extraction thermodynamics of Cu(II) studied at different temperatures (298–313 K). The thermodynamic parameters concerned in this context include changes in the standard free energy ( $\Delta G^\circ$ ), standard enthalpy ( $\Delta H^\circ$ ) and standard entropy ( $\Delta S^\circ$ ) due to the transfer of a unit mole of Cu(II) from the aqueous into the organic phases. The  $\Delta G^\circ$  of Cu(II) extraction at different temperatures were calculated from [38]:

$$\Delta G^\circ = -2.303RT \log K_{\text{ex}} \quad (8)$$

where  $R$  is the universal gas constant ( $8.314\text{ J/mol K}$ ),  $T$  is the thermodynamic temperature and  $K_{\text{ex}}$  is the extraction constant. The logarithmic values of  $K_{\text{ex}}$  from Eq. (8) were computed from Eq. (4) and they were associated to  $\Delta H^\circ$  according to the Van't Hoff equation [38]:

$$\log K_{\text{ex}} = \frac{-\Delta H^\circ}{2.303RT} + \text{constant} \quad (9)$$

Table 3

Thermodynamic data obtained from Cu(II) extraction with SOS.

$T$ (K)	$T^{-1}$ ( $\text{K}^{-1}$ )	$\log K_{\text{ex}}$	$\Delta G^\circ$ (kJ/mol)	$\Delta S^\circ$ (kJ/mol K)	$T\Delta S^\circ$ (kJ/mol)
298	0.00336	12.89	−73.55	0.09081	27.06
300	0.00333	12.81	−73.58	0.09030	27.09
302	0.00331	12.78	−73.90	0.09076	27.41
305	0.00328	12.70	−74.17	0.09075	27.68
313	0.00319	12.49	−74.85	0.09061	28.36

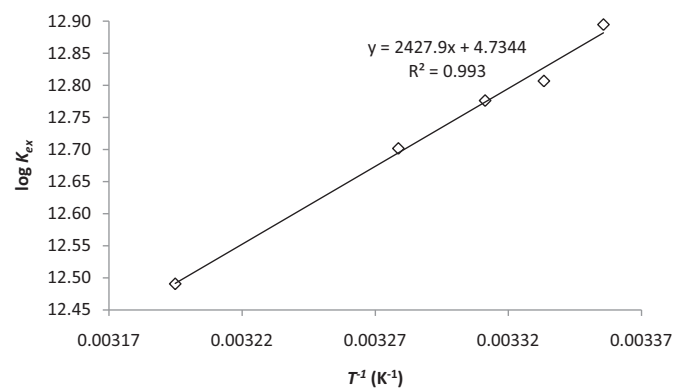


Fig. 9.  $\log K_{\text{ex}}$  versus  $T^{-1}$ .

The corresponding values of  $\Delta S^\circ$  were then calculated by the Gibbs–Helmholtz equation [38]:

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} \quad (10)$$

Finally,  $T\Delta S^\circ$  at various temperatures were evaluated. Table 3 summarizes the thermodynamic data obtained from Cu(II) extraction with SOS. The linearity of Van't Hoff equation (Eq. (9)) was ascertained by plotting  $\log K_{\text{ex}}$  against  $T^{-1}$  (Fig. 9) and the value of  $\Delta H^\circ$  was determined from the slope of this plot as  $-46.49\text{ kJ/mol}$ .

From Table 3 and Fig. 9,  $\log K_{\text{ex}}$ ,  $\Delta S^\circ$  and  $T\Delta S^\circ$  obtained at various temperatures are positive values while  $\Delta G^\circ$  and  $\Delta H^\circ$  are negative values. The negative changes of  $\Delta H^\circ$  and  $\Delta G^\circ$  indicate that the Cu(II) extraction with SOS occurred exothermically and spontaneously in the forward direction. This reaction is termed 'entropy driven' since the favorable entropy overcomes the unfavorable enthalpy ( $T\Delta S^\circ > \Delta H^\circ$ ). The positive  $\Delta S^\circ$  observed in the complexation of Cu(II) with D2EHPA loaded in SOS was related to the extensive disruption of water hydration sphere which released a larger number of water molecules than the number of bound ligands (D2EHPA) [38]. Consequently, the total degrees of freedom of the system was increased by complexation and resulted in a positive value of  $\Delta S^\circ$  [38]. On the other hand, the negative change of  $\Delta H^\circ$  observed was due to the interaction between Cu(II) and D2EHPA molecules [38]. These positive and negative changes of  $\Delta S^\circ$  and  $\Delta H^\circ$  led to the formation of inner sphere structure of Cu(II)–D2EHPA complexes in SOS where Cu(II) and D2EHPA molecules were in direct contact [38]. This result is consistent with the inner sphere structure of various metal–D2EHPA complexes reported in the literatures [17,39].

#### 3.5. Cu(II) stripping from loaded SOS

Fig. 10 shows the effect of various types and concentrations of acids on %S of Cu(II) from SOS loaded with  $494\text{ mg/L}$  ( $7.78\text{ mM}$ ) of Cu(II). Among all acids,  $\text{H}_2\text{SO}_4$  achieves the highest %S throughout the concentrations studied, followed by HCl and  $\text{HNO}_3$ . It reveals that more than 95% of Cu(II) is stripped by  $\text{H}_2\text{SO}_4$  from 1 to 2 M, with the maximum %S of more than 99% observed at 1.5 M. The maximum %S attained by HCl and  $\text{HNO}_3$  are, however, much lower

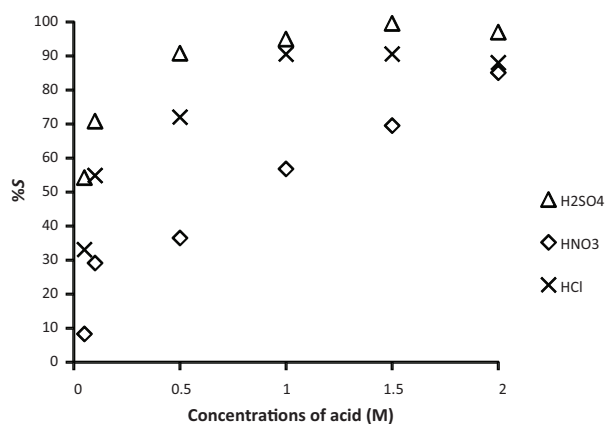


Fig. 10. Effect of various acids on %S of Cu(II) from loaded SOS.

than H<sub>2</sub>SO<sub>4</sub>, where only 90% and 85% of %S are observed at 1.5 M HCl and 2 M HNO<sub>3</sub>, respectively. The greater stripping efficiency of H<sub>2</sub>SO<sub>4</sub> is due to its higher concentration of proton (H<sup>+</sup>) relative to HCl and HNO<sub>3</sub> at the same molarity. This would shift the equilibrium of Eq. (5) more to the left and, thus, enhanced the %S. The effectiveness of dilute H<sub>2</sub>SO<sub>4</sub> (<2 M) in Cu(II) stripping from various D2EHPA-loaded organic solvents has been reported by numerous researchers [40,41]. Stripping of other divalent metal ions using the same acid from various D2EHPA-loaded organic solvents such as Cd(II) [19], Zn(II) [41,42] and Mn(II) [43] has also been reported.

#### 4. Conclusion

In the extraction studies, %E was found not to vary appreciably with initial Cu(II) concentration (25–500 mg/L (0.39–7.88 mM)) but decreased consistently with temperature from 298 to 323 K. The loading capacity of SOS for Cu(II) was found to be 2400 mg/L (37.82 mM) after contacting with fresh aqueous phases containing initial Cu(II) concentration of 500 mg/L (7.88 mM) repeatedly up to 6 contacts. A constant stoichiometry ratio of D2EHPA to Cu(II) of 4:1 in Cu(II)–organic complexes (extracted species) was determined by the equilibrium slope and numerical analyses, and verified by the quantitative analysis with FTIR. The Cu(II)–D2EHPA complexes were found to form inner sphere structures in SOS from the extraction thermodynamic study. In the stripping studies, %S of Cu(II) achieved by various dilute (<2 M) mineral acids (H<sub>2</sub>SO<sub>4</sub>, HCl, HNO<sub>3</sub>) increased with their concentrations. The order of decreasing %S for various types of acids was found to be H<sub>2</sub>SO<sub>4</sub> > HCl > HNO<sub>3</sub> throughout all the concentrations studied, with H<sub>2</sub>SO<sub>4</sub> attaining the highest %S (>99%) at 1.5 M.

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