CHAPTER 4

Leaching of copper, nickel and gold

4. Leaching of copper, nickel and gold

4.1 Two-stage leaching from WPCBs

In this chapter, a two-stage leaching process is developed for the recovery of copper, nickel and gold from ultrasonically cleaned metallic fractions of WPCBs. The base metals within the metallic fractions impacts upon the leaching of precious metals such as gold. Therefore, the leaching of base metals such as copper and nickel was done using nitric acid in the first stage. The leach residue obtained in stage-1 used as raw material for stage-2 for leaching of gold and silver. Optimization of leaching parameters such as time, temperature, type of leachant, concentration of leachant, were also done in both stages. Finally, the kinetics of leaching of copper, nickel and gold were studied to find out the dissolution mechanism and also to calculate experimental activation energies.

4.1.1 Optimization of nitric acid leaching of copper and nickel through Response Surface Methodology

The different factors with various stages for optimization were input by Design Expert-13 software. Total of twenty parametric variants were produced by seeing factorial points (6), corner points (8), and center points (with a replication of 6 times) to develop the acceptability of the model. All the experiments excluding the center point have been carried out three times. The average values of response (Cu and Ni leaching) are shown in Table-4.1. Similarly, the center point was repeated six times, and the response value was measured.

The highest desirability and different numerical combinations has been checked using the optimization program for maximizing the model functions. The leaching efficiencies and desirability was checked additionally for using low molarity of nitric acid. However, the leaching efficiencies for Cu and Ni were found 77.50%, 87.93% with molarity 2.0 respectively and 85.68, 94.99 % with molarity 2.5 respectively. Moreover, the leaching efficiencies of Cu and Ni were 92.11% 98.80% with 3M nitric acid, which is not able to serve the zero waste treatment motto. Therefore, the current study was done with 3.5M the maximum copper and nickel from WPCBs metallic fractions. The desirability (D) value closer to 1 is considered most desirable parameters. In this work, the optimized parameters were obtained at desirability of 0.993 and 1.00 for copper and nickel respectively (figure-4.1&4.2), which basically indicating the applicability of the studied model.

Table 4.1-Central composite design table for the leaching of copper and nickel

	Factor 1	**Factor 2**	**Factor 3**	**Response 1**	**Response 2**
Run	**A: Acid Concentration** (M)	**B: Time** (min)	**C: Temperature** (°C)	**Cu Leaching** (%)	**Ni Leaching** (%)
1	3.5	30	90	83.00	85.60
2	0.5	30	90	51.49	59.31
3	3.5	105	60	88.73	97.99
4	3.5	30	30	63.00	35.44
5	2.0	105	60	76.09	77.96
6	2.0	105	60	74.41	79.23
7	2.0	105	90	82.29	85.69
8	2.0	105	60	74.36	79.02
9	2.0	180	60	88.04	91.36
10	3.5	180	90	97.93	98.36
11	0.5	180	90	58.16	61.36
12	2.0	105	60	76.55	78.32
13	2.0	30	60	63.21	67.09
14	0.5	180	30	42.00	47.65
15	2.0	105	60	75.33	78.00
16	0.5	30	30	16.00	19.67

17	0.5	105	60	47.35	55.76
18	2.0	105	60	75.40	76.93
19	2.0	105	30	62.00	65.13
20	3.5	180	30	96.55	99.53

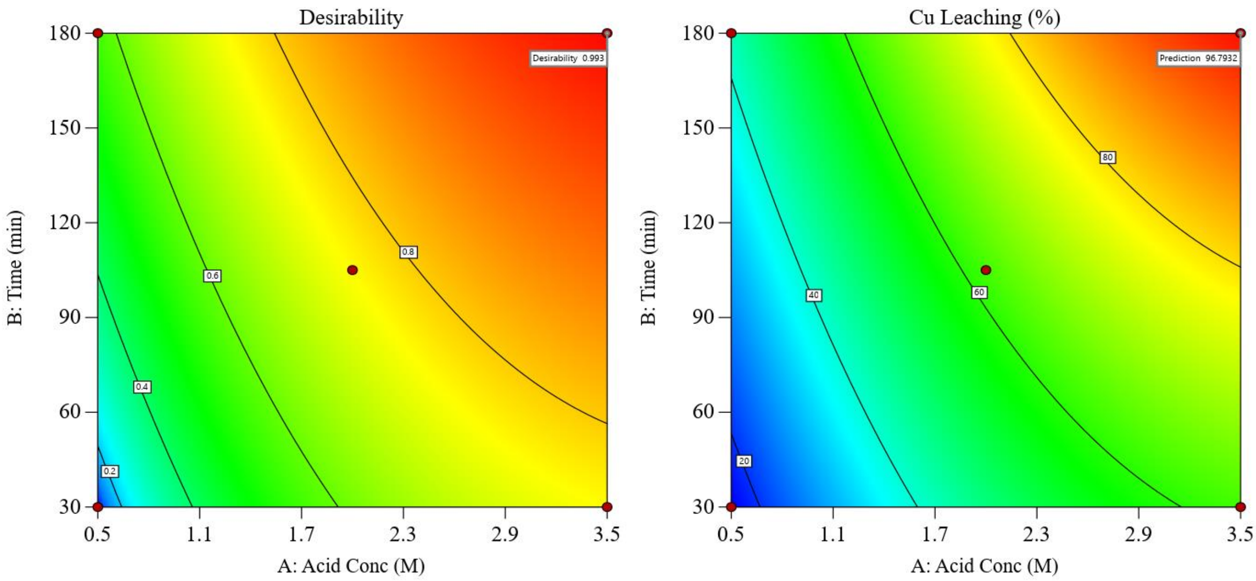

Figure 4.1-Desirability value of copper leaching at optimized parameters

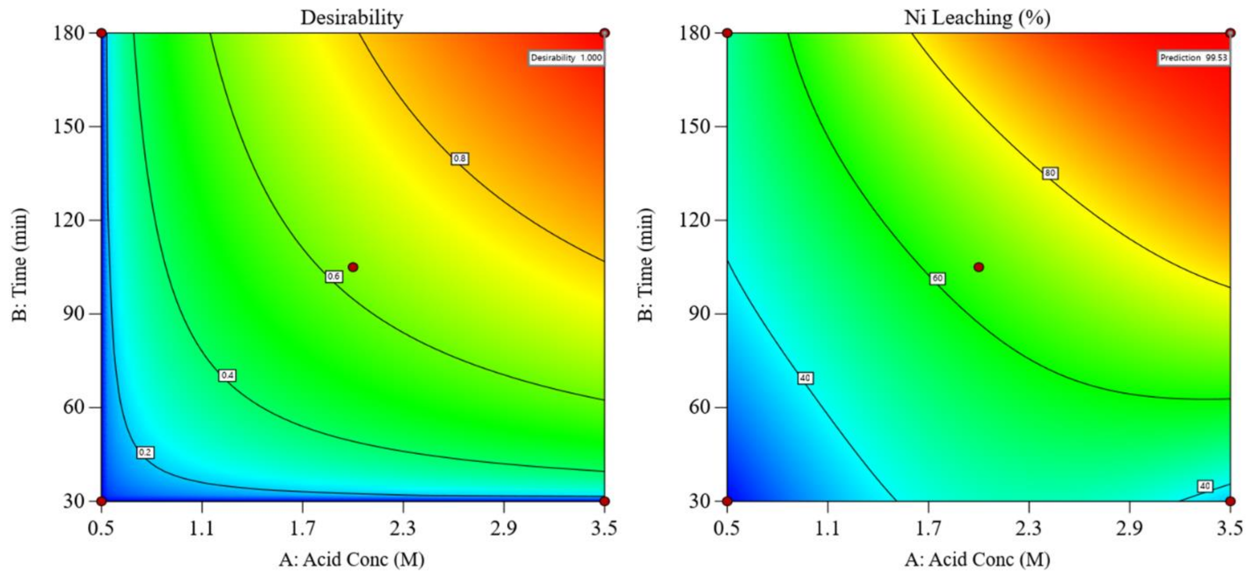

Figure 4.2-Desirability value of nickel leaching at optimized parameters

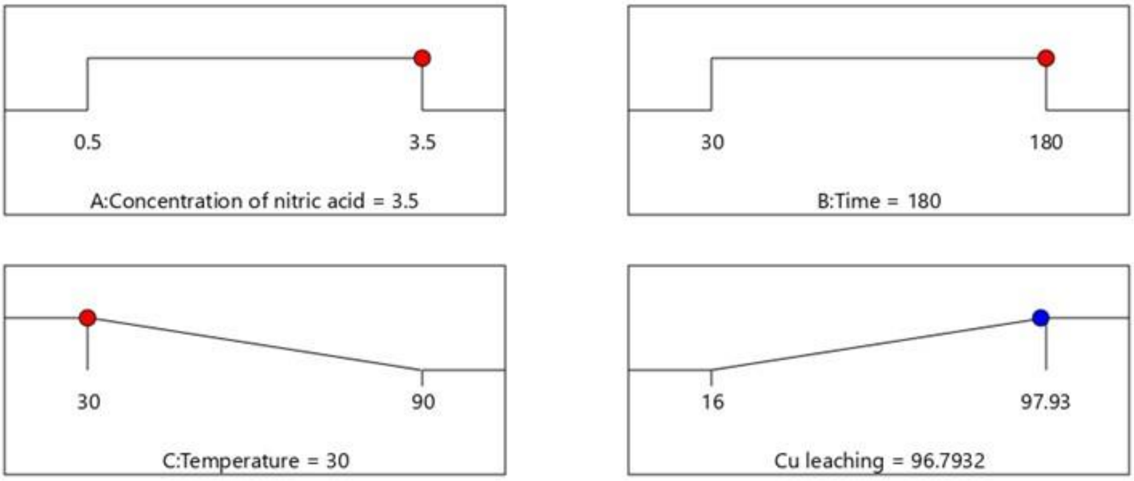

Figure 4.3-Optimum parameters for the copper leaching

From figure-4.3 & 4.4, it can be observed that at a temperature 30°C, with 3.5 M acid concentration, 96.79% of copper and 99.53% nickel could be leached within 180 min via numerical optimization.

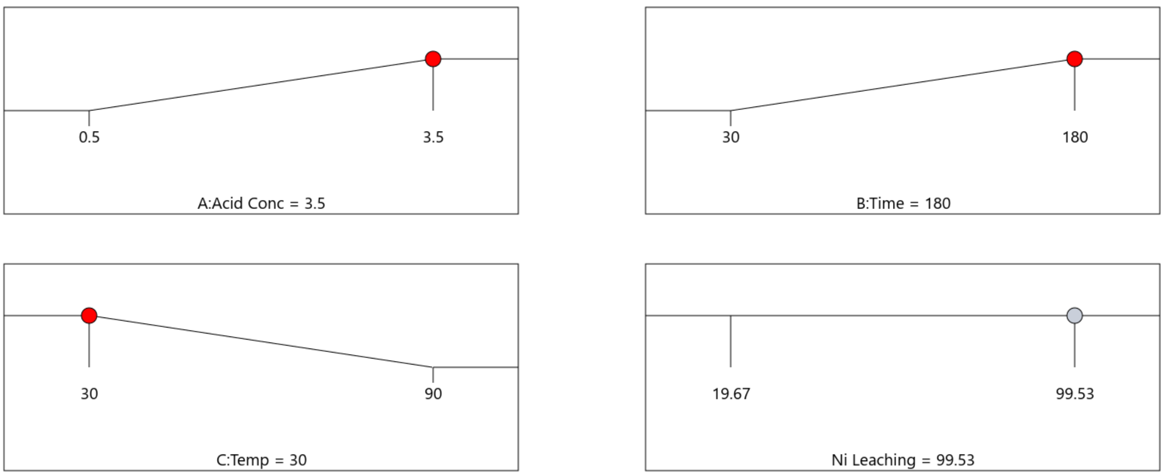

Figure 4.4-Optimum parameters for the nickel leaching

4.1.2 Development of RSM

The higher-order and significant quadratic model was used to fit and assess the particular and individual responses of various factors for copper leaching. The copper leaching was articulated in relation to the factors shown in Eq. (4.1) based on the analysis. Analysis of variance (ANOVA) was used to evaluate how well the regression model fit the data. (Table-4.2).

$$Cu\ leaching = 75.59 + 21.42A + 10.60B + 9.33C + 1.98AB - 3.78AC - 4.74BC - 7.89A^2 - 0.3064B^2 - 3.79C^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots(4.1)$$

Table 4.2-ANOVA quadratic model for copper leaching

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	7492.70	9	832.52	512.36	< 0.0001	significant
A-Acid Concentration	4588.59	1	4588.59	2823.94	< 0.0001	
B-Time	1123.18	1	1123.18	691.23	< 0.0001	
C-Temperature	870.86	1	870.86	535.95	< 0.0001	
AB	31.24	1	31.24	19.23	0.0014	
AC	114.53	1	114.53	70.49	< 0.0001	
BC	180.03	1	180.03	110.79	< 0.0001	
A^2	171.25	1	171.25	105.39	< 0.0001	
B^2	0.2581	1	0.2581	0.1588	0.6986	
C^2	39.43	1	39.43	24.26	0.0006	
Residual	16.25	1 0	1.62			
Lack of Fit	12.39	5	2.48	3.22	0.1128	not significant
Pure Error	3.85	5	0.7708			
Cor Total	7508.95	19				

The **Model F-value** of 512.36 with probability (p) <0.0010 implies the model is significant. The factors such as nitric acid concentration (A), time (B) and temperature (C) also having **P-values** less than 0.0001 specify that the model terms are significant and the impact of them on the recovery of copper are equally distributed. Additionally, the **model F-values** of A, B and C are 2823.94, 691.23 and 535.95 implies the higher the F value indicate the more impact on the recovery of copper. Therefore, from these data, it is observed that the nitric acid concentration is more impact followed by the time and temperature of the leaching process on copper recovery. The higher R^2 values also indicate a higher correlation between the actual and predicted values as shown in Figure 4.5.

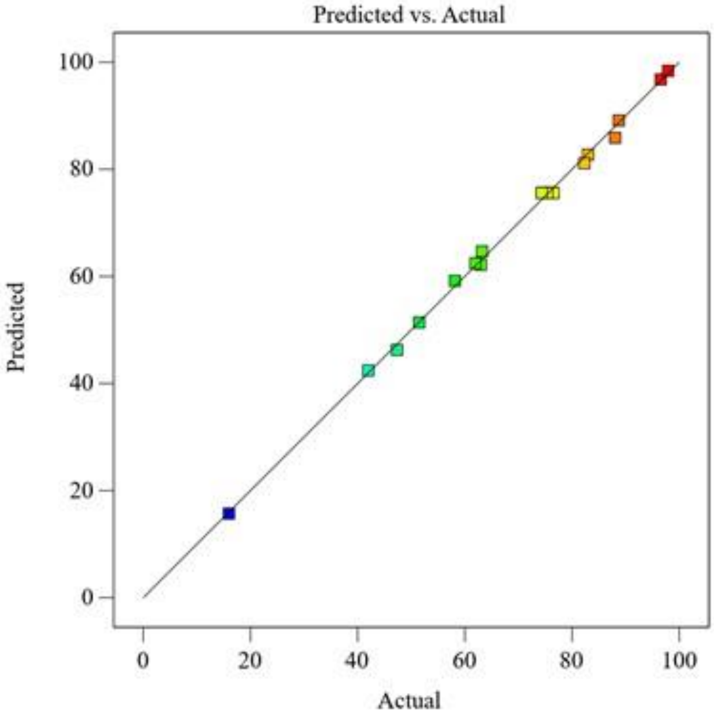

Figure 4.5-Predicted vs. actual plots for copper leaching

Individual responses of several factors for nickel leaching has also been studied through the higher-order and important quadratic model. Eq-4.2 is showing the theoretical nickel leaching in relation to the factors based on the analysis through the software, where A, B and C representing concentration of acid, time and temperature respectively.

$$Ni\ leaching = 78.25 + 21.11A + 12.123B + 10.24C + 5.85AB - 0.5450AC - 9.66BC - 1.37A^2 + 0.9796B^2 - 2.84C^2 - 3.18ABC + 1.23\ A^2B + 2.55A^2C - 4.75AB^2 - 11.65A^2B^2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4.2)$$

Similarly, the evaluation of regression model to fit the data has been done utilizing analysis of variance (ANOVA) as shown in the (Table-4.3)

Table 4.3-ANOVA reduced Quartic model for nickel leaching

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	8385.49	14	598.96	664.84	< 0.0001	significant
A-Acid Conc	891.69	1	891.69	989.76	< 0.0001	
B-Time	294.52	1	294.52	326.91	< 0.0001	
C-Temp	210.30	1	210.30	233.43	< 0.0001	
AB	274.01	1	274.01	304.15	< 0.0001	
AC	2.38	1	2.38	2.64	0.1653	
BC	746.14	1	746.14	828.20	< 0.0001	
A^2	2.82	1	2.82	3.13	0.1373	
B^2	1.44	1	1.44	1.60	0.2620	
C^2	12.04	1	12.04	13.36	0.0147	
ABC	80.65	1	80.65	89.51	0.0002	
A^2B	2.40	1	2.40	2.67	0.1635	
A^2C	10.42	1	10.42	11.57	0.0192	
AB^2	36.06	1	36.06	40.03	0.0015	
A^2B^2	59.20	1	59.20	65.72	0.0005	
Residual	4.50	5	0.9009			
Lack of Fit	1.27	2	0.6373	0.5919	0.6072	not significant
Pure Error	3.23	3	1.08			
Cor Total	8389.99	19				

The Model F-value of 664.84 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. The factors such as nitric acid concentration (A), time (B) and temperature (C) also having **P-values** less than 0.0500 indicate model terms are significant and the impact of them on the recovery of nickel are equally distributed. In this case A, B, C, AB, BC, C^2, ABC, A^2C, AB^2, A^2B^2 are significant model terms. Additionally, the **Lack of Fit F-value** of 0.59 implies the Lack of Fit is not significant relative to the pure error. The higher R^2 values also indicate a higher correlation between the actual and predicted values as shown in Figure 4.6.

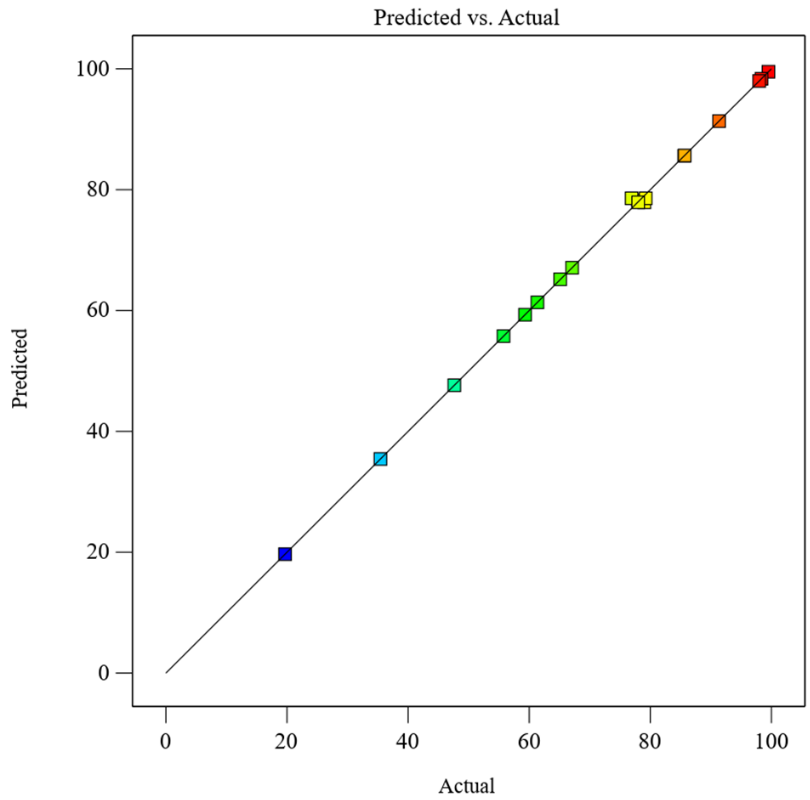

Figure 4.6-Predicted vs. actual plots for nickel leaching

4.1.3 2D and 3D surface plots for model analysis

In addition, three-dimensional response surface plots along with two-dimentional contour plots were drawn in order to attain the precise idea on the combined consequence of variables on the copper and nickel leaching as shown in figures-4.7 & 4.8 **(** Blue colour designates the minimum leaching and the red colour specified the maximium leaching. Figure-4.7 (a,b) depicts that the leaching of copper increases with increasing the concentration of nitric acid (0.5 -3.5 M), time 30 -180 min) and maximizes (96.79%) at 3.5 M nitric acid in 180 min. Similarly, leaching of copper increased with inncreasing the temperature (30 – 90 °C) and nitric acid concentration as shown in figure-4.7 (c,d). However the leaching of copper not much effected by the temperature range except a little deviation. Therefore, 30 °C temperature alongwith the concentration of nitric acid effect has been studied. In addition, the combined consequence of time and temperature is also studied on leaching of copper as shown in figure-4.7 (e,f). Here also, the leaching of copper increses with incresing the time (30-180 min) at 30 °C. Finally, numerical optimization was chosen with the help of RSM to obtain the maximmum leaching efficiency of copper at appropriate comination of temperature, time and acid concentration.

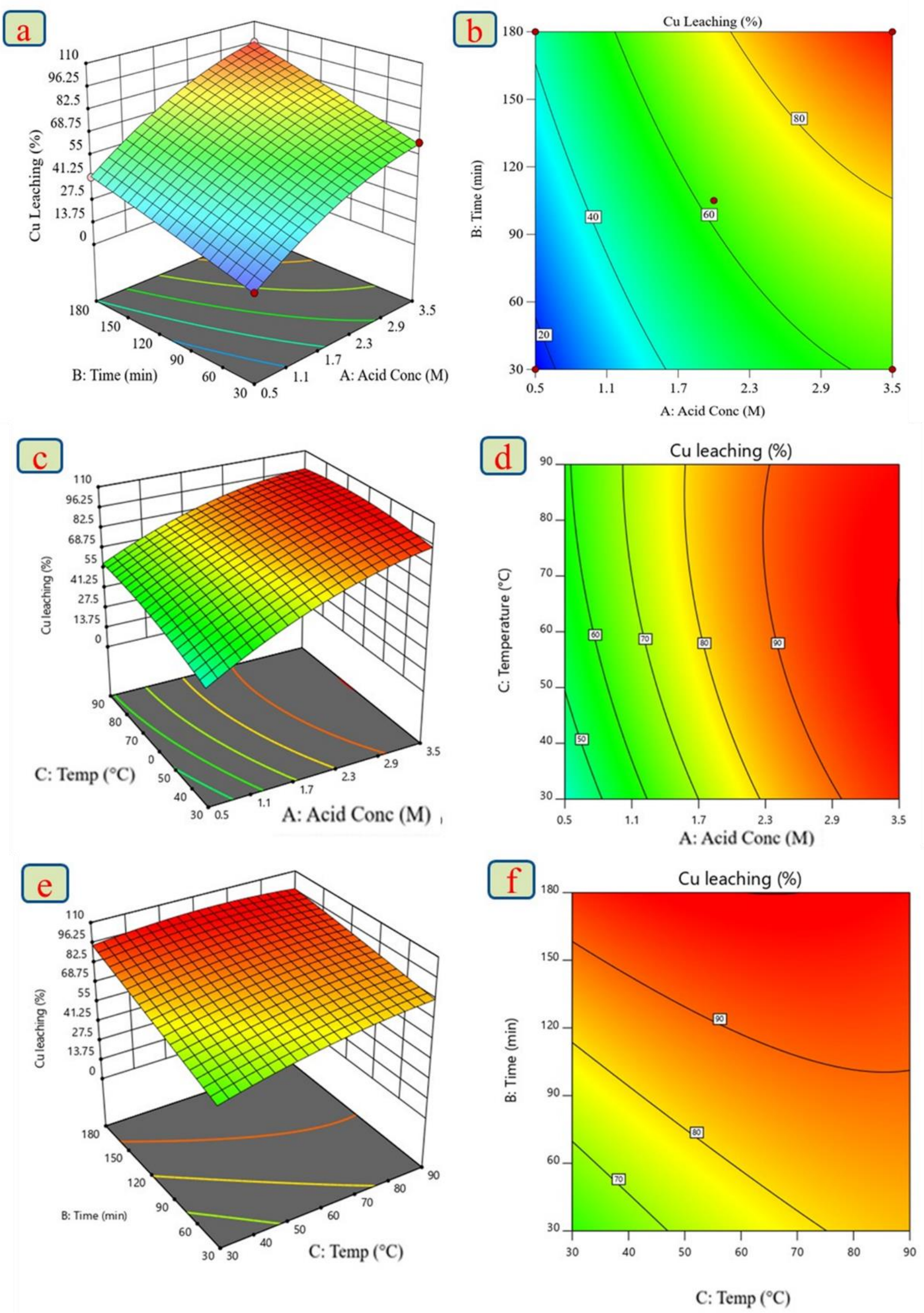

Figure 4.7- 3-D response surface designs and 2D contour designs for the leaching of copper: (a,b) represent a constant temperature (30); (c,d) illustrate a constant time of 180 min; (e,f) represent a constant acid concentration of 3.5M

The combined effect of factors on nickel leaching has also been assessed through graphical representation of the regression equation, 2D contour graphs, and 3-D surface plots. The minimum leaching of nickel has been represented by blue color and red color represents the maximum leaching of nickel from the WPCBs metallic fractions. Leaching of nickel increases with increasing the concentration of nitric acid (0.5-3.5M), time (30-180 min) and maximizes at 3.5 M with in 180 min as shown in figure-4.8 (a,b).

Likewise, Increasing temperature (30-90 °C) also increases the leaching of nickel for the some extent. The effect of temperature and acid concentration on leaching efficiency has been shown in figure-4.8 (c,d). The combined effect of temperature and time on nickel leaching has also been studied and shown in figure- 4.8 (e,f). The leaching efficiency of nickel has increased with increasing leaching time (30-180 min) at 30 °C. The appropriate condition of time, acid concentration, and temperature has been chosen with the numerical optimization through the RSM. The maximum nickel leaching (99.53%) has been observed at a temperature of 30 °C, with 3.5 M acid concentration within 180 min.

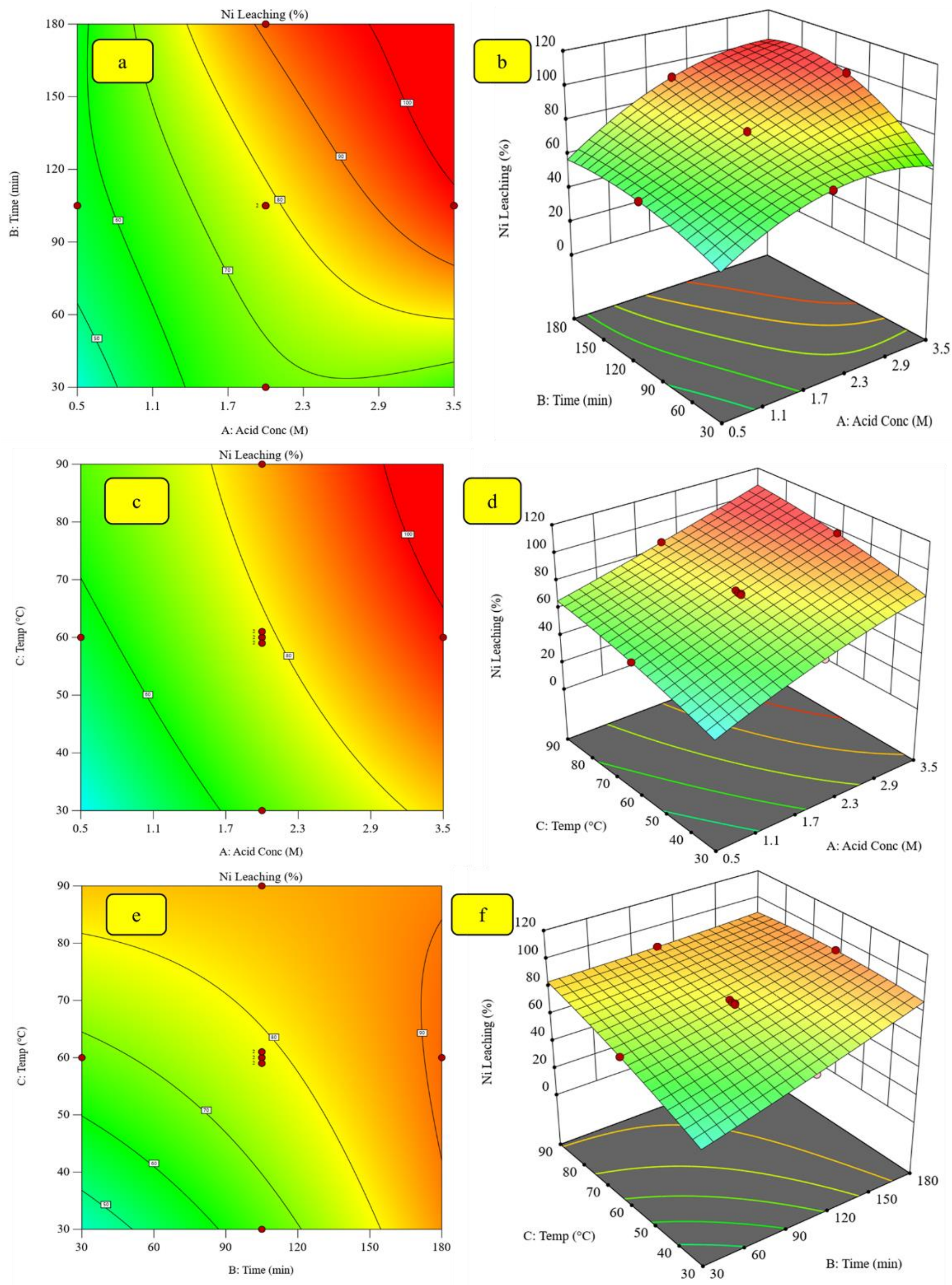

Figure 4.8- 3-D response surface designs and 2D contour designs for the leaching of nickel: (a,b) represent a constant temperature (30 °C); (c,d) illustrate a constant time of 180 min; (e,f) represent a constant acid concentration of 3.5M

4.1.4 Validation of leaching of copper and nickel

The experiments were conducted under the predicted optimum conditions to validate the optimization results through RSM. Design expert-13 software predicted the 96.79% Cu and 99.53% Ni leaching at optimum conditions, which is in closely in agreement with the experimental copper (98.96%) and nickel ((99.50%) leaching efficiency. Hence, the experimental results validated the RSM results (Table-4.4). Other minor elements such as palladium, tin and silver were also found in the first stage leach liquor. However, no gold presence was seen in the leach liquor at the optimum conditions.

Table 4.4-Comparison of calculated results to those from copper and nickel leaching experiments.

S. No.	**Factors**			**Ni Leaching**		**Cu Leaching**	
1	Time (min)	Temp (°C)	Acid Conc. (M)	Experimental (%)	Calculated (%)	Experimental (%)	Calculated (%)
2	180	30	3.5	99.50	99.53	98.96	96.79

From these studies, the optimized parameters for the effective leaching of copper and nickel are mentioned as 3.5 M nitric acid; 30 °C temperature; 180 min residence time; 50 g/L pulp density and agitation speed of 500 rpm. Along with copper and nickel, other elements such as zinc (99.50%), lead (99.50%), cadmium (99.50%), and to a lesser extent of tin (25.0%) and silver (10%) are also dissolved at these optimized parameters (Figure 4.9). Importantly, gold is not dissolved and remains in the residue.

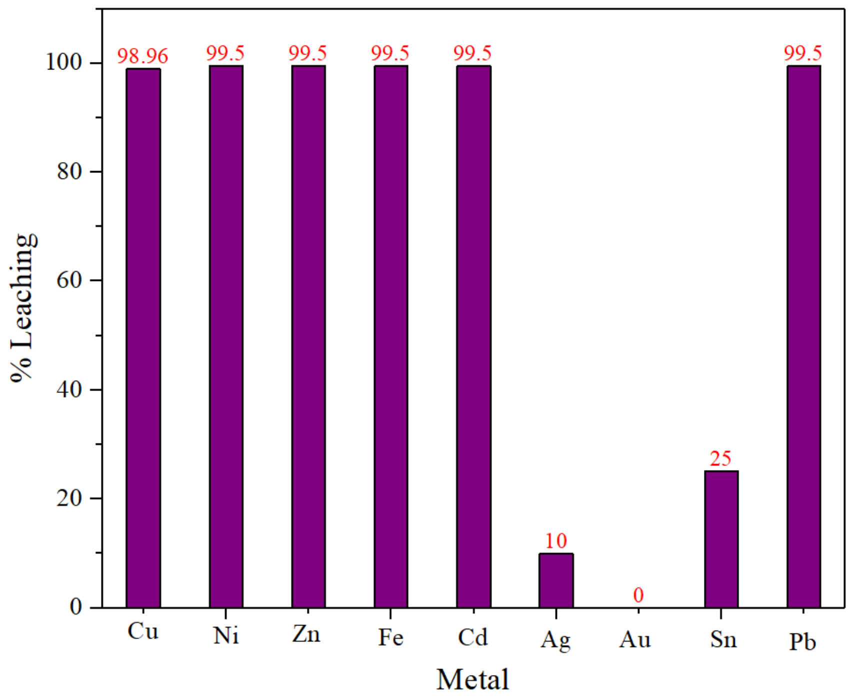

Figure 4.9-Leaching efficiency of various metals in stage-1 leaching [Temp. 30 °C; time 180 min; concentration of nitric acid 3.5 M; pulp density 50 g/L; stirring speed 500 rpm]

4.1.5 Analysis of stage-1 leach residue

The leach residue obtained from the stage-1 leaching was initially analysed with SEM-EDS as shown in Figure-4.10. Dominant non-metallic fractions along with tin, gold, and traces has been observed under the SEM. Consequently, the leach residue was dissolved in aqua regia and analysed by ICP-MS and AAS to know the accurate concentration of metallic fractions. The ICP-Ms and AAS results revealed that the insignificant quantities of copper remained (0.0025 ± 0.001 wt.%), while the other constituents were Au (0.045 ± 0.01 wt%), Ag (0.022 ± 0.01 wt%) and Sn (0.78 ± 0.1 wt%) along with a major non-metallic fraction.

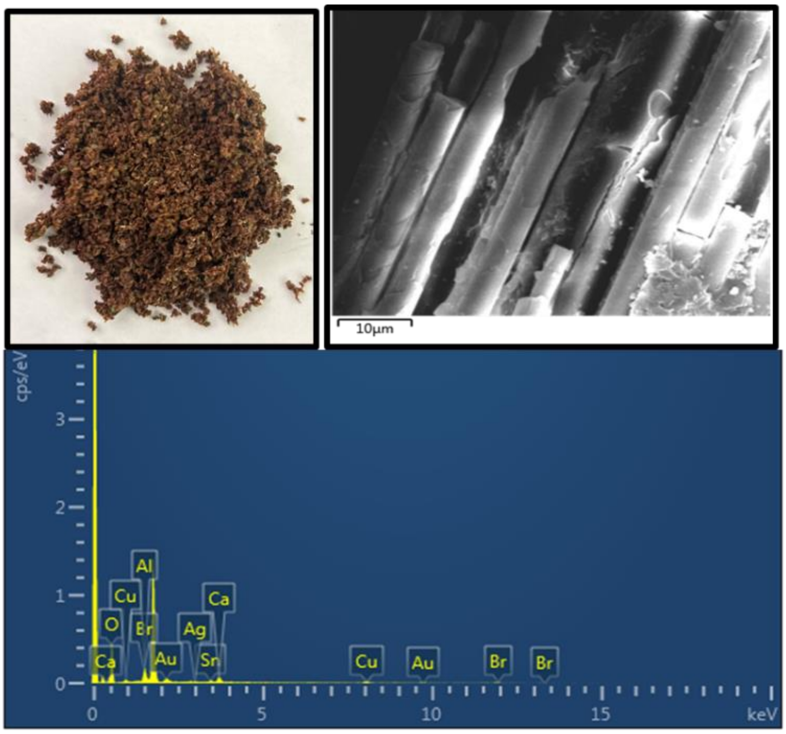

Figure 4.10- SEM (EDS) of leach residue obtained in stage-1 leaching

4.1.6 Kinetic study of copper and nickel leaching

The actual mechanism of copper and nickel dissolution from the metallic rich fractions may be understand by studying the kinetics of the leaching process. The prevalent shrinking-core model was applied to govern the kinetic parameters of a reaction in the present study. Therefore, the analysis of leaching fractions (experimental) verses time were done by plotting several curves utilizing the various shrinking-core models such as diffusion controlled (Eq-4.3) and chemical reaction controlled (Eq-4.4). These two models are usually effective and controls the reaction in solid-liquid systems.

$$1 - \frac{2x}{3} - (1 - x)^{\frac{2}{3}} = K_d t \quad \text{.............................} \; (4.3)$$

$$1 - (1 - x)^{\frac{1}{3}} = K_c t \quad \text{...........................} \; (4.4)$$

Where,

x= fraction of leaching,

K_d=kinetic rate constant for the diffusion-controlled reaction,

Kc is kinetic rate constant for chemical reaction- controlled reaction,

t= reaction time (min).

The experimental leaching fraction values were put in the above kinetic equations and plotted against the leaching time.

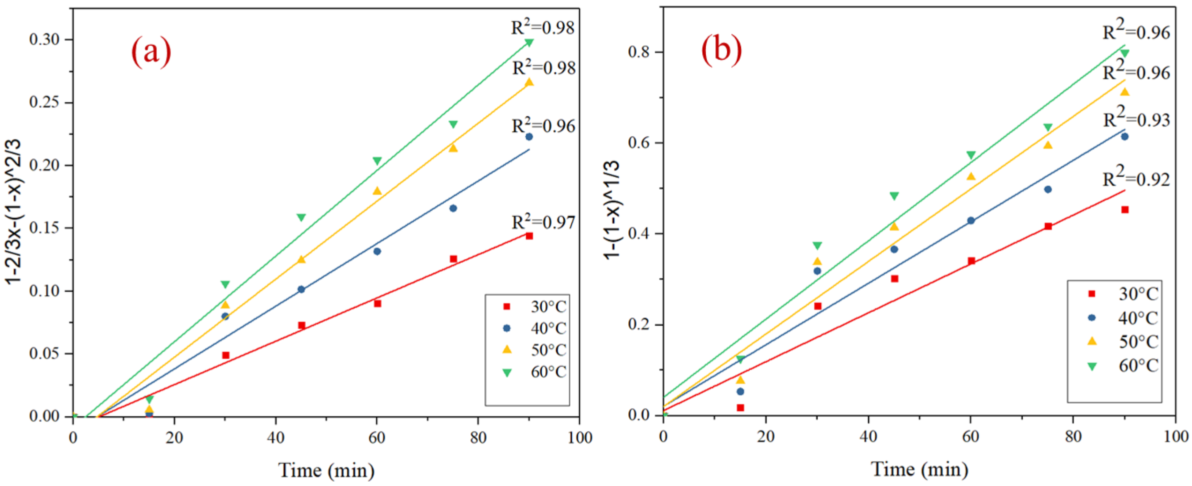

Figure 4.11-Kinetic plots of diffusion control (a) and reaction control (b) models for copper leaching from metallic fractions

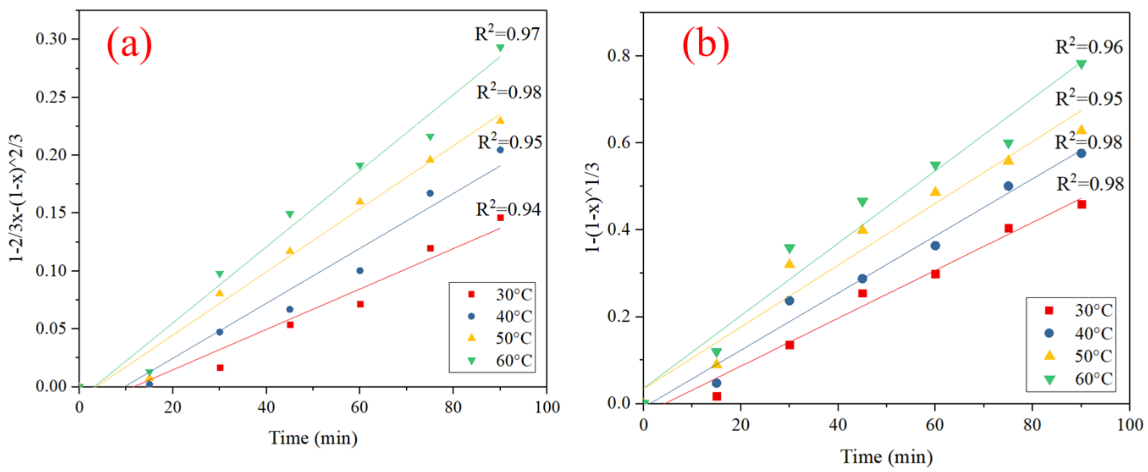

Figure 4.12-Kinetic plots of diffusion control (a) and reaction control (b) models for nickel leaching from metallic fractions

The kinetic equations show a good and nearly identical linear fitting to all of the parameters for the diffusion and chemically controlled surface reaction models used in the optimization of copper (Figure-4.11) and nickel (Figure-4.12) leaching. The R^2 values were compared and it was found that the fit for the diffusion controlled model is not considerably lesser than the fit for the surface-reaction controlled model. Consequently, the range of experimental activation energy is calculated based on the Arrhenius plots for copper (Figure-4.13) and nickel (Figure-4.14) to evaluate the kinetic model of the reaction.

$$k = A\, e^{\left(-\frac{Ea}{RT}\right)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(4.5)}$$

Where,
k = Reaction rate constant,
A= Pre-exponential factor,
E_a= Activation energy,
R= Gas constant

As per the previous studies (Havlik, 2008; Randhawa et al., 2016; Rao et al., 2021c), it is suggested that the activation energies thus calculated should be in the range of 4.18–12.55 kJ/mol for diffusion controlled model and greater than 42 kJ/mol for chemically controlled surface reaction model. In the present study, the calculated activation energy using eq-4.5 for copper leaching from diffusion and reaction model of 19.075, 13.29 kJ/mole and 16.98 and 12.53 kJ/mole for nickel respectively, which is in the predictable values for the mixed mechanism. The calculated activation energy provides compelling evidence that the mixed mechanism governs the suggested leaching mechanism.

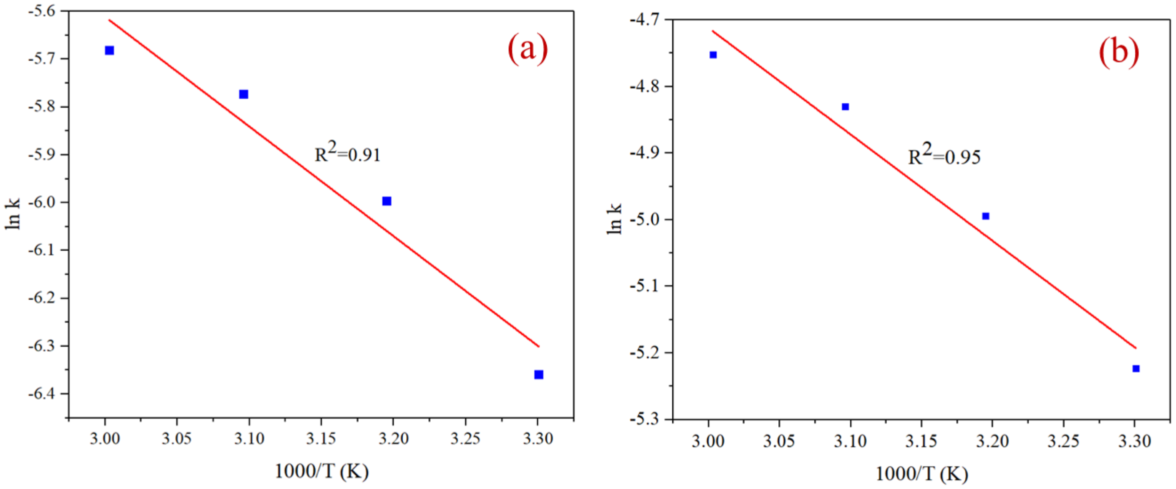

Figure 4.13-Arrhenius plots for copper leaching from metallic fractions in diffusion controlled (a) and reaction controlled (b) conditions

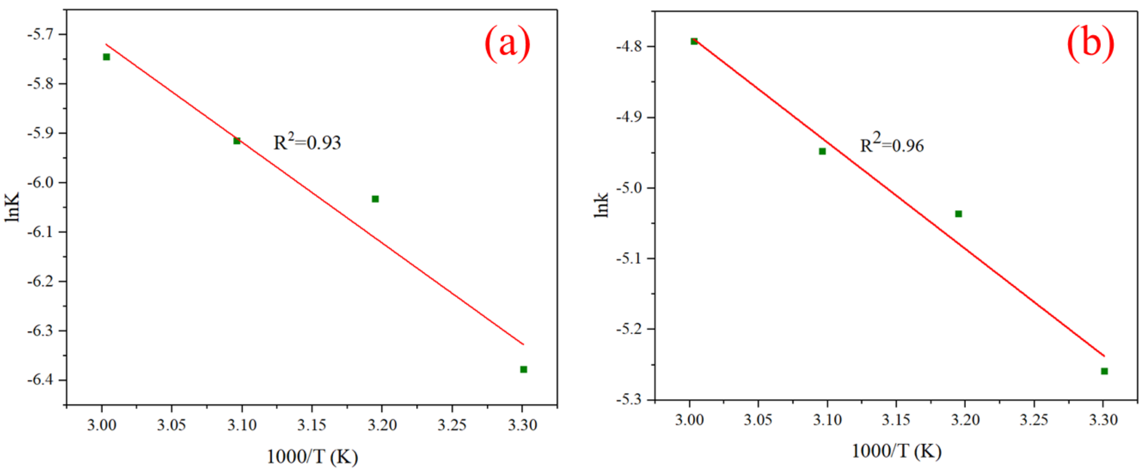

Figure 4.14-Arrhenius plots for nickel leaching from metallic fractions in diffusion controlled (a) and reaction controlled (b) conditions

4.2 Stage-2 leaching: Dissolution of gold

The residue generated in stage-1 leaching was further treated for leaching of precious metals such as gold and silver in Stage-2. Halide leaching of gold is relatively newer and effective route for gold leaching from the secondary resources. The chlorine or bromine are generated in situ by chemical reaction among the acidic reagent and sodium halides and found effective as strong oxidizing agent for gold leaching (Eq. 4.6). Few of previous works reported the feasibility of gold leaching through halide solution (Cui and Anderson, 2020; Encinas-Romero et al., 2015; Harjanto et al., 2019). However, some limitations of chlorine and iodine leaching have also been identified in terms of difficulty in controlling in released chlorine gas, and the severe corrosion issues and higher amount of chlorine and iodine is required to leach out the gold (C. Li et al., 2015).(Cui and Anderson, 2020). In case of bromine leaching, stabilised bromine having lower vapour pressure than liquid bromine has employed for maximum gold leaching from conventional ores (Melashvili et al., 2014). In bromine medium, the oxidation of gold by bromine take place and further it stabilized as gold bromide complex, as represented in Equations (4.6) and (4.7).

$$NaBr + 2H_2SO_4 \rightarrow NaHSO_4 + Br_2 + SO_2 + 2H_2O \qquad (4.6)$$

$$Au + 2\ Br_2\ (aq.) + 4e^- \rightarrow AuBr_4^- + 3e^- \qquad (4.7)$$

Parameters such as leaching reagent, concentration of NaBr, and temperature were studied for the effective extraction of gold.

4.2.1 Variation in the concentration of the oxidising agent

The preliminary stage-2 leaching experiments were carried out at 65 °C for 90 min with 500 rpm stirring speed to study the effect of leaching reagent. The capability of sulphuric acid was initially checked for gold leaching. Therefore, 2.5 M sulphuric acid alone is used as a leachant at the initial stage. Additionally, the effect of adding sodium bromide on gold leaching was also investigated. Hence, the effect of addition of 1 M and 2 M sodium bromides to the sulphuric acid on gold dissolution has also been observed. 7.52% of gold leaching was observed with sulphuric acid, which shows that sulphuric acid is not suitable leachant for the gold leaching. The addition of 1 M sodium bromide increases the leaching efficiency up to 68.70%. Similarly, in the case of 2 M sodium bromide addition, the leaching percentage of gold is 81.86 %. Moreover, the addition of 2.5 M sodium bromide in sulphuric acid solution enhanced the leaching efficiency and maximum gold leaching was seen with this combination due to generation of more stabilised bromine as shown in figure-4.15. Therefore, 2.5 M sulphuric acid with the combination of 2.5 M sodium bromide was chosen for further studies at optimum parameters; 65 °C in 90 min resident time by keeping the stirring speed at 500 rpm.

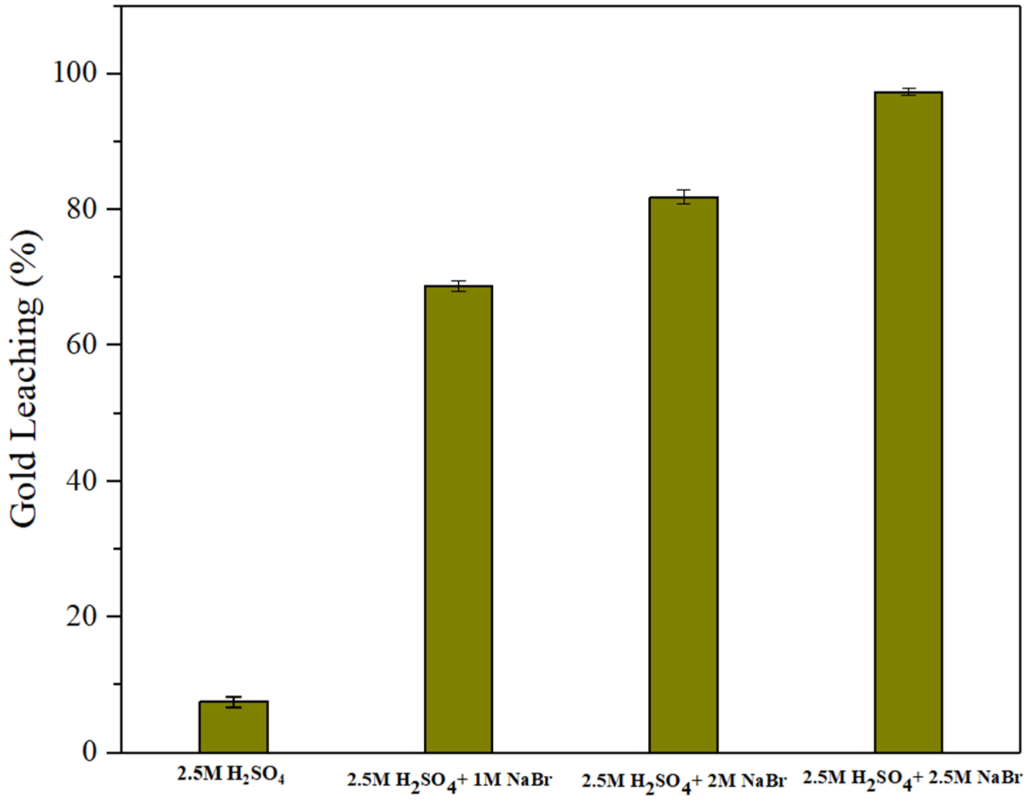

Figure 4.15-Effect of *concentration variation of the oxidising agent* on gold leaching from stage-1 leach residue

4.2.2 Effect of time variation on gold leaching

The effect of concentration of sodium bromide (1-2.5 M) with 2.5M sulphuric acid at 65 °C has also been studied and reported in figure-4.16. The resident time (90 min) and stirring speed (500rpm) was kept constant. Sulphuric acid alone was not able to leach the gold from stage-1 leach residue efficiently. Only 2.3% of gold was leached out in 15 min and it was found constant (7.52) after 75 min. Contrary, leaching is gradually increases from 81.83% to 97.31% with increasing the concentration of sodium bromide from 2 M to 2.5 M and the rate of leaching is constant after 75 min leaching. These observations suggested that the addition of 2.5 M sodium bromide to 2.5 M sulphuric acid is an active leachant for the gold leaching in 75 min at 65° C with an agitation of 500 rpm.

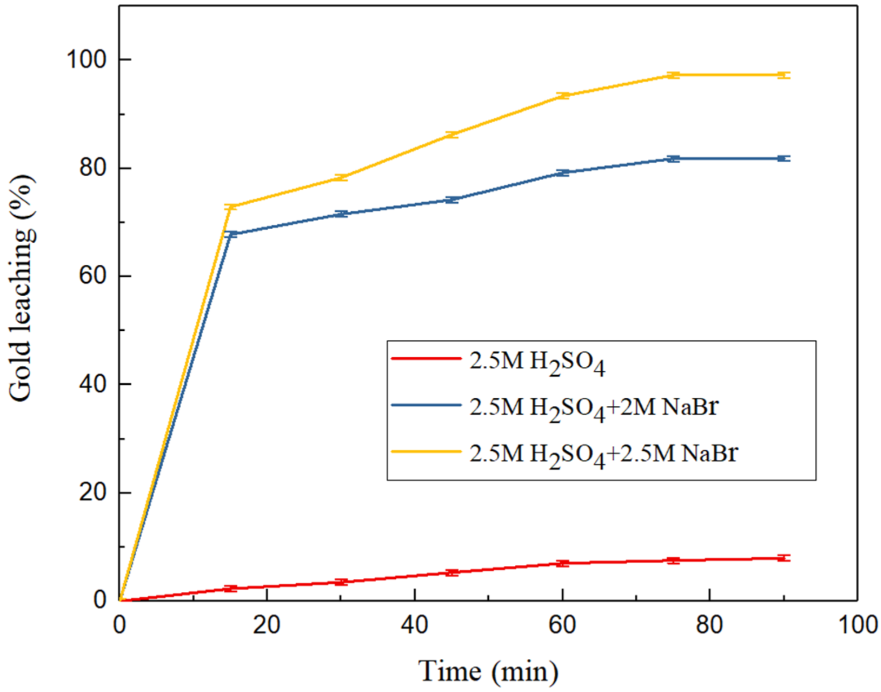

Figure 4.16-Effect of time on gold leaching from stage-1 leach residue

4.2.3 Effect of temperature on gold leaching

The effect of temperature on gold leaching was also explored in the range of 30 to 75 °C. The remaining parameters are 90 min residence time, 2.5 M sulphuric acid with 2.5 M sodium bromide as leaching reagent and 500 rpm agitation speed. Figure 4.17 shows the effect of temperature on leaching efficiency of gold at different residence time. The rate of gold leaching increases gradually from 75.58 to 97.31% by increasing the temperature from 30 to 65 °C in 90 min resident time. However, further increase in temperature shows decreased leaching efficiency (95.13%). This is probably due to the loss of bromine at elevated temperature and longer resident period. Based on these results, 65 °C was chosen as optimised temperature for the maximum and effective leaching of gold.

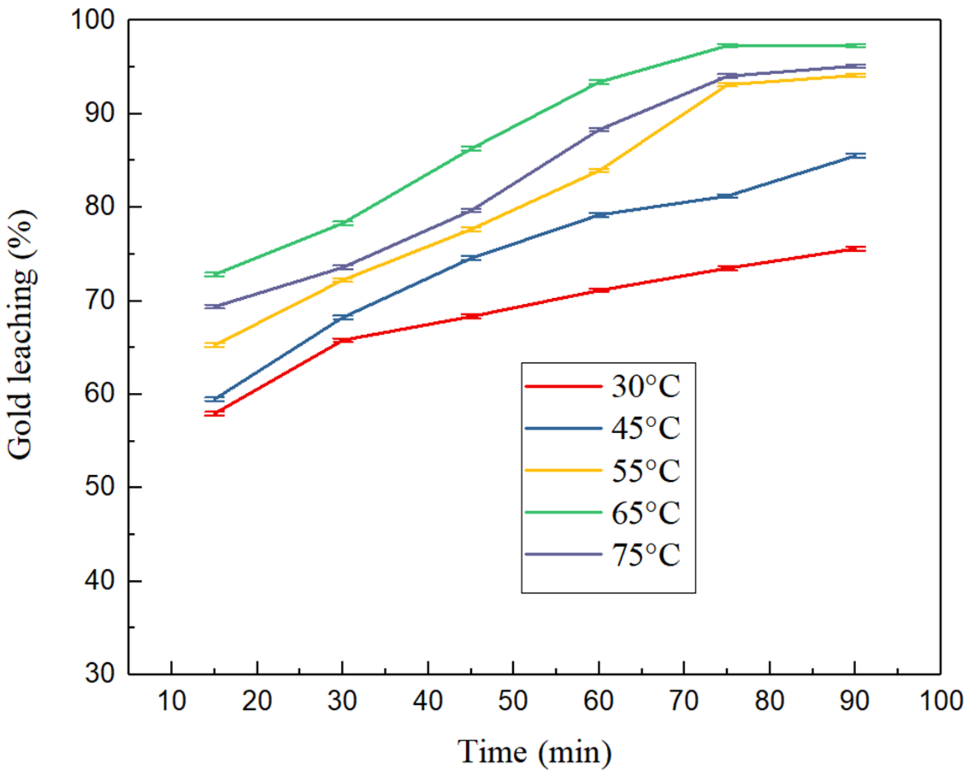

Figure 4.17-Effect of leaching temperature on gold leaching from stage-1 leach residue

4.2.4 Kinetic study of gold leaching

The dissolution of gold from leach residue has also been studied through the kinetics of the leaching process. Again, the prevalent shrinking-core model was applied to find out the kinetic parameters of a reaction in the current study. Therefore, the analysis of leaching fractions (experimental) verses time were done by plotting several curves utilizing the various shrinking-core models such as diffusion controlled (Eq-4.3) and chemical reaction controlled (Eq-4.4), which are usually effective and controls the reaction in solid-liquid systems. Figure-4.18 shows the good and linear fitting to all the parameters for the gold dissolution for the both diffusion and chemically controlled surface reaction models. The R^2 values were compared and found almost similar for both the models. Therefore, the range of experimental activation energy is calculated based on the Arrhenius plots for gold (Figure-4.19) to evaluate the kinetic model of the reaction.

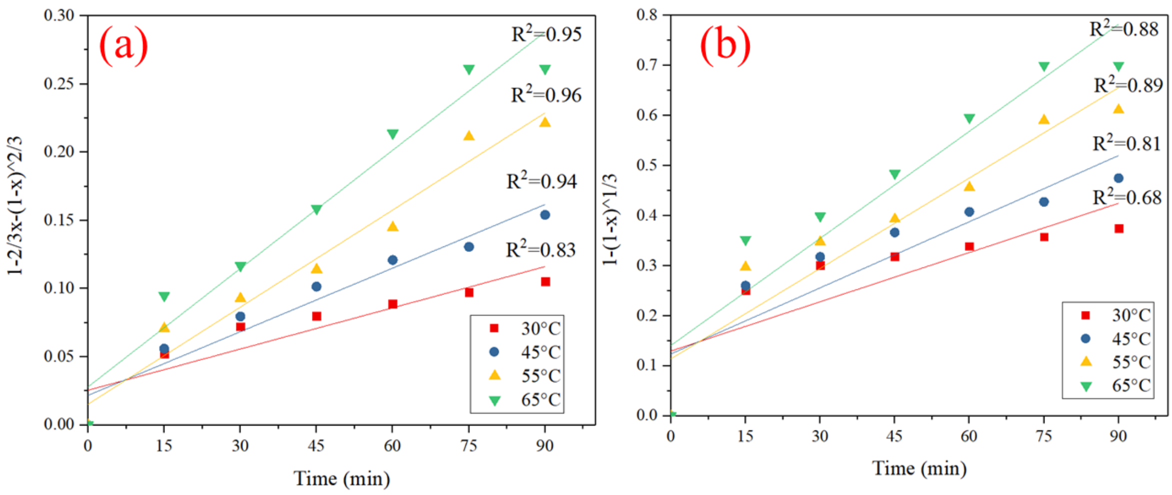

Figure 4.18-Kinetic plots of diffusion control (a) and reaction control (b) models for gold leaching from metallic fractions

The slope values have been obtained by the figure-4.18 and these values were used to calculate the activation energy. The calculated activation energy for diffusion and chemically controlled surface reaction model was 26.41 and 19.42 kJ/mole, which is in the predictable values for the mixed mechanism.

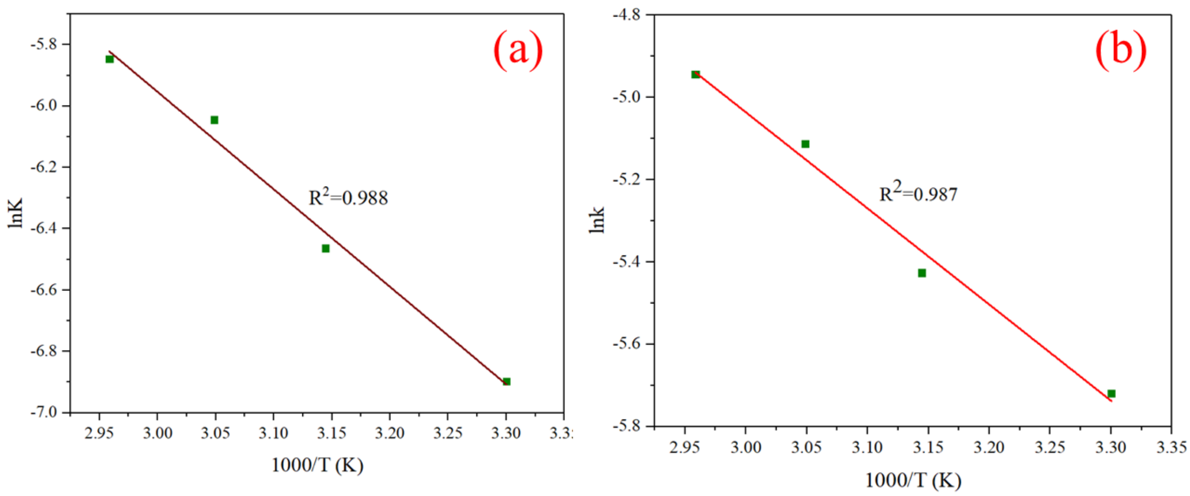

Figure 4.19-Arrhenius plots for gold leaching from metallic fractions in diffusion controlled (a) and reaction controlled (b) conditions

Conclusions

- Successfully demonstrated a metal leaching process that selectively dissolves copper and nickel to leave a gold-rich solid residue in stage-1.
- 98.96% copper and 99.50% nickel were leached out in stage-1 leaching at optimum parameters; 3.5M nitric acid at 30°C, over a 3 h period, for 50 g/L pulp density, and 500 rpm agitation speed.
- In stage-2 leaching, extraction of gold was observed with bromide leaching at acidic conditions.
- 97.31% of gold was leached out from stage-1 leach residue at optimum conditions; 2.5M sulfuric acid with 2.5M sodium bromide at 65°C, over a 75 min period and 500 rpm agitation speed.
- Kinetic studies showed that the leaching of copper and nickel followed mixed model mechanism.
- Similarly, kinetic studies for stage-2 leaching showed mixed mechanism model followed during the leaching of residue.