Optimization of HNO_3 leaching of Copper from old AMD Athlon processors using response surface methodology

Umair Javed[1], Robina Farooq[2]*, Farrukh Shehzad[3], Zakir Khan[1,4]

[1]Department of Chemical Engineering, COMSATS Institute of Information Technology, Defence Road, Lahore, Pakistan

[2]Department of Chemistry, COMSATS Institute of Information Technology, Defence Road, Lahore, Pakistan

[3]Department of Statistics, Islamia University of Bahawalpur, Bahawalpur, Pakistan

[4]Systems Power and Energy, School of Engineering, University of Glasgow, Glasgow, G128LL UK

Abstract

The present study investigates the optimization of HNO_3 leaching of Cu from old AMD Athlon processors under the effect of nitric acid concentration (%), temperature (°C) and ultrasonic power (W). The optimization study is carried out using response surface methodology with central composite rotatable design (CCRD). The ANOVA study concludes that the second degree polynomial model is fitted well to the fifteen experimental runs based on p-value (0.003), R^2 (0.97) and Adj-R^2 (0.914). The study shows that the temperature is the most significant process variables to the leaching concentration of Cu followed by nitric acid concentration. However, ultrasound power shows no significant impact on the leaching concentration. The optimum conditions were found to be 20 % nitric acid concentration, 48.89 °C temperature and 5.52 watt ultrasound power for attaining maximum 97.916 mg/l concentration of Cu leaching in solution.

Key words: Leaching, copper, nitric acid, response surface methodology

1. Introduction

Discarded electronics equipments are rapidly growing worldwide. The technological advancement lead the world to a digital future. The waste of electrical and electronics equipment are increasing from 40 to 70 million tones/year[1, 2]. Electronic waste contains precious metals as well as base metals. The recovery of precious metals from electronic waste is gaining momentum[3, 4]due to the high demand for precious metals for electric and electronic instruments and limited availability of raw material from ores. The computer processors, an advanced micro device (AMD) and RAM are typical examples of these type of wastes. The scrap composition varies from source to source. A PCB of computer can contain approximately 4-7% Fe, 13-20% Cu, 1-5% Al, 0.3-1% Pb, 0.1-1% Ni, 0.026-0.10% Ag and 0.05-0.250% Au along with some other metals [5, 6].

Pyro metallurgical process and hydrometallurgical process are being applied to recover the metals from ores and solid wastes [7, 8]. Pyro metallurgical process consists of different steps like incineration, smelting, roasting, converting and refining to recover the metals. In pyro metallurgicalprocess, metals are recovered without any chemical pre-treatment. The disadvantages associated are high energy requirements, NO_x and SO_x emissions and loss of metals during combustion[9]. Hydrometallurgical process is gaining more attention due to less energy requirements as compared to Pyro-metallurgical process.

During hydrometallurgical process, leaching rates of metals are effected by the kind of leaching agent, concentration and temperature [10, 11]. Different chemicals can be used as leaching agents like cyanides [12-14], sulfuric acid, aqua regia, thiourea [14-16], thiosulfate and their mixtures with other chemicals [17-22]. The leached solution can further be concentrated and purified by different separation process including, precipitation, cementation, solvent extraction and ion exchange. Electrolysis or electrowinning process is the final step of hydrometallurgy for the recovery of metals [9].

Cyanide is very efficient for the leaching process but it is quite toxic as well [14]. To overcome this problem, thiourea and thiosulfate are being studied. Thiosulfate has advantages over cyanide, as it is relatively economical and has less hazardous. However, its leaching mechanism is not well known. Leaching can be enhanced by the presence of some oxidant e.g., hydrogen peroxide along with acids[18]. Thiourea has been used to recover gold from PCBs as a leaching agent[3, 4]. Presence of copper imparts negative impact on the gold extraction. This problem can be eliminated by the pre-treatment. Aqua regia can also be used as leaching agent to leach the gold in the form of gold chloride, but it generates toxic waste that can affect the environment [19, 23]. The leached solution can be concentrated and purified by the different separation process including precipitation, cementation, solvent extraction and ion exchange[5].However, these processes are very complex and gold is not recovered easily from leached solution.

Nitric acid is a good lixiviant for the extraction of copper and other base metals from electronic waste because of its powerful oxidizing effect as compared to hydrochloric acid and sulfuric acid [2, 3, 23, 24]. All base metals can be dissolved in nitric acid leaching except gold.

The leaching rates of copper can be increased using ultrasound waves. Zhang et al (2008) studied the effect of ammonial leaching on copper bearing tailings and reported 13.5 % increase of copper leaching using ultrasound waves [25].Ultrasonic cavitation is affected by temperature, power or intensity, the solvent vapor pressure and nature of the solvent used[18]. It is previously reported that cavitation is better attained at a lower temperature. Solvent vapor fills the cavitation bubbles, which then tend to collapse less violently, that is, the sonication effects are less intense than expected. Hence a compromise between temperature and cavitation must be achieved[26].

Various studies reported on leaching of copper using ultrasonic irradiation and process optimization by using response surface methodology (RSM). However, selective nitric acid leaching of copper from old AMD Athlon processors has never been reported in the literature. Although RSM has been commonly used in searching optimal conditions, there were no reports describing the use of experimental design (Expert-Design Pro) software to optimize such processes. Current study intends to estimate the effect of variables for identifying the optimum conditions using small composite design. To the content of the present study, it is also needed to investigate the effect of ultrasonic radiation at high temperatures on the leaching of copper.

RSM is rapidly replacing one variable–one time approach to the collective effect of all factors on a particular process. It is less laborious and depicts competeeffect of various parameters on the process. Hence, present work is designed to assess the effect of variables such as nitric acid concentration, temperature and ultrasonic power to identify the optimum conditions using small composite design. The interactions among various factors especially ultrasonic power and temperature may not be ignored to get true optimization of the process which ultimately may lead to finding significant and non-significant factors. This will help to ignore the involvement of unnecessary parameters during leaching of copper. The characterization of solid particles is carried out by XRD and concentration of copper in the leached solution is determined by Atomic Absorption Spectroscopy.

2.0 Materials and Methods

2.1 Leaching of copper in nitric acid

Nitric acid was used to fully leach the metals from the AMD Athlon processors. The metal concentrations of the digestion solution were determined using atomic absorption spectrophotometer (G8442AA, Agilent Technologies, USA). X-ray diffraction pattern was investigated on grounded waste PCBs powders by X-Ray diffractometer (X'Pert Powder PANalytical, DY-3805), and the result indicates that the copper in the PCBs exists as metal copper.

Leaching procedures of waste AMD Athlon processors specimen without gold coated pins was shredded to pass the 1mm final fineness for leaching experiment. Analytical grade commercial concentrated nitric acid (50%) was used as received in experiments and was diluted as per requirement. Leaching experiments were carried out with 1.5g crushed AMD Athlon processors in a 300mL conical flask under magnetically stirring at temperature ranges of 25℃ to 50℃ temperature for one hour. The effect of ultrasonic irradiation on the leaching of copper at this temperature range was studied by irradiating the reaction solution at different powers ranges from 0 to 300W.During the process NO_x emissions occurs that could be seen by the brown color gas emitted from the solution (Equation 1). Therefore, reflux condenser was used for re-dissolving these gases in solution.

$$Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O \quad \text{.........(1)}$$

The leached solution was further analyzed for copper metal concentration by atomic adsorption spectroscopy.

AMD Athlon processors contained gold coating pins on small printed circuited chip which were detached and were separately leached in the nitric acid solution. The collected solid particles were washed few times with the distilled water and were placed in a heating oven at 100^{o}C for 1 hour, leaving behind the dry gold particles. The purity of gold was confirmed by X-Ray diffractometer (X'Pert Powder PANalytical, DY-3805). The XRD pattern of the sample suggested the crystalline behavior of gold. The spectrum showed that there was no other metal present except the recovered gold (figure 1). The five dominant peaks of the plane (111), (200), (220), (311) and (222) were dictating the crystalline structure of gold. This pattern exactly matched the standard XRD pattern of gold.

As soon as the coated layer of gold is removed, the metal present inside is now exposed. These pins were separated and then sent for X-Ray diffraction. The major peaks of XRD pattern confirmed the presence of copper like Cu (111), Cu (200) and Cu (220) (figure 2).

2.2 Experimental design and optimization

In this study, the main objective is to apply RSM to build a mathematical model and to maximize leaching concentration of copper (Y, mg/l) from AMD Athlon processors. Response surface methodology (RSM) is a most commonly used procedure to explore functional relation between a set of input variables with the responses and to optimize these response.RSM is used to study the effect of three input variables (factors):nitric acid concentration (X_1, %), temperature (X_2,^oC) and absolute ultrasound power (X_3,W). Two level factorial with small CCRD was used. The small design generated 15 experiments (supplementary Table 1) which are comprised of six axial points, four factorial points and five central points. The minimum and maximum levels of each input variables were selected in accordance with previous studies [2, 4, 6-8, 27]. The coded levels and actual values of input factors are listed in Table 1.The Design-Expert9.4 were used to carry out the optimization study.

The functional relation (mathematical model) is approximated by second order polynomial. Second order polynomial equation can generally be written as:

$$Y = \beta_0 + \sum \beta_i X_i + \sum_{i \neq j} \beta_{i \neq j} X_i X_j + \sum \beta_{ii} X_i^2 + \varepsilon \quad (2)$$

For three input variables, above model can be written as;

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 + \varepsilon \quad (3)$$

Where Y is response variable, X_1, X_2 and X_3 are independent variables. While β_o is a constant, β_1,β_2 and β_3 are linear coefficients, β_{12},β_{13} and β_{23} are cross product coefficients, β_{11}, β_{22} and β_{33} are quadratic coefficients. These coefficients have been estimated through the results of 15 experiments.

Results and discussion:

The data of experimental results through RSM was evaluated through analysis of variance (ANOVA) in order to identify the significance of the model and associated input variables towards the output response. The significance of regressions model, individual input variables towards output response were carried out using F-values, p-values, R^2, Adj-$R^2$and lack of fit. Besides, the interaction of two input variables towards output response was also an important contribution of ANOVA analysis. The interactions were studies through 3D plots by means of surface response. Additionally, the predicted values of output response (copper leaching) were estimated based on the second degree polynomial model equation.

3.1 Model and adequacy check

One of the main objectives of RSM is to build an appropriate mathematical model using data obtained from response surface design. The observed response from 15 experimental conditions is used to estimate a full second order model in this study. This model is suggested by the software from a set of different models based on p-values and F-values. Prior to getting results of the estimated model, necessary assumptions are tested.

Unfortunately, the given data set does not fulfil some of the assumptions. Therefore, power transformation is used and the output response is defined as $Y^* = Y^3$ = (Leaching Concentration)^3.

The diagnostic plots in figure 3 show that there is no outlier in the data and the selected model provide good prediction of response variables.

The estimated equation for output response Y^* in terms of coded factors is given as:

$$\hat{Y}^* = 421019.7 - 67436.9X_1 + 133705.7X_2 + 40919.7X_3 + 37927.9X_1X_2$$
$$+ 94892.2X_1X_3 - 213687.2X_2X_3 - 45946.7X_1^2 - 71139.2X_2^2 + 14890.4X_3^2$$

In the present study, the significant of the proposed model and the input variables towards the output response were analyzed at 95% level of confidence (Table 2). This indicates that the p-value less than 0.05 represent a significant variable term. Generally, low p-values ($p<0.05$) with the high value of F-value indicate that the variable term is statistically significant. In other words, the given effect (source of variation) has a significant effect on the output response. The ANOVA results in table 2 indicate that the second degree polynomial model is significant ($p<0.05$) to the present experimental conditions and associated output responses. It may also conclude that all the variable terms (linear, quadratic and interaction) are collectively statistically significant. Here, low F and high p ($p>0.05$) values and lack of fit show that the model is adequate for predicting leaching concentration of Cu .

The individual terms of nitric acid concentration (X_1, %), temperature (X_2,°C) and absolute ultrasound power (X_3,W) were tested under the hypothesis β_i or $\beta_{ij} = 0$ and the term is significant if $P < 0.05$. In this case, linear effects of nitric acid concentration (X_1, %) and temperature (X_2,°C) are significant whereas the third linear one is not significant ($p > 0.05$). All three interaction effects and quadrate effects of nitric acid concentration (X_1, %), temperature (X_2,°C) are statistically significant. Like linear effect, the quadratic effect of absolute ultrasound power (X_3,W) was also not significant.

In the analysis, the contribution of individual factors and their interactions are of greater importance. It helps to understand the role and impact of different process conditions on output response. Among the individual terms, temperature (X_2) was the high significant terms for leaching concentration followed by nitric acid concentration with the p-value of 0.0011 and 0.0196, respectively. Moreover, temperature (X_2) is the second and third largest contribution due to its linear and quadratic effects respectively. The absolute ultrasound power (X_3) is considered to be non-significant terms with p-value of 0.0953. Besides, the interaction of temperature (X_2)

and absolute ultrasound power (X_3) are highly significant with the p-values of 0.0006 and has the largest contribution in F-value and the total sum of squares.

The fitting of the model is further verified by R^2 and adjusted R^2 (Adj-R^2). The value of R^2 above 0.90 is considered very well for a model. The values of R^2 and adjusted R^2 for this fitted model are 0.97 and 0.91, respectively. The value of R^2 indicates that 96.8% (or refined 91.1%) of the total variation in copper leaching concentration can be explained by these linear, interaction and quadratic effects. So, the model is a good fit and highly significant. Adequate Precision measures the signal-to-noise ratio. A ratio greater than 4 is desirable. Here the ratio is 12.87 which indicate an adequate signal. Finally, R^2, adjusted R^2 and lack of fit test are important factors for model selection.

3.2 Analysis of 3D Response Surfaces

Three dimensional response surface plots (figures 4a-4c) shows the investigation for the interaction of temperature and nitric acid concentration and ultrasound power to the Cu leaching concentration. As shown in figure 4a, the nitric acid concentration was the relatively prompt effect on copper leaching as compared to ultrasound power (figure 4b). Copper leaching linearly increased with increasing nitric acid concentration but decreased more sharply after its mean value. On the other hand, copper leaching slightly increases with increasing temperature. Similarly, in figure 4b, nitric acid concentration shows same effect on leaching concentration (figure 4a) while ultrasound power shows no significant effect on leaching concentration. However, ultrasound power while interacting with temperature shows significant effect on the leaching concentration as shown in figure 4b. Similarly results can be found when temperature varies along the ultrasound power for the leaching concentration.

A 3D plotted surface showed the effects of all possible variations in nitric acid concentration (X_1) and temperature (X_2) on the leaching concentration (Y). The leaching concentration was directly proportional to the concentration of nitric acid at constant ultrasound power (X_3) when considered middle value. However, the effect becomes less over 38% of concentration. Whereas leaching concentration first increased at lower temperatures and then decreased at higher temperature. This may be due to the cavitation effects produced by ultrasound waves which decrease with increasing temperature.

It can be seen that there is a very small change in leaching concentration when both temperature and ultrasound power is increased. This implies that nitric acid concentration is more dominant process variable at given temperature range whereas ultrasonic cavitation stayed insignificant. Nitric acid with the ultrasonic action promotes matrix oxidation which facilitates analytic extraction [18]. However, high temperature helps to disrupt strong solute–matrix interactions and fasten the diffusion rates

3.3 Optimization study

In the present study, numerical optimization is adopted to get optimum conditions. In numerical optimization, combination(s) of input variables (conditions) are determined that optimize response under desired constraints. The desired goals (constraints), limits, weights, and importance for response and input variables are summarized in table 3. The conditions to maximize copper leaching at a minimum percentage of nitric acid concentration are the main objective of this study.

Using ten sets of conditions (supplementary table 2) that maximize predicted leaching concentration, the optimum set is found to be a nitric acid concentration of 20 %, the temperature of 48.89 ºC and ultrasound power of 5.52 watt at maximum leaching concentration of 97.916 mg/l. It can be concluded that the optimum response is confirmed by finding 95% confidence interval of predicted response.

Conclusions

Response surface method (RSM) was carried out to optimize the leaching concentration of copper from old AMD Athlon processors using nitric acid as leaching agent along with temperature and ultrasound power as process variables. Small composite rotatable design (CCRD) was used to carry out the subject study. The ANOVA results indicated that the second degree polynomial model was fitted well to the design process. Variable terms (linear, quadratic and interaction) were collectively statistically significant. All three interaction effects and quadratic effects of nitric acid concentration, temperature was statistically significant. Linear effect and quadratic effect of absolute ultrasound power (X_3, watt) was found to be non-significant. The values of R^2 and adjusted R^2were found to be 0.97 and 0.91 (97% and 91%) respectively. Copper leaching linearly increased with increasing nitric acid concentration but decreased sharply after its mean value. However, copper leaching slightly increased with increasing temperature. Ultrasound power linearly decreased copper leaching with its increasing values. There was very a slight change in copper leached when both temperature and ultrasound power were increased. This implies that nitric acid concentration is a dominant factor. Maximum copper leaching at a minimum percentage of nitric acid concentration was achieved by using 10sets of experimental conditions. The optimum conditions were found to be 20%of nitric acid, 48.89 °C of temperature and 5.52 watt of ultrasound power for attaining maximum 97.916 mg/l concentration of copper leaching in solution. The optimum response was confirmed by finding 95% confidence interval of predicted response.

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Figures and Tables

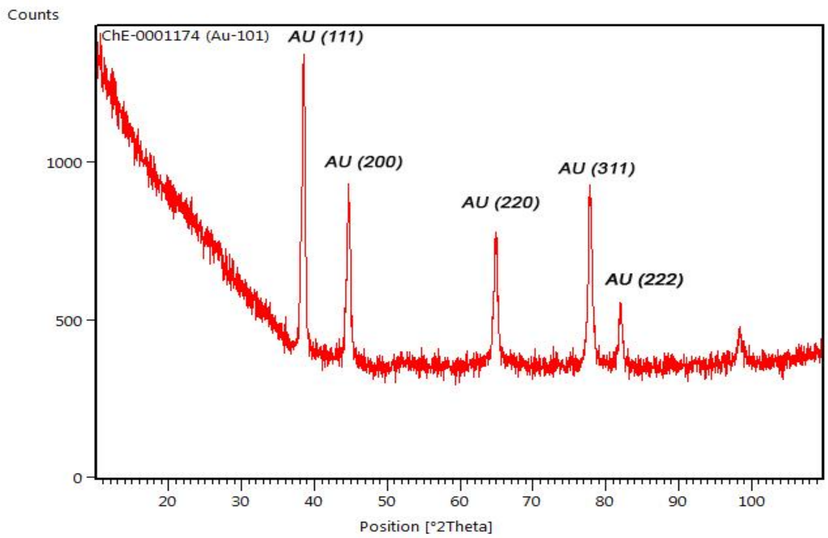


Figure 1 XRD peaks for extracted gold

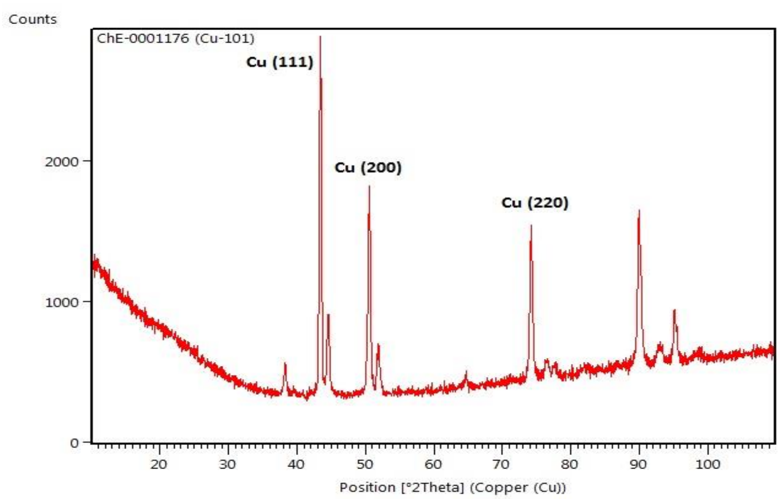


Figure 2 XRD peaks for material (Cu) below gold layer

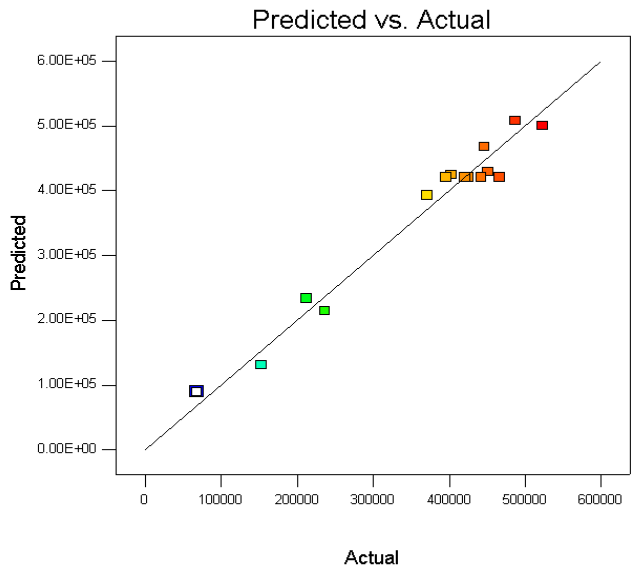
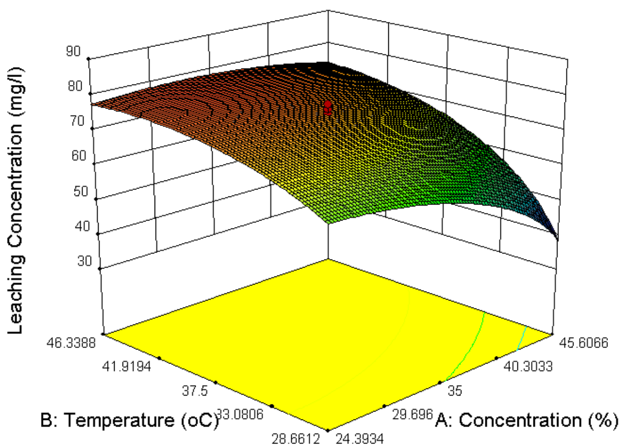
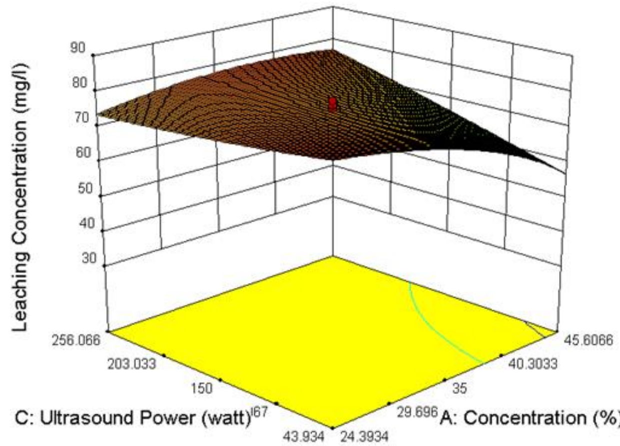


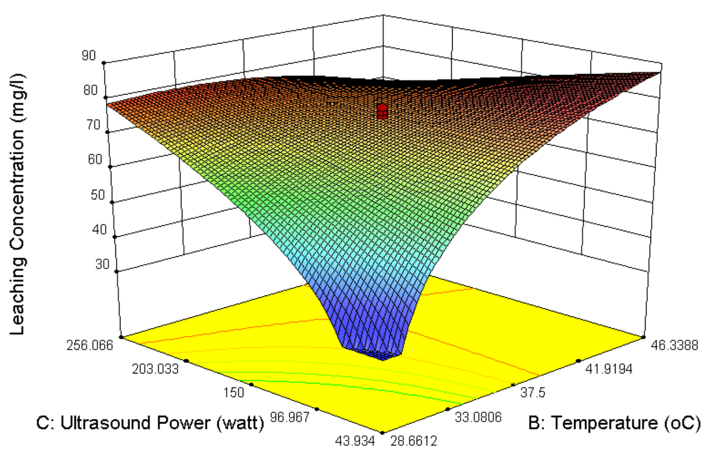
Figure 3 Theoretical values of leaching concentration of Cu predicted from the model vs actual experimental values



(a)



(b)



(C)

Figure 4 Variations in leaching concentration (mg/l) with respect to: (a) temperature andnitric acid concentration (b) ultrasound power andnitric acid concentration (c) ultrasound power & temperature

Table 1 Process input variables

Factor: Uncoded	Coded		Coded Levels: -α	-1	0	+1	+α
Nitric acid concentration (%)	X_1	Uncoded Levels	20	24.3934	35	45.6066	50
Temperature(°C)	X_2		25	28.6612	37.5	46.3388	50
Ultrasonic power(W)	X_3		0	43.9340	150	256.066	300

Table 2. ANOVA results ofleaching concentration as an output response variable

Source	**Sum of Squares**	**df**	**Mean squares**	**F-value**	**p-value**	**Remarks**
Model	2.444E+11	9	2.715E+10	17.09	0.0030	Significant
X_1	1.819E+10	1	1.819E+10	11.45	0.0196	Significant
X_2	7.151E+10	1	7.151E+10	44.99	0.0011	Significant
X_3	6.698E+09	1	6.698E+09	4.21	0.0953	Not Significant
X_1X_2	2.877E+09	1	2.877E+09	1.81	0.2363	Not Significant
X_1X_3	1.801E+10	1	1.801E+10	11.33	0.0200	Significant
X_2X_3	9.132E+10	1	9.132E+10	57.46	0.0006	Significant
X_1^2	1.629E+10	1	1.629E+10	10.25	0.0240	Significant
X_2^2	3.904E+10	1	3.904E+10	24.56	0.0043	Significant
X_3^2	1.710E+09	1	1.710E+09	1.08	0.3471	Not Significant
Residual	7.946E+09	5	1.589E+09			
Lack of Fit	5.205E+09	1	5.205E+09	7.59	0.0511	Not Significant
Pure Error	2.742E+09	4	6.855E+08			
Total	2.523E+11	14				
R^2	0.97					
Adj-R^2	0.91					
Adequate Precision	12.87					

Table 3. Desirability specifications of numerical optimization for CCRD

Variable	Goal	Lower limit	Upper limit	Lower weight	Upper weight	Importance
Nitric acid concentration (%)	in range	20	50	1	1	3
Temperature (°C)	in range	25	50	1	1	3
Ultrasound power (Watt)	minimize	0	300	1	1	3
Copper leaching (mg/l)	maximize	40.75	80.56	1	1	3

Supplementary Table 1.Experimental design with output response variable based on CCRD

Run	X_1	X_2	X_3	X_1(%)	X_2(ºC)	X_3 (Watt)	Leaching concentration (mg/L)	
							Y(actual)	$\hat{Y}$ (predicted)
1	0	0	0	35	37.5	150	73.42	74.94
2	+1	+1	-1	45.60	46.33	43.93	80.56	79.41
3	0	0	0	35	37.50	150	74.92	74.94
4	-α	0	0	20	37.50	150	73.83	75.15
5	+α	0	0	50	37.50	150	59.60	61.60
6	+1	-1	+1	45.60	28.66	256.06	76.69	75.43
7	0	+α	0	35	50	150	76.39	77.62
8	0	0	0	35	37.50	150	77.54	74.94
9	0	0	+α	35	37.50	300	78.66	79.82
10	0	-α	0	35	25	150	40.75	44.75
11	-1	+1	+1	24.39	46.33	256.06	61.82	59.84
12	0	0	-α	35	37.50	0	71.85	73.24
13	-1	-1	-1	24.39	28.66	43.93	53.45	50.75
14	0	0	0	35	37.50	150	75.15	74.94
15	0	0	0	35	37.50	150	76.15	74.94

Supplementary Table 2. Optimum predicted response and desirability

No. of experiments	Nitric acid concentration (%)	Temperature (℃)	Ultrasound power (Watt)	Leaching concentration (mg/L)	Desirability
1	20	48.89	5.52	97.91	1
2	20	47.76	6.95	96.85	1
3	20	46.34	2.36	96.16	1
4	20	45.66	3.09	95.40	1
5	20	45.95	17.96	93.93	1
6	20	46.61	22.67	93.93	1
7	20	44.90	11.58	93.66	1
8	20	47.35	42.44	91.90	1
9	20	48.70	49.96	91.56	1
10	20.	45.04	38.25	90.74	1