Statistical Evaluation of Recovery of Copper from Printed Circuit Board (PCB) by using Hydrometallurgical Method and RSM Model

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Abstract: *This manuscript deals with copper recovery from PCB by using hydrometallurgical methods and its evaluation by developing a quadratic model by using Box –Behnken experimental design and Response Surface Methodology (RSM) considering the factors: the concentration of H_2SO_4 (X1) and H_2O_2 (X2), the solid (X3)/Liquid ratio, times (X4) and temperature. Hydrometallurgical methods are more predictable and calculative in comparison to pyrometallurgical methods. RSM is a collection of statistical and mathematical methods that are useful for the modeling and analyzing engineering problems used in this study. By hydrometallurgical method 85 % of copper can recovered from 20.09 % available in printed circuit board (PCB). Box Behnken design total 27 experiments were performed, a model was developed for optimization of copper recovery. A second order polynomial model was developed using multiple linear regression analysis. This study showed that RSM based on Box-Behnken method is a useful tool for optimizing the operating parameters for copper recovery using leaching process. The statistical data of summary fit shows R Square is 0.99 indicates a better fit to the data. The Adjusts R Square is 0.98 also indicate better correlation in models with all variables. Root Mean Square (RMS) Error estimates the standard deviation of the random error. It was observed the RMS 2.91 and 60.06 mean of response for 27 observations.*
Keywords: *Printed Circuit Board (PCB), Electronic Waste (e-waste), Response Surface Methodology (RSM), Hydrometallurgy.*

I. Introduction

With the industrialization and development society, the dependence on electronic gadgets increases, which causes a big concern to environmentalist. The composition of electronic gadget is heterogeneous in nature and during disposal of it increases environment concern due to leaching of toxic chemicals and metals through it. The physiochemical classification of electronic waste shows it mainly consists of plastic, glass, ceramics, rubber, metal (ferrous & nonferrous), printed circuit board (PCB) concrete etc. In PCB iron & steel constitutes ~ 50% of the electronic waste, plastics ~ 21 %, nonferrous metal ~13 % and other ingredients ~ 16 % [1] and [2]. Non-ferrous metals consist of metals like Cu, Al and precious metals i.e. Ag, Au, Pt, Pd etc. The presence of the number of heavy metals like Pb, Hg, As, Cd, Se, & Cr and flame retardants in significant amount make them potentially hazardous waste [2]. If these hazardous materials are not handled in an environmentally sound manner can create environmental problem [1] and [3].

The increase of electrical and electronic products intake and further obsolescence causes the flooding of electronic waste in society [4]. Since electronic waste life span is very short and every day invention of new technology increases the demand of electronic gadget in market. According to Greenpeace Report India has generated 800,000 tonnes electronic waste in 2012 [5]. Electronic waste is one of the most vastly growing problem in all-around the world and majority of its, are exported to developing countries like India [6]. PCB is base of the electronic industry as it is an important ingredient of nearly all electronic gadgets. PCB are made up of fibre glass, phenolic resin, epoxy resin, Sn, Cu, Sb, Cd, and possibly Pb (solder), resin and/or NH_4Cl (flux), brass/gold/silver (contacts), plastic, aromatic solvents - typically trichloroethylene or acetone(for removing flux), varnish, paint, $FeCl_3$ and various oxides and sulfates resulting from exposure to the environment before sealing [7]. The two dominant constituents of a PCB are fiber glass, which provides insulation & copper provides conductive pathways. Generally in most of gadgets, PCB is typically 1.6 mm in thickness. Motherboards have a multilayer construction, which means they have more than two Cu layers. The process of PCB manufacturing is extremely complicated [8]. PCB contains many electric/electronic components, such as condensers (Ni, Al, Ag, Ta), inductors (Fe, Zn, Cu), resistors (Ni, Cr, Cd, Al, Pb, Ta), relays, diodes (Pb, Ga, Al, In), capacitors (Sn, Cu, Zn), EMI filter (Fe, Cu, Zn) and IC chips (Pb, Ni, Sn, Ga, Al, Ag), Connector (Pb, Ni, Sn), Oscillator (Fe, Ni, Cu), Transistor (Pb, Cu) [9]. As per Central Pollution Control Board (CPCB), PCB scrap contains Cu (16%), Fe (12%), Ni (2%), Pb (2%), Al (7%), Ag (280 ppm), Au (110 ppm) [10]. The unorganized

disposal of the PCB creates havoc in environment by releasing of toxic chemical and during this losses of some valuable metal also occur.

The precious metals contribute the most value in electronic scraps. From an economic point of view, recovery of few precious metals from electronic waste may be beneficial. Hydrometallurgical methods are more predictable and calculative in comparison to pyrometallurgical methods [11], [12] and [13]. Hydrometallurgical processing consists of leaching through acids, recovery of metal by adsorption or ion-exchange or by electro-refining processes and the last step is chemical reduction or crystallization. Generally, base metals are leached in HNO_3 [14]. The most efficient agent used for solder leach is HBF_4 [15]. Copper is leached by H_2SO_4 or Aquaregia [14].

II. Experimental Method

PCB contains hazardous materials in electronic components such as relays, switches, capacitors, or batteries. Such materials include heavy metals (e.g. Pb, Hg, As etc.) which are potentially dangerous in very small concentration also. Magnetic materials also available in such components and create problem during physical separation. Such components were manually dismantled and removed from the PCB before any processing [16]. Schematic of preparing metal powder and leaching processes has shown in Fig.1.

2.1 Dismantling of PCB

PCB was manually dismantled using chisels, hammers, pliers, screwdrivers cutting scissor. PCB were heterogeneous in structure and contained a variety of constituents, such as IC Chips, condensers, capacitors, transistors, resistors, diodes, and connecting jacks which were removed. The weight of motherboard used in this study is 495 g (Fig. 2a). These EECs were mounted on the front-side of the PCB, and soldering metals projected from the back-side of the PCB (Fig. 2b). After dismantling, the weight of PCB was found 207 g. The 288 g of waste components from this PCB was removed (Fig. 2c). Extra care was taken while cutting PCB into pieces by chisels, hammers, pliers, screwdrivers and cutting scissors.

2.2 Cutting and Thermal Treatment of PCB

The PCB was then cut into pieces as small as possible of about 3 cm × 3 cm, 2 cm × 4 cm by pliers, chisel, hammer, clipper as shown in Fig.2d. The PCB cut pieces were then weighed and found 203.49 g. There was a loss of 3.51 g in cutting. The cut pieces of PCB than incinerated in muffle furnace at 600 °C for 15 minutes [17]. After incineration in muffle furnace, the weight of incinerated pieces again taken and found 160 grams. There was losses of 43.49 g indicate presence of carbonaceous material present in PCB. After pyrolysis residues mainly consist of glass fiber, metal and carbon. It could be seen from that the residues obtained after thermal treatment in muffle furnace was composed of pieces of equal dimensions to those of the original ones, and the color of PCB after incineration was changed to completely black (Fig 3a.). This was coke like carbonaceous product formed during the process due to cyclization and secondary repolymerization reactions [18].

2.3 Shredding, Grinding and Size Classification

The particle size of the crushed PCB has significant effects not only on the efficiency of the physical separation equipment, but also on the effectiveness of further treatment involving chemical processes. The shredding of PCB is a fundamental process which liberates particles from different materials in order to allow further processing by other physical and chemical technologies [19]. The next step was the crushing of material to reduce the size of PCB in a Ball mill. Ball Mill was run for 40 minutes for converting all burned pieces into fine powder. The size separation of shredded PCB, cumulative sieve analysis was done as per BSS 1962. Standard sieves are used to separate different fraction by sieve shaker using a series of standard sieve with a pore size of 63 μm to 150 μm. The fine fractions were rich in plastic materials while the metals were fundamentally present in the intermediate fractions with larger particle size range (Fig. 3b). The loss in grinding & sieving is measured significant because fine fractions were rich in plastic materials, fine fractions again incinerated. These fractions were converted into greenish lumps and the ash deposited on backside of these lumps (Fig. 3c). The copper were available in small pieces in PCB fine fractions (Fig. 3d). Classification of different fractions received after grinding and sieving has shown in table 1a. Total material left for density separation and chemical treatment is 133.37 g, while initial weight of PCB was 495 g.

2.4 Separation of Metal and Nonmetal Powder

Separation of metal and nonmetal from pulverized material was carried out by gravity separation method as used by number of researcher due specific gravity difference between metallic and nonmetallic material. The 18.09 g copper was separated and safely recovered by sieving which is 8.74% of PCB sheet weight i.e. 207 g. Out of the remaining material, the material which was more than 63 micron was converted

into less than 63 micron powder by again grinding with pastel mortar to make it in homogeneous range. The powdered materials (115.28 g) were kept in the bottle. One side nipple of bottle was connected by PVC tube to air supply line and the other side was connected to water line. The optimum quantity of air and water were supplied simultaneously and the bottle was kept in stainless steel chamber to collect the overflow water to avoid the separated nonmetal powder. It was found nonmetal powder is separating and the heavy metal particles are settling down. The after 1 hour exercise, the water and air supply was stopped and put to rest for 24 hours. The overflowed water & bottle water was allowed to settle for 24 hours and remaining material in bottle and in bucket was collected separately in a beaker. The separated powder weighed and bottle bottom powders were found 105.4 g and 9.88 g respectively.

2.5 Acid Leaching Procedures of PCB Powder

Acid leaching of metals from e-waste have been extensively investigated using various mineral acids and oxidants combination with acids to enhance metal extraction [20]. Analytical grade commercial H_2SO_4, H_2O_2 (30%) was used for this experiment. Leaching experiments were carried out in a 250 mL conical flask at room temperature (22 °C). Oxidant commonly used in H_2SO_4 system for leaching Cu was H_2O_2 [20]. The overall reaction for Cu dissolution can be expressed by reaction follows Eq. (1):

$$Cu + H_2O_2 + H_2SO_4 \longleftrightarrow CuSO_4 + 2H_2O \text{----------------------(1)}$$
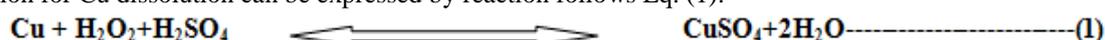
Leaching of Cu from PCB powder was carried out at room temperature (22 °C). There were many factors influencing the leaching of copper such as H_2SO_4 concentration, H_2O_2 concentration, solid/liquid ratio, dimension of particles, leaching temperature and time.

III.   Result & Discussion

A number of experiments were performed in different combinations of acid concentration, H_2O_2 concentration, quantity of metal powder, variation in time and temperature (Table 2). The concentration (ppm) of solution was analyzed by Atomic Absorption Spectrophotometer (AAS-900). The 2 g metal powder was dissolved in 50 mL 98% H_2SO_4 (conc.) solution and reaction time was 2 hours, no H_2O_2 was added for oxidation and room temperature 22 °C (Table 2a). In another sample 2 mL H_2O_2 (30 %) was added for oxidation and other conditions were remaining same. The concentrations of copper were increases by 237.14 % on addition of H_2O_2 indicate a major role of oxidant in leaching of copper. In another experiment H_2SO_4 concentration were varied from 5 to 25%. Leaching of Cu increases with increase of the concentration of H_2SO_4 (Fig. 4a). It was maximum i.e. 82.82% when H_2SO_4 concentration is 25% but 15 % was considered optimum because leaching of copper becomes almost stationary after 15 % (Fig. 4a). It appears that leaching reaches the maximum when the concentration at 15% of H_2SO_4 and then keeps almost constant so that it was decided to use 15% of H_2SO_4 solution for further experimental work (Fig. 4a). In third category the quantity of PCB powder is increased up to 3 g keeping other things same and it was found that the leaching of Cu is decreased with increasing in the quantity of PCB powder (Fig 4b). This was due to change in Solid/Liquid ratio. Leaching rate decreases with the increase in solid PCB powder as in comparison H_2O_2 was not increased, it indicates the significance of the oxidizing agent (Fig. 4b). In fourth experiment we have changed the quantity of H_2O_2. While Cu recovery increases with the increase of H_2O_2 concentration until addition of H_2O_2 reaches to or over 1 mL in 1g metal powder (Fig. 4c). Oxygen produced from the decomposition of H_2O_2 reacts with metal Cu to form CuO, which can further react with H_2SO_4 to form $CuSO_4$. Thus H_2SO_4 and H_2O_2 actively together act as the reactants. In this way, the Cu recovery increases with the increase of their concentrations. The results shows when the volume of H_2O_2 increased, the oxidation process increase results more yield (Fig. 4c). The Cu % was increased up to 91.04 % when quantity of PCB powder was only 1 g and the volume of H_2O_2 was 5 mL. In fifth experiment we have changed the reaction time and rest condition remains same (Table 2e). The result indicates optimum condition achieved within 1-2 hours, no major changes observed with increasing reaction time (Fig. 4d). The copper leaching has no significant increase when the time is extended up to 4 hrs and even one sample was analyzed after 24 hrs, no significant change is found in concentration (Fig. 4d). Based on this phenomenon, the Cu recovery at 2 h was adopted to examine the influence of system variables on it. In the sixth experiment solution temperature changed from 22 °C to 70 °C and no significant change in concentration was found (Table 2f). The temperature has no significant impact on the Cu recovery when it is in a range from 22 °C to 70 °C (Fig 4e). With the increase of the reaction temperature, the reaction and the decomposition of H_2O_2 will be speeded. However, the content of dissolved oxygen in aqueous phase deceases, which results in that there is no significant impact on Cu recovery. In the last experiment the sample is magnetically stirred for 2 hours and it was found that with same conditions about 3% of Cu recovery has increased (Table 2g). It can be summarized from the experimental results above that the optimum condition of leaching Cu is 1 g PCB powder, 100 mL of 15 (wt%) sulfuric acid, 1mL H_2O_2, and reaction for 2 hours at room temperature (22 °C)

3.1 Model Developments
3.1.1 Response Surface Design
Response Surface Methodology (RSM) was used in this experiment to determine the optimum operational conditions required for the recovery of copper from PCB. RSM was used in this experiment to optimize different variable like acid concentration, solid/liquid ratio, H_2O_2 concentration and time factor for recovery of copper from PCB. These designs are helps to solve 2nd order prediction equation for the each surface response. In this model the curvature in the true response function [21]. RSM also quantifies the relationship between the controlling input parameters and the obtained Response Surface [22]. If all variables are assumed to be measurable, the Response Surface can be expressed as follows;

$$y = f(X_1, X_2, X_3, X_4) \text{---(2)}$$

Where X_1 = H_2SO_4 concentration; X_2 = H_2O_2 concentration, X_3 = solid/liquid ratio, X_4 = time and y is the prediction response. The Box-Behnken design is a RSM design [23]. The Box Behnken design indicates copper recovery increases with increase of acid quantity, H_2O_2 quantity, and time but trends are reveres in case of solid/liquid ratio (Table 2).

3.1.2 Statistical Analysis
Response Surface regression procedure was used for experimental results to fit the following quadratic model, providing regression coefficients. In RSM for each response a model is defined that can predict the variable combination between different parameters. The full quadratic model for four variables used in response(y) was described as the following polymeric eq. [24]

$$y = \square_0 + \square_1X_1 + \square_2X_2 + \square_3X_3 + \square_4X_4 + \square_{11}X_1^2 + \square_{22}X_2^2 + \square_{33}X_3^2 + \square_{44}X_4^2 + \square\square_{12}X_1X_2 + \square_{13}X_1X_3 + \square_{14}X_1X_4 + \square_{23}X_2X_3 + \square_{24}X_2X_4 + \square_{34}X_3X_4 \text{--}$$
(3)

Where y = predicted response; α_0 = Constant Coefficient; α_1, α_2, α_3 and α_4 = linear effect coefficients; α_{11}, α_{22}, α_{33} and α_{44} = quadratic effect coefficients; α_{12}, α_{13}, α_{14}, α_{23}, α_{24} and α_{34} = interaction effect coefficients;

3.1.3 Prediction Expression
The prediction expression eq (4) shows the equation used to predict the response and the result of design of experiment. Positive sign in from of the terms indicates synergistic effect; whereas negative sign indicates antagonistic effect [25]

$$(Y = (-29.32) + 3.95 * X1 + (-0.091) * X2 + (-2.09) * X3 + 49.11 * X4 + X1 * [X2 * 0.03] +$$
$$X1*X3*0.01+X2*X3*-0.31+X1*X4*0.36+X2*X4*2.45+X3*X4*-3.28+X1*X1*-0.09+X2*X2*-0.19$$
$$+X3*X3*0.26+X4*[X4*-11.20]\text{--}$$
$$\text{-----------------(4)}$$

3.1.4 Design of experiments
The optimization of experimental design was done using RSMBBD and was used to create a set of designed experiments by JMP software [26]. The BBD was developed based on the combination of a four level (full or fractional) factorial design with an incomplete block design [27] and [28]. The experimental design consisted of all four variables (X_1 = H_2SO_4 concentration; X_2 = H_2O_2 concentration, X_3 = solid/liquid ratio, X_4 = time) with two levels i.e. low (-1) and high (+1) with 27 experimental runs (Table 3).

3.1.5 Response Y: Actual by Predicted Plot
The graph for goodness of fit depends on which type of response used. The actual by predicted plot is for continuous responses shows how well the model fits the data (Fig. 5a). Each leaf is predicted with its mean hence X-coordinates are these means. The actual values form a scatter of points around each leaf mean, a diagonal line represents the locus of where predicted and actual values are the same range (Fig. 5a). For a perfect fit, all the points would be on this diagonal. When validation is used, plots are shown for both the training and the validation sets. While a graph between residual and predicted compares experimental copper recovery efficiency (%) with the predicted values obtained from the model (Fig. 5b). The figures indicate good agreement between the experimental and predicted values of copper recovery efficiency (%).

3.1.6 Summary Fit
The statistical data of summary fit shows R Square is 0.99 indicates a better fit to the data (Table 4). The Adjusts R Square is 0.98 also indicate better correlation in models with all variables (Table 4). Root Mean Square (RMS) Error estimates the standard deviation of the random error. It was observed the RMS 2.91 and 60.06 mean of response for 27 observations (Table 3).

3.1.7 Parameter Estimates

The Parameter Estimates report shows the estimates of the model parameters and for each parameter gives a t test for the hypothesis that it equals zero (Table 4a). These are the estimates of the model coefficients. When there are linear dependencies among model terms, these might be labeled as Biased or Zeroed [21]. Standard Error gives estimates of the standard errors for each of the estimated parameters [21]. The t ratio tests whether the true value of the parameter is zero. The t ratio is the ratio of the estimate to its standard error. Prob > |t| indicates lists the p-value for the test that the true parameter value is zero, against the two-sided alternative that it is not[21].

3.1.8 Residual by Predicted Plot

The plot shows the residuals (which are the observed response values minus predicted values) plotted against the predicted values of Y (Fig. 5b). The residual values scattered randomly about zero. The sorted estimates option produces a version of the parameter estimates report that is useful in screening situations (Table 4b). If the design is not saturated, the sorted estimates report gives the information found in the parameter estimates report, but with the terms, other than the intercept, sorted in decreasing order of significance. The parameter estimates are presented in sorted order, with smallest p-values listed first.

3.1.9. Prediction Profiler

The response Prediction Profiler figure gives a closer look at the response surface to find the best settings that produce the response target (Fig. 6a). It is a way of changing one variable at a time and looking at the effects on the predicted response. The profiler shows prediction traces for each X variable. The vertical dotted line for each X variable shows its current value or current setting. The horizontal dotted line shows the current predicted value of each Y variable for the current values of the X variables. In red current predicted value of response, changes by dragging a factor value. In bracket 95% confidence interval for the mean response.

3.1.10 Sorted Parameter Estimates

Table 5b shows the results of sorted parameter estimates and the terms used in sorted parameters are explained below-a) The sorted estimates option produces a version of the parameter estimates report that is useful in screening situations. b) If the design is not saturated, the sorted estimates report gives the information found in the Parameter Estimates report, but with the terms, other than the intercept, sorted in decreasing order of significance. The parameter estimates are presented in sorted order, with smallest p-values listed first.

3.1.11 Normal Plot

Identifies parameter estimates that deviate from normality, helping you determine which effects are active (Fig. 6b). If a transformation to orthogonality has been applied, the vertical axis represents the Normalized Estimates. These are the orthogonally t-Ratio values found in the Parameter Estimate Population report. Because the estimates are normalized by an estimate of σ, the points corresponding to inactive effects should fall along a line of slope 1. A red line with slope 1 is shown on the plot figure, as well as a blue line with slope equal to the t-Test Scale Lenth PSE (Lenth's Pseudo Standard Error (PSE) is an estimate of residual error due to Lenth) (Fig. 6b). Lenth PSE is provided when the parameter estimates have equal variances and are uncorrelated.

3.2 Estimation of Quantitative Effects of the Factors

RSM is a collection of mathematical and statistical techniques for empirical model building [21]. By careful design of experiments, the objective is to optimize a response (output variable) which is influenced by several independent variables (input variables). An experiment is a series of tests, called runs, in which changes are made in the input variables in order to identify the reasons for changes in the output response[21]. The Surface Profiler shows a three-dimensional surface plot of the response surface (Fig. 7). A response surface model can pinpoint a minimum or maximum response, if one exists inside the factor region. Only two factors can be displayed on a plot and thus X_1 and X_2 become the best candidates for providing a picture of response Y_1. The response can be represented graphically in the three-dimensional space that helps visualize the shape of the response surface. The figure 8a represent the response surface plots of the acid concentration (X_1) and H_2O_2 dosage (X_2) on Cu removal efficiency while PCB powder weight (X_3) and time (X_4) kept constant. The three dimensional response surface plots obtained from second polynomial equation are shown in figure 7a to 7e. The optimum values of the variables were obtained as the response is maximized using the RSM technique. The best response range can be obtained by analyzing the response surface plots. The combined effect of H_2SO_4 concentration and H_2O_2 of the solution on Cu removal efficiency of PCB powder at constant dosage of PCB

powder and time is shown in figure 7a. The Cu removal efficiency increased with increasing the acid concentration of solution. This is due to the increase in the number of binding sites. It is clear from this figure that the percentage of Cu removal increases with increase in H_2SO_4 concentration from 5 to 25 mL. It is noted that the maximum adsorption at all the concentration takes place at H_2SO_4 concentration 25 %. The maximum copper removal efficiency of 88.61 % was observed at constant PCB powder dosage (1g) and time (2 hrs). The figure 7b represents the response surface plots of the acid concentration (X_1) and PCB powder weight (X_3) on Cu removal efficiency while H_2O_2 dosage (X_2) and time (X_4) kept constant. It was observed when acid concentration is increased from 5 % to 25 % and PCB powder dosages were also increased than due to this the Cu removal efficiency is decreased. The figure 7c represent the Response Surface plots of the H_2O_2 dosage (X_2) and time (X_4) in hours on Cu removal efficiency while acid concentration (X_1) and solid/liquid ratio, PCB powder weight (X_3) kept constant. It was observed that when acid concentration is constant and H_2O_2 concentration is increased from 1mL to 5 mL and time was also constant for 2 hours, the Cu removal efficiency is increases drastically due to fully oxidation of Copper ions. The figure 7d represent the three dimensional response surface plots of the H_2O_2 dosage (X_2) and PCB powder weight (X_3) on Cu removal efficiency is studied while acid concentration (X_1) and time (X_4) kept constant. It is observed that when H_2O_2 concentration is decreased and the PCB powder dosage increased that the Cu removal efficiency is decreased drastically. The figure 7e represents the three dimensional response surface plots of the PCB powder weight (X_3) and time (X_4). The Cu recovery efficiency is studied while acid concentration (X_1) and H_2O_2 dosage (X_2) kept constant. It is observed that when H_2O_2 concentration was increased the copper removal efficiency is increased and when H_2SO_4 concentration is increased keeping H_2O_2 dosage (X2) constant Cu removal efficiency also increased.

IV.   Conclusion

The recovery of precious metals can be achieved using the hydrometallurgical method. Size reduction by ball mill gives better results in comparison of results in other studies. The recoverable copper in PCB powder was determined by leaching process in H_2SO_4 using H_2O_2 as an oxidant. The effects of different leaching conditions on copper recovery were studied like (a) effect of dilute H_2SO_4 concentration; (b) effect of the addition of PCB powder; (c) effect of H_2O_2; (d) effect of reaction time; (e) effect of temperature. The optimum leaching condition for 1 g of PCB powder at room temperature (22 ^{o}C) is proposed as following: 100 mL of 15 (wt%) H_2SO_4, 1mL H_2O_2, time 2 hours. Total 30 experiments were performed to determine the optimum copper extraction conditions. At above optimum condition, it could be concluded that by hydrometallurgical 85 % of copper can recovered from 20.09 % available in PCB.

For Box-Behnken design total 27 experiments were performed. The model was developed for optimization of copper recovery. The RSM analysis has been reviewed. RSM can be used for approximation of both experimental and numerical responses. Two steps are necessary, the definition of an approximation function and design of the plan of the experiments. In this work RSM was employed for optimization of copper recovery using leaching process. By using the Box Behnken method, four main parameter including H_2SO_4 concentration, H_2O_2 concentration, solid/Liquid ratio, time and temperature were examined. A second order polynomial model was developed using multiple linear regression analysis. The optimal operating conditions were determined using numerical optimization techniques. For this purpose, the maximum copper recovery was optimized for minimum consumed H_2O_2. Accordingly, the recovery efficiency of copper, 81.82 % in terms of the independent variables was optimized. This study showed that RSM based on Box-Behnken method is a useful tool for optimizing the operating parameters for copper recovery using leaching process.

A review of different design for fitting Response Surface has been given. A desirable design of experiments should provide a distribution of points throughout the region of interest, which means to provide as much information as possible on the problem. A model has been presented to study the extraction process of copper from e-waste. The model allows determining the extraction efficiency of copper from e-waste for given operating conditions. The model presented is very effective and can be used to study the extraction process. The predictions were in excellent agreement with experiment.

Acknowledgement

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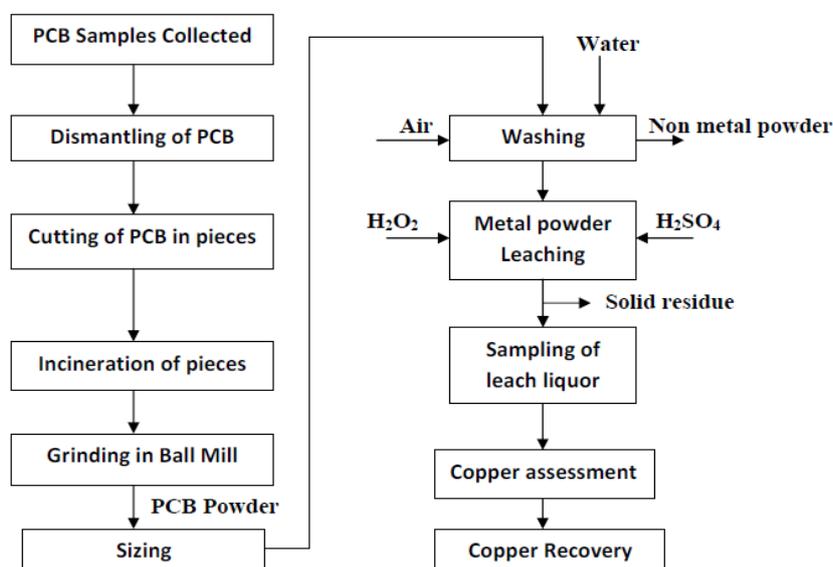
Fig.1. Schematic block diagram of the process route used in the experimental work

Fig 2a. Printed Circuit Boards

Fig.2b. PCB after dismantling

Fig.2c. Dismantled Materials from PCB

Fig.2d. Cut pieces of PCB

Fig.3a.PCB after incineration in muffle furnace

Fig.3b PCB powder of after incineration

Fig.3c. Powder lumps of incinerated PCB
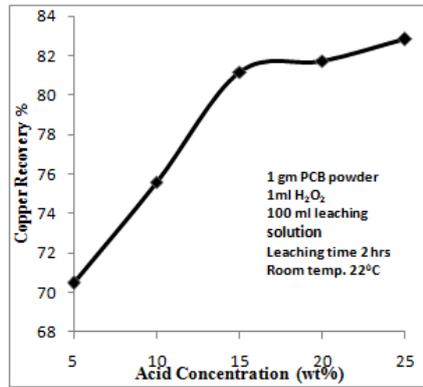

Fig.3d. Photographs of copper present in PCB

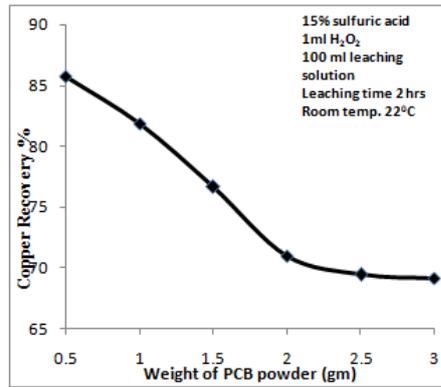**Fig.4a.** Effect of dilute H_2SO_4 conc. on Cu recovery   **Fig.4b.** Effect of the addition of PCB powder
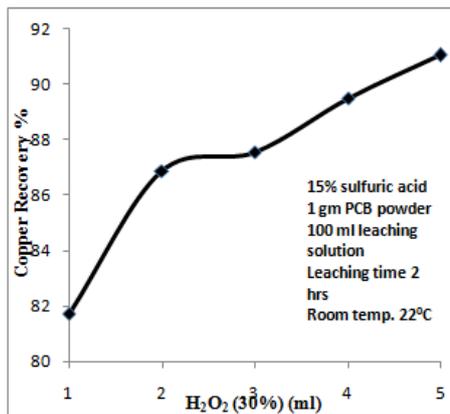

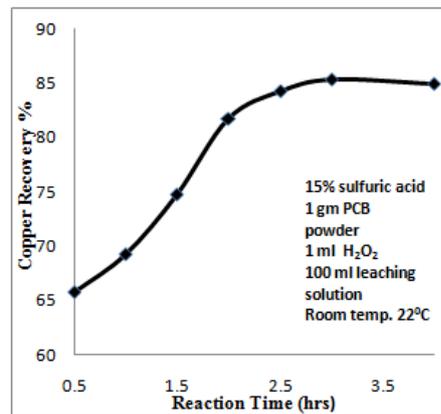**Fig.4c.** Effect of H_2O_2 addition on Cu recovery   **Fig. 4d** Effect of Reaction time on Cu recovery
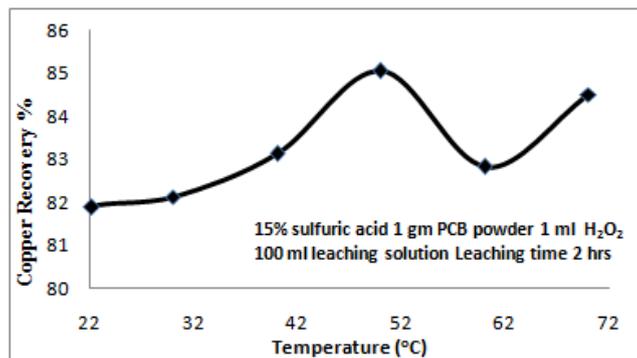

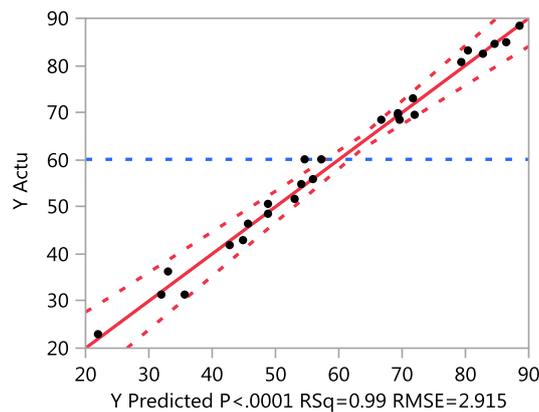**Fig. 4e** Effect of temp on Cu recovery

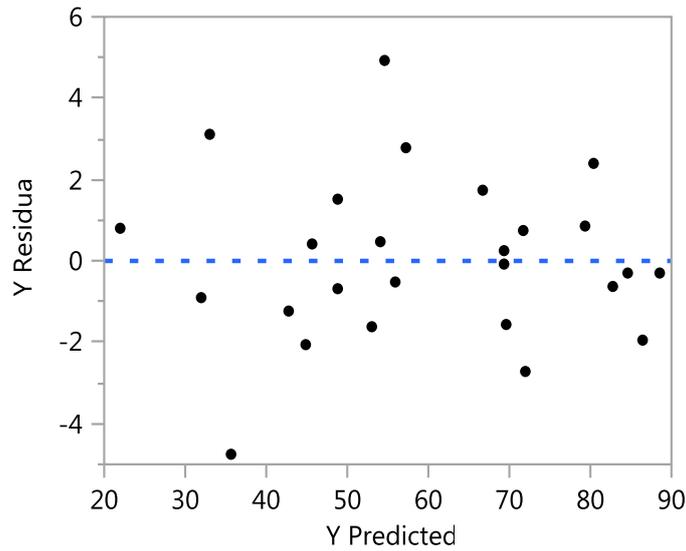**Fig.5a** actual response v/s predicted.

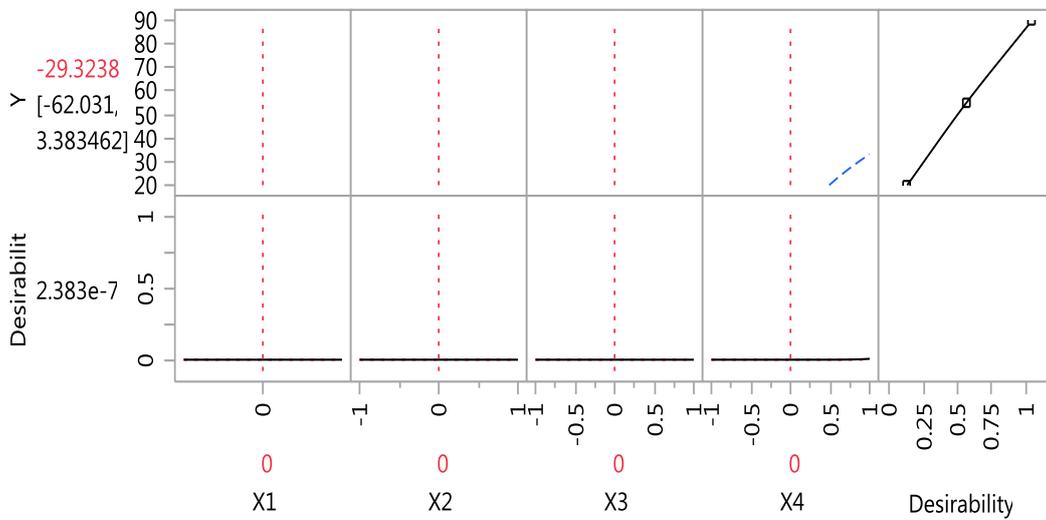**Fig.5b.** Y residual v/s Y predicted
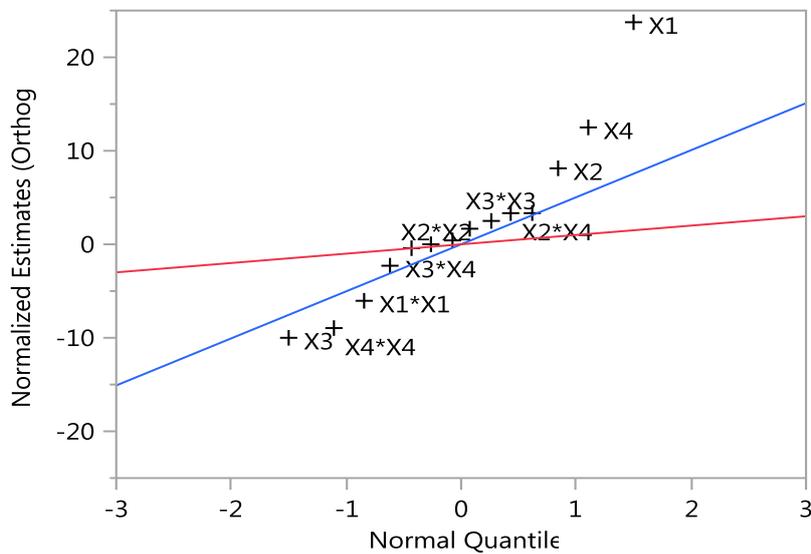
Fig.6a. Prediction Profiler

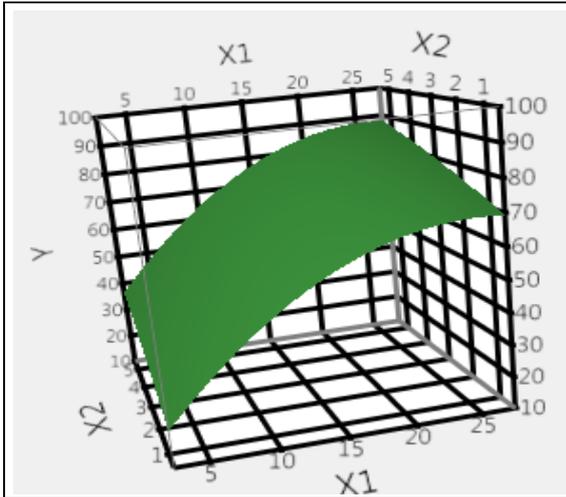**Fig 6b** Normalized Estimates v/s Normal Quantiles

Fig.7a. RS plot when X_3 & X_4 kept constant

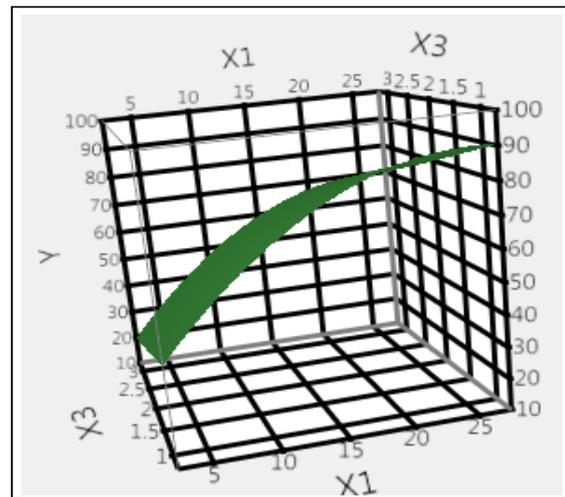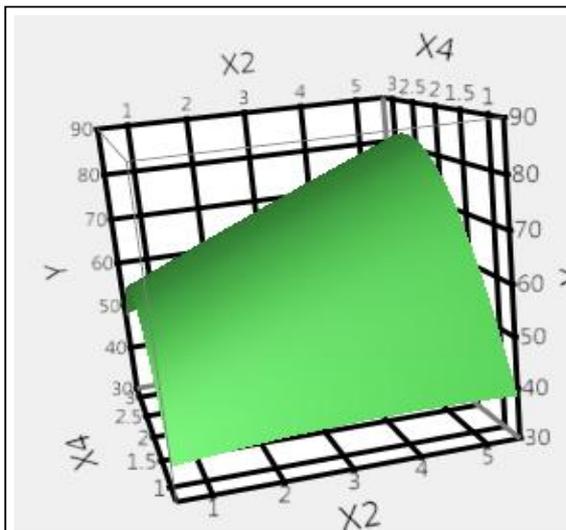**Fig.7b.** RS plot when X_2 & X_4 kept constant

Fig.7c. RS plot when X_1 & X_2 kept constant
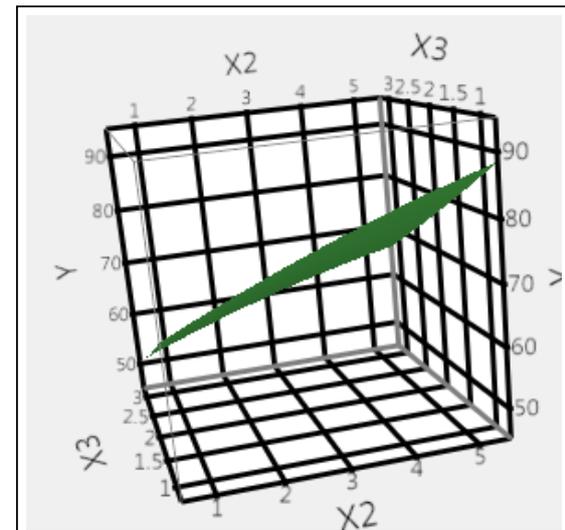

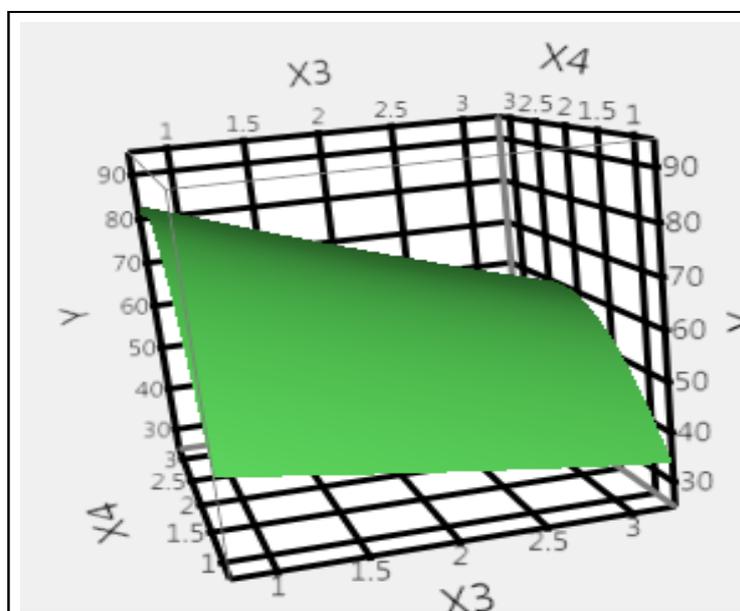**Fig.7**d.RS plot when X_1 & X_4 kept constant

Fig.7e RS plot when X_1 & X_2 kept constant

Table 1a Weight of separated fractions before and after incineration of PCB powder

S. No.	BSS No.	Aperture (μm)	Aperture Range (μm)	Weight (gm) (before incineration)	Weight (gm) (after incineration)
1	100	150	>150	24.89	20.75
2	170	90	90-150	104.49	20.29
3	200	75	75-89	0.39	12.82
4	240	63	63-74	0.49	6.95
5		< 63	< 63	12.29	72.56

Table 1b Weight of different PCB specimen

S. No.	Steps in treatment of PCB	Weight(gm)
1	PCB	495
2	Scrap removed	288
3	PCB Sheet weight after removal of waste material	207
4	Loss in PCB cutting into pieces	3.51
5	Remaining weight of PCB Pieces	203.49
6	Loss in incineration at 600^0C	43.49
7	Weight of PCB pieces after incineration	160
8	Loss in grinding and sieving	17.45
9	Total material after processing	142.55
10	Loss in again grinding, sieving after incineration	9.18
11	Total material left for density separation and chemical treatment	133.37

Table 2 Comparison of Copper Recovery (%) as per Box-Behnken Design.

S. No.	X_1 (Acid conc.) (wt %)	X_2 (H_2O_2) (mL)	X_3 (PCB) (g)	X_4 (Time) (Hours)	Copper Conc. (ppm)	Copper Conc. % (PCB 115.28 g)	Copper Recovery % as experiment	Copper Recovery % as per model
1	25	3	1	2	1795	20.69	88.31	88.61
2	5	1	2	2	1470	8.47	36.16	33.09
3	15	5	2	1	1960	11.29	48.21	48.9
4	15	3	2	2	2815	16.22	69.62	69.37
5	15	1	2	3	2260	13.02	55.59	56.12
6	25	3	3	2	4230	16.25	69.37	72.1
7	15	3	3	3	3660	14.06	60.02	57.25
8	25	1	2	2	2955	17.03	72.69	71.95
9	15	3	2	2	2815	16.22	69.25	69.37
10	5	5	2	2	1875	10.8	46.12	45.74
11	5	3	3	2	2065	7.93	31.07	31.98
12	15	5	1	2	1715	19.77	84.38	84.68
13	15	5	3	2	4175	16.04	68.47	66.74
14	15	3	1	1	1045	12.04	51.41	53.06
15	15	1	1	2	1385	15.96	68.15	69.76
16	15	1	2	1	1745	10.05	42.92	44.98
17	5	3	2	3	1720	9.91	31.07	35.86
18	15	5	2	3	3270	18.84	80.44	79.59
19	5	3	2	1	930	5.36	22.87	22.11
20	15	3	3	1	2540	9.76	41.65	42.9
21	25	3	2	1	2430	14	59.78	54.86
22	5	3	1	2	1025	11.81	50.43	48.91
23	15	3	2	2	2910	16.77	69.25	69.37
24	25	3	2	3	3345	19.28	82.29	82.93
25	15	3	1	3	1685	19.42	82.9	80.53
26	15	1	3	2	3335	12.81	54.69	54.27
27	25	5	2	2	3445	19.85	84.75	86.7

Table 3 Summary of Fit

R Square	0.98853
R Square Adj	0.97514
Root Mean Square Error	2.9158
Mean of Response	60.0689
Observations	27

Table 4a: Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob > |t|
Intercept	-29.3238	15.01148	-1.95	0.0745
X_1	3.948958	0.606973	6.51	<.0001*
X_2	-0.09063	3.034863	-0.03	0.9767
X_3	-2.09292	6.654377	-0.31	0.7585

X_4	49.10958	6.654377	7.38	<.0001*
X_1*X_2	0.02625	0.072895	0.36	0.725
X_1*X_3	0.0105	0.14579	0.07	0.9438
X_2*X_3	-0.30625	0.72895	-0.42	0.6818
X_1*X_4	0.35775	0.14579	2.45	0.0304*
X_2*X_4	2.445	0.72895	3.35	0.0057*
X_3*X_4	-3.28	1.457901	-2.25	0.0440*
X_1*X_1	-0.09229	0.012626	-7.31	<.0001*
X_2*X_2	-0.19281	0.315645	-0.61	0.5527
X_3*X_3	0.26375	1.262579	0.21	0.838
X_4*X_4	-11.1988	1.262579	-8.87	<.0001*

Table 4b: Sorted Parameter Estimates

Term	Estimate	Std Error	t Ratio	t Ratio	Prob > |t|
X_4*X_4	-11.19875	1.262579	-8.87		<.0001*
X_4	49.109583	6.654377	7.38		<.0001*
X_1*X_1	-0.092287	0.012626	-7.31		<.0001*
X_1	3.9489583	0.606973	6.51		<.0001*
X_2*X_4	2.445	0.72895	3.35		0.0057*
X_1*X_4	0.35775	0.14579	2.45		0.0304*
X_3*X_4	-3.28	1.457901	-2.25		0.0440*
X_2*X_2	-0.192812	0.315645	-0.61		0.5527
X_2*X_3	-0.30625	0.72895	-0.42		0.6818
X_1*X_2	0.02625	0.072895	0.36		0.7250
X_3	-2.092917	6.654377	-0.31		0.7585
X_3*X_3	0.26375	1.262579	0.21		0.8380
X_1*X_3	0.0105	0.14579	0.07		0.9438
X_2	-0.090625	3.034863	-0.03		0.9767