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Research Article

RECOVERY OF PRECIOUS METAL FROM WASTE PRINTED CIRCUIT BOARD: UNDERSTANDING THE LEACHING PHENOMENON AND ITS OPTIMIZATION

Ravi Patel, Abhipsa R Makwana
The Maharaja Sayajirao University of Baroda, Gujarat, India
**Corresponding author: abhipsamakwana78@gmail.com*

ABSTRACT

Recovery of precious metals from printed circuit boards (PCBs) using lixivient (thiourea) was after adsorption on low-cost adsorbent prepared from waste tea powder. The influence of particle size of PCB (<75 μm-75-150 μm), thiourea dose (10-90 ml for 0.5g of PCBs), pulp density (0.00125-0.01125 g/ml), contact time (6-24 hr), ferric ion dose (0-0.15 molar) and RPM (50-225) were studied for gold and silver leaching under batch mode. PCB sample with smaller particle size (>75 μm) leached higher amounts of gold and silver in the solution. Preliminary experiments showed 80 ml 0.5M TU dose best for leaching at pH 1.9-2.0 and at pulp density of 0.00125 g/ml after 15 h leaching time. Presence of 0.15 M ferric ions increased gold leaching rate. Leached liquor based on above discussed conditions showed an average of 2.220 mg/g of gold and 0.447 mg/g of silver leaching from 1g sample of PCBs. Optimization of thiourea dose, pulp density, ferric-ion concentration was carried in RSM through Box-Behnken Design. Second order quadratic polynomial model was developed for gold and silver using Design Expert Software to maximize both gold and silver recoveries. The optimum conditions suggested by model were found to be 100 ml 0.5M TU, 0.00125 g/ml pulp density and 0.15M ferric ion concentration. Adsorptive recovery of leached metal using low-cost pretreated waste tea powder was examined. Waste tea powder was found an effective material for recovery of metals from the leached liquor. Results of metal recovery on adsorbent were reported through SEM, EDS analysis.

Keywords: E-waste, PCBs, Leaching, RSM, Adsorption, Recovery.

1. INTRODUCTION

The composition of e-waste is diverse and falls under 'hazardous' and 'non-hazardous' categories. The physical composition of e-waste is very diverse and contains over 1000 different substances, which falls under organic and inorganic fractions. Heavy metals form a significant part of inorganic fraction accounting for 20-50% [1]. E-waste consists of hazardous metallic elements like lead, cadmium, chromium, mercury, arsenic, selenium and precious metals like silver, gold, copper and platinum. Overview indicates that manufacturing of mobile phones and personal computers consumes 3% of gold and silver mined worldwide each year; 13% of the palladium and 15% of cobalt [1]. Whether hazardous or precious, heavy metals are non-renewable and finite resource and therefore eventually become very valuable. A PCB is a printed circuit board, a key component in electronics to build electronic devices. Printed circuit board (PCB) contains various metals of interest. PCBs can be considered as a significant secondary raw material for precious and special metals.

From an economical point of view, recovery of precious metals from PCBs is attractive because the content of precious metals in waste [2-4].

In the past recent years, much attention has been keen to the development of techniques for recycling of E-waste. In this, the most active research on the recovery of metals from waste PCBs and electronic scraps has been focused on hydrometallurgical with adsorption techniques which are reportedly more environment friendly, predictable, and easily controlled due to mild working conditions. In addition, hydrometallurgy leads to a higher recovery rate due to relative ease in leaching of product and the possibility of cascading. [5-9]. In general, leaching is the key step of PCB recycling through hydrometallurgical route which involves extraction of metal values into aqueous solution. Though the process has some environmental consequences to be considered, chemical leaching is rapid and efficient over biological leaching. Consequently, chemical leaching is the process that should be considered for efficient leaching of metals from E-wastes by the utilization of less toxic chemicals [10].

The recent interest on thiourea leaching of gold and silver has probably been insisted mainly due to less toxicity than cyanide, organic material, high efficiency and the cationic properties of the complex so that the most exciting applications appear in the field of ion exchange and adsorption [10]. The leaching of gold, silver through TU or any other material depends on different parameters like TU dose, pulp density, P^H, temperature, presence or absence of external oxidant, etc., that can affect the leaching rate of metals. [10]. The optimization of this factors is very important to obtain maximum leaching rate of metals by consuming minimum chemicals. Optimizing these parameters by OFAT approach can give optimum condition for leaching, but it does not give the interaction effect of different governing variables on leaching. To study the interaction effect on leaching of metals RSM approach is widely used in water and wastewater treatment processes. That can be also applied to the leaching or extraction of metals from PCBs.

Present study reports preliminary study to understand the influence of particle size of PCB, thiourea dose, pulp density, contact time, ferric ion dose and RPM on gold and silver leaching under batch mode. Based on preliminary study, optimization of thiourea dose, pulp density, ferric-ion concentration was carried in RSM through Box-Behnken Design. Adsorptive recovery of leached metal using low-cost pretreated waste tea powder has been reported. Waste tea powder was found an effective material for recovery of metals from the leached liquor.

2. MATERIALS AND METHOD

2.1. Materials

All chemicals were used as received without further purification. The specifications of chemical used are (i) Thiourea (98%), Molecular weight – 76.12 g/mol, Formula- $NH_2(CS)NH_2$, Supplier- Finar chemicals, Ahmedabad. (ii) Ferric sulphate (98%), Molecular weight- 399.88 g/mol, Formula- $Fe_2(SO_4)_3.H_2O$, Supplier- Suvidhanath laboratories, Baroda.

2.2. Analytical methods

The extracted amount of metals through different lixiviants in whole work were analyzed in AAS (ECIL-AAS4141as per standard method, 22nd edition of "standard methods for the examination of water and wastewater", American public health association, Washington, DC.

Samples of waste tea powder and copper powder after the experiments were observed with a scanning electron microscope (SEM) coupled with an energy dispersion spectroscopy (EDS) (E JEOL JSM-5610LV, Oxford instrument, England). Prior to the SEM analysis, the samples were dried always.

2.3. Pretreatment of PCBs

For the recovery of gold, silver and copper in this study nearly 500g scrap of waste computers RAM and processors is purchased from local scrap market. As we discussed earlier particle size of PCBs effects greatly on leaching, so the two sets of same material of about 200g PCBs are grounded to a size ranging from 10 to 20 mm and then it is further reduce by crushing in a mixture and sieved in two sieve range of <75 μ and 75-150 μm.

2.4. Qualitative analysis of PCBs

2.4.1. Analysis with aqua regia and HNO_3

For this analysis some amount of crushed PCBs was diluted to aqua-regia solution made from concentrated HCl and HNO_3 and in 1+1 HNO_3 also for 24 hours. Then it was filtered and leached liquor is analyzed with AAS for leached metal contents from the waste.

2.5. Leaching experiment

2.5.1. Batch study and optimization

The leaching experiment was carried through batch process using conical flask and shaking in rotary flask shaker for a given time period and at room temperature.

In the present work the experiment were carried with the both sieved sizes of <75 μ and 75-150 μ. The varying volume of leached liquor was mixed with the weighed amount of powdered sample (0.5g) in a conical flask, and the heterogeneous mixture was shaken in a rotary flask shaker at a room temperature for given time period to evaluate the effect of various parameters on the leaching reaction. The samples were then filtered and metal concentration in the filtrate was measured after proper dilution with distilled water. The factors affecting the leaching reaction include concentration of thiourea (TU), pulp density, shaking time, presence or absence of external oxidant, RPM. These factors were thoroughly examined by OFAT approach. The effect of the 0.5M TU dose (10 to 90 mL), pulp density (0.00125 to 0.01125 g/ml), shaking time (3, 6, 9, 12, 15 & 24hr), ferric ion presence (0.005M to 0.15M) and RPM (50, 150, 225) were studied in this section. Since thiourea is not stable and easy to decompose in alkaline solution in whole experiment the P^H was adjusted to 1.9-2.0 using 0.05M H_2SO_4.

*2.5.2. **Experimental design for RSM and data analysis***

The Box–Behnken design (BBD) with response surface methodology (RSM) was used to investigate the effect of the five important process variables namely, TU dose, pulp density and Ferric ion concentration. The BBD is an economical, efficient and rotatable quadratic design where factor combinations are at the midpoints of the edges and at the center [11, 12].

The central points are used to estimate the experimental error and to perform the model adequacy check. Gold in mg/g was considered as the response parameters. Range of process variables based on one-factor-at-a-time concept as studied earlier was chosen. Table 1 shows the independent variables along with their coded values used in RSM. The BBD factorial design with five replicates at central point is presented in Table 2.

Table 1. Experimental range and levels of the independent variables

Variable	**Factors**	**Coded levels**		
		-1	**0**	**+1**
TU dose (ml/g of PCB)	x_1	60	80	100
Pulp density(mg/ml)	x_2	0.001	0.00125	0.0015
Ferric ion concentration (M)	x_3	0.1	0.15	0.2

Table 2. Design matrix

Run	Process Variables		
	x_1:TU dose	x_2:Pulp Density	x_3:Ferric Ion Molarity
1	60	0.001	0.15
2	100	0.001	0.15
3	60	0.0015	0.15
4	100	0.0015	0.15
5	60	0.00125	0.1
6	100	0.00125	0.1
7	60	0.00125	0.2
8	100	0.00125	0.2
9	80	0.001	0.1
10	80	0.0015	0.1
11	80	0.001	0.2
12	80	0.0015	0.2
13	80	0.00125	0.15
14	80	0.00125	0.15
15	80	0.00125	0.15
16	80	0.00125	0.15
17	80	0.00125	0.15

To estimate the contribution of the three variables, experimental data were analyzed and fitted to the following second-order polynomial model using Design Expert 10.0 software:

$$y = \beta_0 + \sum_{j=1}^{k}\beta_j x_j + \sum_{j=1}^{k}\beta_{jj} x_j^2 + \sum_{j=1}^{k}\sum_{i=1}^{i<j}\beta_{ij} x_i x_j + \varepsilon \qquad (1)$$

where *y* represents the predicted response; *xi* and *xj* are the independent variables, ˇ0, ˇ*j*, ˇ*jj* and ˇ*ij* are regression coefficients for intercept, linear, quadratic and interaction coefficients respectively, ε is the error and *k* is the number of variables studied [13, 14].

2.6. Recovery of leached gold, silver and copper.

2.6.1. Recovery of leached metals by cementation

Leached metals from PCBs by thiourea solution was subjected to cementation. In cementation recovery of gold and silver by copper powder were carried by taking various amount of copper powder. In 50 ml of leached liquor various amount in range of 10 mg to 60 mg was taken and subjected to shaking for 24 hrs. Recovery is calculated by initial and final concentration of leachate.

2.6.2. Recovery of leached metals by adsorption using waste tea powder

After the leaching of gold, silver, copper and other metals by thiourea solution, for the recovery of gold, silver and copper adsorption technique was tested. In that waste tea powder was used as adsorbent. The adsorption tests were carried out on batch mode. For that pretreatment of adsorbent and experiment method were carried out as below.

2.6.3. Pretreatment of adsorbent

Leached gold, silver, copper and other metal can be adsorbed through natural adsorbent like waste tea powder, coffee powder, bagasse, rice husks etc. To recover the leached gold, silver, and copper it was subjected to adsorption process. In this study low cost adsorbents like waste tea powder was used for this purpose in batch mode study.

Pretreatment is necessary to ensure the higher adsorption capacity of adsorbents. For that waste tea powder is brewed in hot water for 10 min. and then filtered tea leaves are dispersed in 0.01M HNO_3 solution for 2 h. Then filtered and washed with deionized water. This process of cleaning and filtering will repeated for regeneration. The residue will air dried in sunlight. To activate it, is subjected to oven at 110°C for 2 h.

2.6.4. Batch mode adsorption experiments

Experiments for adsorption test of precious and base metals from varying amount of waste tea powder were carried in batch mode. For this, the heterogeneous mixture in range of 10 to 100 mg of dry adsorbent and 50 ml leached liquor solution containing 197 mg/l of copper, 2.642 mg/l of gold and 0.617 mg/l of silver was shaken using a rotary flask shaker for 15 h at constant room temperature. Then, the adsorbent was separated by filtration and the aqueous solutions were analyzed for their metal content. From the measured initial and final concentrations of metal ions, percentage adsorption (%A) of each metal ion on the adsorbent was calculated. The test was carried for 6 h and for 24 h keeping all other conditions constant to check the effect of time.

3. RESULTS AND DISCUSSION

3.1. Qualitative analysis of PCBs

The results of a qualitative analysis of PCBs with aqua-regia solution made from concentrated HCl and HNO_3 and in 1+1 HNO_3 also for 24 hours are shown in Table 3.

Table 3. Amount of leached metals (mg/g) in aqua regia and 1+1 HNO_3 from PCB powder

Element	Amount leached by Aqua regia (mg/g)	Amount leached with 1+1 HNO_3 (mg/g)
Au	2.5	0.065
Ag	0.632	0.330
Cu	85.81	82.34

3.2. Preliminary optimization of leaching parameters

Initial optimization of variables affecting leaching of gold, silver and copper using thiourea such as particle size, TU dose, pulp density, reaction time, ferric ion concentration and shaking speed were carried by OFAT approach.

3.2.1. Effect of particle size

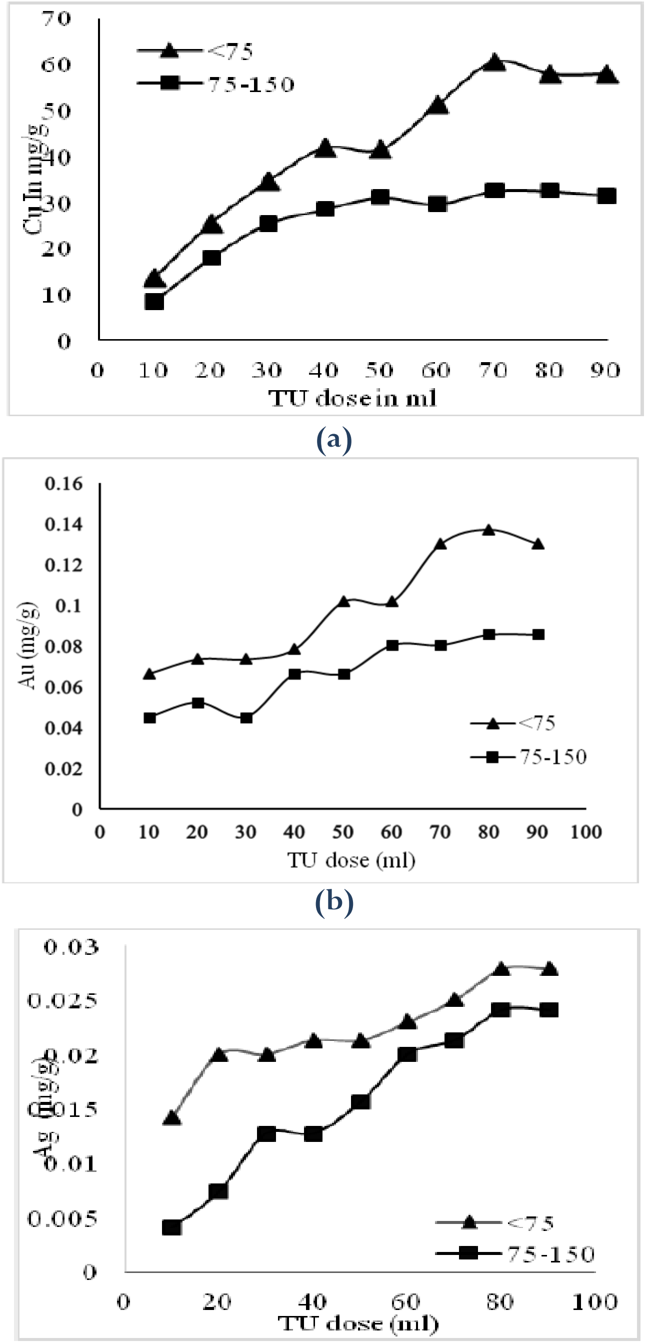
The effect of particle size of gold, silver and copper was examined by using the PCBs of two different sizes (<75μ, 75-150μ). Keeping other parameters such as TU-0.5 M, RPM-200, pH-1.9-2.0 for 24h of shaking.

The results are presented in table 4, from which it is found that the fraction with <75 μ size yielded highest quantity of dissolved gold, silver and copper.

Table 4. Amount of leached metals (mg/g) in 0.5M TU from two different sizes of PCB powder

Elements	Amount Leached (mg/g)	
	Particle size (μm)	
	<75	75-150
Au	0.571	0.342
Ag	0.329	0.164
Cu	91.53	61.98

According to Gurung et al., 2013 [10], smaller the particle size more will be the dissolution of metals. This fact was also found in this work. This is because of high surface area of the small particle size and subsequently a higher proportion of metals contacted to the leached liquor. For further experiments we worked on both size of PCB powder to study the behavior of that on different parameters of leaching through thiourea. So the other parameter's optimization study were carried on two sizes as 75 µm and 75-150 µm.



(a)

(b)

(c)

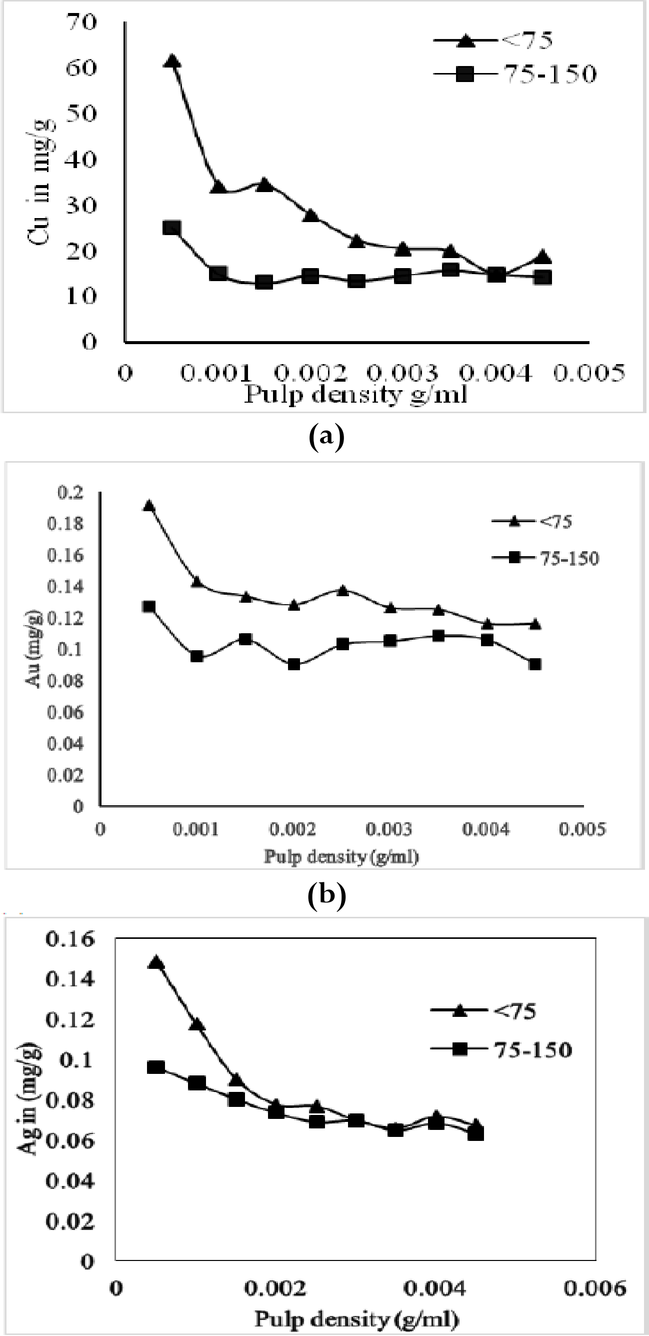
Fig. 1. Effect of 0.5M TU dose on (a) copper (b) gold (c) silver leaching from PCB sample, pH= 1.9-2.0, Pulp density= 0.01 g/ml, shaking time= 3 h, shaking speed= 200 RPM, Room temperature

Fig. 1(a) shows the results of the effect of Tu dose at 0.5 M concentration ranging from 10 ml to 90 ml for 1g of PCB sample for the both particle sizes . From the figure it is seen that the leaching of the copper increases with the increasing TU dose but not effective after 70ml. Fig. 1(b) shows the results of the effect of TU dose on the leaching of gold which is not much effective when it is higher than 80 ml. The reason for leaching of copper from PCB by thiourea which has potential of leaching of gold and silver was the acidic condition of the solution that was adjusted. Similarly the amount of silver leached (Fig. 1(c)) was found to be maximum at 80 ml of 0.5 M TU at pH 1.9-2.0 for the both sizes and at higher dose slight decrease in leached silver was found for <75µ size. It is important to note that the action of TU on gold is effective only at proper TU dose, where dissolution of gold proceeds smoothly and the maximum recovery is achieved. So for the leaching of gold 80 ml of 0.5M TU is recommended dose. This because the use of concentrated thiourea solution hindered the leaching process due to precipitation. In addition, keeping in view the low consumption of reagent, using 80 ml of 0.5 M TU solution is effective for silver and gold leaching. As per M. Gurung et al., 2013 and Ha et al., 2010 [10, 15] the leaching rate of metals increases with increase in lixiviate dose up-to optimum value after that no further increase was seen and for above all cases same thing has been reported that with increase in TU dose the leaching rate of copper, gold and silver increases and stopped after specific dose.

3.2.2. Effect of pulp density

Fig. 2(a), (b) and (c) shows the results of the effect of pulp density (0.00125 g/ml to 0.01125 g/ml) on copper, gold and silver leaching while keeping other variable constant and shaking for 3 h. It was found that for both sizes all metals leaching was maximum at lower pulp density of 0.00125 g/ml. At 0.00125 g/ml pulp density the copper leaching was very high than higher pulp densities as studied in this. For the <75µ size at 0.00125 g/ml copper leaching is almost 3 times higher than 0.0025 to 0.0225 g/ml pulp density and for 75-150µ size it is also higher than higher pulp density as shown in fig. 2(a).

This is because of more lixiviant available to react with the metals in powderd PCB sample, so the more metal can react with TU and get leached. Gurung et al., 2013 [10], studied the effect of pulp density on leaching of metals from PCBs through different materials and concluded that when pulp density are lower or the liquid medium is high compare to solid phase, the leaching of metals increases due to effective mass transfer.



(a)

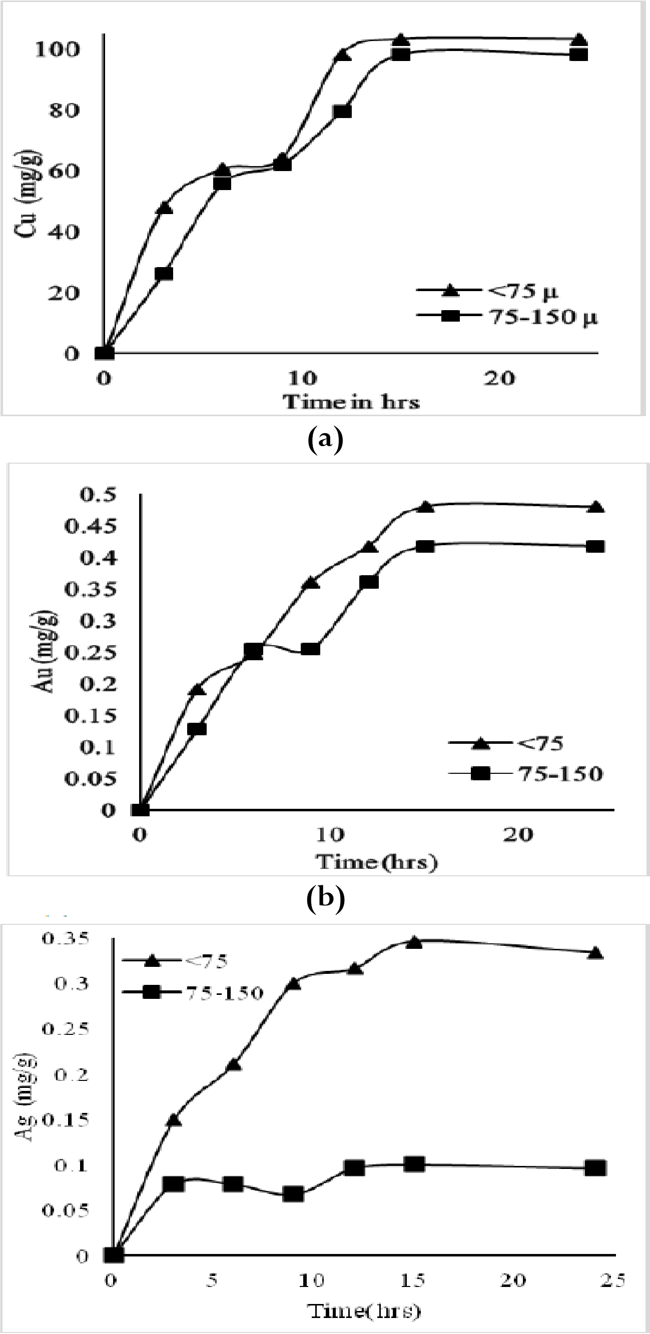
(b)

(c)

Fig. 2. Effect of pulp density on (a) copper (b) gold (c) silver leaching from PCB sample, 0.5M TU= 80ml, pH= 1.9.-2.0, shaking time= 3 h, shaking speed= 200 RPM, Room temperature

3.2.3. Effect of shaking time

Fig. 3(a), (b) and (c) shows the effect of shaking time on copper, gold and silver respectively from the PCB sample at pulp density of 0.00125 g/ml. The shaking time given were 3h, 6h, 9h, 12h, 15h, and 24h. As per the Gurung et al., 2013 [10], with an increase in leaching time the metals extraction also increases and after optimum value no further increase was shown. In this work results also shows that leaching is increases with increase in time for copper, gold and silver leaching increases up to 15hrs and after that until 24hrs no increase was found. Hence for copper, gold and silver leaching 15hrs time was considered an optimum time.



(a)

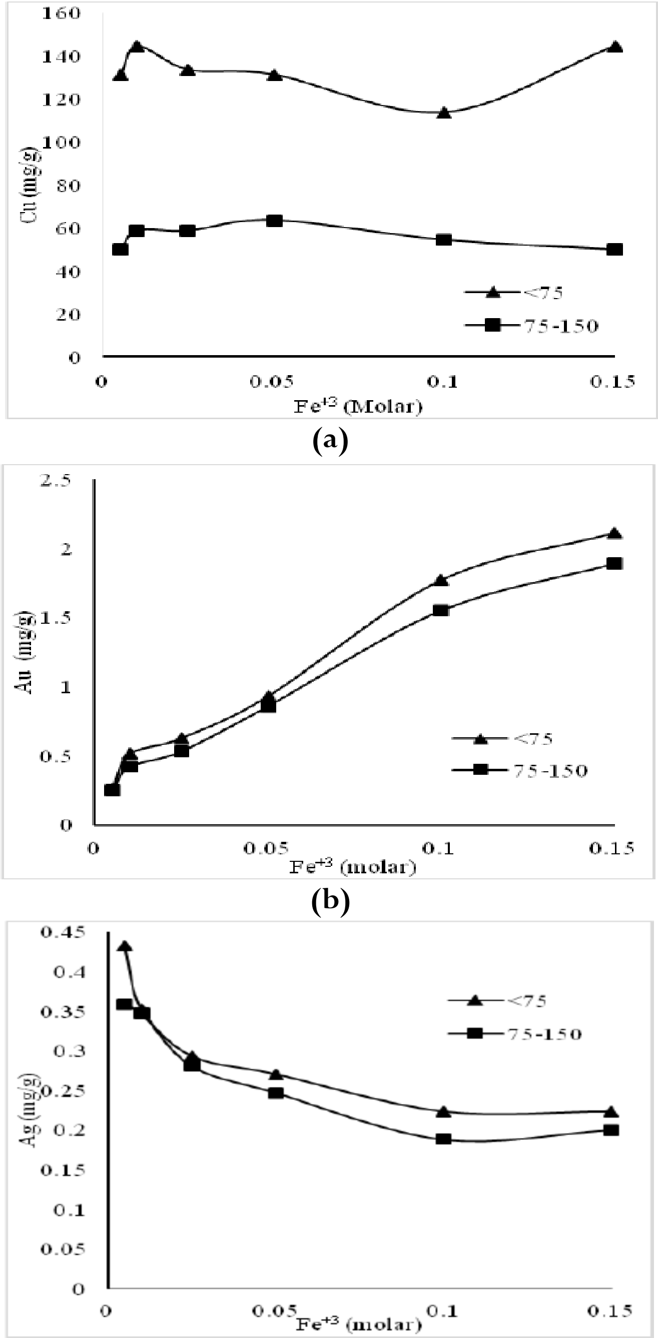
(b)

(c)

Fig. 3: Effect of shaking time on (a) copper, (b) gold, (c) silver leaching from PCB sample Pulp density= 0.00125 g/ml, 0.5M TU = 80ml, pH= 1.9.-2.0, shaking speed= 200 RPM

3.2.4. Effect of external oxidant-ferric ion concentration

Fig. 4(a), (b) and (c) show the effect of presence of ferric ion (0.01M to 0.15M) as an external oxidant on leaching of copper, gold and silver for 15hrs time.



(a)

(b)

(c)

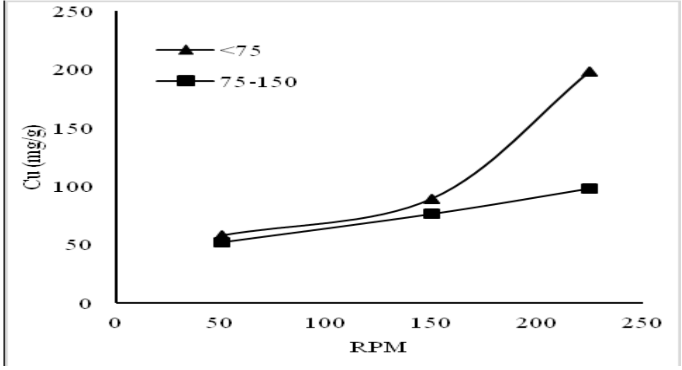
Fig. 4. Effect of presence of ferric ion on (a) copper, (b) Gold, (c) silver leaching from PCB sample 0.5M TU= 80ml, pH= 1.9-2.0, pulp density= 0.00125 g/ml, shaking time= 15 h, shaking speed= 200 RPM

It can be seen from the Fig. 4(a) that the presence of ferric ion as an external oxidant does not affect the copper leaching. Not enough changes found in copper leaching with change or increase in ferric ion concentration.

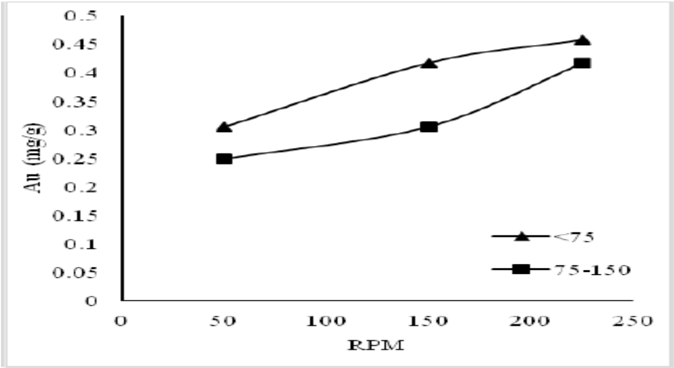
Gold and silver dissolution in acidothiourea solution is known to be an electrochemical reaction catalyzed by the presence of ferric ion [16, 17]. The role of ferric ion in the complexation process is to facilitate the oxidation of metallic gold and silver to aurous (Au^+) and argentous (Ag^+) ions, respectively. Reports have shown that ferric sulfate can best speed up the leaching reaction and TU in the presence of ferric ions exhibits a potential improvement over the use of TU alone for gold leaching [10, 16]. Huyhua et al. 1989 and Gurung et al., 2013 [10, 18] found that the leaching of gold with TU in the presence of ferric sulfate as an oxidant was up to four times faster than TU alone in air. The dissolution of gold and silver is dependent on the oxidant concentration. Fig. 4(b) and (c) shows the effect of the presence of ferric ion on the leaching efficiency of acidothiourea leachate towards gold and silver respectively. In the absence of ferric ion, the extraction increased sluggishly with time at the beginning of the leaching and it attained the equilibrium within 15 h. It can be seen that with increase in ferric ion concentration from 0.01M to 0.15M the leaching of gold was increased. In the absence of ferric ion gold leaching was 0.48 mg/g and within 15 h for <75 µ size. Within 15h of time gold leaching was almost four times higher (2.22 mg/g) and silver leaching was found decreasing with increase in ferric ion concentration. It may be because of higher oxidation potential. Accordingly, 0.15M ferric ion concentration in acidothiourea solution was found to be the optimum concentration for the leaching of gold in our experimental conditions. For silver it was 0.01M. For silver leaching it can be seen that there was no positive effect of ferric ions on the leaching of silver. Rather, the dissolution efficiency was slightly decreased. These results suggest that the proper amount of ferric ion oxidant, necessary for the oxidation of silver, is supplied by the feed material itself. The difference in leaching behavior of gold and silver in the presence of an oxidizing agent is attributable to the respective ORP values of these metals [10). Since gold has lower oxidation potential values than silver, it seems reasonable that the presence of external oxidizing agent enhances the gold leaching

3.2.5. Effect of shaking speed

To examine the effect of shaking speed on the leaching rate of copper, gold and silver the test was carried out by varying the shaking speed from 50, 150 to 225 rpm using 0.5 M TU at 0.00125 g/ml pulp density. Fig. 5(a), (b), (c) shows the effect of shaking speed on the amount of copper, gold and silver extraction respectively.



(a)



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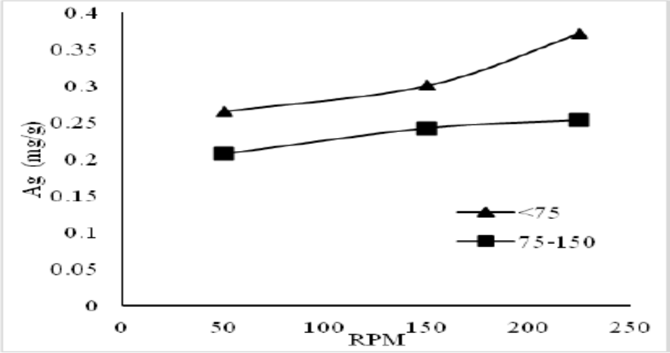


(c)

Fig. 5 Effect of shaking speed on (a) copper, (b) gold and (c) silver leaching from PCB 0.5M TU= 80ml, pH= 1.9-2.0, pulp density= 0.00125 g/ml, shaking time= 15 h, Ferric ion = 0.15 M

According to Fujiwara et al., 2007 [19] increasing the shaking or agitation speed can increase the adsorption of metals. This may be contributed to the fact that shaking or agitation of the leaching solutions improved the mass transfers and accelerated the leaching of metals. In this study the results also indicate that the leaching rate is increases with increase in shaking speed for all copper, gold and silver metal, which suggests that the shaking speed of 225 rpm is sufficient to provide adequate particle suspension.

3.3. RSM model development and its validation

Seventeen runs were conducted based on the experimental design. Experimental results of leached gold in mg/g are presented in Table 5.

Table 5. Design matrix along with predicted and actual values

	Process variables			Response: Leached Gold (mg/g)	
Run	x_1:TU dose	x_2:Pulp Density	x_3:Ferric Ion Molarity	Actual value	Predicted value
1	60	0.001	0.15	1	1.03
2	100	0.001	0.15	2.5	2.45
3	60	0.0015	0.15	1.41	1.46
4	100	0.0015	0.15	1.64	1.61
5	60	0.00125	0.1	1.1	1.12
6	100	0.00125	0.1	2	1.91
7	60	0.00125	0.2	1.68	1.58
8	100	0.00125	0.2	2.2	2.37
9	80	0.001	0.1	1.31	1.35
10	80	0.0015	0.1	1.5	1.53
11	80	0.001	0.2	2.22	2.19
12	80	0.0015	0.2	1.64	1.6
13	80	0.00125	0.15	2.01	2.09
14	80	0.00125	0.15	2	2.09
15	80	0.00125	0.15	2.06	2.09
16	80	0.00125	0.15	2.28	2.09
17	80	0.00125	0.15	2.11	2.09

The observed removals were used to compute the models using second order polynomial given in Eq. (2). The models for results of leached gold in mg/g in terms of coded factors were determined as follows:

$$\text{Gold (mg/g)} = 2.0916+0.39375x_1-0.105x_2+0.22875x_3-0.3175x_1x_2-0.1925x_2x_3 -0.1883x_1^2-0.2658x_2^2-0.1583x_3^2 \quad (2)$$

The ANOVA test indicated that quadratic models described well the gold leaching.

The ANOVA results for above quadratic models along with *p*-values and *F*-values are presented in Tables 6, respectively. Fisher test was used to evaluate the significance of each factor and their interaction with each other. Values of "Prob. > F" less than 0.0500 indicate model terms are significant [20]. Coefficients with *p*-value greater than 0.1were considered statistically insignificant [20].

Table 6. Analysis of variance (ANOVA) test for Gold leaching (mg/g)

Source	Sum of Squares	df	Mean Square	F Value	p-value	
					Prob > F	
Model	2.947579	9	0.32750	31.1547	<0.0001	significant
A-TU dose	1.240312	1	1.24031	117.986	<0.0001	
B-Pulp Density	0.0882	1	0.0882	8.39016	0.023098	
C-Ferric Ion Molarity	0.418612	1	0.41861	39.8211	0.000400	
x_1x_2	0.403225	1	0.40322	38.3574	0.000448	
x_1x_3	0.0361	1	0.0361	3.43406	0.106278	not significant
x_2x_3	0.148225	1	0.14822	14.1001	0.007121	
x_1^2	0.149292	1	0.14929	14.2016	0.006996	
x_2^2	0.297472	1	0.29747	28.2975	0.001099	
x_3^2	0.105511	1	0.10551	10.0369	0.015749	
Residual	0.073586	7	0.01051			
Lack of Fit	0.021575	3	0.00719	0.553086	0.672928	not significant
Pure Error	0.052011	4	0.01300			
R^2 = 0.9756, R^2 adjusted = 0.9443, R^2 predicted = 0.8588, AP = 18.13, CV% = 5.69						

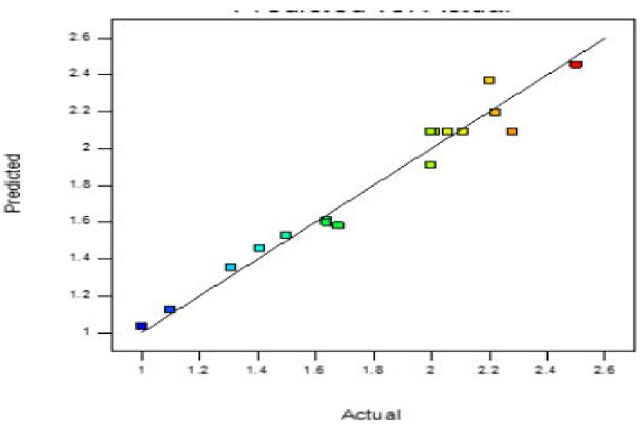


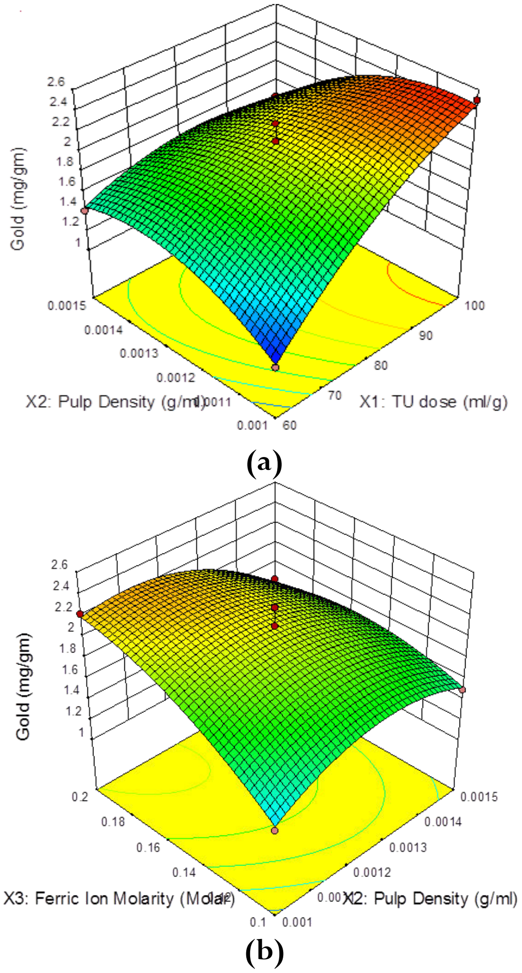
Fig. 6 Plot of predicted v/s actual value of leached gold (mg/g)

As can be observed from Tables 7, the *p*-values for all the models were less than 0.05 and thus models for gold leaching was found to be significant with 95% confidence interval. The lack of fit (LOF) compares the residual error to the pure error from the central points in the experimental design points, and therefore should be insignificant.

The ANOVA results for LOF show *p*-value more than 0.05, suggesting insignificant LOF. Coefficient of determination R^2 is the parameter to determine the overall efficiency of model prediction. In this work R^2 values obtained for all the models were high (R^2=0.9756), which ensure good correlation between observed values and model predicted values.

Further, R^2 value should be in reasonable agreement with R^2 adjusted. [20] suggests that when R^2 and R^2 adjusted differ reasonably, there is a good chance that insignificant terms have been included in the model. Myers et al., 2009 [14] explains that R^2predicted shows pre-diction capability of the model for new responses and hence both R^2 and R^2 predicted should be in reasonable agreement with each other. For developed model, R^2, R^2adjusted and R^2 predicted do not differ considerably. Adequate precision (AP) can be defined as the ratio of the range of the predicted values of the design points to the average standard deviation of all predicted response and should be greater than 4 for a good model [21]. This is satisfied in this model. The coefficient of variance (CV) defines reproducibility of the model and is the ratio of the standard error of estimate to the mean value of the observed response. If CV of the model is not greater than 10%, model can be considered reproducible [22], and in the present study, CV values were well below 10%.

The plots of actual and predicted values of the leached gold from PCB in mg/g of PCB showed very good agreement between observed and predicted values (Fig.6). Therefore, the quadratic models represented by Eq. 6 could be used to predict the leaching of gold in mg/g of PCB, under the studied experimental conditions.



(a)

(b)

Fig. 7.Response surface plots for gold leaching as a function of (a) pulp density and TU dose at 0.2 M ferric ion (b) pulp density and ferric ion concentration at 80 ml of 0.5M TU dose

Figs. 7 (a) and (b) depicts the various response surface plots for the recovery gold from PCBs. The curvature nature of the curves showed that there was an interaction between the response and the individual variables. The results are shown in Figs. 7 (a) and (b), in which two parameters were varied within the experimental range, while other factors were fixed at the center level. The response surface plots show the nature and extent of the interactions of the different components.

Fig. 7(a) shows the 3D plot of the TU dose (mg/ml) and pulp density while keeping the ferric ion concentration of 0.2 M constant at the central level. Accordingly, increasing the TU dose improves Au leaching and decrease in pulp density also improves gold leaching. But if the TU dose is higher and pulp density is higher gold leaching is not so effective due to increase in solids increases the consumption of reagent. This conclusion is in good agreement with that reports by other researchers [10]. Fig. 7(b) demonstrates the Au recovery as a function of pulp density and ferric ion concentration while keeping TU dose at 80 ml constant at the central level. As can be seen that Au recovery affected by ferric ion concentration. At lower pulp density the effect of ferric ion concentration is positive at the same time at higher pulp density this effect is getting indistinct. It can be seen that the ferric ion concentration has the most influence on Au recovery at lower pulp density. Increasing ferric ion concentration increases the gold leaching, this is due ferric ion oxidizes gold and silver easily.

3.3.1. Process optimization

Response surface methodology is based on the strategy of multiple response optimizations. It converts the multiple responses into a single one by combining the individual responses into a composite function followed by its optimization [23]. Optimization was done based on the desirability function approach. Desirability function-based approach consists of converting each response into individual desirability functions (d) that are then aggregated into a composite function (D) which is usually a geometric or an arithmetic mean. [23].

Ideally, it should be equal to 1 but practically should be close to 1. In Design expert 10 software five different goals – maximum, minimum, fixed tar-get, within the range or none – can be set to each variable and response. In the present study, TU dose, pulp density and ferric ion concentration being the governing parameters of operating efficiency. TU dose was set to be within the range of 60-100 mL/g PCB.

Pulp density was set to be minimize as 0.001 g/ml and ferric ion concentration was set to be within the range. The desired goal for response leached Gold was set as maximum. The optimum conditions predicted by the models are presented in Table 7. Confirmatory tests were carried out in duplicate and the mean values are presented in Table 7.

Table 7. Optimum conditions for gold leaching

	TU dose (ml/g)	Pulp density (g/ml)	Ferric ion molarity	Au recovery (mg/g)	Desirability
Predicted	100	0.001	0.2	2.717	0.849
Observed	100	0.001	0.2	2.645	-

Results of the confirmatory tests gave 2.645 mg/g gold at the optimum conditions, which was close to the values predicted by the regression models developed.

3.4. Recovery of gold and silver from leached liquor

Leached gold, silver and copper from thiourea leaching are subjected to cementation by copper powder and adsorption by waste tea powder for possible recovery. The results obtained by both type recovery processes are explain below.

3.4.1. Recovery of gold, silver by cementation using copper powder

Various studies on cementation reported that Cu, Pb, Zn, Ni, and Fe have potentiality to form the metal thiourea complexes, $Cu[CS(NH_2)_2]_4^{2+,}$ $Pb[CS(NH_2)_2]_4^{2+,}$ $Zn[CS(NH_2)_2]_2^{2+}$, $Ni[CS(NH_2)]_4^{2+,}$ and $Fe[CS(NH_2)_2]_2^{3+}$, respectively [10,24] . But, as thiourea solution is less sensitive to base metals, (as compared to the content of total dissolution with aquaregia) were leached along with gold and silver [10]. It is desirable that the leached gold and silver should be selectively recovered from thiourea solutions containing the base metals.

Cementation is one of the most effective and economical techniques widely employed in hydrometallurgical processes of solution streams, including the recovery of precious metal values from pregnant leached liquors. The advantages of the cementation process include its relative simplicity, ease of control and its ability to recover valuable metals. For gold and silver cementation, there are two simultaneous reactions. The cationic gold and silver in the complexes $Au[SC(NH_2)_2]^{2+}$ and $Ag[SC(NH_2)_2]^{3+}$ are reduced to elemental gold and silver, while the oxidation of less noble metals such as Cu, Fe, Zn, and Al, supplies the necessary electrons for the reduction reaction [10].

The standard reduction potential of Zn (-0.76 V) and Fe (-0.44 V) are lower than that of Ni (-0.26 V), Pb (-0.13 V), Cu (+0.34 V), Ag (+0.80 V), and Au (+1.50 V), Zn and Fe were considered unsuitable for the cementation process as they would reduce and precipitate some base metals along with gold and silver[10].

From this values copper appeared more desirable because it is relatively inexpensive and has lower reduction potential than those of gold and silver but higher reduction potential than that of other base metals. Consequently, copper is expected to selectively reduce gold and silver over base metals from the leached liquor for the present cementation process.

The experiment of cementation by copper was carried by taking Cu powder within range of 0.1 mg/ml to 0.6 mg/ml range at room temperature for 24 hrs. The results of cementation test for the recovery of gold and silver using copper powder are shown in fig. 8.

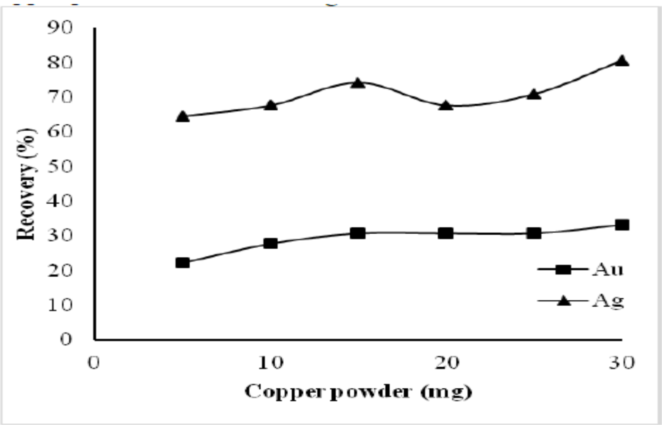


Fig. 8. Recovery of (a) gold and (b) silver by cementation with copper powder. Leached liquor = 50 ml, shaking speed = 200 rpm, Time = 24 h at room temperature

From the Fig. 8 it can be seen that 80 % recovery of silver was achieved at 0.6 mg/ml Cu powder dose, while at 0.6 mg/ml of Cu dose only about 33 % gold can be recovered.

The difference in ORP values of Au (+1.50 V), silver (+0.80 V) and Cu (+0.34 V) is the reason of this feat. From the results it is clearly observed that total Au recovery requires higher amount of copper powder. So for that investigation of a new viable method for recovery of gold and silver from leached liquor is in need.

Cementation process by copper of gold and silver from leached liquor reduces the silver (I) and gold (I) to their elemental form by following reactions [10].

$$2Au\,[CS(NH_2)_2]_2^{+} + Cu \longrightarrow Cu^{2+} + 2Au + 4CS(NH_2)_2 \quad (3)$$

$$2Ag\,[CS(NH_2)_2]_3^{+} + Cu \longrightarrow Cu^{2+} + 2Ag + 6CS(NH_2)_2 \quad (4)$$

Copper powder after the cementation was analyzed by SEM and EDS for material composition as shown in Fig. 9(a) and (b) respectively.

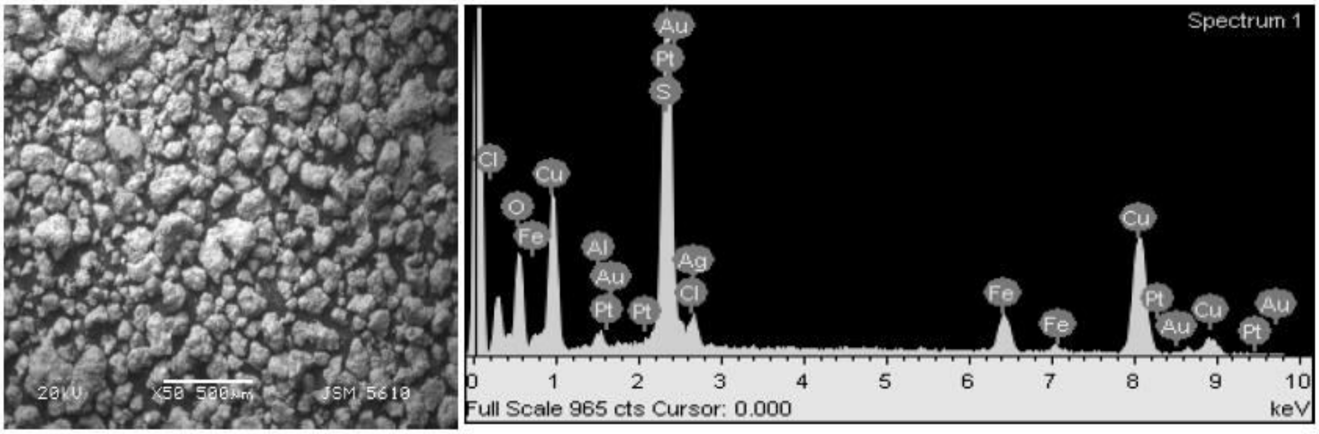


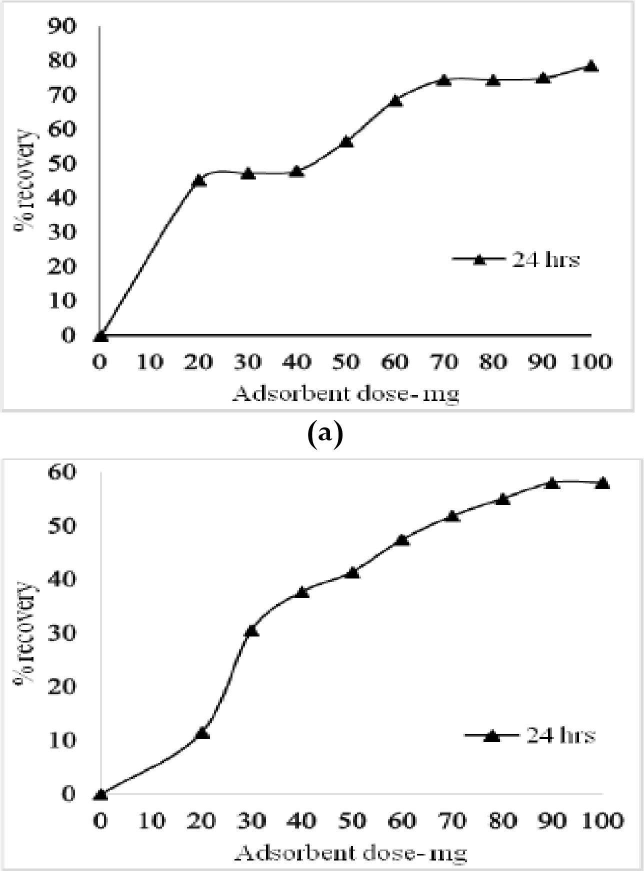
Fig.9 (a) SEM image (X50) and (b) EDS spectrum of residues after cementation by copper powder

3.4.2. Adsorption of leached metals using waste tea powder

3.4.2.1. Effect of adsorbent dose

The possibility of adsorptive recovery of dissolved gold and silver was investigated also by waste tea powder as adsorbents and the results are presented in Fig. 10. The results indicate that the percentage of gold and copper adsorption increased with the increase in adsorbent dose. As seen from figure after 1.4 mg/ml of adsorbent dosage Cu recovery remains constant at higher dosages. And Au recovery remains constant after 1.6 mg/ml of adsorbent dosage. For the silver results were not effective that can be seen from graph. The experiment was carried for 24 hrs, as seen from the graphs copper recovery achieved in 24 hrs was 78.5 %. For gold, in 24 hrs recovery achieved was about 57 %.

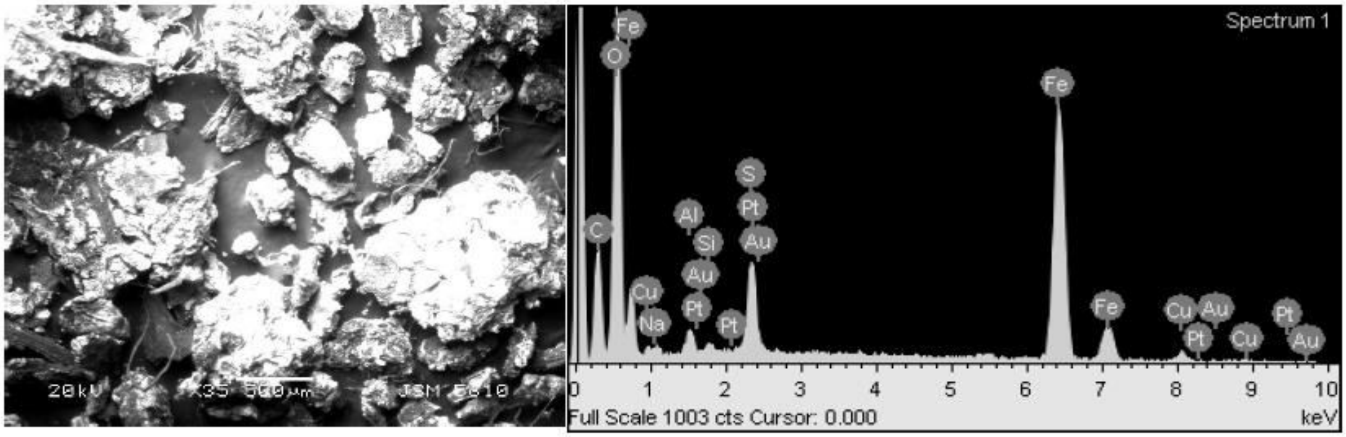
For the study of adsorbed metals onto waste tea powder from leached liquor, the dried waste tea powder after adsorption experiment subjected to EDS and SEM analysis. Fig 11(a) shows the digital micrograph image of waste tea powder after the adsorption from leached liquor. Fig. 11 (b) shows the EDS spectrum in which we can see sharp peaks of gold and copper which is the evidence of adsorption of gold and copper on waste tea powder. Presence of Fe peaks was due to ferric ions presence in solution which was added as oxidant.



(a)

(b)

Fig.10. Adsorption of (a) copper, (b) gold from thiourea leachate by waste tea powder, leached liquor = 50 ml, shaking speed = 200 rpm at room temperature



(a) **(b)**

Fig.11 (a) SEM image (X35) and (b) EDS spectrum of waste tea powder taken after adsorption.

4. CONCLUSION

The results of our study on process affecting parameters of the thiourea leaching for leaching of copper, gold and silver from PCB sample, and the subsequent recovery of dissolved metal led to the following conclusions.

1. Acidic solution of thiourea found as an effective alternative compared to conventional cyanide leaching of gold.
2. For all the parameters both sizes (<75 µm and 75-150 µm) of powdered PCBs were studied and smaller particle size found effective for leaching of copper, gold and silver through thiourea solution.
3. The elemental gold present in scraps of PCB sample was effectively leached with 80 ml of 0.5 M thiourea solution for 1g of powdered PCB sample in pH 1.9-2.0.
4. Pulp density also played an important role in leaching of gold and silver. Higher gold and silver leaching was found at lower pulp density.
5. Thus, the best conditions for the leaching as per OFAT study for gold at < 75 µm size were found to be 0.5 M TU in 0.05 M H_2SO_4 at pulp density (weight of PCBs/volume taken) of 0.00125 g PCB/mL at room temperature for 15 h. The leaching was achieved four times higher when 0.15M ferric ions were added. Based on above conditions leaching of 1 g PCB crush was carried and 2.22 mg/g of gold leaching was reported.
6. Effective leaching of silver was achieved at 80ml of 0.5 M thiourea solution for 1g of powdered PCB sample in pH 1.9-2.0 at pulp density of 0.00125 g/ml in 15 h. However, the presence of ferric ions as oxidizing agents had no beneficial effect for leaching. Silver leaching was not found so rapid, 0.447 mg was extracted from 1g of <75 µm size of PCB in 15 h. For 75-150 µm size of powdered PCB extraction of silver was 0.376 mg/g.
7. Further statistical optimization of TU dose, pulp density and ferric ion concentration on gold leaching from powdered PCB was carried using RSM. Second-order quadratic polyniomial model, representing the gold recovery expressed as a function of these three variables, was developed using Design Expert DX10 software. A statistical analysis (ANOVA) was carried out to study the effects of the individual variables as well as their combined interactive effects and quadratic effect on gold leaching. The results showed that the effects of the individual variables, their quadratic terms, and all the interactions among the variables were statistically significant. Model suggested 100 ml/g TU dose 0.001 g/mL pulp density and 0.2 molar ferric ion as optimum condition with 2.717 mg/g predicted gold leaching. Actual gold leaching was observed to be 2.645 mg/g which is in good agreement with the predicted value.
8. Therefore this study has shown that the development of mathematical models for gold leaching process based on statistics can be useful for predicting and understanding the effects of experimental factors. It can be stated that RSM could efficiently be applied for the modeling and optimization of gold leaching process.
9. Leached liquor obtained as per optimum conditions suggested by RSM study is used to do recovery of precious metal through cementation using copper powder and through adsorption using waste tea

powder. Cementation was found to be effective for silver recovery; a larger amount of copper powder was required for gold recovery. Accordingly, cementation is not applicable for the precipitation and recovery of gold from Au–TU complex solution.

10. The extracted gold from the leached liquor was adsorbed quantitatively on waste tea powder. Analysis of waste tea powder by EDS after adsorption also showed the presence of gold that adsorbed from leached liquor.

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