REMOVAL OF COPPER FROM AQUEOUS SOLUTIONS USING REACTIVE EXTRACTION

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MASTER OF TECHNOLOGY
IN
CHEMICAL ENGINEERING

by

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CERTIFICATE

This is to certify that the thesis entitled "**Removal of Copper from Aqueous Solution using Reactive Extraction**" is an authentic record of my own work carried out as a curriculum requirement for the award of degree of Master of Technology in Chemical Engineering from Thapar University, Patiala, under the supervision of Dr. Dipaloy Datta, Assistant Professor and Dr. Avinash Chandra, Assistant Professor, Department of Chemical Engineering, Thapar University, Patiala for the session 2013-2015.

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ABSTRACT

The thesis is concentrated on the use of reactive extraction for purification of aqueous streams containing Copper(II) ions. Dissolved Cu^{2+} ions are removed from the aqueous solution with the help of TBP as the reactive extractant. Benzene is used as the diluent to decrease the viscosity of the TBP. The effect of various parameters on removal percentage, namely, initial copper concentration, extractant percentage in extractant-dilutent mixture, O/A ratio, pH and temperature were studied. A percentage extraction of 98% was obtained under the optimized conditions (initial Cu^{2+} concentration =20ppm, O/A ratio = 3:1, pH = 6, temperature = 25°C, extractant concentration = 1.825mol L^{-1}). A two stage stripping process was also undertaken at 70°C to strip the aqueous solution received after the extraction tests and to reuse the clean extractant solvent for subsequent reactive extraction tests. 4N H_2SO_4 was used as the stripping agent. Thermodynamic analysis was done for the process which inferred that the process is exothermic and is favourable at low temperature and also forms a stable Cu-TBP complex.

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ABBREVIATIONS

TBP	Tri-butyl phosphate
D2EHPA	di-2-ethylhexyl phosphoric acid
AAS	Atomic Absorption Spectrophotometer
O/A	Organic phase/ Aqueous phase
ppm	Parts per million
K_{eq}	Equilibrium constant for extraction
K_D	Distribution coefficient
$Cu^{2+}{}_{aq}$	Copper concentration in aqueous phase
TBP_{org}	Tri-butyl phosphate in organic phase
R	Universal gas constant
ΔH	Enthalpy change
ΔS	Entropy change
T	Temperature
V_{org}	Volume of organic phase
A	Interfacial area
k_L	Mass transfer coefficient
t	Time
$C_{org}{}^{*}$	Interfacial concentration of Cu^{2+}
Corg	Concentration of Cu^{2+} in organic phase
k	Rate constant
α, β	Order of reaction with respect to Cu^{2+} and TBP respectively
D_{HC}	Diffusion coefficient of Cu^{2+} in benzene
Ha	Hatta Number

CHAPTER – 1

INTRODUCTION

Solvent extraction is one of the most efficient methods used to remove, separate and concentrate metallic species from aqueous media [1, 2]. Reactive extraction has come a long way since the 1970s and in the last decade there has been a tremendous advance in the usability of reactive extraction to hydrometallurgy. There are more than 40 chemicals (Cyanex 921, Cyanex 272, D2EHPA, TBP etc) that can be used as an extractant in order to remove metals from the aqueous stream [2, 3]. Numerous studies have been carried out to investigate the reactive extraction of various metals from aqueous streams generated from industrial effluents.

In reactive extraction, the extractant is used to remove the metals from the aqueous streams by making a complex with them. The extractant replaces, partially or fully the coordinated water molecules around the metal ions and form organically soluble species [4]. The extractant is expected to have high distribution coefficient and dependence on pH in the system that is chosen [5].

Futility of reactive extraction process lies in the reusability of the extractant after the extraction process is over. The organic phase that is formed after it extracts the metal ions by forming metallic complexes are stripped with strong acids such HCl, H_2SO_4, HNO_3 etc. or strong bases like NaOH. Like extraction the stripping is also an ion-exchange phenomena and also pH dependent. The stripping agent breaks the metal-extractant complex in organic phase and frees the extractant of the metal ion by rejecting the ion to the aqueous phase [6].

Copper is an important metal which is vital as well as toxic to the biological systems[7, 8]. Many human activities produce industrial effluents which contain Copper such as mining, metal processing and finishing, electroplating, printed circuit board manufacturing etc. which when untreated can pose as a serious environmental risk [9, 10]

Tri-butyl phosphate is an extractant of organo-phosphorus group. TBP is readily soluble in lots of organic solvents but is slightly soluble in water, It has high affinity for water of around 3.22 – 3.43 M/100 gm TBP and it dissolves most nitrates, rare earth metals and transitional elements but not basic metals. It works well in extracting metallic elements of Ac and La families and lots of heavy metals. It is chemically stable and has resistance to strong acids, strong bases and radiation. With a dipole moment of 3.07 Debye units and high capacity to supply electron, TBP is capable to form complexes with metal ions [11].

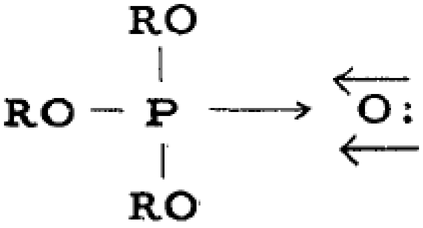

Fig 1.1 Structure of TBP [11]

CHAPTER – 2

LITERATURE SURVEY

Huang *et al.* (1986) [12] studied use of di-2-ethylhexyl phosphoric acid as an extractant to remove zinc from sulphate medium. Kinetic study was done using a constant facial area cell. Extraction and stripping rates were measured and that led to development of rate expressions and a probable mechanism for the process. A simple extraction regime was proposed using the nature of the extractant used and the mechanism for the formation of complexes of zinc. The interfacial step was the controlling step. The mass-action constant which was calculated in this study agreed with the extractant constant which was calculated in the previous equilibrium study. Total sulphate concentration's effect on the extraction was studied too.

Woller *et al.* (1996) [13] used quinolines (LIX 26) and oximes (LIX84) as extractants to remove heavy metals namely, Cu, Cr, Cd, Ni, Zn and Pb in one step from the waste water i.e. landfills. They investigated the stoichiometry of the extracting reaction, selectivity of metals in extraction process and phase separation. They also conducted extraction and re-extraction experiments using a continuously operated mixer settler.

Devi *et al.* (1997) [14] used Na-Cyanex 272 as the extractant for solvent extraction of zinc and manganese from sulphate solutions. Extraction of Zn^{2+} and Cu^{2+} ions increased with the increasing pH and observed a linear pattern with the increase in extractant concentration till 0.05M.

Zhang *et al.* (1998) [15] used a leaching process with 2M HCl at 95°C and the leaching liquor was subjected to solvent extraction by 25% D2EHPA in kerosene diluent at pH = 2. The rare earth metals were stripped from the organic phase by 2M HCl and after it, oxalic acid was added for rare earth metals precipitation. Ni and Co was also recovered by the solvent extraction and cobalt was stripped by HCl. Co and Ni both were precipitated as oxalates. Rare earth metal recovery reached 98% whereas Co and Ni yields reached 98% and 99.9% respectively.

Zhang *et al.* (1999) [16] studied a process in which they employed a leaching stage in which the leaching liquor formed was subjected to solvent extraction by 25% D2EHPA in kerosene diluent at pH=2.5. The organic phase was stripped by 1M H_2SO_4. 25% Cynanex at pH=4.1 was also used as the extracting solvent to recover Ni and Co. The organic phase was stripped with 0.5M H_2SO_4 and Co and Ni were precipitated as oxalates. RE recovery observed was around 94%.

Reddy *et al.* (1999) [17] showed a process to remove nickel using PC-88 as the solvent extractant with kerosene as diluent. With three stages of extraction, 99% of nickel was extracted under the optimized conditions of extractant concentration of 1M neutralised to 50% and O/A = 2.2. A stripping test was also done to recycle the extractant with H_2SO_4 as the stripping agent and O/A was fixed at 5. Stripping yield was observed >99.98%.

Juang *et al.* (1999) [18] studied the use of Aliquat 336 as an extractant to extract Cu^{2+}-NTA chelated anions with the help of solvent extraction. The distribution ratios of Cu^{2+} were calculated. Effect of different parameters like pH, amine concentration and temperature were studied. With the increase in pH distribution ratios first increased and then decreased. Non ideality of organic phase was discussed and enthalpy of extraction process was found out.

Kyuchokov and Szymanowski (2000) [19] used a mixture of two extractants – a chelating and basic or solvating extractant and employed reactive extraction to remove copper(II) and zinc(II) from acidic solutions. They proposed a series of step which enabled the recovery and separation of Cu and Zn which is as follows – Firstly, metal chlorocomplex, solvates or ion pairs were formed and thus the chloride media was extracted. Secondly, Chloride ions were scrubbed by a aqueous solution with a fixed pH and metal ions were transferred to the chelate. Finally, the organic phase was stripped with sulphuric acid and the extractant was recovered.

Kyuchokov *et al.* (2000) [20] used alkyl-8-hydroxyquinoline (KELEX 100) as the reactive extractant to remove zinc and copper from the chloride solutions. There are three stages and in all three of them the separation was possible. The necessary conditions for the separation to take place in all three of the stages were discussed by them. Amongst these three steps, the stripping stage was the most efficient. An ammonical solution was used as a scrubbing agent to scrub chloride from the organic phase. After it, Zn was selectively stripped by 0.25-0.8M sulphuric acid and Cu was stripped at 3 M sulphuric acid at the O/A ratio of 1.

Mhaske *et al.* (2001) [21] studied the extraction of palladium, rhodium received from spent catalyst using Cyanex 921 as an extractant from aqueous HCl medium. Studies were performed in the presence and as well absence of Tin (II) chloride. Extraction of individual elements were performed separately initially to see the effects of different variables namely, HCl concentration, tin (II) chloride concentration, equilibrium time, stripping agents and intial concentration of elements. Finally, a synthetic solution was prepared similar to the composition of leachate from spent catalyst and a process was developed for the same.

Mansur *et al.* (2002) [22] proposed a equilibrium model for the reactive extraction of Zn(II) with the help of D2EHPA as extractant and n-heptane diluent which was considered a test system by the European Federation of Chemical Engineering. Statistical analysis of estimated parameters supports the model. Two consecutive reactions were supposed to give two zinc complexes and when the situations change from extraction to stripping their relative proportions also change. Newton's method was used to solve the model and direct search data fitting method of Hooke and Jeaves is employed to estimate the paremeters. The model predicted the concentration of aqueous phase with relative error less than 11% when activity coefficient of 1.0 was assumed.

Kongolo *et al.* (2003) [23] used solvent extraction to remove Co and Zn from copper sulphate solution which has 2 g L^{-1} Cu^{2+}, 1 g L^{-1} Co^{2+}, 8.4 g L^{-1} Fe^{2+} and 12.60 g L^{-1} Zn^{2+}. LIX 984 was used to extract copper and H_2SO_4 was used as stripping agent. Subsequently, iron was precipitated with $CaCO_3$ and afterwards Co and Zn were extracted with D2EHPA and was stripped by H_2SO_4. Removal percentage of more than 95%, 90% and 90% were observed for Cu, Co and Zn respectively.

Tsakiridis and Agatzini (2004) [24] used 20% Cyanex 301 as reactive extractant which was diluted in Exxsol D-80 with 5% TBP and used it to extract cobalt and nickel from sulphate solution. They used a one stage process with pH=2, temperature=50°C and O/A ratio=1. Manganese was co-extracted and it was scrubbed off. After it, Co and Ni were stripped by 5M HCl and a stripping yield of 99.2% for Ni and 99.6% for Co was observed. The stripping was done at temperature=50°C and O/A ratio=2. In another paper by the same authors, they described the reactive extraction of Al in the presence of Co, Mg and Ni from sulphate solution with the same extractant described earlier. The removal percentage of Al was found to be 99.5% in a single step with pH = 3, temperature = 40°C and O/A ratio of 1. After scrubbing with water, Co and Mg were stripped from the organic phase. 99.6% stripping yield was obtained when 2M H_2SO_4 was used as the stripping agent at a temperature of 40°C with O/A ratio of 2:1.

Fang *et al.* (2004) [25] studied a liquid emulsion membrane process which uses 3,5-di-isopropyl salicylic acid (DIPSA) and tri-isobutyl phosphine sulphide (TIBPS) as carriers and as a precipitant ammonium sulphide $(NH_4)_2S$ was employed. Sulphide ions have a reactive nature with cadimuim ions in the aqueous (internal) which increased the cadmium recovery significantly and minimised the zinc impurities. This process was used to enrich low concentrated cadmium from a solution of highly concentrated zinc ions. A single stage process gave a cadmium recovery of 98% at 99.6% cadmium sulphide content under optimum conditions.

Reddy and Priya (2005) [26] used reactive extraction to remove Cu, Ni and Zn using LIX 841 from sulphate solutions. LIX 841 proved to be an effective extractant for selective separation of Cu, Ni and Zn. A flow sheet was also developed by them to remove the metals which had extraction efficiency and stripping yield > 99.5%.

Reddy *et al*. (2005) [27] used LIX 841 as an extractant and developed a flow sheet for separation and subsequent recovery of Cu(II), Zn(II) and Ni(II) from sulphate solution. They found out that selective separation of Cu(II), Zn(II) and Ni(II) was a function of equilibrium pH when LIX 84 I was used as an extractant. For Cu(II) the pH required was 4, Zn(II) required a pH of 9 and Ni needed a pH of 7.5 to be extracted. Under optimum conditions and in two stage contact operation the Cu(II), Zn(II) and Ni(II) extraction efficiency was found to be 99.4%, 99.81% and 99.4% respectively. A two stage stripping test was also performed for Cu(II), Zn(II) and Ni(II) with H_2SO_4 as the stripping agent and under optimum conditions the stripping yield was 99.94%, 99.7% and 99.93% respectively. They also designed a complete extraction and stripping flow sheet with efficiencies > 99%.

Mellah and Benachour (2006) [28] studied the solvent extraction of zinc and cadmium from phosphoric acid solutions using di-2-ethylhyhexyl phosphoric acid as the extractant and kerosene as the diluent. Different parameters namely, the extractant concentration, the O/A ratio and pH were varied and their effect on removal percentage was observed. Factorial design and Yates algorithm for non-linear regression were applied and the extraction was described by the equations $Zn_{aq}^{2+} + 1.5(H_2A_2)_{org} \rightarrow ZnA_2(HA)_{org} + 2H_{aq}$ + and $Cd_{aq}^{2+} + 1.25(H_2A_2)_{org} \rightarrow CdA_2(HA)^{1/2}$ org $+2H_{aq}^{+}$.

Ryszard, C. and Jan, S. (2007) [29] used di(2-ethylhexyl)pyridine-2,4-dicarboxylate (S), ACORGA CLX-50 (S) and LIX 54 (HL) used separately and in 1 : 1 mole/mole mixtures to extract Cu(II) from chloride solutions when the water activity, a_w and aqueous phase total concentration, σ of dissolved species were kept constant. They found that with these solvents Cu(II) extraction was high even when water activity was low and the extraction strongly depended on chloride concentration. At a pH of 2.4–3.9, LIX 54 had a low extraction capability and was not much affected by chloride concentration. For ACORGA CLX-50, in the chloride concentration range of 3-4M around 90% and 50% of Cu were extracted for $a_w = 0.617$ and $\sigma = 12$ M, and $a_w = 0.835$ and $\sigma = 8$ M respectively. Most of the chloride ions transferred to aqueous phase and simultaneously, Cu got converted from the solvate $CuCl_2S_2$

in the chealate CuL_2 when it was subjected to scrubbing by water at pH more than 4. Finally, 25-75g L^{-1} H_2SO_4 was used to strip copper and the organic phase was recycled.

Li *et al.* (2009) [30] described a process which included a leaching stage to obtain RE. Other metals like RE, Zn and Fe were extracted by solvent extraction with 20% P_2O_4 as the extractant in kerosene diluent, Co and Ni were scrubbed by 0.5 M of sulphuric acid and other RE were removed by stripping with HCl. After it, reactive extraction was again carried out to separate Co and Ni by 20% Cyanex 272 in kerosene. It was followed by the concentration and precipitation of the spherical nickel hydroxide. Sulphuric acid (1M) was used to strip Co and was concentrated with the formation of $CoSO_4$.

Fontana and Pietrelli (2009) [31] used the extractant HEHEPA and kerosene diluent to remove rare earth metals from chloride media. The order of the extraction under optimum conditions was Tb > Gd > Eu > Sm.

Xie *et al.* (2009) [7] studied the extraction of Cu^{2+} from waste cyanide solution with the help of LIX 7820 as an extractant. Low pH favoured the extraction but with high cyanide to copper ratio the extraction efficiency decreased. The solvent was also able to extract very strongly the zinc and nickel from the cyanide solution but showed weak affinity for iron cyanide complex. This process can be utilized for the extractional recovery of copper and cyanide from waste solutions of cyanide. After the extraction, the left over cyanide solution can be recycled back to cyanidation process.

Long *et al.* (2010) [32] used D2EHPA in sulphonate kerosene as an reactive extractant to remove zinc from sulphate solution. Zn extraction increased with pH, D2EHPA volume fraction and O/A ratio. The optimum conditions were pH = 2, 20% D2EHPA, O/A ratio = 1, contact time = 8 min, rpm = 200 and settling time = 10 minutes which lead to removal percentage of 38% which increased to 75% when saponified D2EHPA was used. Stripping tests were done with 196 g/L H_2SO_4 and 88.60% zinc 1.76% ferric ions were recovered.

Rodrigues and Mansur (2010) [33] developed two leaching stages which yielded 80-85% rare earth metals and 95-100% Ni for the first stage and in the second stage these values increased to 87% for rare earth metals and 100% for Ni. After leaching and filtration were performed, rare earth metals were precipitated with sodium hydroxide so that the leach liquor can be recovered. In the end, solvent extraction was performed with 0.5M D2EHPA at pH=3 and then by >0.6M Cyanex at pH = 5.7 to separate Cd, Co and Ni from the leach liquor. Around 97.8% rare earth metals were recovered.

Singh *et al.* (2011) [34] used a liquid membrane containing D2EHPA, a complexing agent to remove Cu, Ni and Zn simultaneously from an aqueous stream. Maximum extraction obtained for Zn, Cu and Ni was 98.8%, 95.8% and 95% respectively when the process was done under optimum conditions. With the increase in source phase concentration the distribution coefficients also increased. The highest distribution coefficient of 250, 150 and 50 was observed for Zn, Cu and Ni respectively for their initial concentration of 500 mg L^{-1}. A decrease in the final source phase concentration was observed with the increase in the pH difference. Minimum final source phase concentration of 25, 20 and 15 mg L^{-1} respectively for Ni, Cu and Zn was obtained for a pH difference of 4. A transport period of 5000 seconds gave the lowest source phase concentration of 60, 40 and 10 mg L^{-1} for Ni, Cu and Zn respectively. The maximum removal rate followed the pattern Zn > Cu > Ni under optimum conditions.

Zhu *et al.* (2012) [35] employed Versatic 10 and LIX 63 as solvent extractant to separate copper from Iron in solutions of high chloride concentration in a synergistic solvent extraction system (SSX). The SSX system selectively extracted copper over iron and other metals acting as impurity and transferred the extracted copper to a sulphate solution in which the copper was recovered by conventional electrowinning. It was proposed that copper exists as $CuCl_2$(neutral molecule) in high chloride solutions which forms complexes via a solvating mechanism with the organic components of the system.

Zhu *et al.* (2012) [36] described a synergising solvent extraction system (SSX) with Versatic 10, LIX 63 and TBP in Shellsol D70 as solvent extractant which was used to separate nickel, copper, cobalt and zinc from solutions with high chloride concentration. In this system, 95% of copper was extracted and around 12% Ni and negligible Co, Mn and Ca were extracted. The organic phase was scrubbed with water and loaded strip liquor was produced suitable for copper electrowhinning. In another SSX system, Alamine 336 and TBP in Shellsol D70, 99% Zn, 43%Mn and 87% Co were extracted (pH=3.5) from the Copper less raffinate of the first SSX system. After stripping, the cobalt, zinc and manganese can be separated by conventional solvent extraction or ion exchange process. A third SSX system comprising of the same solvents was used to extract Ni from the copper-cobalt-zinc less raffinate of the second SSX system. Around 98% of Ni was recovered in single contact. A process flow sheet was also developed to recover the Cu, Co, Ni and Zn from high chloride concentration solutions.

Innocenzi *et al*. (2012) [37] used D2EHPA and Cynanex 272 in n-dodecane as diluent to separate dissolved Ni from Mn and Zn from the solution formed after leaching of NiMH batteries. They found out that D2EHPA was a better extractant as compared to Cyanex 272. The extraction efficiency of > 99% for Zn and > 95% Mn was achieved at optimum conditions. When a two stage counter current flow was employed the extraction efficiency of Zn and Mn increased to 100% and 95% respectively and the remaining raffinate contained 80% of intial Ni concentration. The Zn and Mn were stripped from organic phase with 4M sulphuric acid and the yield was >99% for Ni and Zn and for Mn, it was 98%. In the end, a flow sheet was proposed to describe the whole process.

Kavitha *et al.* (2012) [38] used D2EHPA as carrier, DOP as plasticizer and CTA as polymer to study the permeation of Copper ions through polymer inclusion memembrane (PIM). The effects of various parameters namely, initial Cu(II) concentration, strip phase H_2SO_4 concentration and membrane D2EHPA concentration on transport were studied and it was found that transport of Cu(II) increased with the increase in feed Cu(II) concentration, increase in strip phase H_2SO_4 concentration. It increased to a certain value with the increase in membrane D2EHPA concentration. They also studied the kinetics of the Cu (II) transport and stability studies of membranes were also carried out.

Baba *et al.* (2013) [39] used a combination of TBP and Cyanex-272 as solvent extractants to recover Pb(II) and Zn(II) from galena ore leachate. The basic studies showed that extraction increased with the increase in pH, temperature and extractant concentration. Extraction yield of 92.1 ± 0.2% was observed for Pb(II) by 1mol/L TBP in MIBK at pH = 5 and for Zn(II) it was around 94.6 ± 0.2% by 0.032mol/L Cyanex 272 in kerosene at pH = 3. Stripping yield of 94.5 ± 0.2% Pb (II) and 94.6 ± 0.2% Zn(II) was obtained when the organic phase(TBP and Cyanex-272) was stripped with 0.1 mol/L HCl. Finally, an extraction scheme was proposed.

Devi *et al.* (2014) [40] used the extractant 5-nonylsalicylaldoxime and 2-hydroxy-5-nonylacetophenone oxime (LIX®973 NS-LV) in kerosene diluent to extract Cu(II) from chloride solution. Effect of Parameters namely, shaking time, extractant concentration, HCl concentration and salt concentration were studied. Under optimum conditions of extraction time = 2minutes and extractant percentage = 10% the separation of copper having initial concentration of 0.05M Cu(II) with 0.05M either Fe(II) or Fe(III) and 0.05M [Fe(II)+Fe(III)] was studied. The Fe(II) showed no extraction and on the other hand for Fe(III) separation factor of 25.13 was obtained when 0.005M HCl was used and Separation factor increased to 7325 when 0.5M sodium sulphate was used.

Jha *et al.* (2014) [41] used LIX 84 above pH = 2 in a single stage to separate Cu from sulphate leach solution. The other metals present in sulphate leach solution, namely Zn, Cd and Ni were extracted by 2.5% Cyanex 302. It was found at pH of 2.1, it extracted Zn and Cd together and left Ni in the raffinate. Cd and Zn were being able to be selectively stripped out by 10% HCl and 10% H_2SO_4 respectively. The extraction increased with increase in pH and O/A ratio.

Table 2.1. Copper removal using solvent extraction in various studies

Initial Cu^{2+} concentration	Extractant	Solvent	Optimum pH	% Removal	Ref.
1.5×10^{-3} M	N,N'-p-phenylene bis (5-amino-2-methyoxy-phenol)	Chloroform and Nitrobenzene	6	100	[5]
2×10^{-4} mol dm^{-3}	2-(o-hydroxyphenyl)benzothiazole	Chloroform + water	7	100	[6]
250 mg L^{-1}	LIX 7820	Quaternary amine Aliquat 336 + 4-nonylphenol	9.5	90	[7]
500 mg L^{-1}	D2EHPA	Soybean oil + TBP (Phase modifier)	4	98	[9]
0.1 mg L^{-1}	LIX 26 and LIX 84	Kerosene and Chloroform	2	100	[13]
1.57 mM	ALIQUAT 336	Kerosene	6.5	98	[18]
14 g L^{-1}	Versatic 10 + LIX 63	Shellsol D70	-	95	[35]
12.4 g L^{-1}	LIX63, Versatic 10 + TBP	Shellsol D70	0.5	95	[36]
15.4×10^{-4} mol L^{-1}	D2EHPA	dichloromethane	4.5	70	[38]
0.92 g L^{-1}	LIX 84	kerosene	2.65	98.73	[41]

CHAPTER – 3

EXPERIMENTAL STUDY

The equilibrium and the kinetic studies are based on the results obtained from the experiments performed. The experimental methodology that is followed to obtain the extraction properties for the extraction of Cu^{2+} from its aqueous solutions is described in this chapter. In the experiments, firstly, it was tried to observe the effect of various parameters like extractant-diluent concentration, initial Cu^{2+} concentration, aqueous to organic ratio, pH and temperature on the removal efficiency of Cu^{2+} and secondly, the efficiency of extractant in removing Cu^{2+} after being stripped was studied.

3.1 Materials and equipments

Table 3.1 List of materials used in the study

Chemical	**IUPAC Name**	**MW/ kg kmol^{-1}**	**Density /kg m^{-3}**	**Viscosity /cP**	**Supplier**	**Purity (%*w*)**
Copper Sulphate (anhydrous)	Copper(II) Sulphate	159.60	360	-	Loba Chemie Private Limited, India	98
Tri-*n*-butyl phosphate (TBP)	Tri-*n*-butyl phophate	266.32	970	3.4(25^{0}C)	Spectrochem, India	99
Benzene	Cyclohexa-1,3,5-triene	78.11	972.7	0.6076 (25 ^{0}C)	Spectrochem Private Limited, India	99.5

Sulphuric acid	Sulphuric acid	98	1840	26.7 (20^0C)	Spectrochem Private Limited, India	98
Sodium Hydroxide	Sodium hydroxide	40	2130	-	SD fine chemicals private limited, India	97

Distilled water used to prepare the aqueous solutions of various concentrations of Cu^{2+}, is procured from S. D. Fine-Chem Ltd., India.

The equilibrium extraction experiments are carried out in the conical flasks (RANKEM, India) of 100 mL which were placed in a temperature controlled water shaker bath (LSB-24) of Spectralab, India. Temperature was maintained constant inside the shaker at 298 K according to the type of equilibrium experiments. The ingredients of these flasks were separated by using a pipette of 5ml after the extraction is complete. The initial and equilibrium pH values of aqueous solutions are measured using a digital pH-meter of MRC Scientific Instruments (86555), India. The final concentration of Cu^{2+} in the aqueous phase was determined by Atomic Absorption Spectrophotometer GBC 932AA, Australia.

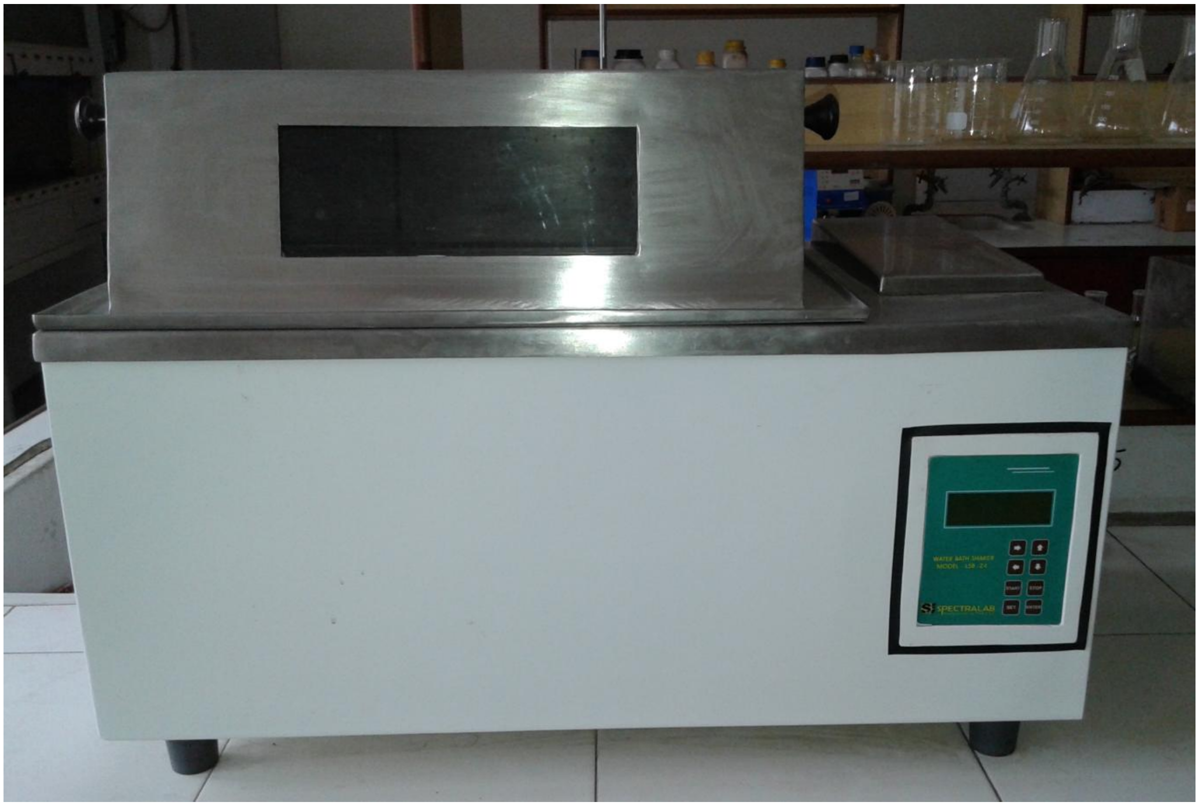

Fig.3.1. Temperature controlled water shaker bath (LSB-24) of Spectralab, India.

3.2 Experimental Procedure

3.2.1 Variation of parameters

The ranges of parameters used in this study are determined as such, to simulate the conditions of actual industrial waste water streams. The upper limit of the aqueous phase copper concentration has been taken to be 100 mg L^{-1} which is in the range of the maximum concentration of Cu^{2+} found in the waste water streams. The lower limit is chosen to be 20 ppm which is generally the minimum concentration of Cu^{2+} found in these waste water streams and beyond which the concentration is too low to be separated fruitfully. Different concentrations of the Cu^{2+} are made from the stock solution of 100 mg L^{-1}. The TBP(extractant) and dilutent(benzene) are mixed together as TBP is highly viscous and benzene when mixed with it decreases its viscosity. The TBP amount in the mixture was varied as 10 to 50% (0.365 to 1.825 mol L^{-1}). Organic phase (TBP-Benzene mixture) and aqueous phase (initial Cu^{2+} solution) are varied in the ratio of 1:3 to 3:1 in order to see it's effect on the removal efficiency of Cu^{2+}. In order to see the effects of pH, the pH of the aqueous phase was varied from 2 to 11. 4N H_2SO_4 was used to ceontrol the acidity while 4N NaOH was used to make the solution basic when needed. The extraction experiments were done at a temperature range of 298 K to 333 K to see the effect of temperature on the extraction efficiency.

3.2.2 Cu^{2+} Removal by Reactive Extraction

A 100 ppm solution was prepared by mixing 0.125 gm. of cupric sulphate in 500 ml of solution. 60 ppm and 20 ppm solution were prepared by serial dilution and were kept in separate 500 ml beakers. 20 ml of each solution was taken and 10%, 30% and 50% TBP-Benzene mixture was added to each of them and the extraction of Cu^{2+} was carried out by keeping all the solutions in the incubator shaker for 3 hrs at 298K. After 3 hrs, 5ml of aqueous phase was taken out of the Extract-raffinate mixture using a pipette making sure no organic materials comes along with it. Concentration of Cu^{2+} in the final aqueous phase is determined using the AAS. Percentage extraction was calculated using the formula

$$\frac{\mathrm{Cu}^{2+}_{\mathrm{initial}}\ (\mathrm{aqueous}) - \mathrm{Cu}^{2+}_{\mathrm{final}}\ (\mathrm{aqueous})}{\mathrm{Cu}^{2+}_{\mathrm{initial}}\ (\mathrm{aqueous})} \times 100$$

3.2.3 Stripping of Organic Phase

The extract phase was taken out after the extraction experiment and put into beakers. The extract phase containing the TBP-Benzene and Cu^{2+} was mixed with 4 M H_2SO_4 in the ratio of 2:1. The mixture was then put in the shaker for around 1 hour. It was then allowed to settle so that the newly formed aqueous and organic phases can be separated. The organic phase was separated from the mixture and the extraction experiments were completed in the same way like the original extraction experiments. The aqueous stream was analysed and the final concentration of aqueous stream was found with AAS and removal percentage was calculated.

CHAPTER – 4

RESULTS AND DISCUSSION

4.1. Effect of Various Parameters on the Extraction of Cu^{2+}

The effect of contact time (0 to 180 min), O/A phase ratio (1:1 to 3:1 and 1:3 to 3:1), equilibrium pH (2 to 11), initial Cu^{2+} concentration (20 to 100 mg L^{-1}) and TBP concentration (0.365 mol L^{-1} to 1.825 mol L^{-1}) on the extraction of Cu^{2+} has been investigated and the results are reported in Figs. 4.1-4.5.

4.1.1. Effect of Contact Time

The reactive extraction experiments were carried out at a time range of 10 to 300 min. The operating conditions for these experiments were [TBP] = 0.365 mol L^{-1}, O/A ratio = 1:1, initial concentration of Cu = 20mg L^{-1}, equilibrium pH = 6.0 ±0.1 and at temperature of 298K. The removal percentage of Cu increased with the increase in the contact time till 120 minutes and then it stayed constant at 99.45%. The equilibrium was set at 120 minutes. A contact time of 180 minutes was taken in all the other experiments to make sure the equilibrium is reached (Fig.4.1)

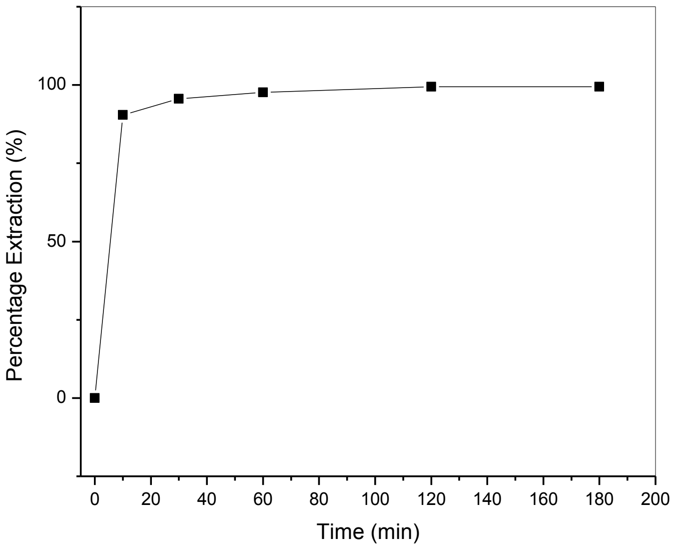

Fig. 4.1. The effect of contact time on the removal percentage of Cu^{2+} . [TBP] = 0.365 mol L^{-1}, O/A ratio = 1:1, $Cu^{2+}_{initial}$ = 20 mg L^{-1}, pH = 6.0 ± 0.1 and temp. = 298K

4.1.2. Effect of O/A phase Ratio

The operating conditions used were [TBP] = 0.365 mol/L and 1.825 mol/L, and equilibrium pH = 6 at 298 K. The O/A phase ratio was varied between 1:3 and 3:1. The results are shown in Fig. 4.2. The extracted metal percentage increased with increasing the O/A phase ratio. The variation of the phase ratio from 1/3 to 3/1 lead to an increase in the percentage of extracted metal from 89.65 to 96 % and from 94.85 to 98.75 % for Cu^{2+} (20 ppm) at TBP concentration of 0.365 mol/L and 1.825 mol/L, respectively. For a fixed initial copper concentration in aqueous stream, as the amount of organic phase is increased, more Cu-TBP complex can be formed because of abundance of TBP and as a result of this, the extraction percentage increases.

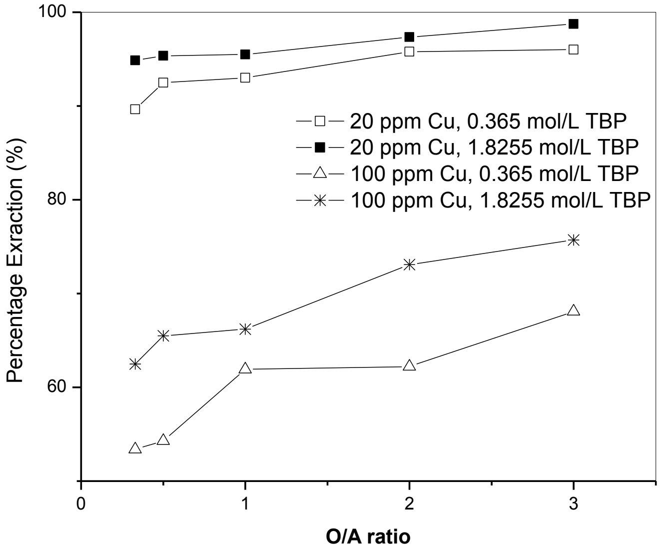

Fig. 4.2. Influence of the O/A phase ratio on the Cu^{2+} extraction when [TBP] = 0.365 mol L^{-1} and 1.825 mol L^{-1}, contact time = 120 mins, $Cu^{2+}_{initial}$ = 20 mg L^{-1} and 100 mg L^{-1} , pH = 6.0 ± 0.1 and temp. = 298K

4.1.3. Effect of Equilibrium pH

In order to study the effect of pH on the extraction efficiency, the operating conditions were fixed as $Cu_{initial}$ = 20 mg L^{-1} and 100 mg L^{-1}, TBP concentration = 0.365 mol L^{-1} and 1.825 mol L^{-1} and O/A ratio = 1:1 at temperature = 298 K. The pH was varied from 2 to 11. Fig. 4.3. Inferences that at pH of 6 the extraction is highest and for $Cu_{initial}$ = 20 mg L^{-1} and extractant concentration of 1.825 mol L^{-1} it was the highest at 96.5%. The graph also inferences that for low $Cu_{initial}$ values effect of pH is more prominent. A possible explanation can be stated as at low pH values the protons act in competition with Cu^{2+} to form weak bonds with the TBP which has a slightly negative charge owing to its dipole moment and at high pH values Cu^{2+} ions tries to accept electrons from the solution resulted due to increased basicity.

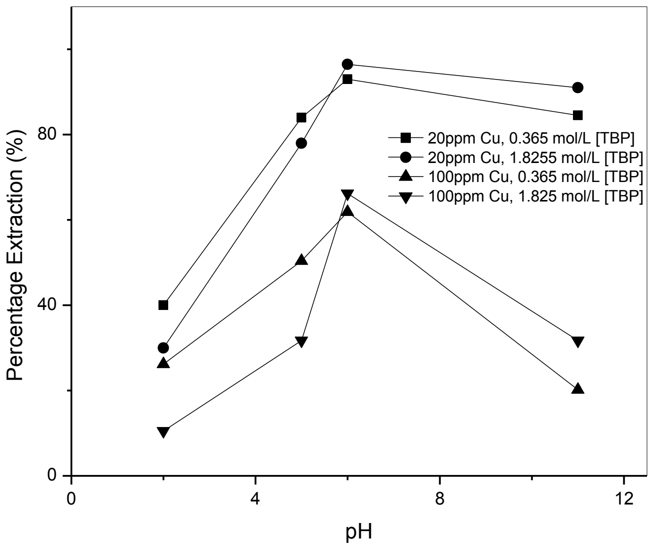

Fig. 4.3. Influence of the pH on the Cu^{2+} extraction when [TBP] = 0.365 mol L^{-1} and 1.825 mol L^{-1} , contact time = 120 mins , $Cu^{2+}_{initial}$ = 20 mg L^{-1} and 100 mg L^{-1}, O/A ratio = 1:1 and temp. 298K.

4.1.4. Effect of TBP Concentration and initial Cu^{2+} concentration

The effect of TBP concentration on the extraction ratio of Cu^{2+} was studied in the range of 0.365 mol L^{-1} to 1.825 mol/L. The operating conditions used were: equilibrium pH = 6.0 ± 0.1 and O/A phase ratio = 1:1 at 298 K. It was observed that the extraction percentage increased with increase of extractant concentration (Fig. 4.4). In the extractant concentration range, the increase was from 93 to 96.5 % at 20 mg L^{-1} initial Cu^{2+} concentration but a lower extraction is observed at 100 mg L^{-1} of initial Cu^{2+} concentration (61.9 to 66.2 %). Extraction percentage decreases with the increase in initial concentration of Cu^{2+} for a fixed extractant concentration because at equilibrium most of the Cu^{2+} ions present in lower initial concentrations of aqueous phase makes Cu-TBP complex whereas at higher initial concentrations because of the increase in Cu^{2+} ions but for the same extractant concentration, only a few Cu^{2+} ions are able to make Cu-TBP complex and rest are left in the aqueous phase. That leads to an decrease in the percentage extraction. For a fixed initial concentration of Cu^{2+} , the percentage extraction increases with the increase in extractant concentration as more TBP molecules are available for every Cu^{2+} ions in the aqueous phase.

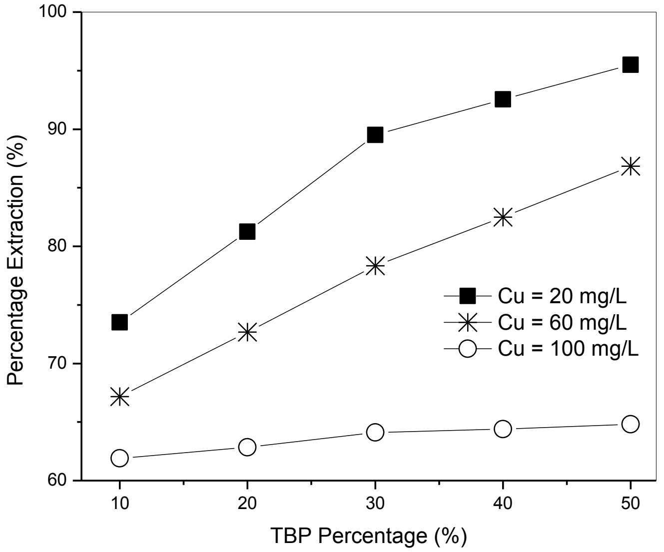

Fig. 4.4. Effect of the TBP concentrations on the Cu^{2+} extraction. pH = 6.0 ± 0.1, contact time = 120 min, $Cu^{2+}_{initial}$ = 20 mg L^{-1}, 60 mg L^{-1} and 100 mg L^{-1} , O/A ratio = 1:1 and temp. 298K.

4.1.5. Effect of Temperature

The temperature was varied from 298 K to 333 K to study its effect on removal percentage of Cu. The operating conditions were: initial Cu^{2+} concentration = 20 and 100 mg/L, extractant concentration = 10 and 50 mol/L, pH = 6.0 ± 0.1 and O/A phase ratio = 1:1. With an increase in the temperature a decrease in removal percentage (Fig. 4.5) was observed. It was observed that extraction is higher when the temperature is low and it decreases as the temperature is increased concluding that extraction process is more favourable at low temperature.

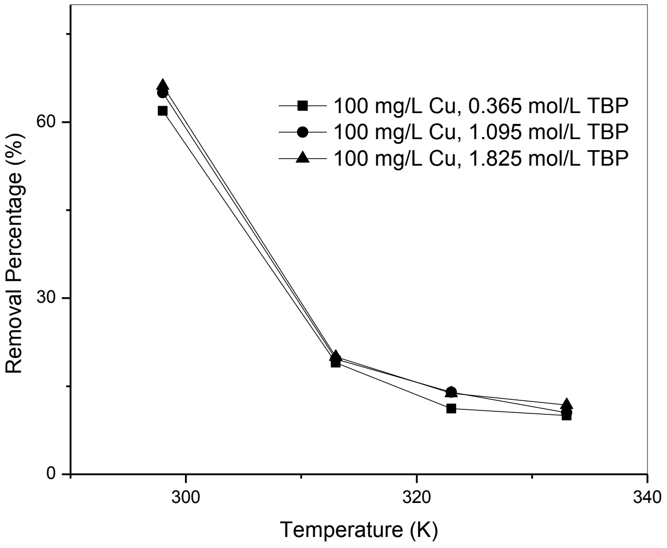

Fig.4.5a

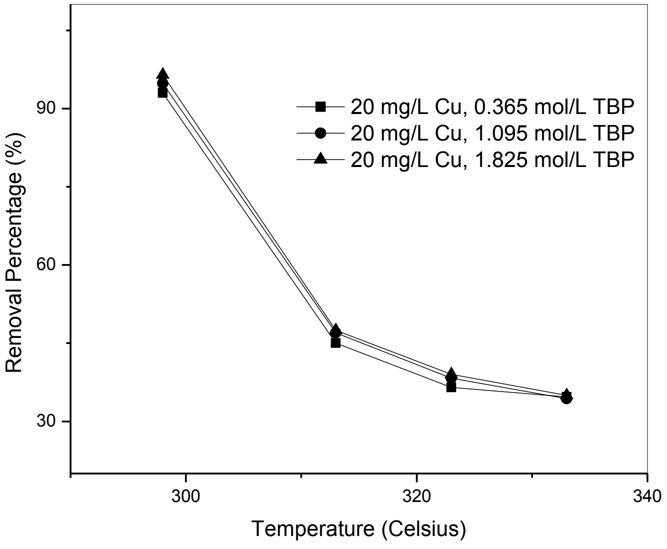

Fig.4.5b

Fig. 4.5. Effect of temperature on the removal percentage of Cu^{2+}. pH = 6.0 ± 0.1, contact time = 120 min, O/A ratio = 1:1 and [TBP] = 0.365 mol L^{-1} (10%), 1.095 mol L^{-1} (30%) and 1.825 mol L^{-1} (50%), (a) $Cu^{2+}_{initial}$ = 20 mg L^{-1} (b) $Cu^{2+}_{initial}$ = 100 mg L^{-1}

4.2. Regeneration of Extract Phase

A two stage stripping process with H_2SO_4 as the stripping agent was performed to observe the reusability property of the extractant. The operating conditions were: O/A ratio = 1:2, stripping agent concentration = 4N and temperature = 343K. After each stage, fresh H_2SO_4 was used to strip the organic phase after the phase the phase separation. The organic phase separated after phase separation from each stage was used for extraction experiment under the operating conditions of: initial Cu^{2+} concentration = 20 mg L^{-1} and 100 mg L^{-1}, extractant concentration (received from stripping experiments) = 0.365 mol L^{-1} and 1.825 mol L^{-1}, O/A phase ratio = 1:1 at 298 K. Removal percentage decreased with the increase in number of stages. 1st stage highest removal percentage of 9% and 31% was obtained for intial Cu^{2+} concentration of 20 mg L^{-1} and 100 mg L^{-1} respectively. 2nd stage highest removal percentage of 6.5% and 18.3% was obtained for 20 mg L^{-1} and 100 mg L^{-1} respectively.

4.3 Reaction Stoichiometry and Equilibrium

The cation exchange is the principal mode of action of the phosphoric extractant during the extraction reaction. The oxygen atom of the phosphoryl group P=O ensures coordination with the ions extracted by forming chelating products [28]. It also plays an important role when the extraction is carried out, starting from the strongly acidic aqueous solutions, since TBP behaves like a solvating agent. It is assumed that the solubilities of the extractant and the Cu-TBP complex in the aqueous phase are negligible and that the species extracted are not associated with each other. The mechanism for the extraction of Cu^{2+} metal ion from the aqueous phase can be given as [22, 42]:

$$\mathrm{Cu}_{\mathrm{aq}}^{2+} + m\mathrm{TBP}_{\mathrm{org}} \leftrightarrow (\mathrm{Cu} \bullet \mathrm{TBP}_{m})_{\mathrm{org}} \qquad (4.1)$$

Where, *m* is the number of molecules of extractant engaged in the reaction. The equilibrium constant of the extraction reaction, K_{eq}, can be given as a function of molar concentration, provided that the ionic strength of the aqueous solution is constant.

$$K_{\text{eq}} = \frac{[(\text{Cu} \bullet \text{TBP}_m)_{\text{org}}]}{[(\text{TBP})_{\text{org}}]^m [\text{Cu}^{2+}]_{\text{aq}}} \qquad (4.2)$$

The distribution coefficient (K_D) on molar concentration scale is expressed in terms of the total concentration of the Cu^{2+} in all its possible forms in the aqueous phase, $[Cu^{2+}]_{aq}$ and organic phase, $[Cu^{2+}]_{org}$ given as:

$$K_{\text{D}} = \frac{[(\text{Cu} \bullet \text{TBP}_m)_{\text{org}}]}{[\text{Cu}^{2+}]_{\text{aq}}} \qquad (4.3)$$

$$K_{\text{D}} = K_{\text{eq}} [(\text{TBP})_{\text{org}}]^m \qquad (4.4)$$

Taking the logarithm of the above equation, one obtains:

$$\log K_{\text{D}} = \log K_{\text{eq}} + m \log[\text{TBP}]_{\text{org}} \qquad (4.5)$$

This equation is the defining statement for the equilibrium studies of the Cu^{2+} metal extraction. Thus a straight line plot between $\log K_{\text{D}}$ on the y-axis and log $[TBP]_{org}$ on the x-axis, would give the slope, i.e, the number of molecules of TBP (m) reacting with Cu^{2+} ion. The linear graph in Fig. 4.6 between log K_D and log $[TBP]_{org}$ will give the intercept and slope values which will lead to values of m and K_{eq} for 298 K .

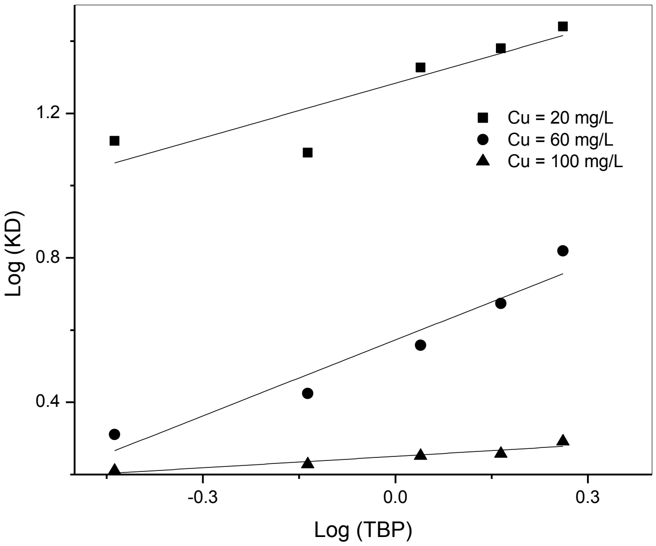

Fig. 4.6. Linear plot between log $(TBP)_{org}$ and log (K_D) when pH = 6.0 ±0.1, contact time = 120 mins , $Cu^{2+}_{initial}$ = 20 mg L^{-1}, 60 mg L^{-1} 100 mg L^{-1} , O/A ratio = 1:1, [TBP] = 0.365 mol L^{-1} (10%), 1.095 mol L^{-1} (30%) and 1.825 mol L^{-1} (50%) at temp. 298 K

The m and K_{eq} values comes out as follows -

Table 4.1. m and K_{eq} values at 298 K to find out the reaction stoichiometry

Initial Cu^{2+} concentration, ppm	m	**Intercept**	K_{eq}
20	0.50468	1.28344	19.20613601
60	0.70085	0.5726	3.737661783
100	0.10558	0.25036	1.779754091

The average value of m comes out to be 0.77037 and the reaction stoichiometry present itself as

$$Cu^{2+}_{aq} + 0.77037TBP_{org} \leftrightarrow (Cu \bullet TBP_{0.77037})_{org} \qquad (4.6)$$

4.4 Thermodynamic Analysis

Over a temperature range if the enthalpy and entropy of reaction are assumed to be constant, the equilibrium constant for the extraction can related to temperature by the Van't Hoff equation [43]–

$$\ln K_{eq} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \qquad (4.7)$$

This equation can be presented as a linear plot between ln K_{eq} and 1/T and the slope and intercept values will give the apparent enthalpy and entropy of the reaction respectively.

K_{eq} values can be determined the methodology described in unit 4.3 for different temperatures namely 298, 313, 323 and 333K as shown in figure 4.7,4.8,4.9 and 4.10. Henceforth, a linear plot can be developed between the ln K_{eq} and 1/T values as shown in figure 4.11.

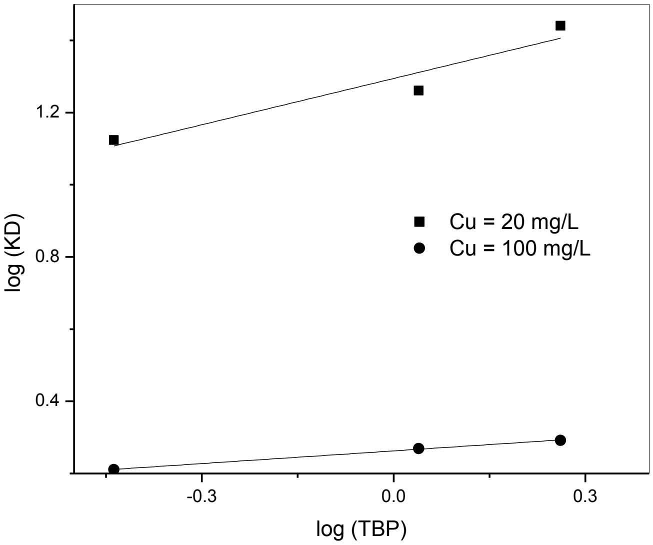

Fig. 4.7. Linear plot between log $(TBP)_{org}$ and log (K_D) at 298K

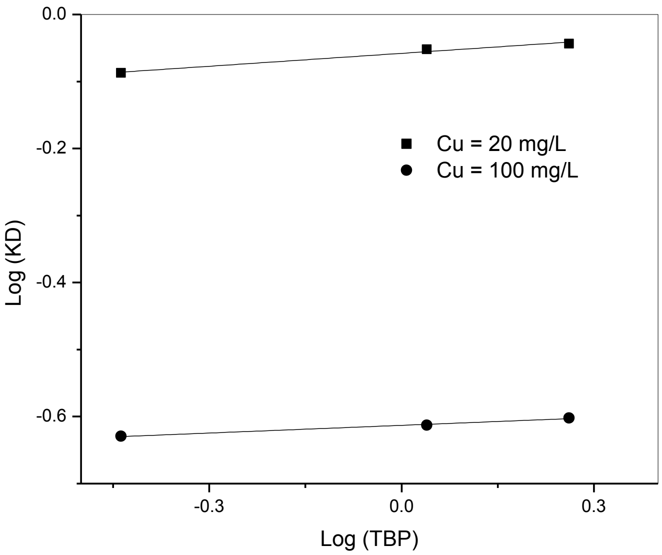

Fig. 4.8. Linear plot between log $(TBP)_{org}$ and log (K_D) at 213K

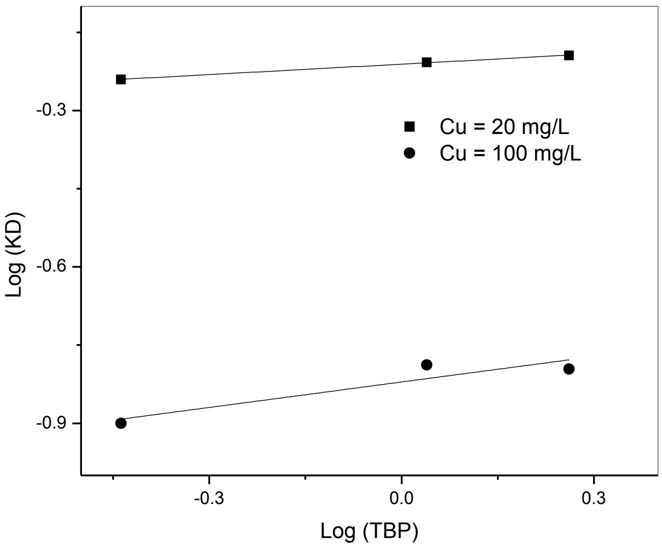

Fig. 4.9. Linear plot between log $(TBP)_{org}$ and log (K_D) at 323K

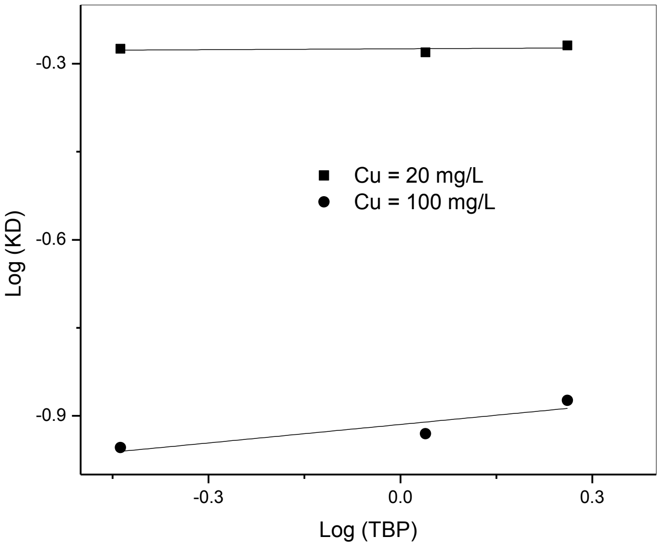

Fig. 4.10. Linear plot between log $(TBP)_{org}$ and log (K_D) at 333 K

Table 4.2. *m* and K_{eq} values for different temperatures

$Cu^{2+}_{initial}$, mg L^{-1}	***m***		**Intercept**		***Keq***	
Temp, K	**20**	**100**	**20**	**100**	**20**	**100**
298	0.427	0.117	1.294	0.262	19.697	1.830
213	0.064	0.038	-0.058	-0.613	0.874	0.243
323	0.066	0.162	-0.211	-0.820	0.615	0.151
333	0.005	0.104	-0.274	-0.914	0.531	0.121

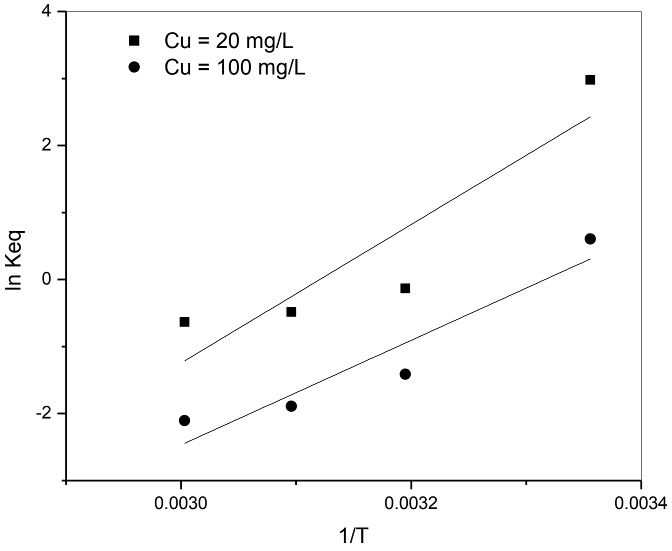

Fig. 4.11. Linear plot between ln K_{eq} and 1/T to find the values of enthalpy change and entropy change

Table 4.3. Enthalpy change and entropy change for the extraction

Intial Cu^{2+} Concentration (ppm)	**Enthalpy Change ($kJ\ mol^{-1}$)**	**Entropy Change ($J\ mol^{-1}\ K^{-1}$)**
20	-85.88	-267.99
100	-64.84	-215.03

It can be seen that enthalpy change is -85 $kJ\ mol^{-1}$ which shows that the extraction reaction is exothermic and low temperatures would favour the extraction experiments. A low value of entropy change further informs us that the system is well ordered because of the formation of Cu-TBP complex.

4.5 Determination of mass transfer coefficient

For better understanding of the movement of Cu^{2+} ions from aqueous phase to organic phase, it is imperative to determine the mass transfer coefficient. As TBP has low distribution coefficient in water [44] we can safely assume that resistance offered by aqueous diffusion film is negligible. The only resistance that the transport of Cu^{2+} ions will get will be by organic diffusion film. From the definition of mass transfer rate, we can write that –

$$\frac{V_{org}}{A} \cdot \frac{dC_{org}}{dt} = k_L\left(C_{org}{}^{*} - C_{org}\right) \tag{4.8}$$

and simplifying it,

$$\ln\left(\frac{C^{*}{}_{org}}{C^{*}{}_{org} - C_{org}}\right) = \frac{k_L A}{V_{org}} \cdot t \tag{4.9}$$

It depicts a linear plot between $\ln\left(\frac{C^{*}{}_{org}}{C^{*}{}_{org} - C_{org}}\right)$ and t which gives $\frac{k_L A}{V_{org}}$ as the slope. As Interfacial area and organic phase volume are known, k_L can be found out.

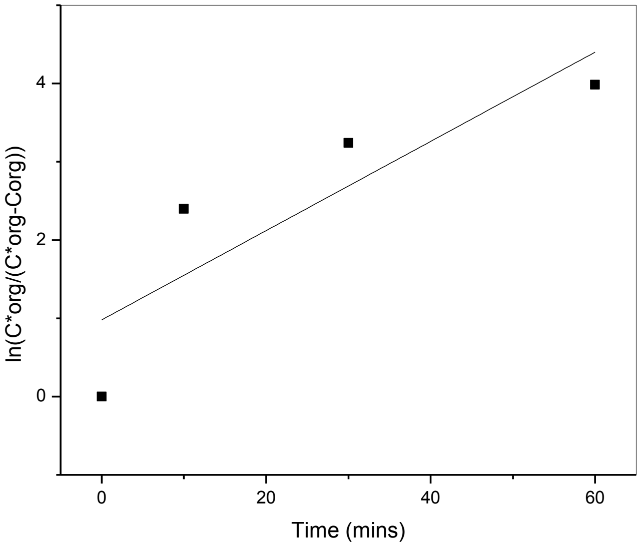

Fig. 4.12. Linear plot between $\ln(C_{org}{}^{*}/(C_{org}{}^{*} - C_{org}))$ and time to find k_L

The value of k_L comes out to be 9.07 x 10^{-4} m s^{-1}. A high value of mass transfer coefficient means the mass transport of Cu^{2+} is an integral part of the Cu^{2+} transport from aqueous phase to the organic phase.

CHAPTER – 5

CONCLUSIONS

Experiments were performed to remove Cu^{2+} from aqueous streams with the help of TBP as the extractant.

Extraction yield better results when initial concentration of Cu^{2+} is low and the maximum removal percentage was observed for initial Cu^{2+} concentration of 20 mg L^{-1}.

Extractant concentration has a minimum effect on removal percentage when initial Cu^{2+} concentration is high and at low initial Cu^{2+} concentration increase in extractant concentration gives rapid rise in removal percentage. Maximum removal percentage of 95% was observed when initial Cu^{2+} concentration was 20 mg L^{-1} and extractant concentration was 1.825 mol L^{-1}.

Variation of O/A ratio has prominent effect on higher initial concentration of Cu^{2+} although the removal percentage in this case was lower as compared to cases of lower initial concentration of Cu^{2+}.

Variation of pH showed that extraction process was unfavourable at both high and low pH values and had maximum removal percentage at a pH of 6. A possible explanation can be stated as at low pH values the protons act in competition with Cu^{2+} to form weak bonds with the TBP which has a slightly negative charge owing to its dipole moment and at high pH values Cu^{2+} ions tries to accept electrons from the solution resulted due to increased basicity.

Extraction process proceeded very fast in the first 60 minutes and equillibrium was reached at 120 minutes and the extraction percentage reached 98% for initial Cu^{2+} concentration of 20ppm and extractant concentration of 0.365 mol L^{-1}.

Stoichiometric analysis was able to give the extraction mechanism and it can be represented as

$$\mathrm{Cu}_{\mathrm{aq}}^{2+} + 0.77037\mathrm{TBP}_{\mathrm{org}} \leftrightarrow (\mathrm{Cu} \bullet \mathrm{TBP}_{0.77037})_{\mathrm{org}}$$

Thermodynamic analysis showed that the extraction process was a exothermic reaction and low temperature favoured the extraction which was also proved by the analysis of effect of temperature variation on removal percentage which showed that as the temperature was increased from 298K to 333K the removal percentage decreased. Thermodynamic analysis also proved the formation of stable Cu-TBP complex which was substantiated by the low entropy change for the system.

The mass transfer coefficient was calculated and it came out as 9.07×10^{-4} m s^{-1} which is a relatively high value for reactive extraction process which inferences that mass transfer plays an important role in the transport of Cu^{2+} ions.

CHAPTER – 6

SCOPE OF FURTHER STUDY

Stripping process is a necessary part of the reactive extraction process. It allows the reusability of the used extractant. It is dependent on pH, temperature, type of stipping agent used and the concentration of the stripping agent. A proper plan can be developed to make the stripping process effective.

Kinetics of the reactive extraction process can be found out by initial rate law method following the rate equation as follows –

$$r_{C_o} = k\left[Cu_{aq}{}^{2+}\right]^{\alpha}.[TBP_{org}]^{\beta}$$

After finding out the rate law, Hatta No. can be found out following the equation –

$$Ha = \frac{\sqrt{1.11 \cdot k\left[Cu_{aq}{}^{2+}\right]^{\alpha}.[TBP_{org}]^{\beta}D_{HC}}}{k_L}$$

The value of Hatta number will then determine whether the regime of reactive extraction will be reaction controlled or mass transfer controlled [45].

CHAPTER – 7

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