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Selective extraction, separation and recovery of Cu(II) in presence of Zn(II) and Ni(II) from leach liquor of waste printed circuit board using microcapsules coated with Cyanex 272

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Abstract−The study was conducted to optimize the selective extraction and recovery of Cu(II) in the presence of Zn(II) and Ni(II) from the leach liquor of waste printed circuit boards (PCBs). The extraction experiments were carried out according to 2^4 factorial design of experiment to optimize the extraction factors. The design was analyzed using MINITAB to determine the main effects and interactions of the chosen extraction factors. The factors chosen were: extraction pH, amount of Cyanex 272 in dispersed phase during MC-Xs preparation, amount of MC-Xs and temperature. The pH, amount of MC-Xs and temperature were found to be statistically significant. The optimized experimental conditions for the Cu(II) extraction in presence of Zn(II) and Ni(II) were extraction pH 6.0, amount of Cyanex 272 in dispersed phase 3 g, amount of MC-Xs 2.5 g and Temperature 45 °C. Factorial design of experiment was also carried out to determine the Cu(II) stripping factors from the loaded MC-Xs using H_2SO_4 solution. The liquid-liquid extraction Cu(II) was conducted with the prime aim to evaluate the nature of Cu(II) complex extracted by Cyanex 272. Results showed that the extraction species is $[Cu(HA_2)(Ac)\cdot 2HA]$. Finally, a complete process for the separation and recovery of Cu(II), Zn(II) and Ni(II) from the leach liquor of waste PCBs was conducted based on the optimized experimental condition and effect of pH on extraction.

Key words: Copper, Cyanex 272, Factorial Design, Microcapsules, Printed Circuit Board

INTRODUCTION

The interest in determining the trace of heavy metals from waste materials has increased immensely due to their limited ore resource, economical values and environmental impacts. Metal ion recovery from waste materials is now a major concern of policy-makers, environmentalists, and engineers in terms of environmental protection and metal resource as well as economic benefit. Among the various types of waste materials, concern on waste printed circuit boards (PCBs) is increasing worldwide due to the significant increase of generation, serious negative impacts for environment as well as metals resource [1-3]. PCBs contain many valuable metals, where the metals content is about 28% [2]. Among these valuable metals, PCBs contain 10-30% copper, depending on the source and type of the circuit board [1,2,4-6]. Hence, the recovery of Cu(II) from the PCBs is bearing considerable interest not only for the treatment of the waste PCBs but also for the recovery of a valuable metals.

Numerous studies have been conducted worldwide to define the selective extraction separation and recovery process of Cu(II) from waste PCBs including mechanical process, pyrometallurgical process and hydrometallurgical process [5-8]. Among the methods applied, the hydrometallurgical process offers significant advantages over other processes [5,9]. However, selective recovery of Cu(II) has been obtained in presence of Zn (II) and Ni(II) from leach liquor of PCBs using microcapsules coded with Cyanex 272 (MC-Xs) batchwise [1]. From the study, one can observe that the classical batch extraction system requires many experimental runs in each of the variables to optimize experimental conditions that lead to economical loss as well as being time consuming.

In almost all branches of science and engineering, there are many variables influencing the processes, and hence a quantitative assessment of their efficiency is required. The conventional approach utilized in the investigation of process variables is one variable at a time. This method can potentially miss some important aspects of the variables contributing to the response, which usually involves interactions between or among the factors that are being investigated. Statistical analysis, specialty factorial design of experiments and analysis of the variance approach can be highly applicable for this purpose, since factorial design of experiments and analysis of the variance are effective techniques to study any process behavior. Usually, they are most efficient to estimate the effects of several variables simultaneously, where one variable is varied at a time in the general method [10]. In factorial design of experiments, experiments are conducted in an organized manner and analyzed systematically to obtain the yields with much needed information that can be applied for the optimization purpose through analysis. In analysis of variance, factors are estimated by yields analysis obtained for all the coefficients (main effects and all relevant interactions of factors) in 2-level full or fractional factorial experiments [10,11]. Then, the

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analysis is able to declare the optimum experimental conditions of each of the variables with significant effects and intersections of the factors by incorporating a certain confidence level [10].

It is, therefore, of interest to use factorial design of experiments and analysis of the variance to obtain the optimal extraction and separation performance and to determine the optimum experimental condition of extraction of Cu(II), Zn(II), and Ni(II) from the leach liquor of PCBs using MC-Xs. Therefore, in the present study, experiments were conducted according to 2^4 factorial design, and the design was analysis using MINITAB (version 14) to determine the experimental conditions of Cu(II) in the presence of Zn(II), and Ni(II) using MC-Xs. The extraction mechanism of Cu(II) with Cyanex 272 was also evaluated in the present study. However, the content of Cyanex 272 in MC-Xs was not controlled during the preparation. Hence, the extraction mechanism was evaluated in liquid-liquid extraction system with prime aim to observe the nature of Cu(II) complex extracted by Cyanex 272.

EXPERIMENTAL SECTION

1. Reagents

Cupric sulfate ($CuSO_4 \cdot 5H_2O$) with the purity above 99% was obtained from Labjax chemical Ltd. Extractant Cyanex 272 (92%), i.e., bis (2, 4, 4-trimethylpentyl) phosphinic acid was obtained from Cytec Industries Inc., Canada. Dichloromethane was obtained from Mallinckrodt Chemicals, USA. Gum arabic used was obtained from Sigma Aldrich. Polystyrene used was obtained from Beijing Yanshan petrochemicals co., Ltd. All other chemicals used were of at least reagent grade.

2. Apparatus

The mixing of aqueous and organic phases in liquid-liquid extraction was carried out using a wrist-action flask shaker (SFI, Stuart Scientific). The MC-Xs were characterized by using an optical microscope equipped with a digital camera and scanning electron microscopy (JEOL JSM 6400, Model-6210). All batch experiments were performed using hotplate stirrer (Harmony, Japan, Model HTS-1003). The pH of aqueous solutions was measured with a digital pH meter (Eutech Instrument, Singapore, Model 300/310). An atomic absorption spectrophotometer (AAS) (Perkin Elmer, Model Analyst 700) was used for the analysis of metal ions values in the aqueous solutions.

3. Liquid-liquid Extraction of Cu(II)

The liquid-liquid extraction of Cu(II) was conducted from the synthetic aqueous solution. The organic phase was prepared by diluting Cyanex 272 in hexane. 10 milliliters aqueous solution containing Cu(II) ion and equal volume of organic solution containing desired concentration of Cyanex 272 were shaken and equilibrated at room temperature (25±1 °C) for 30 minutes. After disengagement phase, the raffinate was separated and the equilibrium pH was measured. The Cu(II) ion concentration in the aqueous phase was analyzed by AAS after the desired dilution with 0.1 M HNO_3. The concentration of Cu(II) ion in the organic phase was calculated by the difference between the Cu(II) ion concentration in the aqueous phase before and after extraction. The distribution ratio (D) was calculated at the Cu(II) ion present in the organic phase to that of in the aqueous phase at equilibrium.

4. Leaching of Waste Printed Circuit Boards

Leaching studies were carried out following the same procedure of our previous study [1]: 100 ml of ammoniacal alkaline solution [NH3-$(NH_4)_2SO_4$] and 400 mg crushed PCBs were taken in a 500 ml round bottom flask, fitted with water cooled condenser and stirrer, which was immersed in oil bath maintained at 60±1 °C for 24 hours. Concentrations of Cu(II), Zn(II) and Ni(II) contents in the leach liquor were determined by AAS and found to be 535.01 ppm, 18.28 ppm and 15.23 ppm, respectively.

5. Extraction of Metal Ions from the Leach Liquor of Waste PCBs Using MC-Xs

MC-Xs were prepared following the optimized preparation conditions of MC-Xs as described elsewhere [1]. Later, the prepared MC-Xs were used to extract metal ions in from the leach liquor of waste PCBs. 20 milliliters of aqueous sulfate solution containing metal ions and desired amount of MC-Xs were mixed together in 100 ml stoppered conical flasks. The mixer was stirred using a hotplate magnetic stirrer for 30 minutes and then separated by filtration. The time was found sufficient to reach chemical equilibrium as verified in our previous study [1]. The metal ions concentrations in the aqueous phase were measured by AAS after the desired dilution with 0.1 M HNO_3, and the metal ions concentrations in MC-Xs were estimated by difference.

The pH value of the aqueous solution was adjusted with H_2SO_4 or NaOH solution, and kept constant concentration of CH_3COO^- (Ac^-) to be 0.25 M by adding calculated amounts of CH_3COOH (Ac) as a buffer agent. The temperature was controlled using a thermostated bath.

6. Stripping of Cu(II) from the Loaded MC-Xs

In the case of Cu(II) stripping from the metal ions loaded MC-Xs using diluted sulfuric acid in batchwise, 1 g of metal ions loaded MC-Xs and diluted sulfuric acid containing desired acid concentration were mixed together following the solid to liquid ratio of 1 : 10 and 1 : 20. The mixture was stirred using a hotplate magnetic stirrer for 30 minutes and then separated by filtration. After filtration, the metal ions concentrations in the filtrate were estimated by AAS and the metal ions concentrations MC-Xs were estimated by difference.

7. Statistical Analysis

The results are generally expressed as percentage of metal ions extraction and stripping. The batch extraction and stripping of Cu(II) in presence of Zn(II) and Ni(II) were carried out according to 2^4 and 2^2 factorial design of experiments, respectively. The experimental results obtained were analyzed using Minitab (version 14) to define the significant effects and interactions of the factors.

RESULTS AND DISCUSSION

1. Liquid-liquid Extraction

Since Cyanex 272 is an acidic extractant, the pH plays an important role in the extraction. Therefore, it is important to investigate the effect of pH to evaluate the extraction behavior.

Extraction of Cu(II) from the aqueous sulfate-acetate solution was carried out using 0.1 M Cyanex 272 at 1 : 1 phase ratio within the initial pH (pH_{ini}) range 2.5-5.5 (equilibrium pH range 3.2-5.3). The effect of distribution ratio (D value) on equilibrium pH is shown in Fig. 1. The figure shows that the D value increased with increasing the pH equilibrium. The plot was linear with the slope of 1.18, indicating the release of a mole of H^+ from the extractant for ex-

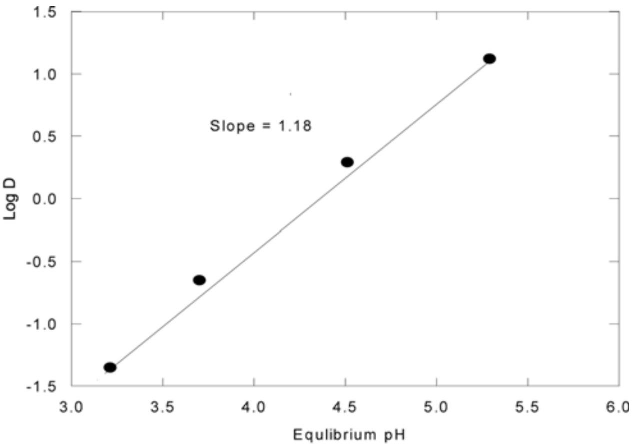

Fig. 1. Effect of distribution ratio on equilibrium pH in liquid-liquid extraction of Cu(II). Initial aqueous phase: [Cu(II)]= 750.48 ppm; [SO]=1 M; [Ac$^-$]=0.25 M; Organic phase: [H_2A_2] =0.1 M; O:A=1. S=1.18.

traction of a mole of Cu(II).

Since the extractant, Cyanex 272, is a liquid cation exchanger as well as chelating agent and can extract a diverse range of metal ions [12], the significance of Cyanex 272 concentration dependence is of prime importance to evaluate the extraction mechanism.

The effect of Cyanex 272 concentration on the percentage of extraction of Cu(II) from aqueous sulfate-acetate solution was studied with varying extractant concentrations. The dependence of distribution ratio on the Cyanex 272 concentration is given in Fig. 2. The figure shows that the distribution ratio increased with increasing Cyanex 272 concentration in organic phase. The plot of log D vs. log [H_2A_2] illustrated the slope of 1.71, indicating the association of two moles of dimer Cyanex 272 for the extraction of a mole of Cu(II) into the organic phase.

The dependence of distribution ratio on Cu(II) ion concentration was studied with varying Cu(II) concentration in the aqueous phase. The Cyanex 272 concentration and the pH in the aqueous phase were kept constant at 0.1 M and 4.5, respectively. The plot for the dependency of log D on log [Cu(II)] is shown in Fig. 3. As can be seen, the distribution coefficient decreased with increasing of Cu(II) concentration in the aqueous phase. This might have happened because of the formation of non-extractable and undissociated Cu^{2+}-Ac^- or Cu^{2+} SO_4^{2-} species in the aqueous phase at higher concentration, which decreased the distribution ratio [4].

The dependence of distribution ratio on acetate ion (Ac^-) concentration for the Cu(II) extraction was studied with varying acetate ion concentration in two different experimental conditions. The plot of log D vs. log [Ac^-] shown in Fig. 4 highlights the distribu-

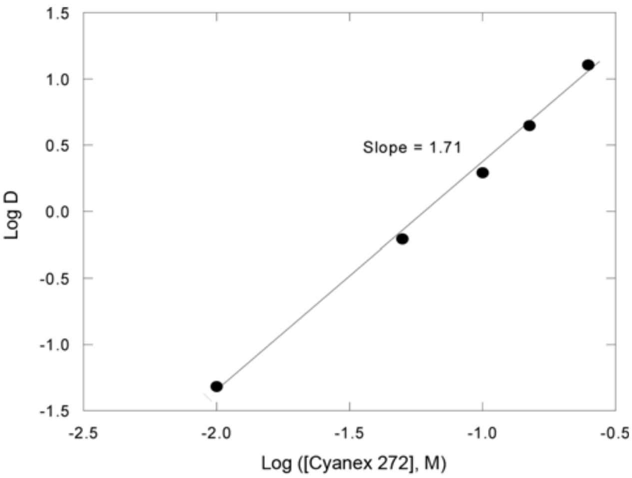

Fig. 2. Dependence of distribution ratio on Cyanex 272 concentration in organic phase in liquid-liquid extraction of Cu(II). Initial aqueous phase: [Cu(II)]=751.75 ppm, [SO]=1 M, [Ac$^-$] =0.25 M, pH$_{ini}$=4.5, O:A=1, S=1.71.

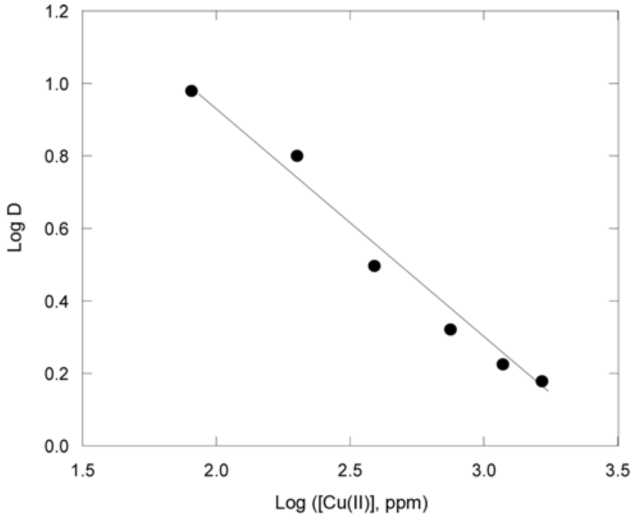

Fig. 3. Dependence of the distribution ratio of [Cu(II)] in aqueous phase in the liquid-liquid extraction of Cu(II). Initial aqueous phase: [SO_4^{2-}]=1 M, [Ac$^-$]=0.25 M, pH$_{ini}$=4.5; Organic phase, [H_2A_2]=0.1 M; O:A=1; S=− 0.65.

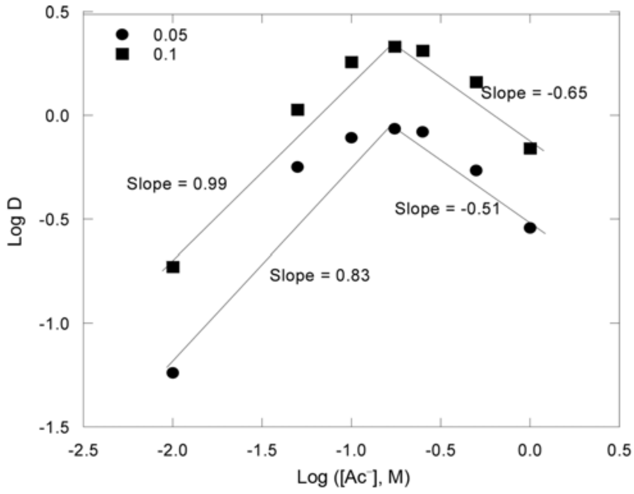

Fig. 4. Plot of log D vs. log [Ac$^-$] in the liquid-liquid extraction of Cu(II). Initial aqueous phase: (●) [Cu(II)]=740.95 ppm, (●) pH$_{ini}$=4.5; (■) [Cu(II)]=904.26 ppm, (■) pH$_{ini}$=5.0; Organic phase, (●) [H_2A_2]=0.1 M, (■) [H_2A_2]=0.05 M; [SO_4^{2-}]=1 M; A:O=1; (●) S=0.99 and −0.65, (■) S=0.83 and −0.51.

tion coefficient, which increased with increasing acetate ion concentration in the aqueous phase from 0.01 M to 0.175 M; thereafter the distribution coefficient decreased with increasing acetate ion concentration.

The decrease of the distribution coefficient with an increase of the acetate ion concentration in aqueous phase suggested that at higher acetate ion concentration, Cu(II) might exist as $[Cu(Ac)_2]$ species, and this species formed extractable $[Cu(Ac)(HA_2)\cdot 2HA]_{org}$ species with a fraction mechanism of one Ac^- liberation process. As the concentration of Ac^- ion increased in the aqueous phase, the non-extractable $[Cu(Ac)_2]$ species was formed gradually [4]. The formation of the $[Cu(Ac)_2]$ species in the aqueous phase reduced the concentration of Cu(II), resulting in the reduction of the distribution coefficient. At lower acetate ion concentration, Cu(II) might exist as $[Cu(Ac)]^+$ or Cu^{2+} species and the species formed extractable $[Cu(Ac)\cdot(HA_2)\cdot 2HA]_{org}$ species with participation one mole Ac^-.

From the results it can be postulated that Cu(II) was extracted via flowing reaction:

At higher acetate ion concentration region:
$[Cu(Ac)_2]_{aq}+2H_2A_2=[Cu(Ac)(HA_2)\cdot 2HA]_{org}+Ac^-+H^+$

At lower acetate ion concentration region:
$Cu^{2+}_{aq}+2H_2A_2+Ac^-=[Cu\ (Ac)(HA_2)\cdot 2HA]_{org}+H^+$.

The effect of distribution ratio on sulfate ion concentration for Cu(II) extraction was carried out by varying the sulfate ion concentration. The plot of log D vs. log $[SO_4^{2-}]$ is shown in Fig. 5, which shows that the distribution ratio was not dependent on sulfate ion concentration, which indicates that there was no effect of sulfate ion concentration on Cu(II) extraction within the studied experimental conditions. However, the distribution ratio was found to be decreasing at higher sulfate ion concentration region (0.1-0.5 M), while at lower sulfate ion concentration region (0.02-0.1 M) the distribution ratio was independent [4]. This variation of results obtained might be the variation of metal ion concentration and the extraction pH in aqueous phase.

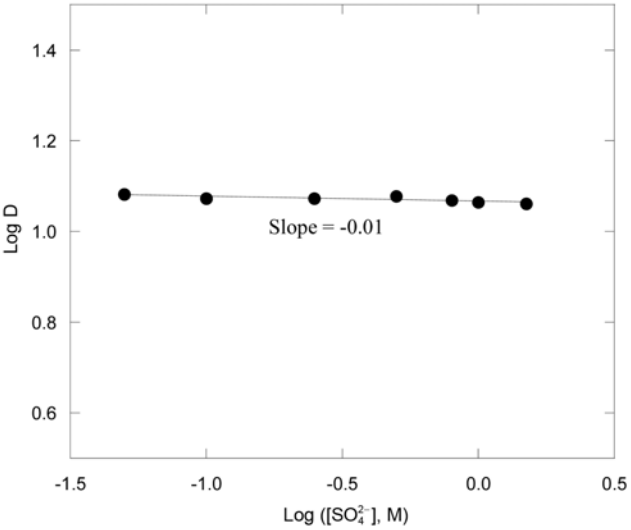

Fig. 5. Effect of distribution ratio on sulphate ion concentration in the liquid-liquid extraction of Cu(II). Initial aqueous phase: [Cu(II)]=740.95 ppm, [Ac$^-$]=0.25 M, pH$_{ini}$=5.5; Organic phase: [H$_2$A$_2$]=0.1 M; A:O=1; S=−0.01.

1-1. Extraction Mechanism

Cyanex 272 is a di-alkyl derivative of phosphinic acid. It acts as a mono-acetic chelating agent. Cyanex 272 considered as a dimeric (H_2A_2) in nonpolar solvents [13], and then the extraction equilibrium reaction may be considered as follows:

$$Cu^{2+}+2H_2A_{2(org)}+Ac^-\Leftrightarrow[Cu(HA_2)Ac\cdot 2HA]_{org}+H^+ \tag{1}$$

The equilibrium constant K_{ex} of the above reaction can be given:

$$K_{ex}=\frac{[Cu(HA_2)(Ac)\cdot 2HA]_{(org)}[H^+]}{[Cu^{2+}]_{aq}[H_2A_2]^2_{(org)}[Ac^-]} \tag{2}$$

Eq. (2) can be expressed as:

$$K_{ex}=\frac{D[H^+]}{[H_2A_2]^2_{(org)}[Ac^-]} \tag{3}$$

Where, $D=\frac{[Cu(HA_2)(Ac)\cdot 2HA]_{(org)}}{[Cu^{2+}]_{aq}}$

Taking logarithms and re-arranging, Eq. (3) takes the form:

$$logD=logK_{ex}+2log[H_2A_2]_{(org)}+log[Ac^-]+pH \tag{4}$$

The slopes of the plots of log D versus equilibrium pH in Fig. 1 and log D versus log $[H_2A_2]$ in Fig. 2 agree with the mechanism and the extracted species is $Cu(HA_2)(Ac)\cdot 2HA$.

2. Preparation of MC-Xs

The MC-Xs prepared and the preparation conditions and its morphology were discussed elsewhere [1]. In the present study, MC-Xs was prepared following the optimized preparation conditions as determined in Bari et al. [1]. Typical SEM photograph of the prepared MC-Xs is shown in Fig. 6. The figure shows that the MC-Xs are spherical and have sufficient rigidity with narrow size distribution.

3. Effect of Extraction pH on the Extraction of Cu(II), Zn(II) and Ni(II) from the Leach Liquor of PCBs Using MC-Xs

Effect of equilibrium pH on the percentage of Cu(II) extraction in presence of Zn(II) and Ni(II) from the leach liquor of waste PCBs using MC-Xs was investigated. The results obtained are shown in

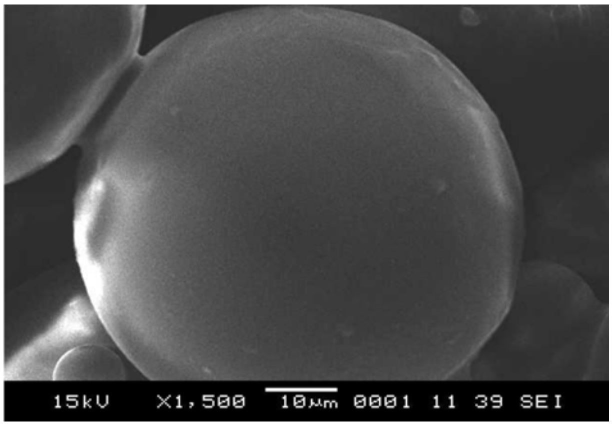

Fig. 6. Scanning electron micrographs of MC-Xs. Composition of disperse phase: PS: CH$_2$Cl$_2$:Cyanex 272=4 g: 50 mL: 3 g: continuous phase: 1 wt% gum arabic solution; agitation speed:400 rpm.

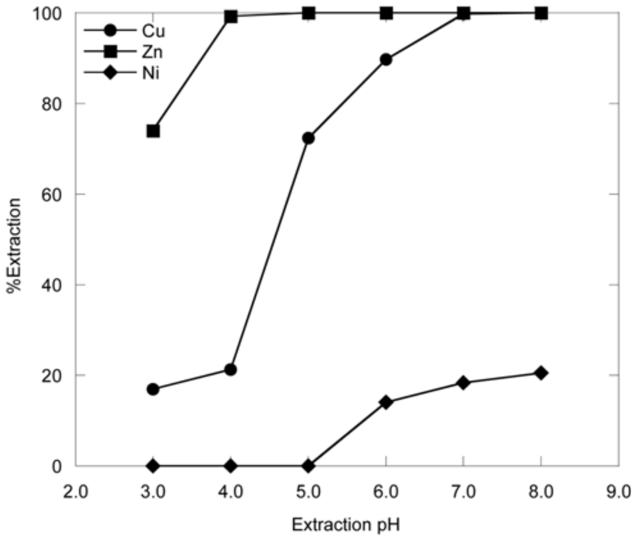

Fig. 7. Effect of pH on the extraction Cu(II), Zn(II) and Ni(II) from the leach liquor of waste PCBs using MC-Xs. Initial aqueous phase: [Cu(II)]=535.01 ppm; [Zn(II)]=18.28 ppm; [Ni (II)]=15.23 ppm; [SO$_4^{2-}$]=1 M, [Ac$^-$]=0.25 M; Organic phase: amount of Cyanex 272 in dispersed phase=2 g, amount of microcapsules=2 g; S : L=1 : 10; Temperature=45 °C.

Fig. 7. It was found that the percentage of extraction increased with increasing extraction pH. The figure also shows that Cu(II) extraction was significantly increased with the extraction pH at the pH range 4 to 7. Almost 100% Cu(II) and Zn(II) extraction was achieved at extraction pH 7 and 4, respectively. The extraction of Ni(II) was started at extraction pH 6 and reached about 20% at pH 8.

4. Statistical Study in Extraction Process

Extraction pH, amount of Cyanex 272 and amount MC-Xs have significant effect on Cu(II) extraction [1]. Besides, temperature also played an important role on metal ions extraction [4]. One study reported that Cu(II) extraction efficiency increased with increasing temperature up to 45 °C and thereafter the efficiency decreased with increasing temperature [14]. Hence in the present study, experimental variables such as aqueous pH, amount of Cyanex 272 in dispersed phase during MC-Xs preparation, amount of MC-Xs and temperature were chosen for statistical analysis to determine the significant effects and their interactions of Cu(II) extraction in presence of Zn(II), and Ni(II). The factors studied and their levels are shown in Table 1. Parameters, which were kept constant during the experimentations are as follows: [Cu(II)]=535.01 ppm; [Zn(II)]=18.28 ppm; [Ni(II)]=15.23 ppm; [SO$_4^{2-}$]=1 M and [Ac$^-$]=0.25 M.

The main response under investigation was the percentage of Cu(II) extracted in MC-Xs. As can be seen in Table 2, in all runs of the factorial design, the optimum about 100% of Cu(II) extraction was obtained in presence of Zn(II) and Ni(II). Zn(II) was 100% extracted under these experimental conditions, whereas nickel extraction did not exceed 15%. Therefore, statistical analysis was performed for the optimization of chosen extraction factors only for Cu(II) extraction purpose.

To determine the main effects and interactions of the Cu(II) ex-

Table 1. Cu(II) extraction using MC-Xs- Maximum and minimum levels of variables

Factor	Variables	Low level	High level	Units measured
A	Extraction pH$_{ini}$ (pH)	5.0	6.0	pH units
B	Amount of Cyanex 272 (HA)	2.0	3.0	g
C	Amount of MC-Xs (MC-Xs)	1.5	2.5	g
D	Temperature (T)	25	45	^{o}C

Table 2. Full 2^4 factorial design of experiments for the extraction of Cu(II) in presence of Zn(II), Fe(III) and Ni(II) using MC-Xs

Treatment code	Copper extraction (mg/L)				% Copper extraction (Y)
	Before extraction	After extraction			
		I	II	Average	
(1)	535.01	41.68	39.43	40.55	92.42
A	535.01	22.15	25.31	23.73	95.56
B	535.01	33.65	36.11	34.88	93.48
AB	535.01	16.10	19.21	17.65	96.70
C	535.01	33.97	36.54	35.25	93.41
AC	535.01	20.61	17.01	18.80	96.48
BC	535.01	29.53	31.41	30.47	94.30
ABC	535.01	17.44	20.01	18.72	96.50
D	535.01	28.62	30.23	29.42	94.50
AD	535.01	12.25	14.82	13.53	97.47
BD	535.01	30.55	27.5	29.02	94.57
ABD	535.01	13.48	11.50	12.49	97.66
CD	535.01	26.43	23.65	25.04	95.34
ACD	535.01	9.79	6.15	7.97	98.51
BCD	535.01	25.31	21.99	23.65	95.58
ABCD	535.01	1.18	4.01	2.59	99.51

Table 3. Full 2^4 factorial design analysis for optimization Cu(II) extraction factors using MINITAB

Treatment code	Effect	Coeff.	S.E.	T	P
(1)		96.5611	0.13038	740.59	0.000
A	3.0697	1.5348	0.13038	11.77	0.000
B	0.2628	0.1314	0.05831	2.25	0.039
C	0.4441	0.2220	0.03616	6.14	0.000
D	2.3081	1.1541	0.13038	8.85	0.000
AB	−0.0272	−0.0136	0.05831	−0.23	0.819
AC	−0.0122	−0.0061	0.03616	−0.17	0.868
AD	0.8513	0.4256	0.13038	3.26	0.005
BC	−0.0091	−0.0045	0.01617	−0.28	0.783
BD	0.1156	0.0578	0.05831	0.99	0.336
CD	0.2075	0.1037	0.03616	2.87	0.011
ABC	−0.0103	−0.0052	0.01617	−0.32	0.754
ABD	0.2525	0.1263	0.05831	2.17	0.046
ACD	0.1844	0.0922	0.03616	2.55	0.021
BCD	0.0712	0.0356	0.01617	2.20	0.043
ABCD	0.0494	0.0247	0.01617	1.53	0.146

S=0.365932, R^2=98.17% R^2_{adj}=96.45

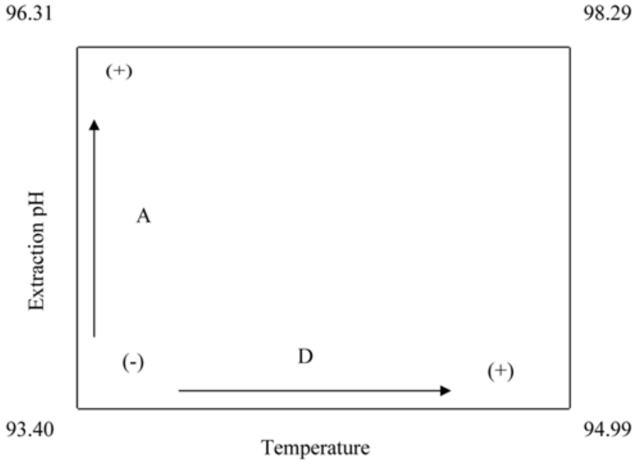

Fig. 8. Two-way tables showing the interactions AD.

traction factors, the design was analyzed using MINITAB. The results obtained are shown in Table 3. The main effects A, C, D, and the two-factor interactions AD were found to be statistically significant at α=0.01. In the range of variable studied, the pH (A) has the largest effect following the temperature (D) with a wide gap separating them from the remaining contrasts. It should be stressed, however, that because of statistically significant interactions, the main effects should not be individually interpreted, but the interacting variables should be considered jointly [10].

The nature of the interactions AD is indicated by two-way tables in Fig. 8, which obtained average levels of the other variables. The interaction AD occurred because at the high temperature, the increase in extraction pH causes higher Cu(II) extraction. The existence of statistically significant interactions meant such a model, based on the main effects only, will not be suitable and the space surface is curved in the particular region of the present design [15].

Based on the above analysis, the suggested “best” fitting model for Cu(II) extraction in presence of Zn(II), NI(II) and Fe(III) using MC-Xs in the ranges of variables studied and under the present conditions of experimentation, is the following:

$$Y=96.56+0.77X_1+0.11X_2+0.58X_3+0.21X_1X_3$$

Where Y is the predicted value of the percentage of Cu(II) extracted in MC-Xs, and the coded variables X_1, X_2 and X_3 are related to the natural variables by the following equations:

$$X_1=pH-\frac{6.0}{0.5}$$

$$X_2=MCX_s-\frac{2.0}{0.5}$$

$$X_3=T-\frac{30}{10}$$

Based on the statistical analysis of the results, the optimum conditions for the Cu(II) extraction in the presence of Zn(II), Fe(III) and Ni(II) using MC-Xs were determined as follows: pH_{ini}=6.0, amount of Cyanex 272 in dispersed phase=3 g, amount of MC-Xs=2.5 g and Temperature=45 °C.

5. Optimization of the Stripping Factors

Acid concentration played an effective role in metal ions stripping from the loaded MC-Xs [1]. Cu(II) stripping efficiency decreased with increasing H_2SO_4 concentration. Optimum about 100% Cu(II) stripping was obtained in presence of Zn(II), Fe(III) and Ni(II) from the loaded MC-Xs at H_2SO_4 concentration of 0.1 and 0.5 M [1]. However, in the present study, Cu(II) stripping was carried out in presence of Zn(II), Fe(III) and Ni(II) from the loaded MC-Xs following 2^2 factorial design of experiments to optimize the stripping factors. The variables were chosen and their levels for the study are given in Table 4. The parameter which was constant during the study was Cu(II) concentration (532 ppm).

Table 4. Minimum and maximum levels of Cu(II) stripping factors from Loaded MC-Xs

Factor	Variables	Low level	High level	Units measured
A	$[H_2SO_4]$	0.1	0.5	M
B	S/L ratio	1 : 10	1 : 20	gml^{-1}

Table 5. Full 2^2 factorial design of experiments for Cu(II) stripping from the loaded MC-Xs

Treatment code	$[Cu^{2+}]_{MC\text{-}Xs}$ concentration (mg/L)				% Cu(II) recovery
	Before stripping	After stripping			
		I	II	Average	
(1)	532	0.80	1.21	1.0	99.79
A	532	1.72	1.16	1.44	99.54
B	532	1.59	0.43	1.01	99.81
AB	532	1.51	0.62	1.06	99.80

The result under investigation was the percentage of Cu(II) stripped from the loaded MC-Xs. The concentrations of Cu(II) in loaded MC-Xs before and after stripping and their recoveries are given in Table 5. As can be seen, the optimum about 100% Cu(II) stripping was obtained under the present experimental conditions, which proves strippability of MC-Xs using diluted sulfuric acid. The design was analyzed using MINITAB (version 14), and the results obtained are in Table 6, which shows that none of the factors was found to be statistically significant at α=0.01. This practically means that the results differed only because of experimental error and that a stripping study of Cu(II) in presence of Zn(II), and Ni(II) can be conducted under any combination of the factor values within the ranges studied.

6. Separation and Recovery of Cu(II) in Presence of Zn(II) and Ni(II) from the Leach Liquor of PCBs

The optimized experimental conditions of Cu(II) extraction factors obtained from the statistical analysis were approached to carry

Table 6. Full 2^2 factorial design analysis for optimization Cu(II) stripping factors using MINITAB

Treatment code	Effect	Coeff.	S.E.	T	P
(1)		99.1175	0.4546	218.03	0.000
A	−1.1850	−0.5925	0.4546	−1.30	0.262
B	−1.1000	−0.5500	0.4016	−1.37	0.243
AB	−0.9400	−0.4700	0.4016	−1.17	0.307

S=0.141995, R^2=54.84% R^2_{adj}=20.97%

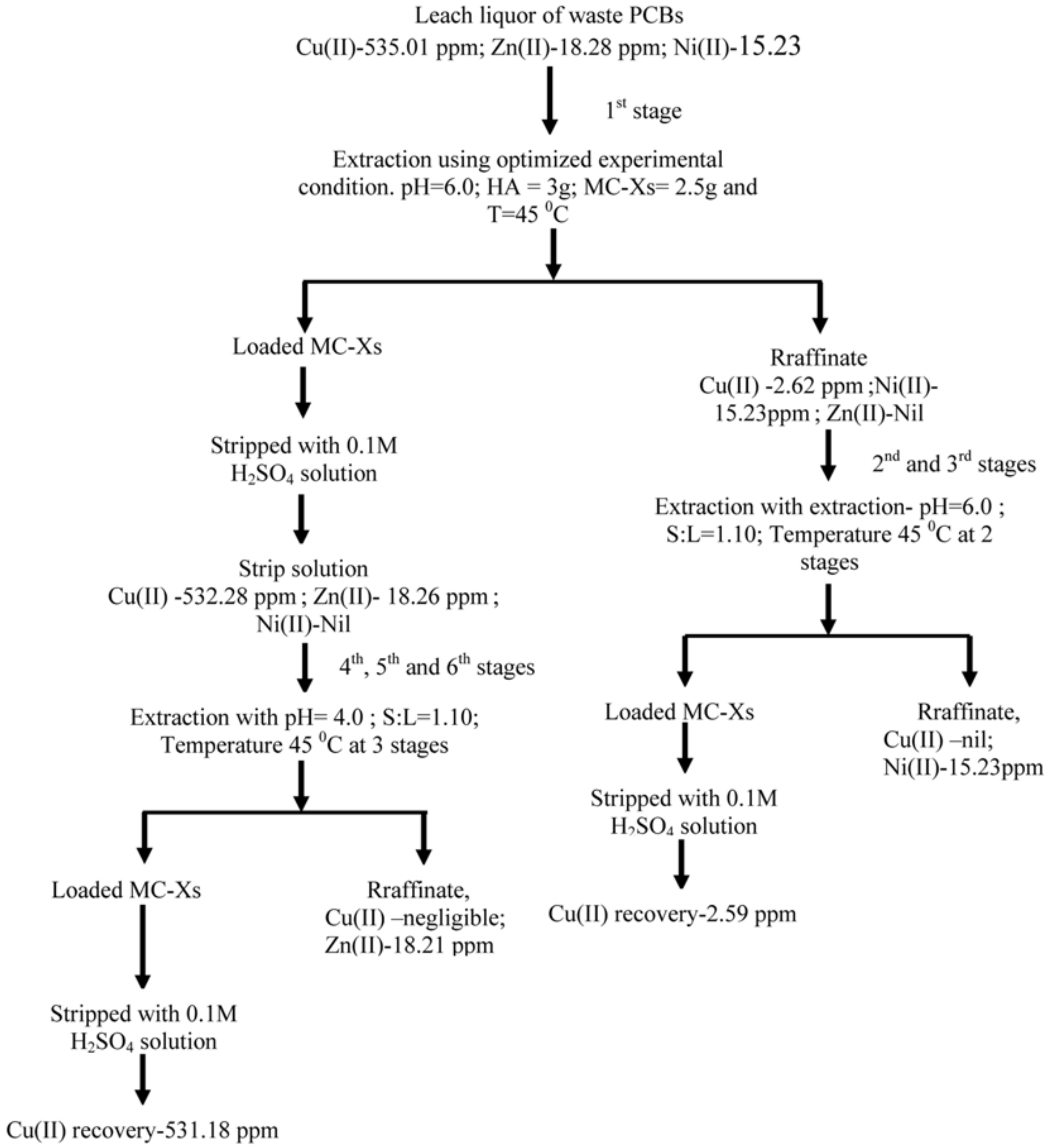

Fig. 9. Flow chart for the separation and recovery of Cu(II), Zn(II) and Ni(II) from the leach liquor of waste PCBs. Amount of Cyanex 272 in dispersed phase (HA)=2 g; S : L=1 : 10.

out for the Cu(II) extraction in presence of Zn(II), Ni(II) from the leach liquor of waste PCBs. Thereafter, the separation and recovery of Cu(II), Zn(II) and Ni(II) was performed based on the effect on extraction pH (Fig. 7) batchwise using MC-Xs containing 2 g Cyanex 272 in dispersed phase. Results obtained are shown in Fig. 9. At the 1st stage, extraction study was conducted from the leach liquor waste PCBs using optimized experimental conditions, i.e., pH 6.0, amount of Cyanex 272 in dispersed phase 3 g, amount of MC-Xs 2.5 g and temperature 45 °C. It was found that 99.51% Cu(II) and 100% Zn(II) were loaded in MC-Xs under the optimized experimental conditions, whereas the rest of the Cu(II) and 100% Ni(II) remained in the raffinate. Subsequently, Cu(II) and and Ni(II) were successfully separated from the raffinate at pH 6.0, S : L ratio 1 : 10 and temperature 45 °C in two extraction stages (2nd and 3rd stages). Then Cu(II) was recovered from the loaded MC-Xs using 0.1 M H_2SO_4 solution at S : L of 1 : 10. The loaded MC-Xs obtained at the 1st extraction stage were stripped with 0.1 M H_2SO_4 solution at S : L of 1 : 10. About 99% Cu(II) was separated from the strip solution in three extraction stages at pH 4.0, S : L ratio 1 : 10 and temperature 45 °C. Subsequently, the separated Cu(II) was recovered using 0.1 M H_2SO_4 solution at S : L of 1 : 10. Finally, the flowchart shows the selective recovery of Cu(II), Zn(II) and Ni(II) from the leach liquor of waste PCBs was 99.77%, 99.62% and 100%, respectively.

CONCLUSIONS

The results obtained from liquid-liquid extraction study using diluted Cyanex 272 indicated that pH, Cyanex 272 concentration, Cu(II) concentration and acetate ion concentration play an important role on Cu(II) extraction. However, there was no effect found of sulfate ion concentration under the studied experimental conditions.

The nature of Cu(II) complex extracted by Cyanex 272 showed that the extracted species was [Cu(HA_2)(Ac)·2HA]. The statistical design and analysis of experiments showed that extraction pH, amount of MC-Xs and temperature in the main effects and two factor interactions between extraction pH and temperature were statistically significant. The optimum experimental condition of Cu(II) extraction factors in presence Zn(II), Ni(II) and Fe(III) using MC-Xs was pH_{ini} 6.0, amount of Cyanex 272 in dispersed phase 3 g, amount of MC-Xs 2.5 g and temperature 45 °C. The statistical design of experiments of Cu(II) stripping from the loaded MC-Xs showed that none of the studied factors were statistically significant. Finally, the proposed process for the separation and recovery of Cu(II), Zn(II) and Ni(II) from the leach liquor of waste PCBs showed the selective recovery of 99.77%, 99.62% and 100%, respectively.

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