Selective and Efficient Solvent Extraction of Copper(II) Ions from Chloride Solutions by Oxime Extractants

Z. Kaboli Tanha[a], M. Koorepazan Moftakhar[a], M.R. Yaftian[a],* and N. Noshiranzadeh[b]

[a]Phase Equilibria Research Laboratory, Department of Chemistry, Faculty of Science, University of Zanjan, P.O. Box: 45371-38791, Zanjan, Iran

[b]Organic Chemistry Research Laboratory, Department of Chemistry, Faculty of Science, University of Zanjan, P.O. Box: 45371-38791, Zanjan, Iran

Oxime extractants 3-*tert*-butyl-2-hydroxy-5-methyl benzaldehyde oxime (**HL^1**) and 3-*tert*-butyl-2-hydroxy-5-methoxy benzaldehyde oxime (**HL^2**) were synthesized and characterized by conventional spectroscopic methods. Suitable lipophilic nature of the prepared extractants allowed examining the ability of these molecules for extraction-separation of copper from its mixture with normally associated metal ions by performing competitive extraction experiments of Cu(II), Co(II), Ni(II), Zn(II), Cd(II) and Pb(II) ions from chloride solutions. Both ligands transfer selectively the copper ions into dichloromethane by a cation exchange mechanism. Conventional log-log analysis and isotherm curves showed that Cu(II) ions are extracted as the complexes with 1:2 metal to ligand ratio by both extractants. Verification of the effect of the organic diluent used in the extraction of copper ions by **HL^1** and **HL^2** demonstrated that the extraction efficiency varies as: dichloromethane ~ dichloroethane > toluene > xylene > ethylacetate. Time dependency investigation of the extraction processes revealed that the kinetics of the extraction of copper by **HL^2** is more rapid than that of **HL^1**. The application of the ligands for extraction-separation of copper ions from leach solutions of cobalt and nickel-cadmium filter-cakes of a zinc production plants was evaluated.

Keywords: Copper ions, Solvent extraction, Oxime, Selective separation, Recovery

INTRODUCTION

Copper is one of the first metals ever known and used by humans. It has made crucial contributions to sustaining and developing society since the dawn of civilization. This metal is used in building construction, power generation and transmission, electronic product manufacturing, and the production of industrial machinery and transportation vehicles. Copper wiring and plumbing are integral to the appliances, heating and cooling systems, and telecommunications links used every day in homes and businesses [1]. Beside the economically importance of copper, it is known as an essential trace element found in small amounts in a variety of cells and tissues with the

highest concentrations in the liver [2]. Another vital aspect of this metal is its toxicity to living organisms [3]. Copper is a widespread heavy metal contaminant of the environment [4]. These aspects of the role of copper in the human societies affirm the recovery and removal of copper from water and wastewater solutions are important from both economical and environmental points of view.

Solvent extraction is now widely accepted as a process for the recovery of metal ions from aqueous solutions for hydrometallurgical and environmental applications [5]. It is a powerful technique of preconcentration and separation pertaining to analytical applications [6]. The success in such techniques, with respect to efficiency and selectivity, depends crucially on the extractant used.

Acidic extractants including, as instance, organo-phosphorus compounds [7], pyrazolons [8], β-diketones [9]

_____
*Corresponding author. E-mail: yaftian@znu.ac.ir

and carboxylic acids [10] have been used for extraction-separation of metal ions from various sources. Oximes are a group of efficient acidic extractants which their extracting properties have been vastly investigated in solvent extraction-separation of a variety of metal ions [11-16], particularly towards copper ions [17-20]. The potentials of various types of such extractants with different efficiency and selectivity were the motivations for synthesis of a variety these extractants and their use in metal ion solvent extraction process, from the past years [21-22] to date [23-25]. These variety and continuity in studies concerning on the application of oximes can be attributed to their efficiency, simple method of synthesis from inexpensive materials, and more important the possible switching their extracting properties towards a variety of metal ions by preparing, almost, unlimited types of these molecules bearing common hydroxime ligating functions. Such potentials and highlights provoked us, in continuation of previous studies concerning on the application of oximes in the extraction of metal ions [14,15,26], the preparation of two oxime extractant named 3-*tert*-butyl-2-hydroxy-5-methyl benzaldehyde oxime (**HL**^{1}) and 3-*tert*-butyl-2-hydroxy-5-methoxy benzaldehyde oxime (**HL**^{2}). The chemical structure of **HL**^{1} and **HL**^{2} are shown in Fig. 1. These extractants were used for selective extraction-separation of copper ions from chloride solutions. To the best of our knowledge, these extractants did not use previously in the solvent extraction studies of metal ions.

The stoichiometry of the extracted species was characterized and the effect of parameters influencing the extraction efficiency including aqueous phase pH, type of electrolyte used in the aqueous phase, organic diluent dissolving the extractants and time is investigated and discussed. The applicability of the extractants for recovering copper from a sea water sample and from two leached solutions of cobalt and nickel-cadmium filter-cakes zinc production plants was examined.

EXPERIMENTAL

Reagents and Materials

For synthesis of the extractants 2-*tert*-butyl-4-methyl-phenol and 2-*tert*-butyl-4-methoxyphenol (Fluka, Buchs, Switzerland) were used. Dichloroethane, dichloromethane,
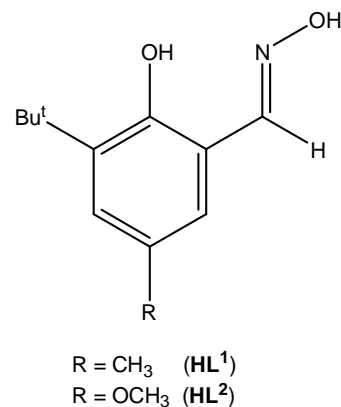

R = CH$_3$ (**HL**^{1})
R = OCH$_3$ (**HL**^{2})

Fig. 1. Chemical structure of 3-*tert*-butyl-2-hydroxy-5-methyl benzaldehyde oxime (**HL**^{1}) and 3-*tert*-butyl-2-hydroxy-5-methoxy benzaldehyde oxime (**HL**^{2}).

ethylacetate, xylene (mixture of isomers) and toluene (Merck, Darmstadt, Germany) were organic diluents examined in solvent extraction experiments. They were washed twice with distilled water, for removing the stabilizers and saturation with water, before being used for extraction experiments. Hydroxylammonium chloride, ethanol, sodium hydroxide, sodium chloride, sodium sulfate, potassium nitrate, hydrochloric acid, nitric acid and sulfuric acid (Merck, Darmstadt, Germany) were used in this study. The stock solutions of metal nitrates (0.01 M) were prepared by dissolving an appropriate amount of corresponding nitrate salts (Merck, Darmstadt, Germany). These solutions were standardized by complex formation titration [27]. Working solutions were prepared by appropriate dilution of the stock solution.

Apparatus

^{1}H NMR measurements were performed on a FT-Bruker (AVC 250 MHz) spectrometer and data were referenced relative to residual protonated solvent (7.26 ppm for CDCl$_3$). A Shimadzu UV-Vis 160 spectrophotometer was used for absorbance measurements. FT-IR spectra were recorded on a Unicam (Matson 1000) spectrometer. A Varian (220AA) flame atomic absorption spectrometer (air/acetylene flame) was used for metal ions determinations. A Metrohm (model 780) digital pH meter equipped with a combined glass electrode was used for the

pH adjustments. Separation of the phases was assisted by a centrifuge Heraeus (model Labofuge 300).

Synthesis of the Studied Oximes

The extractants HL^1 and HL^2 were synthesized based on the known method of Reimer-Tiemann [28] for preparation of corresponding salicylaldehyde derivatives. It is a two steps procedure. At the first step a solution of 2-*tert*-butyl-4-methylphenol (5.000 g, 26.0 mmol) and 2-*tert*-butyl-4-methoxyphenol (5.000 g, 24.0 mmol), for synthesis of HL^1 and HL^2, respectively, in EtOH (15 ml) was refluxed with NaOH (10.000 g, 250 mmol) dissolved in 21 ml of distilled water and CHCl$_3$ (4.2 ml) for 2 h. The productions of this step (aldehydes) were separated by column chromatography and their purities were checked by thin layer chromatography. Yield: 0.700 g (14%) and 0.550 g (11%) for HL^1 and HL^2, respectively. The produced aldehydes were then refluxed with hydroxylammonium chloride (1.000 g, 7.175 mmol) and sodium acetate (2.000 g, 24.3 mmol) in H$_2$O/EtOH (1:1) for 2 h. The final productions were extracted by ethyl acetate (yield: 90% for both oximes). Characterization of HL^1: UV-Vis. (CH$_2$Cl$_2$): 318 nm, FT-IR (KBr): ν_{O-H} = 3330.7 cm^{-1}, ν_{C-H} = 2961.5 cm^{-1}, $\nu_{C=N}$ = 1630.0 cm^{-1}, $\nu_{C=C}$ = 1446.15, 1630.7 cm^{-1}, ν_{C-O} = 1261.5 cm^{-1}. ^{1}H NMR (CDCl$_3$) (Fig. 2a): δ (ppm) 1.50 (s, 9H, CH_3), 6.87, 7.15, (s, 2H, ArH), 8.22 (s, 1H, ArCHNOH), 8.70 (s, 2H, OH). Characterization of HL^2: UV-Vis. (CH$_2$Cl$_2$): 333 nm, FT-IR (KBr): ν_{O-H} = 3384.6 cm^{-1}, ν_{C-H} = 2961.5 cm^{-1}, $\nu_{C=N}$ = 1615.3 cm^{-1}, $\nu_{C=C}$ = 1453.8, 1638 cm^{-1}, ν_{C-O} = 1253.8 cm^{-1}. ^{1}H NMR (CDCl3) (Fig. 2b): δ (ppm) 1.34, (s, 9H, CH$_3$), 6.54-6.95 (s, 2H, ArH), 7.26 (s, 1H, ArCHNOH), 8.20 (s, 2H, OH).

Distribution of the Extractants

Equal volumes of aqueous phase (0.1 M NaCl, adjusted at pH 2-8) and organic phase (5×10^{-3} M HL^1 and HL^2 in CH$_2$Cl$_2$) was stirred for 30 min, at 25 °C. The phases were separated by centrifugation and the percentage of the oxime remained in the organic phase was determined, after appropriate dilution, by UV-Vis. absorption measurements at 318 and 333 nm for HL^1 and HL^2, respectively.

Extraction Experiments

Solvent extraction experiments were carried out in stoppered glass tubes immersed in a thermostated water bath (25.0 ± 0.1 °C) using equal volumes (5 ml) of the aqueous and organic phases. The ionic strength of the aqueous phases was adjusted by sodium chloride at 0.1 M. The pH of the aqueous phases was controlled by addition of hydrochloric acid or sodium hydroxide solutions (0.1 M). It was confirmed that the extraction equilibrium was reached after 20 min under continuous magnetically stirring the solutions. After separation of the phases, the equilibrium pH was determined. The metal concentrations remained in the aqueous phase and that in the organic phase, after stripping with 5 ml nitric acid solution (0.05 M), were determined by a flame (air/acetylene) atomic absorption spectrometry.

RESULTS AND DISCUSSION

Distribution of the Studied Oximes

Lipophilic nature of a ligand plays an important role for choosing it as an extractant in solvent extraction processes. In order to investigate this characteristics of the oximes HL^1 and HL^2, their distribution between aqueous phase (0.1 M NaCl) and dichloromethane as a function of aqueous phase pH (in the range 2-8) has been investigated. These results confirmed that the extractants remain totally in the organic solvent and thus they can be considered suitable for solvent extraction scopes.

Selectivity of the Extractants towards Heavy Metals

Preliminary competitive extraction experiments of Cu(II), Co(II), Ni(II), Zn(II), Cd(II) and Pb(II) ions (1×10^{-4} M, each) from sodium chloride (0.1 M) into dichloromethane solutions of HL^1 and HL^2 (5×10^{-3} M) as a function of aqueous phase pH were performed (Fig. 3). This investigation allows evaluating the selectivity presented by the studied extractants towards the metal ions under experimental conditions. Both of the ligands showed an excellent selectivity towards copper ions. Such selectivity towards copper(II) ions of oxime extractants is well documented [22]. The main difference in the extractive properties of HL^1 and HL^2 is observed towards cobalt ions. At pH 8, about 40% of cobalt ions were extracted by HL^1, whereas HL^2 did not present such ability. The excellent selectivity presented by the prepared ligands towards copper
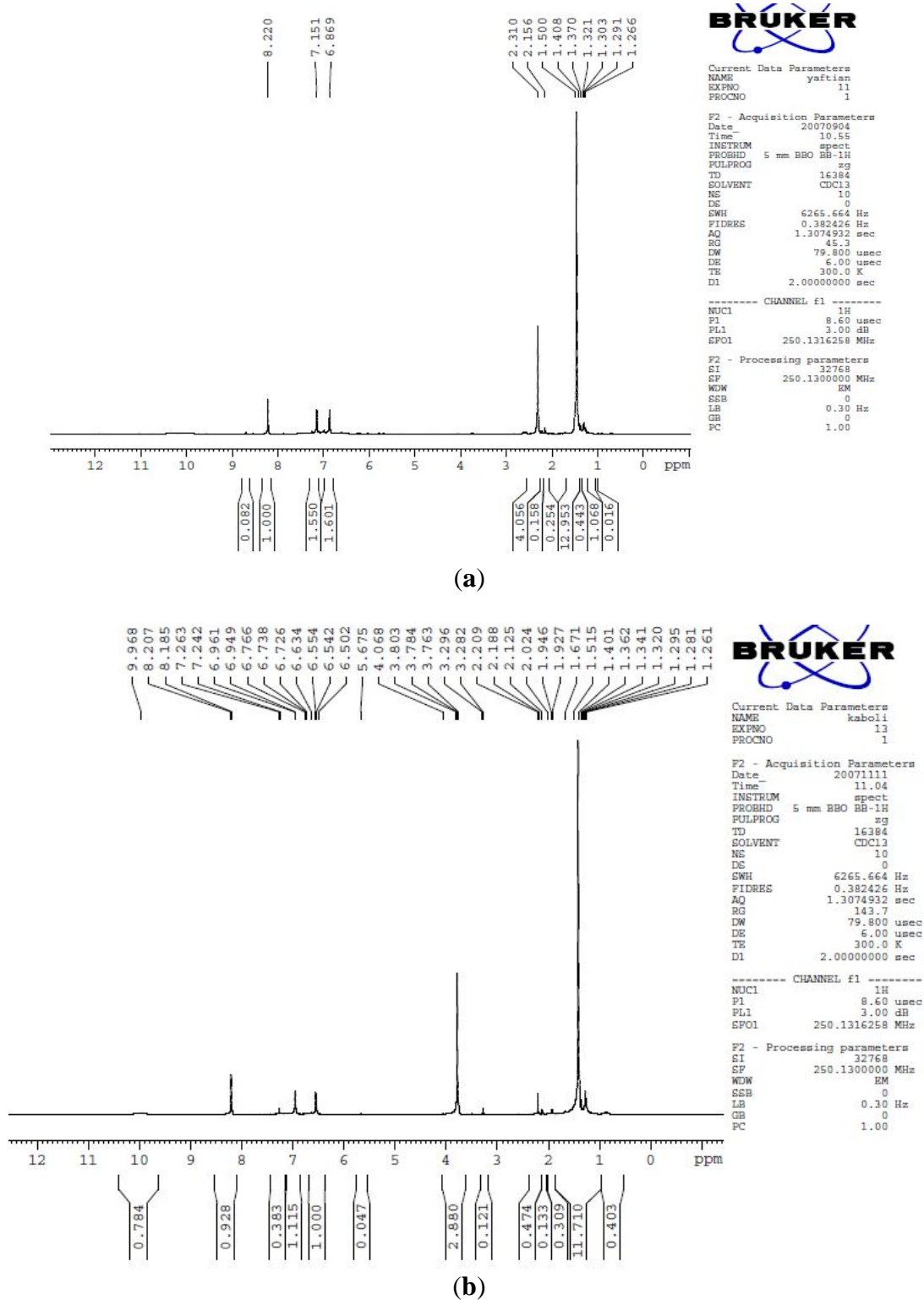
(**a**)

(**b**)

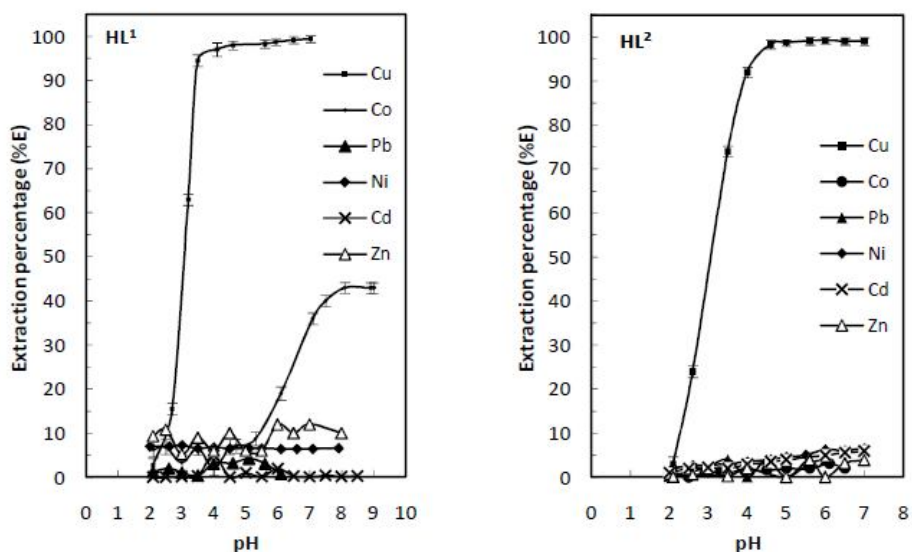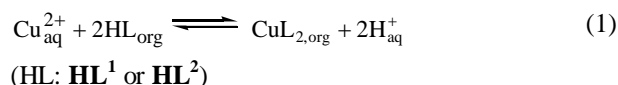**Fig. 2.** ^{1}H NMR spectra of H**L**[1] (a) and H**L**[2] (b).

Fig. 3. Results of the competitive extraction of Cu(II), Co(II), Pb(II), Cd(II), Zn(II) and Ni(II) ions (1×10^{-4} M) from sodium chloride (0.1 M) solutions by **HL^1** and **HL^2** (5×10^{-3} M) as a function of aqueous phase pH, after 20 min magnetically stirring of the phases, at 25 °C.

ions motivated the examination of the efficiency of **HL^1** and **HL^2** as extractant for selective separation of copper ion from normally associated metal ions. It is seen that the extraction efficiency increases with aqueous phase pH. This reveals a cation exchange mechanism (see next section). A quantitative extraction of copper ions was achieved by adjusting the aqueous phase at pH > 4.

Characterization of the Extracted Copper Complexes

Considering the pH dependency of the extraction of copper ions by the studied extractants, the following equilibrium can be assumed for describing the extraction process:

$$Cu^{2+}_{aq} + 2HL_{org} \rightleftharpoons CuL_{2,org} + 2H^+_{aq} \qquad (1)$$

(HL: **HL^1** or **HL^2**)

where the subscripts 'aq' and 'org' denote 'aqueous' and 'organic' phase, respectively, in which the species are present. Corresponding extraction equilibrium constant is defined as:

$$K_{ex} = \frac{[CuL_2]_{org}[H^+]^2_{aq}}{[Cu^{2+}]_{aq}[HL]^2_{org}} \qquad (2)$$

By introducing;

$$D = \frac{[CuL_2]_{org}}{[Cu^{2+}]_{aq}} = \frac{[Cu]_{org}}{[Cu]_{aq}} \qquad (3)$$

The logarithmic expression of Eq. (2) is:

$$logD = logK_{ex} + 2log[HL] + 2pH \qquad (4)$$

The slope of the plots of logD *vs*. pH, at constant ligand concentration, and logD *vs*. log[HL], at constant pH, allows characterizing the stoichiometry of the extracted copper complexes into the organic phase (Fig. 4). The slopes are near to 2 for both plots confirm the stoichiometry suggested by the extraction reaction equilibrium shown by Eq. (1).

The isotherm curves of the extraction of copper ions by the studied extractants **HL^1** and **HL^2** (5×10^{-5} M) were drawn by plotting the variation of $[Cu(II)]_{org}/[HL]_0$ as a function of initial copper concentration ($[Cu(II)]_0$) in the

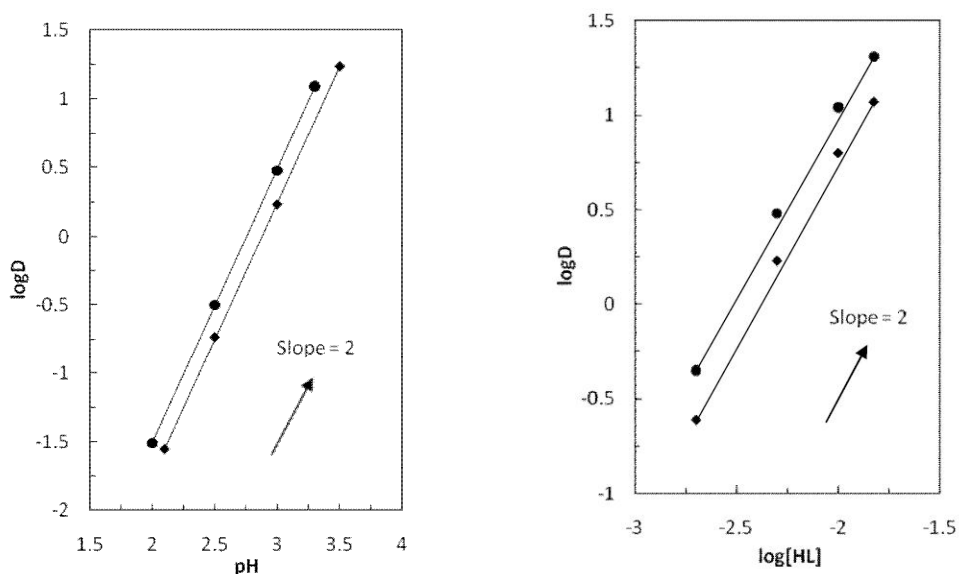**Fig. 4.** Plot of logD *vs.* pH at a constant ligand concentration (5×10^{-3} M), and logD *vs.* log[**HL**], at pH 3, for the solvent extraction of copper ions (initial concentration 1×10^{-4} M) from sodium chloride (0.1 M) solution by **HL**^{1} (♦) and **HL**^{2} (●) in dichloromethane, after 20 min magnetically stirring of the phases, at 25 °C.

aqueous phase, at pH 4. It was seen an increase in $[Cu(II)]_{org}/[HL]_0$ values by increasing the initial copper concentration up to a ratio of about 0.5 for both extractants. This outcome was a further confirmation for the stoichiometry of 1:2 (copper to ligand) for the extracted species.

Effect of Organic Diluents

Selection of an organic diluent is a decisive parameter for designing successful solvent extraction processes. The effect of this parameter was investigated by examination of dichloromethane, dichloroethane, xylene (mixture of isomers), toluene, and ethyl acetate as diluent of **HL**^{1} and **HL**^{2} for the extraction of copper ions from sodium chloride solution (Fig. 5). This investigation showed the extraction efficiency in the studied diluents varies as: dichloromethane ~ dichloroethane > toluene > xylene > ethylacetate. Although these results have been obtained by performing extraction experiments, they cannot be interpreted by considering individually the physicochemical characteristics of the investigated organic solvents such as their polarities

or their dipole moments. This complexity and difficulty for giving a clear reason for the observed order of the extraction efficiencies in the examined organic diluents come from the intervention of various parameters affecting the solute-solvent interactions determining the role of an organic diluent in a solvent extraction process [29].

Time Dependency of the Extraction Process

Kinetics of a solvent extraction process depends on both the kinetics of the chemical reactions occurred in the phases or at the interface, and the rate of diffusion of the species in the interfacial layers [29]. In an extraction process of a metal ion with a chelating reagent a part of the solvation water molecules can be removed from the metal ion and a coordination compound, which is soluble in the organic phase, is formed. Besides, the extractant can dissociate and, together with the extractant-metal complex, can undergo changes in aggregation in the organic phase. Thus, at least one of the chemical steps of the overall reaction mechanism may be slow in comparison with the diffusion rate and therefore the kinetics of the extraction process would
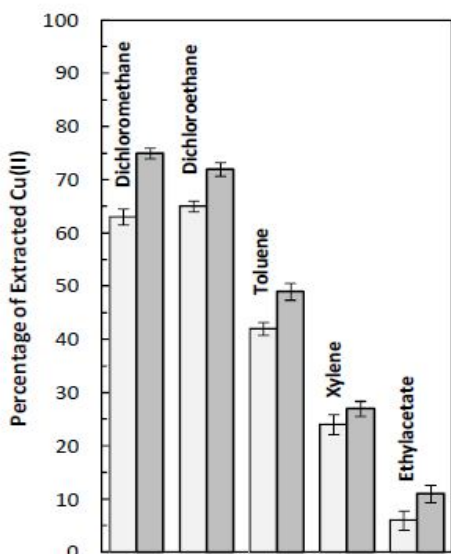
Fig. 5. Effect of diluents on the extraction efficiency of copper ions $(1 \times 10^{-4}$ M) from sodium chloride aqueous phase (0.1 M) by HL^1 (pale gray columns) and HL^2 (dark gray columns) $(5 \times 10^{-3}$ M) at pH 3. Contact time 20 min and temperature 25 °C.
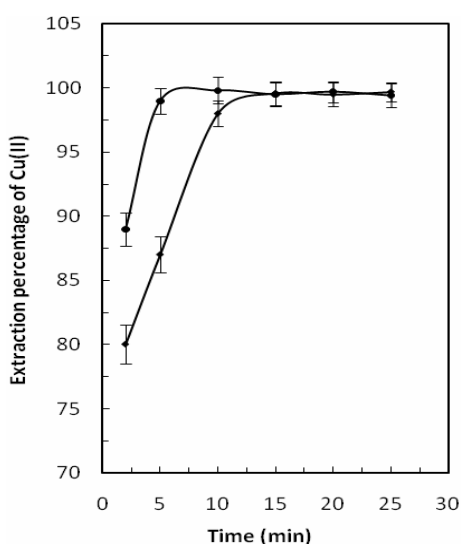

Fig. 6. Time dependency of the extraction of copper ions (initial concentration 1×10^{-4} M) from sodium chloride (0.1 M) aqueous solution adjusted at pH 4, into 5×10^{-3} M of solution of HL^1 (◆) and HL^2 (●) in dichloromethane, at 25 °C.

depend on the chemical reaction rate. Previous studies on the solvent extraction of copper ions by chelating reagents allow considering the interfacial reactions of copper ions by the extractants are slow with respect to the diffusion rate [30-32]. Although the kinetic investigation of the solvent extraction of copper with the studied extractants was not the aim of this study, the verification of the time dependency of the extraction processes was performed for a comparative investigation of the kinetics of the interfacial extraction reaction of copper ions by HL^1 and HL^2 extractants.

Depending on the kinetics of the interfacial reactions the extraction process may depends on the contact time of the aqueous and organic phases. In order to determine appropriate time for the extraction experiments (equilibrium time), the extraction of copper ions from aqueous phase including sodium chloride (0.1 M), adjusted at pH 4, into a dichloromethane solution of the studied extractants as a function of time was investigated (Fig. 6). It is found that the kinetics of the extraction of copper by HL^2 is more rapid than that of HL^1. In fact, the equilibrium conditions are obtained after 10 and 5 min magnetically stirring of the aqueous phase with the organic phases containing HL^1 and HL^2, respectively. However, the experiments were followed with a contact time of 20 min for ensuring that the equilibrium condition is attained.

Effect of Electrolyte on the Extraction Processes

A probable influence of the electrolyte used in the aqueous phase was assessed by extraction of copper ions (1 $\times 10^{-4}$ M) from the aqueous phase containing 0.1-0.5 M of NaCl, NaNO$_3$, Na$_2$SO$_4$ and KNO$_3$ adjusted at pH 4, into dichloromethane solution of the studied oximes $(5 \times 10^{-3}$ M). The results showed that the extraction efficiency is not considerably influenced by the type of electrolyte in the aqueous phase. An interpretation for these observations can be given by the lack of participation of chloride, nitrate and sulfate anions in the coordination sphere of the extracted metal ions, the inability of the studied ligands to complex sodium and potassium ions and thus the absence of competition between copper ions and these cations, and finally the relatively constant activity coefficients of the species involving in the extraction reaction in the studied ionic strength range.

Stripping of the Extracted Copper Complexes from the Organic Phase

The back-extraction of the extracted metal ions from the organic phase is important in solvent extraction procedures. In fact this step in the solvent extraction processes is crucial for lowering the organic solvents used in such processes on one hand, and the limitation of the metal analysis in the organic phase, on the other hand. As the extraction processes in the present work were based on a cation exchange mechanism and could be controlled by variation the aqueous phase pH, it was suggested that the stripping process could be taken place by acid solutions as strippant.

In order to select a suitable stripping reagent, the extracted copper ions (100%) under optimized conditions (aqueous phase: initial concentration of copper ions 1×10^{-4} M, NaCl 0.1 M, pH 4; organic phase: **HL**^{1} and **HL**^{2} 5×10^{-3} M in dichloromethane; contact time 20 min; temperature 25 °C), was stripped by using 5 ml of hydrochloric, nitric and sulfuric acids (0.03 M). The highest amount of stripped copper ions from the loaded organic phase was achieved by sulfuric and nitric acid solutions, with respect to that of hydrochloric acid solution (Table 1).

The effect of nitric acid concentration was examined by using different solutions in the range of 0.01-0.1 M. It is found that 5 ml solution of 0.05 M nitric acid can strip quantitatively the loaded organic phase (Table 2).

Applications

The applicability of the studied extractants for the recovery of copper ions was tested by extraction of these ions from leach solutions of two types of solutions obtained by leaching the residues of zinc production plants (cobalt and nickel-cadmium filter-cakes), and a spiked sea water sample solution.

The filter cakes (2 g each) were dissolved in 10 ml of concentrated hydrochloric acid. The solutions were evaporated in order to for diminishing the acid contents. Then, distilled water (150 ml) was added to the samples. After 24 h, the solution was passed through a filter paper, and the solution was diluted to about 200 ml with distilled water. After adjusting its pH to 5 by using sodium hydroxide solution (0.1 M), its final volume was increased to 200 ml. Analysis of the metal contains in the samples are given in Table 3. A volume of 25 ml of the prepared solutions was in contact with 25 ml of organic phase (1×10^{-2} M **HL**^{1} or **HL**^{2} in dichloromethane). These phases were mechanically stirred for 20 min. The phases were then separated and centrifuged. After stripping the organic phases with 0.05 M nitric acid, the metal ion contents were analyzed with flame atomic absorption spectrometry. The results based on triplicate experiments in Table 4, confirm the ability of the studied ligands for the selective extraction of copper ions in such samples.

The sea water sample was taken from Caspian sea (Hasan Rood area, Guilan province-Iran). The sample was passed through a filter paper, and then copper ion (1×10^{-4} - 1×10^{-3} M) was injected to the solution. The pH of this solution was adjusted to 5. The extraction procedure was

Table 1. Application of Different Acid Solutions as Stripping Agent for Copper Ions from Loaded Organic Phase[a]

Acid	Cu(II)% stripped from organic phase containing[b]	
	HL^1	**HL**^{2}
HCl	77.4	72.6
HNO$_3$	95.3	92.8
H$_2$SO$_4$	94.7	90.2

[a]Extraction: 5 ml aqueous phase (1×10^{-4} M Cu(II), 0.1 M NaCl, pH 4); 5 ml organic phase (5×10^{-3} M **HL**^{1} and **HL**^{2} in dichloromethane); 30 min stirring the phases. Stripping: 5 ml loaded organic phase, 5 ml acid solutions (0.03 M). [b]Standard deviation $<\pm1.1\%$.

Table 2. Application of Different Concentration of Nitric Acid Solutions as Stripping Agent for Copper Ions from Loaded Organic Phase[a]

Concentration (M)	Cu(II)% stripped from organic phase[b]	
	HL^1	**HL^2**
0.01	69.8	71.6
0.03	95.3	92.8
0.05	98.9	100.0
0.07	99.5	100.0
0.10	100.0	98.9

[a]Experimental conditions: see the footnote of Table 1. [b]Standard deviation <±1.3%.

Table 3. Concentration of the Main Metals in Leached Solutions of Filter-cakes Samples of Zinc Production Plants, their Extracted Concentration and the Extraction Percentage by the Studied Extractants

Metal ion	Concentration in solution of					
	Leached Co filter-cake (M)	Extracted metal ion		Leached Ni-Cd filter-cake (M)	Extracted metal ion	
		Concentration (M)	E (%)[a]		Concentration (M)	E (%)[a]
Cu(II)	4.72×10^{-5}	4.40×10^{-5}	95.2	3.31×10^{-4}	3.03×10^{-4}	91.7
Mn(II)	1.62×10^{-2}	1.12×10^{-4}	6.9	3.46×10^{-4}	n. d.[b]	-
Fe(II)	4.66×10^{-5}	n. d.[b]	-	1.43×10^{-5}	n. d.[b]	-
Co(II)	1.78×10^{-3}	0.43×10^{-4}	2.4	5.10×10^{-5}	n. d.[b]	-
Ni(II)	1.19×10^{-4}	n. d.[b]	-	5.80×10^{-3}	0.63×10^{-4}	1.1
Zn(II)	1.68×10^{-2}	0.82×10^{-3}	4.9	3.48×10^{-2}	2.73×10^{-4}	0.8
Cd(II)	1.96×10^{-4}	n. d.[b]	-	1.10×10^{-2}	3.05×10^{-4}	2.8
Pb(II)	2.22×10^{-4}	n. d.[b]	-	3.47×10^{-4}	n. d.[b]	-

[a]Standard deviation < ±1.5%. [b]n. d. means not detectable.

Table 4. Results of the Recovery of the Spiked Copper Ions from Sea Water Samples

Spiked Cu(II) concentration (M)	Extracted Cu(II) by **HL^1**		Extracted Cu(II) by **HL^2**	
	Concentration (M)	E (%)[a]	Concentration (M)	E (%)[a]
1×10^{-4}	9.79×10^{-5}	97.9	9.86×10^{-5}	98.6
5×10^{-4}	4.91×10^{-4}	98.2	4.87×10^{-4}	97.4
1×10^{-3}	9.84×10^{-4}	98.4	9.92×10^{-4}	99.2

[a]Standard deviation <±1.8%.

run by contacting the aqueous phase with dichloromethane solution of **HL^1** and **HL^2** (0.01 M), for 20 min. The phases were then separated and the organic phase was stripped by 5 ml nitric acid 0.05 M. The copper content of the stripping solution was determined by FAAS. The results confirm the suitability of the proposed procedures for recovering the copper ions from a complex matrix as sea water.

CONCLUSIONS

The extractive properties of 3-*tert*-butyl-2-hydroxy-5-methyl benzaldehyde oxime (**HL^1**) and 3-*tert*-butyl-2-hydroxy-5-methoxy benzaldehyde oxime (**HL^2**) towards copper(II) ions were investigated. The present study is a further confirmation that oximes are a kind of valuable acidic extractants for the extraction of copper ions. The analysis of the extraction data reveals a cation exchange mechanism for the extraction process with a 1:2 (metal to ligand) stoichiometry for the extracted complexes by both studied oxime. The studied extractants were capable to separate copper ions from its mixtures with other normally associated metal ions. These molecules can be used for selective extraction-separation of copper ions from complex real samples.

REFRENCES

[1]   Ullman's Encyclopedia of Industrial Chemistry, Wiley-VCH, Weinheim, 2003.

[2]   J.R. Turnlund, Am. J. Clin. Nutr. 67 (1998) 960S.

[3]   L.M. Gaetke, C.K. Chow, Toxicology 189 (2003) 147.

[4]   A. Zümriye, İ.A. İşoğlu, Process Biochem. 40 (2005) 3031.

[5]   M. Aguilar, J.L. Cortina (Eds.), Solvent Extraction and Liquid Membranes, CRC Press, New York, 2008.

[6]   Z. Marczenko, M. Balcerzak, Separation, Preconcentration and Spectrophotometry in Inorganic Analysis, Elsevier, Amsterdam, 2000.

[7]   S.J. Yoon, J.G. Lee, H. Tajima, A. Yamasaki, F. Kiyono, T. Nakazato, H. Tao, J. Indust. Eng. Chem. 16 (2010) 350.

[8]   R. Meera, M.L.P. Reddy, Solvent Extr. Ion Exch. 22 (2004) 761.

[9]   W. Fu, Q. Chen, Q. Wu, H. Hu, L. Bai, Hydrometallurgy 100 (2010) 116.

[10] C.Y. Cheng, Hydrometallurgy 84 (2006) 109.

[11] A. Parus, K. Wieszczyck, A. Olszanowski, Sep. Sci. Technol. 46 (2010) 87.

[12] C.Y. Cheng, Hydrometallurgy 84 (2006) 117.

[13] A. Dakshinamoorthy, P.S. Dhamia, P.W. Naik, N.L. Dudwadkar, S.K. Munshi, P.K. Dey, V. Venugopal, Desalination 232 (2008) 26.

[14] P. Rafighi, M.R. Yaftian, N. Noshiranzadeh, Sep. Purif. Technol. 75 (2010) 32.

[15] A. Parus, K. Wieszczycka, A. Olszanowski, Hydrometallurgy 105 (2011) 284.

[16] N. Sehati, Z. Shiri-Yekta, A.A. Zamani, M.R. Yaftian, N. Noshiranzadeh, Sep. Sci. Technol. 47 (2012) 670.

[17] B. Sengupta, R. Sengupta, N. Subrahmanyam, B. Sengupta, R. Sengupta, N. Subrahmanyam, Hydrometallurgy 81 (2006) 67.

[18] K. Klonowska-Wieszczycka, A. Olszanowski, A. Parus, B. Zydorczak, Solvent Extr. Ion Exch. 27 (2009) 50.

[19] K. Wieszczycka, M. Kaczerewska, M. Krupa, A. Parus, A. Olszanowski, Sep. Purif. Technol. 95 (2012) 157.

[20] K. Wieszczycka, M. Krupa, A. Olszanowski, Sep. Sci. Technol. 47 (2012) 1278.

[21] G.A. Kordosky, K.D. MacKay, R.B. Sudderth, J.M. Sierakoski, Liquid-liquid Recovery of Copper Values Using Alpha-hydroxy Oximes, US Patent US4507268 A, 1965.

[22] J. Szymanowski, Hydroximes and Copper Hydrometallurgy, CRC, Boca Raton, 1993.

[23] M. Krupa, K. Wieszczycka, A. Wojciechowska, A. Olszanowski, Sep. Sci. Technol. 50 (2014) 654.

[24] M. Virnig, J. Bender, N.C. Emmerich, Methods of Metal Extraction Using Oximes, US Patent US8945490 B2, 2015.

[25] S. Pradhan, S. Mishra, Metal. Res. Technol. 112 (2015) 202.

[26] M. Hami Dindar, S.A.M. Fathi, M.R. Yaftian, N. Noushiranzadeh, J. Hazard. Mater. 179 (2010) 289.

[27] J.A. Dean, Analytical Chemistry Handbook,

McGraw-Hill, New York, 1995.

[28]   H. Wynberg, Chem. Rev. 60 (1960) 169.

[29]   J. Rydberg, C. Musikas, G.R. Choppin, Principles and Practice of Solvent Extraction, Marcel Dekker, New York, 1992.

[30]   D.S. Flett, Acc. Chem. Res. 10 (1977) 99.

[31]   H.-Y. Lee, S.-K. Ihm, D.-H. Lee, Solvent Extr. Ion Exch. 5 (1987) 55.

[32]   R.-S. Juang, I.-P. Huang, Sep. Sci. Technol. 35 (2000) 869.