Studies on the Extraction of Copper (II) by Pyrazoloquinazolinone Derivatives from Aqueous Solutions

Khawassek Y.M., Cheira M.F. * and Mahmoud G.M.
Nuclear Materials Authority, P.O. Box 530, El-Maadi, Cairo, EGYPT

Abstract

Pyrazoloquinazolinone type extractants are effective reagents for extraction of Cu (II) ions from aqueous solutions. In this respect, extraction of copper (II) ions with 2-amino-3-(4- (X) phenyl azo)-8,9-dihydro-8,8-dimethyl-7H-pyrazolo [1,5-a] quinazolin-6- one (XPQ), (X= Br, Cl, OCH$_3$ or CH$_3$) were studied. The optimum studied extractants concentrations were found at 0.04% BrPQ, 0.045% ClPQ, 0.05% OCH$_3$PQ and 0.055% CH$_3$PQ in carbon tetrachloride as a diluent. Highly extraction efficiency were found at pH 2, 1/1 O/A ratio and 5 min. shaking time at room temperature. BrPQ was selected as an appropriate structure of reagents to extract Cu (II) species. The proposed method was used in extraction of copper (II) ions in some standard reference geologic samples.

Keywords*: Copper (II) ions, solvent extraction, separation, determination.*

Introduction

Copper is the 25th most abundant element in the earth crust. It is found in earth mainly in the form of chalcopyrite (CuFeS$_2$) associated with other sulphides, such as pyrite (FeS). Copper was used as thermal conductors, electrical conductors, building material and an important constituent of various metal alloys. In view of that it was necessary to monitoring the copper in different field areas, also used in the manufacture of water pipes. Moreover, its alloys were used in jewellery and for coins[1]. In view of lack of mineral resources, efforts are increasingly being made to explore alternate resources. It can be extracted as a byproduct from various sources.

In recent years, extraction, separation and recovery of Cu (II) ions by solvent extractions had been carried out. Two different series of N-donor pyrazole ligands had used in liquid-liquid extraction of Cu (II) ions from aqueous solution using methylene chloride as a diluent[2]. Pyrazole derivatives were currently the subjects of several studies in extraction of copper (II) ions[3-7]. Various reagents were used for extraction of copper ions in environmental and geologic samples such as LIX 860[8], LIX 841[9], LIX 54[10], N,N-bis (2-hydroxy-5-bromobenzyl)-1,2-diamine propane[11], iso nitroso actophenone-2-amino benzoyl hydrazone[12]. Copper (II) ions were also extracted from nitric acid solution with 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (HPMBP) as a cation carrier by liquid membrane emulsion (LME)[13]. Equilibrium, structure and hydrolytic activity for complexes of copper (II), zinc(II) and nickel (II) with imidazole containing reagent and inositol derivatives were used 1-octylimidazole and 1-octyl-2-methylimidazole for extraction of Zn (II), Ni (II) in different organic solvents[14]. A new imidazole reagent, benzo[15-crown-5]-1H-imidazole [4,5f] [1,10] phenanthroline was synthesized as well as prepared complexes

Co (II), Ni (II), Cu (II) and the complex structure found to be (2:1)[15].

The present work aimed to study of Cu (II) ions extraction efficiency from aqueous solution using new synthesized pyrazoloquinazolinone derivatives. The factors controlling the extraction process were determined and then applied upon geologic samples.

Material and Methods

Instruments: Spectrophotometer (Metertech Inc. SP-8001) was used for copper control analysis. The concentration of Cu (II) ions in the aqueous or stripping solutions was spectrophotometrically analyzed using carprizone and ammonium citrate[16]. The synthesized heterocyclic compounds (extractants), the organometallic complex after extraction, as well as the extractant after stripping were analyzed using a Shimadzu FTIR8101 PC infrared spectrophotometer.

All the chemicals were of analytical grade and the double distilled water was used in all experiments.

Synthesis of Extractants: Four multidentate compounds namely 2-amino-3-(4- (X) phenyl azo)-8,9-dihydro-8,8-dimethyl-7H-pyrazolo [1,5-a] quinazolin-6- one (XPQ), (X= Br, Cl, OCH$_3$ or CH$_3$) were prepared. For this purpose, one ß-diketone namely; 2- ((dimethyl amino) methylene)-5,5-dimethyl cyclohexane-1,3-dione (enamindione) was selected as starting materials. The formation of the four compounds was assumed to take place via an initial Michael addition of the exocyclic amino group in the 4-aryl azo-3,5 diaminopyrazole derivatives to the α,β-unsaturated in the enamindione. It yielded the corresponding acyclic non-isolable intermediates which undergo

cyclization and aromatization to form the four products BrPQ, ClPQ, OCH$_3$PQ and CH$_3$PQ[17].

Extraction Procedure: The prepared standard solution of Cu (II) ions was subjected to several solvent extraction experiments by shaking with the synthesized extractants in carbon tetrachloride. The loaded organic solvents were then contacted with different acidic and alkaline stripping solutions to back extract the copper species from the solvents under the relevant conditions. Factors affecting the extraction and stripping efficiencies of Cu (II) ions with the prepared extractants were investigated. It involved diluents type, aqueous solution pH, solvent concentration, contact time, temperature.

Results and Discussion

Effect of Diluents Type: Different organic diluents such as toluene, carbon tetrachloride, benzene, chloroform, methylene chloride, cyclohexane, n-hexane and xylene were employed for the extraction of Cu (II) ions. The other factors were kept constant at 0.05% extractants concentrations, (1/1) O/A ratio and 5 min. shaking time. The highest extraction efficiency of Cu (II) ions was obtained using carbon tetrachloride and methylene chloride diluents due to their polarities of bonds (table 1). In this study, carbon tetrachloride was chosen as a diluent because of a better phase separation. The four bonds of carbon tetrachloride (CCl$_4$) are polarity, but the molecule is non-polar because the bond polarity is canceled by the symmetric tetrahedral shape. When other atoms substituted some of the Cl atoms, the symmetry is broken and the molecule becomes polar as methylene chloride (CH$_2$Cl$_2$)[18].

Effect of pH: The effect of pH was studied in the range of 1 – 13 while the other experimental factors were fixed at 0.05% extractants concentrations/CCl$_4$, (1/1) O/A ratio and 5 min. shaking time. The results shown in figure 1 indicate that maximum extraction efficiency of Cu (II) ions from its aqueous solutions attained at pH 2 to all of the workable extractants.

Effect of Extractant Concentration: Extraction of 5 μg/ml Cu (II) ions was also investigated with varying the concentration of the synthesized BrPQ, ClPQ, OCH$_3$PQ and CH$_3$PQ/CCl$_4$ within the range of 0.005 to 0.2%. The other parameters pH 2, (1/1) O/A ratio for 5 min. shaking time were kept constant.

The obtained results illustrated in figure (2) reveal that, maximum extraction efficiencies of Cu (II) ions occurred with BrPQ and ClPQ extractants whereas the percentage extraction efficiency reached 99.0 and 96.5% at 0.04 and 0.045% concentrations, respectively. On the contrary, 90.4 and 85.6% Cu extraction efficiencies occurred at 0.05 and 0.055% concentrations of OCH$_3$PQ and CH$_3$PQ extractants, respectively.

Effect of Organic/Aqueous Ratio: This factor was studied in the range from O/A = 4/1 to 1/4 (figure 3). Contacting equal volumes of the organic and aqueous phases for 5 min. were led

to 99.2, 96.5, 90.3 and 85.5% Cu extractions efficiencies for the workable extractants BrPQ, ClPQ, OCH$_3$PQ and CH$_3$PQ respectively. The ratio of 1:1 was applied for an efficient extraction of Cu (II) ions from their solutions.

Effect of Contact Time: To study this effect, equal volumes from copper solution and the studied extractants were shaken from 1 to 30 min. It was found that loading of Cu (II) ions occurred within few minutes. As can be seen in figure 4 the extraction efficiencies of Cu (II) ions gradually increased by increasing the contact time till 5 min., which reached constant values of 98.9, 96.2, 90.15 and 85.4% for BrPQ, ClPQ, OCH$_3$PQ and CH$_3$PQ reagents respectively. As a result, the optimum shaking time for maximum extraction efficiencies of Cu (II) ions was 5 minutes.

Effect of Temperature: The extraction of Cu (II) ions was studied at different temperatures ranged from 30 to 60 ℃ upon the studied extractants at pH 2, (1/1) O/A ratio for 5 min. shaking time. It was observed that increasing the temperature up to 60 ℃ did not affect the extraction efficiency of Cu (II) ions (table 2). This behavior may probably attributed to strong metal-extractant complexes which remain stable even at high temperature. Hence all extractions procedures carried out at room temperature.

The ability of BrPQ to extract Cu (II) ions was found to be markedly higher than the other compounds ClPQ, OCH$_3$PQ and CH$_3$PQ because the atomic radius of Br ion is larger than of the other groups.

Loading Capacity of Extractants: The maximum loading capacity of organic phase containing extractants was determined by contacting the four extractants with fresh aqueous 100 μg/ml copper (II) ions at pH 2, (1/1) O/A ratio, 5 min. shaking time at room temperature. When both phases were separated, Cu (II) ions concentration was determined and the same organic phase reused for subsequent extraction with the same fresh aqueous solution. After successive contacts between organic and aqueous phases, the organic phase was become saturated with copper (II) ions.

The obtained results showed that a maximum concentration of 370, 310, 274 and 230 μg/ml of Cu (II) ions using 0.04% BrPQ, 0.045% ClPQ, 0.05% OCH$_3$PQ and 0.055% CH$_3$PQ/CCl$_4$ could be loaded after four stages (figure 5).

Effect of Foreign Ions on Cu Extraction: The effect of associated ions that may present in matrix solution and may cause interfering effect during the extraction of Cu (II) ions was studied (table 3). It was obvious that, more than 10 μg/ml of foreign ions, Cu (II) ions can be extracted in the presence of the studied ions by using the four extractants. Above this concentration, some cations such as Fe^{3+}, Ti^{4+}, Ni^{2+}, Co^{2+}, V^{6+}, Th^{4+} and U^{6+} impart little interfering effect.

Stripping Experiments: Series of experiments were carried out to back extract Cu species into the aqueous phase from the loaded organic phases. Some relevant factors were studied to find out the stripping characteristics on the extracted copper (II) ions.

Determination of Proper Stripping Agent: Different concentration of sulphuric acid and alkalis were shaken with the loaded organic solvents at an (O/A) ratio 1/1 for 5 minutes to obtain the more concentrated strip solutions (table 4). The results reveal that, potassium hydroxide exhibited the highest stripping efficiency of copper (II) ions from the four loaded extractants.

Effect of Potassium Hydroxide Concentration: Different concentration of potassium hydroxide ranged from 5.0 to 15.0% was contacted with equal volumes of the working loaded solvents BrPQ, ClPQ, OCH$_3$PQ and CH$_3$PQ for 5 minutes. Stripping efficiency of copper (II) ions gradually increased until attaining maximum values of 99.4, 92.9, 88.5 and 83.7% for BrPQ, ClPQ, OCH$_3$PQ and CH$_3$PQ extractants, respectively, using 10% KOH stripping agent concentration (table 5).

Effect of Contact Time: Potassium hydroxide (10%) was used to strip Cu (II) ions from the working loaded solvents by shaking equal volumes of both phases for different intervals time ranging 1 to 20 minutes. Maximum stripping efficiency was obtained at 3 minutes contact time (table 6).

Effect of O/A Ratio: To study this factor, the O/A ratio was varied from 4/1 to 1/4 while the other factors of 10 % potassium hydroxide and 3 min. shaking time were kept constants. The following stripping efficiencies (99.8, 94.0, 90 and 87.5%) were attained at O/A ratio 1/1 for BrPQ, ClPQ, OCH$_3$PQ and CH$_3$PQ extractants, respectively. The results showed that, the best stripping efficiency of Cu (II) ions was at O/A ratios 1/1 (table 7).

IR Analysis: The free ligands BrPQ, ClPQ, OCH$_3$PQ and CH$_3$PQ/CCl$_4$, besides the loaded and the back-washed extractants were analyzed using infrared spectroscopy to compare the differences in their peaks positions and intensities (table 8).

The sharp N=N peaks present in BrPQ, ClPQ, OCH$_3$PQ and CH$_3$PQ disappeared after extraction but reappeared after stripping, which may be due to the formation of the metal complex via azo group. IR analysis revealed that the ketone groups present in BrPQ, ClPQ, OCH$_3$PQ and CH$_3$PQ almost kept its positions after extraction and stripping which indicates that it was not involved in the complex formation.

Extraction and determination of Cu (II) in some standard reference samples: The proposed methods using BrPQ, ClPQ, OCH$_3$PQ and CH$_3$PQ were used for the separation and determination of Cu (II) ions in some standard reference geologic (JB-2 and JB-3) samples[19]. The results given in table (9) reveal that, the concentration of copper (II) ions was approximately equals its reference value, (RSD = 0.64 and 0.79%). The results indicate that the proposed method can be reliably used for the extraction of Cu (II) ions efficiently. The relative standard deviation is widely used in analytical chemistry to express the precision and repeatability of an assay.

Table-1
Effect of diluents on the extraction of Cu(II) ions

Diluents type	z			
	BrPQ	**ClPQ**	**OCH$_3$PQ**	**CH$_3$PQ**
Toluene	40.21	38.54	32.25	23.39
Carbon tetrachloride	96.34	94.32	90.45	85.21
Benzene	30.26	26.43	20.12	15.81
Chloroform	23.52	20.49	16.56	10.45
Methylene chloride	95.34	93.76	86.94	83.23
Cyclohexane	29.34	26.54	21.03	18.67
n-Hexane	27.42	22.26	17.98	11.56
Xylene	29.12	26.93	20.33	14.67

Results are mean of triplicate value, Cu (II) = 5 µg/ml and phase ratio (A/O)=1/1,shaking time= 5 min.

Table-2
Effect of temperature on extraction efficiency of Cu(II)

Temp. ºC	Extraction efficiency %			
	BrPQ	**ClPQ**	**OCH$_3$PQ**	**CH$_3$PQ**
30	99.00	96.49	90.35	85.67
40	98.81	96.41	90.01	85.43
50	98.62	96.25	90.00	85.68
60	98.75	96.34	90.31	85.54

Results are mean of triplicate value, Cu (II) = 5 µg/ml and phase ratio (A/O)=1/1, shaking time = 5 min.

Table-3
Effect of interfering ions on the extraction efficiency of 5 μg/ml Cu (II) ions

Ions (μg/ml)	Extraction efficiency, %											
	BrPQ			ClPQ			OCH$_3$PQ			CH$_3$PQ		
	10 μg/ml	50 μg/ml	100 μg/ml	10 μg/ml	50 μg/ml	100 μg/ml	10 μg/ml	50 μg/ml	100 μg/ml	10 μg/ml	50 μg/ml	100 μg/ml
Si^{4+}	99.0	99.0	99.0	99.0	99.0	99.0	99.1	99.0	99.0	99.0	99.0	99.0
Ca^{2+}	99.1	99.0	99.0	99.0	99.0	99.0	99.0	99.0	99.0	99.0	99.0	99.0
Mg^{2+}	99.1	98.0	98.0	99.1	98.3	98.0	99.1	98.2	98.0	99.1	98.2	98.0
Na$^+$	99.2	99.0	99.0	99.1	98.6	98.1	99.2	98.3	99.1	99.7	99.1	99.0
K$^+$	99.8	98.9	98.0	99.7	99.2	99.0	99.1	98.2	98.0	99.5	99.0	98.1
P^{5+}	99.7	99.3	99.0	99.2	99.0	98.1	99.4	99.0	98.3	99.2	99.0	98.2
Mn^{2+}	99.7	99.1	99.0	99.3	98.9	98.1	99.1	98.5	98.1	99.3	98.8	98.3
NH$_4^+$	99.6	99.3	99.0	99.2	99.0	98.5	99.2	99.0	98.3	99.7	99.0	98.4
Al^{3+}	99.3	98.8	98.1	99.1	98.7	98.4	99.1	98.9	98.5	99.1	98.9	98.3
Fe^{3+}	99.6	93.2	83.6	99.7	91.1	81.4	99.6	90.6	80.3	99.4	90.2	80.1
Ti^{4+}	99.9	94.3	87.4	99.2	95.4	88.4	99.9	95.8	88.3	99.9	95.2	88.4
Ba^{2+}	99.0	98.3	98.0	99.2	99.0	98.3	99.2	98.8	98.4	99.6	99.0	98.4
Cr^{3+}	99.2	99.1	99.0	99.2	99.0	98.5	99.4	99.2	99.0	99.5	99.2	99.0
Ni^{2+}	99.0	96.3	90.2	99.1	96.2	90.4	99.0	96.1	90.3	99.1	96.2	90.8
Co^{2+}	99.2	95.5	89.4	99.2	96.3	90.4	99.1	96.7	90.2	99.1	95.7	90.5
V^{5+}	99.2	96.2	90.6	99.2	96.3	90.3	99.4	97.2	90.1	99.5	97.1	91.1
Th^{4+}	99.2	97.1	90.3	99.3	96.5	90.7	99.3	96.7	90.3	99.7	96.7	90.6
U^{6+}	99.1	96.6	90.1	99.5	96.4	90.6	99.4	96.8	90.1	99.4	96.4	90.1
Mo^{6+}	99.5	99.2	98.7	99.3	99.0	99.0	99.1	98.1	98.3	99.1	99.0	98.6
Sc^{3+}	99.3	99.0	98.8	99.4	99.0	99.13	99.4	99.3	99.1	99.2	99.0	98.3

Table-4
Effect of stripping agent type on the stripping efficiency of Cu (II) ions

Stripping agent	Stripping Efficiency, %			
	BrPQ	ClPQ	OCH$_3$PQ	CH$_3$PQ
H$_2$SO$_4$ (0.5, 1, 2 mole/L)	nil	nil	nil	nil
H$_2$SO$_4$ (5 mole/L)	50.5	46.3	40.1	30.2
NH$_4$OH (33%)	69.5	65.3	61.7	56.9
NaOH (5%)	85.2	80.9	76.6	72.8
KOH (5%)	90.8	87.7	83.5	79.3

Table-5
Effect of KOH concentration on the stripping efficiency of Cu (II) ions

KOH Conc.%	Stripping Efficiency, %			
	BrPQ	ClPQ	OCH$_3$PQ	CH$_3$PQ
5.0	90.7	87.7	83.6	79.3
7.5	95.3	90.6	86.2	81.6
10.0	99.4	92.9	88.5	83.7
15.0	99.4	92.9	88.5	83.7

Table-6
Effect of contact time on the stripping efficiency of Cu (II) ions

Contact Time, min	Stripping Efficiency, %			
	BrPQ	ClPQ	OCH$_3$PQ	CH$_3$PQ
1	90.2	85.5	80.8	76.6
3	99.8	94.0	90.3	87.5
5	99.8	94.0	90.3	87.5
10	99.8	94.0	90.3	87.5
15	99.8	94.0	90.3	87.5
20	99.8	94.0	90.3	87.5

Table-7
Effect of O/A ratio on the stripping efficiency of Cu (II) ions

| O/A ratio	Stripping Efficiency, %			
	BrPQ	**ClPQ**	**OCH$_3$PQ**	**CH$_3$PQ**
4/1	67.2	63.0	60.1	55.2
3/1	78.5	74.4	70.8	65.6
2/1	86.3	85.6	81.9	76.4
1/1	99.8	94.0	90.3	87.5
1/2	99.8	94.0	90.3	87.5
1/3	99.8	94.0	90.3	87.5
1/4	99.8	94.0	90.3	87.5

Table-8
Infrared Data for the used synthesized extractants before, after extraction and stripping

| Synthetic Complex	Condition	Major Group (Aliphatic)					
		C – H	**C=O**	**C=N**	**C=N**	**N=N**	**NH**
BrPQ	Before extraction, cm^{-1}(vs)	2945.5	1700.5	1628.6	1618.9	1928.7	3276.6
	After extraction, cm-1(m)	2945.5	1687.5	1600.3	1608.4	-	3271.8
	After stripping, cm^{-1}(m)	2950.0	1687.5	1600.3	1608.4	1928.7	3271.8
ClPQ	Before extraction, cm^{-1}(vs)	2933.6	1668.7	1630.0	1555.6	1922.6	3267.8
	After extraction, cm^{-1}(m)	2934.8	1660.5	1620.6	1550.4	-	3260.7
	After stripping, cm^{-1}(m)	2940.5	1660.5	1620.6	1550.4	1922.6	3260.7
OCH$_3$PQ	Before extraction, cm^{-1}(vs)	2938.5	1665.4	1618.8	1554.8	1923.4	3267.5
	After extraction, cm^{-1}(m)	2936.6	1663.9	1618.8	1552.9	-	3263.7
	After stripping, cm^{-1}(m)	2936.0	1663.9	1618.8	1553.9	1924.5	3263.7
CH$_3$PQ	Before extraction, cm^{-1}(vs)	2930.0	1684.8	1620.7	1600.8	1925.7	3267.9
	After extraction, cm^{-1}(m)	2928.7	1683.5	1616.5	1600.8	-	3266.8
	After stripping, cm^{-1}(m)	2928.7	1683.5	1616.5	1600.8	1925.7	3266.8

Table-9
Determination of Cu (II) ions in standard reference samples using spectrophotometric technique

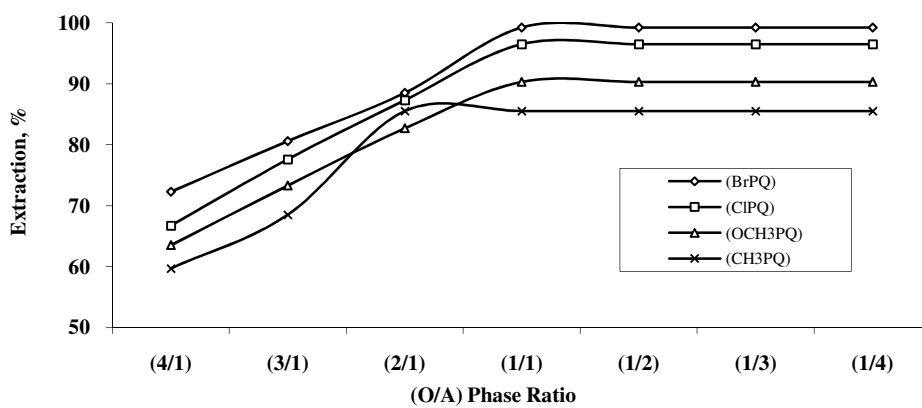| Samples	Certified value[19] (µg/ml)	Determined value (µg/ml)	Standard deviation, S	RSD, %
JB-2	225	222.9	1.43	0.64 %
JB-3	194	192	1.53	0.79 %

Relative standard deviation=100S/$\overline{x}$ (n=3), S= standard deviation and $\overline{x}$ = average
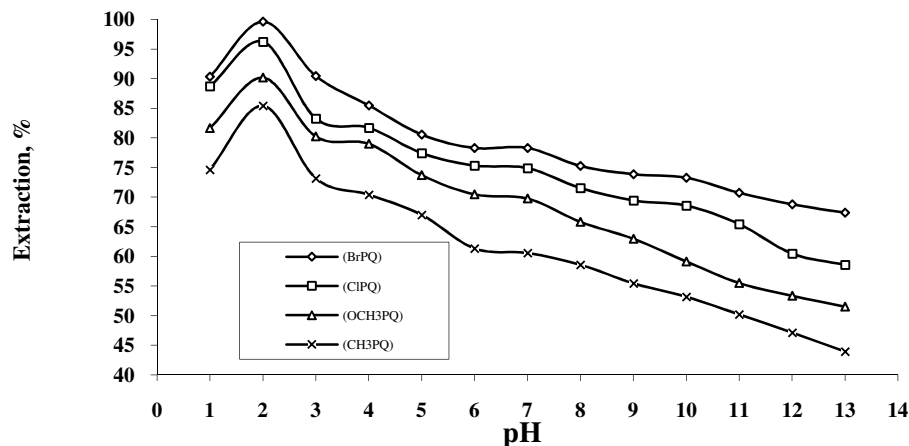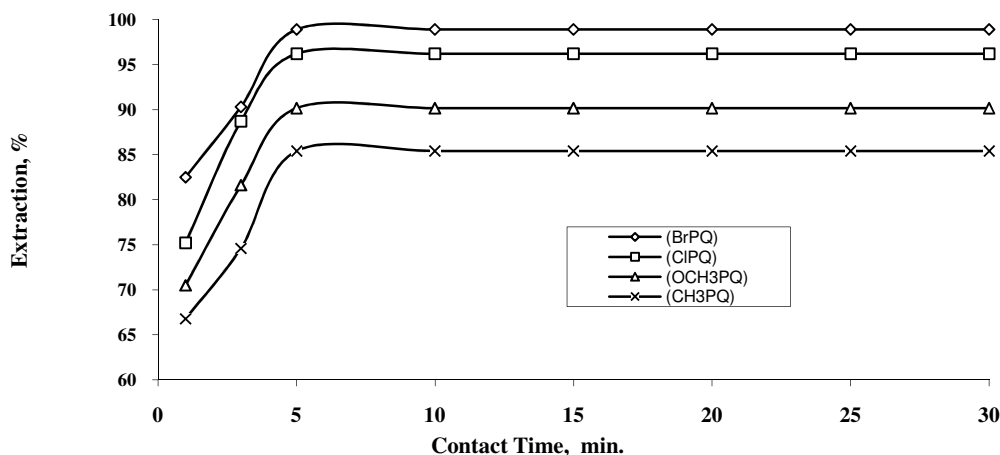
Figure-1
The effect of pH on the extraction efficiency of Cu (II) ions
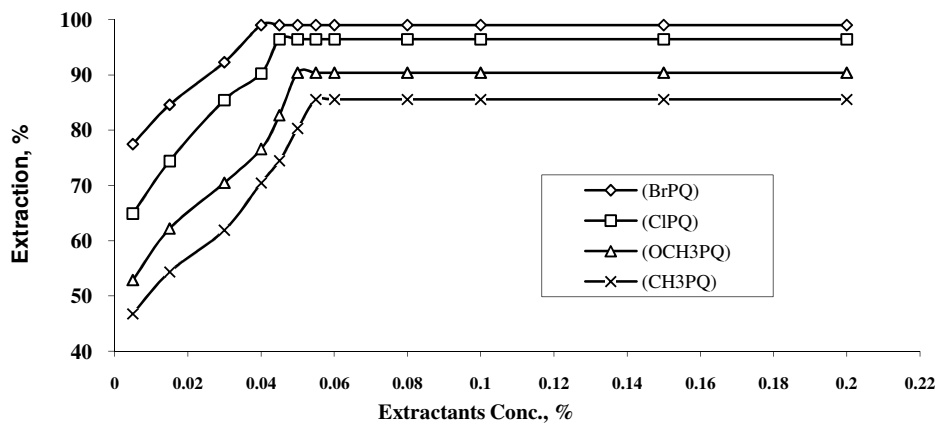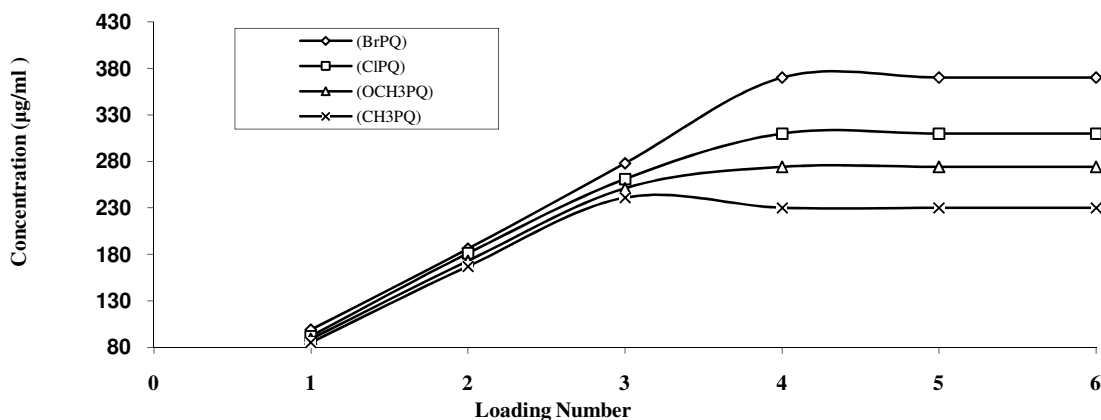

Figure-2
Effect of BrPQ, ClPQ, OCH₃PQ and CH₃PQ concentrations on the extraction efficiency of Cu (II) ions

Figure-3
Effect of O/A ratio on the extraction efficiency of copper ions

Figure-4
Effect of contact time on the extraction efficiency of Cu (II) ions

Figure-5
The effect of loading number on the copper (II) ions concentration of the organic phases of BrPQ, ClPQ, OCH$_3$PQ and CH$_3$PQ in carbon tetrachloride

Conclusion

The synthesized multidentate compounds can be fairly used for extracting Cu species from geologic matrices. The optimum conditions were found at pH 2, the optimum solvent concentrations of BrPQ, ClPQ, OCH$_3$PQ and CH$_3$PQ are 0.04, 0.045, 0.05 and 0.055%, respectively, O/A ratio is 1/1 and shaking time is 5 min. at room temperature. The maximum loading capacity showed that, the organic solvent was fully loaded with the copper (II) after four contacts between the aqueous and the organic phases.

By using the optimum conditions, extraction and determination of copper (II) ions in standard reference geologic (JB-2 and JB-3) samples were carried out.

References

1. Pantnaik P., Handbook of Inorganic Chemical, McGraw-Hill Companies, Inc., 577 **(2003)**

2. Bouabdallah I., Zidane I., Hacht B., Touzani R. and Ramdani A., Liquid -liquid extraction of copper (II), cadmium (II) and lead (II) using tripodal N-donor pyrazole ligands, *ARKIVOC*, **11,** 59 **(2006)**

3. Roqai M.C., Grandmont G.J.G. and Brunette J.P., Extraction of indium(III) from chloride and nitrate media with 3-phenyl-4-benzoylisoxazol-5-one, HPBI, and tri-n-octylphosphine oxide, *Analusis*, **26,** 74 **(1998)**

4. Kitano T., Sohrin Y., Hata Y., Mukai H., Wada H. and Ueda K., Highly selective extraction of Cu(II) and Zn(II)

using [B(3-iPrpz)$_4$]⁻ (iPrpz = isopropylpyrazolyl), *Polyhedron*, **23**, 283 **(2004)**

5. Lopez C., Ponce P., Molinari A. and Oliva A., Further studies on the solvent extraction of copper (II) with dithiocarboxylate derivatives of pyrazol, *Bol. Soc. Chil. Quim.*, **46**, 1 **(2001)**

6. Oliva A., Molinari A., Zúñiga F. and Ponce P., Studies on the Liquid–Liquid Extraction of Nickel(II), Zinc(II), Cadmium(II), Mercury(II) and Lead(II) with 1-Phenyl-3-hydroxy-4-dodecyldithiocarboxylate-5-pyrazolone, *Microchimica Acta*, **140**, 201 **(2002)**

7. Touzani R., Ramdani A., Ben-Hadda T., El Kadiri S., Maury O., Le Bozec H. and Dixneuf P.H., Efficient synthesis of new nitrogen donor containing tripods under microwave irradiation and without solvent, *Synth. Commun.*, **31(9)**, 1315 **(2001)**

8. Veeratana D. and Sohu H.Y., Solvent extraction equilibriain the CuSO$_4$-H$_2$SO$_4$-H$_2$0-LIX 860-kerosene system, *Minerals Engineering*, **11**, 821 **(1998)**

9. Stefanova V., Iliev P., Mroz W. and Stefanov B., Copper (II) extraction from multicomponent sulphuric-acid solutions by means of LIX84I, *Journal of the University of Chemical Technology and Metallurgy*, **45(1)**, 99 **(2010)**

10. Alguacil F. T. and Alonso M., Recovery of copper from ammoniacal/ammonium sulfate medium by LIX 54, *Journal of Chemical Technology and Biotechnology*, **74**, 1171 **(1999)**

11. Kara D. and Alkan M., Preconcentration and separation of copper (II) with solvent extraction using N,N'-bis (2-hydroxy-5-bromo-benzyl)1,2 diaminopropane, *Micro Chemical Journal*, **71**, 29 **(2002)**

12. Gup R. and Giziroglu E., Metal complexes and solvent extraction properties of isonitrosoacetophenone 2-aminobenzoylhydrazone, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, **65**, 719 **(2006)**

13. Hamzah B., Jalaluddin N., Wahab A. W. and Upe A., Copper(II) Extraction from Nitric Acid Solution with 1-Phenyl-3-methyl-4-benzoyl-5-pyrazolone as a Cation Carrier by Liquid Membrane Emulsion, *E-Journal of Chemistry*, **7(1)**, 239 **(2010)**

14. Lenarcik B., Rauckyte T. and Kserzkowska A., The comparison of the extraction process of Zinc (II) and Nickel (II) complexes with 1- octylimidazle and 1- octyl - 2- methylimidazole, XVIII-th ARS SEPARATORIA – Zioty Potok, Poland, **(2003)**

15. Erdon I., Demirhan N. and Avcata U., Synthesis and characterization of a new Imidazole ligand and its complexes with cobalt (II), and copper (II), *synthesis and reactivity in inorganic, metal organic and nano metal chemistry*, **36, 7**, 559 **(2006)**

16. Marczenko Z., Spectrophotometric Determination of Elements, John Wiley and sons Inc., New York, 250 **(1976)**

17. Mahmoud G.M., Synthesis of some ketones and their applications in the extraction of some nuclear elements from acid media, Ph. D. Thesis, Cairo university, Faculty of Science, 156 **(2008)**

18. Smallwood I.M., Handbook of organic solvent properties, John Wiley and Sons Inc. New York, 306 **(1996)**

19. Ando A., Kamioka H., Terashima S. and Itoh S., Values for GSJ rocj reference samples "Igneous Series", *Geochemical Journal*, **23**, 143 **(1989)**