

The Extraction and Recovery of Copper (II) with Tertiary Amines

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Summary: The work describes a comparative study with various high molecular weight tertiary amines to develop a hydrometallurgical method for the extraction and recovery of copper (II) from different aqueous acidic media. Limits such as, the effect of acid, extractant, and stripping agents concentration, time of contact, and diverse ions were optimised. Maximum percentage extraction and recovery of copper (II) ions were achieved with 5% solution of trioctylamine in benzene.

Introduction

New and versatile techniques of liquid-liquid extraction have been developed in the past few years. This has been referred to as "Liquid ion exchanger". The use of high molecular weight amines and amine salts has been made for the removal of mineral acids, organic acids, complex metal acids from aqueous solutions, and organo-phosphorous acids for removal of cations. Separation using liquid ion exchangers might be said to date from 1948, when Smith and Page [1] published their paper entitled "The acid bonding properties of long chain aliphatic amines". However, interest in their application in industrial processes for the recovery of metals is relatively recent. This procedure has also been used commercially for the extraction of metals from ores and metallic minerals. A number of research papers have been published in the field of inorganic-analytical chemistry of copper metal. Most of these studies have been confined to the characterisation, thermodynamics, mechanism and co-ordination of the copper and copper group metals in the form of their chelates and metals complexes [2-37]. The present work deals with the application of hydrometallurgical method for the extraction and recovery of copper (II) from synthetic mixtures with 5% solution of trioctylamine in benzene.

Results and Discussion

Effect of acid concentration

The effect of acid (HCl) concentration in molar range (0.5M-10.0M) was studied, and 99% extraction was noted at 7.5M concentration of HCl, using 5% trioctylamine in benzene.

Effect of Shaking time

The effect of shaking time, in the range 0.50-5.00 minutes, was carried out after optimising the effect of hydrochloric acid concentration. The results are presented in Fig.1.

Effect of phase-volume ratios

The phase-volume ratio (V_{org}/V_{aq}) was varied by keeping the volume of organic phase as constant [10 ml (in 5 ml + 5 ml portions)], and changing the volume of the aqueous phase from 5 ml up to 30 ml. The ratio 1:2 was found to be the most suitable ratio for efficient extraction of Cu (II). The data are depicted in Fig.2.

Effect of extractant concentration

The effect of extractant (TOA in benzene) concentration in molar range (0.01M-0.23M) was also carried out after optimising the effect of acid (HCl) concentration, shaking time and phase-volume ratio. These observations are presented in Fig.3.

Effect of copper concentration

Furthermore studies were also carried out to see the effect of copper concentration, 10 to 100 μ g, on the overall extraction with TOA in benzene. Minor difference was noted in the extraction efficiency above 50 μ g. The effect is illustrated in Fig.4.

Effect of organic solvents

Various organic solvents were used as diluent for trioctylamine and benzene was found to be the

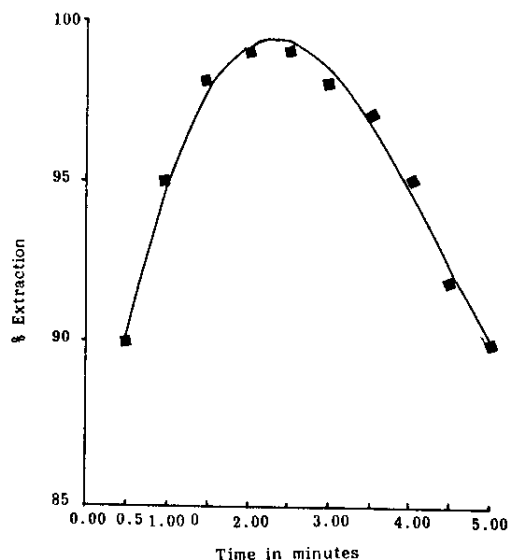


Fig. 1: Effect of shaking time on % extraction of Cu(II) with TOA.

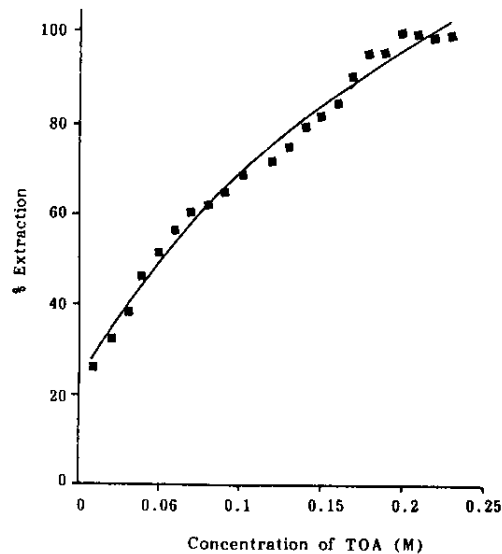


Fig. 3: Effect of TOA concentration on % extraction of Cu(II).

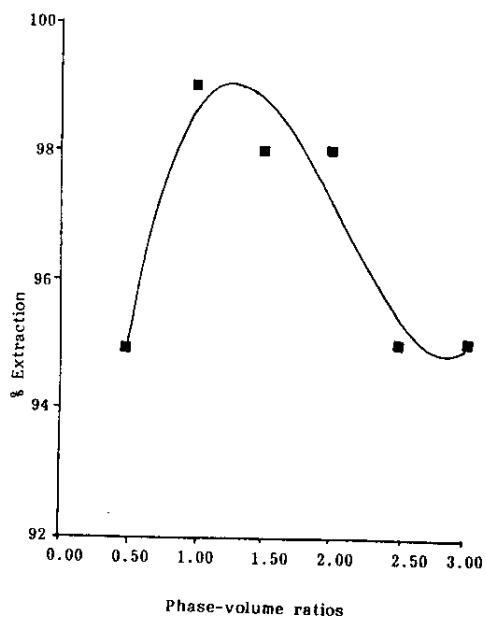


Fig. 2: Effect of phase-volume ratio (Org:Aq.) on % extraction of Cu(II).

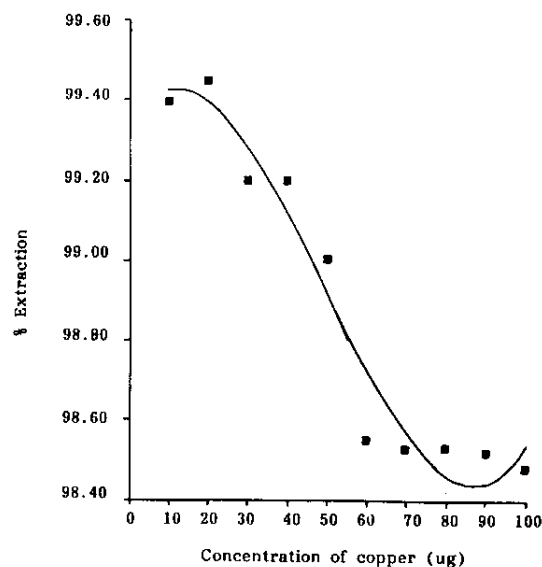


Fig. 4: Effect of copper concentration on % extraction of Cu(II).

Table-1 Instrumental conditions for copper

Conditions	Copper
Lamp current (mA)	7.5
Wavelength (nm)	324.8
Spectral slit (nm)	1.3
Oxidant pressure (kg/cm^2)	1.60
Fuel pressure (kg/cm^2)	0.30
Burner height (mm)	7.5

most suitable. The effect is summarised in the form of Table-2.

Effect of diverse ions

The copper concentration ($20\mu\text{g}$) was kept constant and the effect of diverse ions, in the range $100\text{-}1000\mu\text{g}/\text{ml}$ (25-50 fold excess), that may

Table- 2. Effect of various organic solvents on % Extraction of Copper (II)

S. No.	Solvents/Diluents	Conc. of copper (μg)			
		Added	Found	Extracted	% Extraction
1.	Toluene	20.00	4.52	15.48	77.40
2.	Carbon tetrachloride	20.00	5.65	14.35	71.75
3.	Butane-1-ol	20.00	16.78	3.22	16.10
4.	Methyl Isobutyl Alcohol	20.00	13.95	6.05	30.25
5.	n-Pentane	20.00	3.01	16.99	84.95
6.	propanol	20.00	9.80	10.20	51.00
7.	Butyl Alcohol	20.00	10.93	9.07	45.35
8.	Methyl Benzol	20.00	6.31	13.69	68.45
9.	2-Methyl-propanol (I)	20.00	15.65	4.35	21.75
10.	Chloroform	20.00	5.84	14.16	70.80
11.	Ethylene Dichloride	20.00	3.20	16.80	84.00
12.	Cyclohexane	20.00	4.14	15.86	79.30
13.	o-xylene	20.00	3.96	16.04	80.20
14.	p-xylene	20.00	3.95	16.05	80.25
15.	Methyl Isobutyl-ketone	20.00	6.41	13.59	67.95
16.	Dioxane	20.00	10.93	9.07	45.35
17.	Trichloroacetic Acid	20.00	3.58	16.42	82.10
18.	Benzene	20.00	0.10	19.10	99.50

TABLE- 3 Effect of diverse ions on % extraction of copper (II)

S.No.	Diverse ions	Conc. of diverse ions	Concentration of copper (μg)			
			Added	Found	Extracted	% Extraction
1.	Zn	100	20.00	1.90	19.10	90.50
		500	20.00	2.90	17.10	85.50
		1000	20.00	2.97	17.03	85.15
2.	Co ²⁺	100	20.00	1.25	18.75	93.75
		500	20.00	2.57	17.43	87.15
		1000	20.00	3.21	16.79	93.95
3.	Cr ³⁺	100	20.00	0.83	19.17	95.85
		500	20.00	3.36	16.64	83.20
		1000	20.00	3.77	16.23	81.15
4.	Mn ²⁺	100	20.00	0.35	19.65	98.25
		500	20.00	1.58	18.42	92.10
		1000	20.00	3.77	16.23	81.15
5.	Fe ²⁺	100	20.00	0.20	19.80	99.00
		500	20.00	0.20	19.80	99.00
		1000	20.00	0.20	19.80	99.00
6.	Fe ³⁺	100	20.00	0.20	19.80	99.00
		500	20.00	0.20	19.80	99.00
		1000	20.00	0.30	19.70	98.50
7.	Ca ²⁺	100	20.00	0.25	19.75	98.75
		500	20.00	2.77	17.23	86.15
		1000	20.00	2.37	17.63	88.15
8.	Mg ²⁺	100	20.00	0.23	19.77	98.85
		500	20.00	0.77	19.23	96.15
		1000	20.00	1.98	18.02	90.10
9.	Cd ²⁺	100	20.00	1.55	18.45	92.25
		500	20.00	1.56	18.44	92.20
		1000	20.00	1.49	18.51	92.55
10.	Al ³⁺	100	20.00	0.20	19.80	99.00
		500	20.00	0.40	19.60	98.00
		1000	20.00	0.70	19.30	96.50

S.No.	Diverse ions	Conc.of diverse ions	Concentration of copper (μg)			
			Added	Found	Extracted	% Extraction
11.	Pb ²⁺	100	20.00	0.55	19.45	97.25
		500	20.00	2.77	17.23	86.15
		1000	20.00	2.78	17.22	86.10
12.	Si ⁴⁺	100	20.00	0.76	19.24	96.20
		500	20.00	2.97	17.03	85.15
		1000	20.00	2.78	17.22	86.10
13.	Bi ²⁺	100	20.00	0.93	19.17	95.85
		500	20.00	1.17	18.83	94.15
		1000	20.00	1.06	18.94	94.70
14.	Sn ²⁺	100	20.00	0.23	19.77	98.85
		500	20.00	2.77	17.25	86.15
		1000	20.00	3.75	16.25	81.25
15.	Ti ⁴⁺	100	20.00	0.39	19.61	98.05
		500	20.00	1.97	18.03	90.15
		1000	20.00	2.06	17.94	89.70
16.	W ⁶⁺	100	20.00	1.76	18.24	91.20
		500	20.00	4.96	17.04	85.20
		1000	20.00	3.19	16.81	84.05
17.	V ⁵⁺	100	20.00	2.51	18.49	94.45
		500	20.00	2.17	17.83	90.15
		1000	20.00	2.96	17.04	85.20
18.	U ⁶⁺	100	20.00	0.83	19.17	95.85
		500	20.00	2.36	17.64	88.20
		1000	20.00	2.37	17.63	88.15
19.	Eu ³⁺	100	20.00	0.67	19.33	96.65
		500	20.00	2.96	17.04	85.20
		1000	20.00	2.97	17.03	85.15
20.	Sm ³⁺	100	20.00	0.39	19.69	98.05
		500	20.00	1.57	18.43	92.15
		1000	20.00	1.27	18.73	93.65
21.	Ni ²⁺	100	20.00	0.53	19.47	97.35
		500	20.00	0.83	19.17	95.85
		1000	20.00	0.85	19.15	95.75
22.	Au ⁺	100	20.00	0.29	19.71	98.55
		500	20.00	0.80	19.20	96.00
		1000	20.00	0.85	19.15	95.75
23.	Ba ²⁺	100	20.00	0.60	19.40	97.00
		500	20.00	0.85	19.15	95.75
		1000	20.00	1.48	18.52	92.60
24.	Ag ⁺	100	20.00	0.84	19.16	95.80
		500	20.00	1.17	18.83	94.15
		1000	20.00	1.48	18.52	92.60
25.	Na ⁺	100	20.00	1.00	19.00	95.00
		500	20.00	2.00	18.00	90.00
		1000	20.00	3.90	16.10	80.50
26.	K ⁺	100	20.00	0.50	19.50	97.50
		500	20.00	1.00	19.00	95.00
		1000	20.00	1.00	19.00	95.00

probably cause interference during the extraction and recovery of the metal with TOA in benzene was studied. It was noted that Fe(II) and Fe(III) do not interfere even if present in the 50 fold excess. Similar results were achieved with Al(III) when present in 5-20 fold excess. Mn (II), Ca (II), Mg (II), Sn (II), Au (II), Ti (IV), Pb(II), Ba(II), Sm (III) and K (I) also do not interfere if present in the 5 fold excess. However, this trend decreases by 10 to 15% if the diverse ions concentration is increased from 25 to 50 fold excess. Moreover, the % extraction of copper decreases from 4-15% due to the presence of Si (IV), W (VI), U(VI), Eu(III), Cr (III), Zn (II), Co(II), Na(I) and Cd(II) but this diversity is not so pronounced in case of Bi(II), V(V), Ni (II) and Pb (II) and show minor diverse effect. These observations are tabulated in Table-3.

Analysis of synthetic mixtures

As a final check on the method, various synthetic mixtures were prepared and analysed following the foregoing procedure. The data are given in Table-4.

Single extraction with 5 ml of 5% tertiary amines from different acidic media

The extraction studies of copper from various acidic media were made with 5ml of 5% solutions of tribenzylamine and triethylamine in chloroform, and alamine-336, aliquat-336, and trioctylamine in benzene. Maximum extraction was obtained with 5% solution of trioctylamine in benzene from acidic chloride medium. The comparative studies are illustrated in Fig.5.

Single extraction with 10 ml of 5% trioctyl amine from various acidic media

Further studies were carried out with 10 ml of the trioctylamine in benzene from different acids (HCl, HNO₃, H₂SO₄ and HClO₄.) The extraction in chloride system was found to be the maximum. The results are summarised in Fig.6.

Table- 4 Analysis of synthetic mixtures for copper (II)

Concentration of copper(μg)				Other elements present(μg)
S.No.	Present	Recovered	% Recovery	
1.	20.00	19.80	99.00	Ca: 100, Mg:100, SiO ₂ : 100,Al:100, Fe:100, Na:100, K:100, Ni:100, Co:100, Mn:100, Pb:100, Cr:100, Ag:100, Au:100, Ti:100, Zn:100, Ca:100
2.	20.00	19.91	99.55	Ca:100, Mg:100
3.	20.00	19.94	99.70	Ca:100, Mg:100, SiO ₂ :100
4.	20.00	19.73	99.65	Ca:100, Mg:100, SiO ₂ :100, Al:100
5.	20.00	19.93	99.75	Ca:100, Mg:100, SiO ₂ :100, Al:100, Fe:100
6.	20.00	19.96	99.80	Ca:100, Mg:100, SiO ₂ :100, Al:100, Fe:100, Na:100
7.	20.00	19.88	99.40	Ca:100, Mg:100, SiO ₂ :100, Al:100, Fe:100, Na:100, K:100
8.	20.00	19.87	99.35	Ca:100, Mg:100, SiO ₂ :100, Al:100, Fe:100, Na:100, K:100, Ni:100
9.	20.00	19.88	99.40	Ca:100, Mg:100, SiO ₂ :100, Al:100, Fe:100, Na:100, K:100, Ni:100
10.	20.00	19.92	99.60	Ca:100, Mg:100, SiO ₂ :100, Al:100, Fe:100, Na:100, K:100, Ni:100, Co:100
11.	20.00	19.95	99.75	Ca:100, Mg:100, SiO ₂ :100, Al:100, Fe:100, Na:100, K:100, Ni:100, Co:100, Mn:100
12.	20.00	19.94	99.70	Ca:100, Mg:100, SiO ₂ :100, Al:100, Fe:100, Na:100, K:100, Ni:100, Co:100, Mn:100, Pb:100
13.	20.00	19.85	99.25	Ca:100, Mg:100, SiO ₂ :100, Al:100, Fe:100, Na:100, K:100, Ni:100, Co:100, Mn:100, Pb:100, Cr:100
14.	20.00	19.83	99.15	Ca:100, Mg:100, SiO ₂ :100, Al:100, Fe:100, Na:100, K:100, Ni:100, Co:100, Mn:100, Pb:100, Cr:100, Ag:100
15.	20.00	19.73	98.65	Ca:100, Mg:100, SiO ₂ :100, Al:100, Fe:100, Na:100, K:100, Ni:100, Co:100, Mn:100, Pb:100, Cr:100, Ag:100, Au:100
16.	20.00	19.79	98.95	Ca:100, Mg:100, SiO ₂ :100, Al:100, Fe:100, Na:100, K:100, Ni:100, Co:100, Mn:100, Pb:100, Cr:100, Ag:100, Au:100, Ti:100

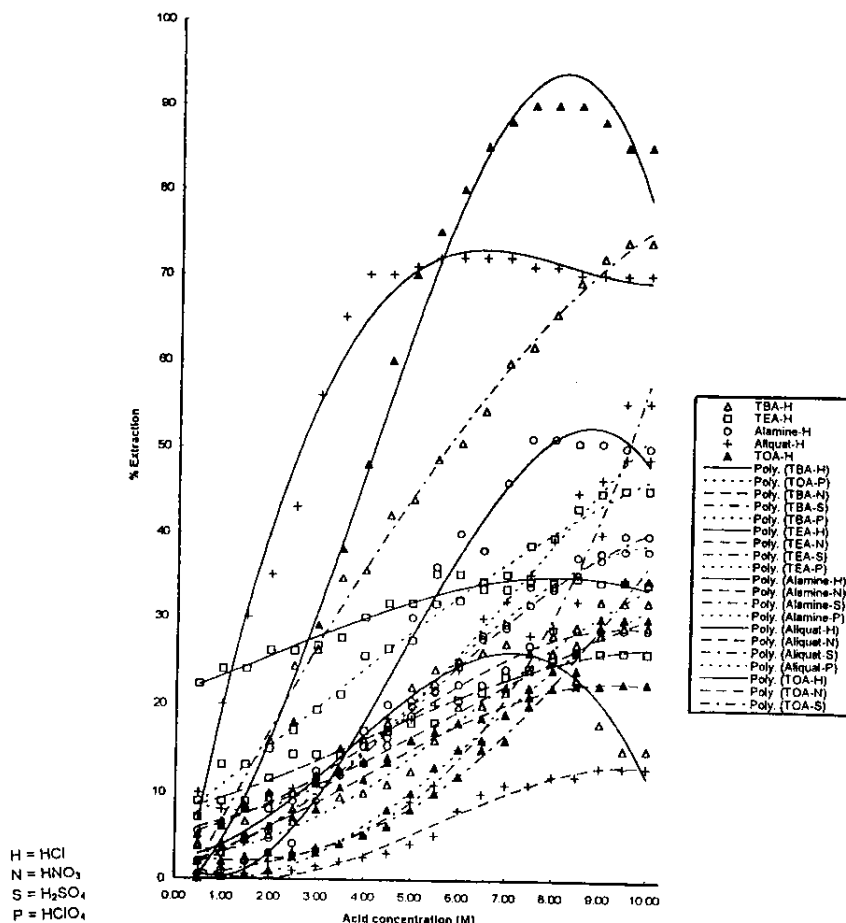


Fig. 5: Single extraction of Cu(II) with 5 ml of 5% tertiary amines from various systems.

Extraction in portions with 10 ml of 5% trioctylamine in benzene from different acidic media

Furthermore extraction studies were performed in portions (10 ml divided in 5 ml portions) with 5% solutions of trioctylamine in benzene from various aqueous acidic media. Extraction in portion enhances the percentage from 95 to 99 in chloride system. The data obtained are depicted in Fig.7.

Recovery of copper from organic phase back into aqueous phase was carried out using dilute solutions (0.05-1.00M) of HCl, HNO₃, H₂SO₄ and HClO₄. Maximum recovery was 99 % with 0.1 M solution HCl. The comparative data obtained from these investigations are depicted in Fig. 8.

Experimental

Instrumentation

Hitachi Polarized Zeeman atomic absorption spectrophotometer (Model Z-8000) in the flame-mode was used throughout these studies. Instrumental conditions are summarised in Table-1.

Reagents

All the reagents and solvents used were of analytical grade. All aqueous solutions were prepared in distilled water. All working solutions were prepared by dilution as required.

Copper (II) solution was prepared by dissolving the requisite amount of the copper metal

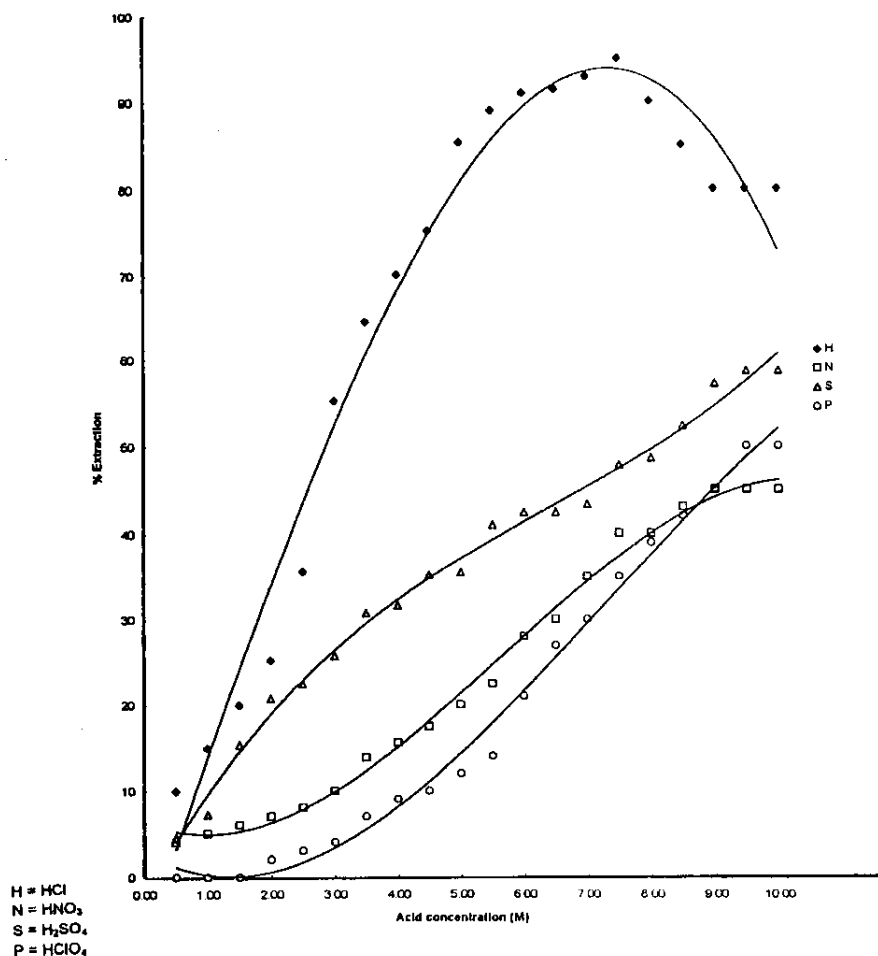


Fig. 6: Single extraction of Cu(II) with 10 ml of 5% trioctylamine (TOA) in various systems.

in 1:1 HCl and was standardised by the Iodimetric method. The working standards and the blanks were acidified to the same extent as the samples. 5% solution of Analar grade tertiary amines supplied by BDH were prepared by dissolving in thiophene free benzene and chloroform.

Procedure

13.6 ml of pure and concentrated hydrochloric acid (73% sp. gr. =1.19) were added to the aqueous solution containing known amount (20 μ g) of Cu (II) in a 100 ml separating funnel. The solution was diluted to 20 ml with distilled water, so that the final HCl concentration is 7.5M. 5 ml of 5% TOA in benzene solution were added to the resulting

acidic aqueous solution. The two phases were shaken manually or on a mechanical shaker for 2 minutes and left over for an hour, so that the two phases may get complete separation and attain equilibrium. The loaded organic amine phase was separated from the acidic aqueous phase into a dried beaker after passing through a Schwarzband \varnothing 5.5 cm filter paper to remove the suspended water droplets. Fresh 5 ml of 5% TOA in benzene were added to the aqueous phase left in the separating funnel and the extraction was made again as earlier. The two batches of the loaded organic amine phases were combined and stripped with 0.10M HCl. The stripped aqueous solution as well as the aqueous phase left in the separating funnel, were analysed for

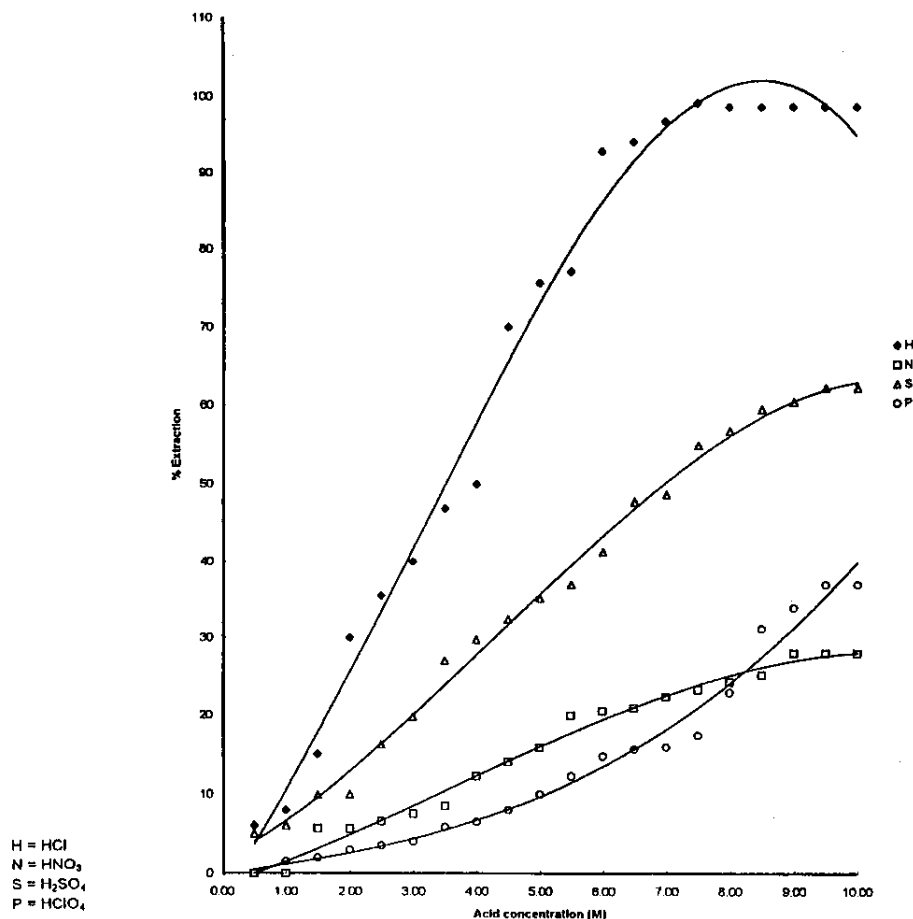


Fig. 7: Double extraction of Cu(II) with 10 ml (in 5 ml + 5 ml portions) of 5% TOA/benzene from various systems.

Cu (II). using atomic absorption spectrophotometry. The percentage extraction of Cu (II). was calculated from the difference of the known amount (20 μ g) of Cu (II) added and left if any in the barren raffinate. Similarly the percentage recovery of Cu (II) was calculated from the known amount of Cu (II) added and the amount recovered back into the aqueous phase.

Conclusion

It can be concluded from the preceding investigations that copper ion makes colourless chloro-complex with HCl at a specific molar concentration (7.5 M). The chloro-complex formed being anionic in nature is quantitatively extracted into the liquid ion exchanger (trioctylamine). It is obvious that 99% copper is quantitatively extracted

into the organic amine phase from the synthetic mixtures even in the presence of 25 fold excess of most of the interfering metal ions. The same percentage of copper content is also recovered with a dilute solution of HCl (0.10 M) as its chloride salt. The hydrometallurgical method is being successfully applied for the extraction and recovery of copper from indigenous copper ore (containing 0.5% Cu). The experimental details and the data obtained will be presented in the form of a research publication. The technology developed is economically feasible by regeneration and recycling of the used solvent just after washing with distilled water. The overall reaction between copper (M) and tertiary amines (R_3N) may be represented by the following equations.



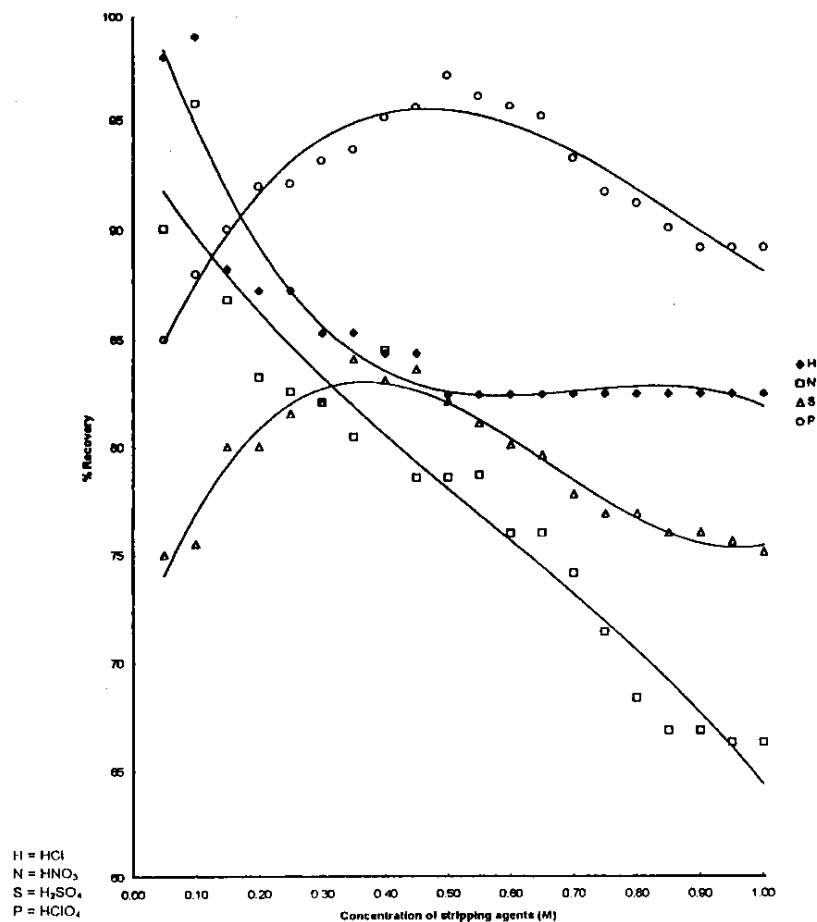
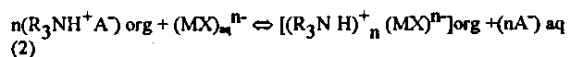


Fig. 8: Effect of stripping agents concentrations on % recovery of Cu(II).



where R_3N = Tertiary amine

$H^+ A^-$ = An inorganic acid

$(MX)_m^{n-}$ = Anionic complex, where, M is a metal ion and X is a ligand.

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