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PROCESS OPTIMIZATION OF NICKEL EXTRACTION FROM HAZARDOUS WASTE

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Abstract: Zinc plant residue is a hazardous waste which contains high quantity of nickel and other valuable metals. Process parameters such as reaction time, acid concentration, solid-liquid ratio, particle size, stirring speed and temperature for nickel extraction from this waste were optimized using factorial design. Main effects and their interactions were obtained by the analysis of variance ANOVA. Empirical regression model was obtained and used to predict nickel extraction with satisfactory results and to describe the relationship between the predicted results and the experiment results. The important parameters for maximizing nickel extraction were identified to be a leaching time solid-liquid ratio and acid concentration. It was found that above 90% of nickel could be extracted in optimum conditions.

INTRODUCTION

The industrial processing residues are the most important sources of environmental contaminations. Some of these wastes are recyclable and recycling the valuable part of these wastes instead of landfill depositing is an important issue from both environmental and economic point of views [1–3]. Zinc plant residue is a hazardous waste containing considerable amounts of metals, such as zinc, cadmium and nickel. It has been shown that the zinc plant residue poses potential environmental risks because it exhibits significant heavy metals solubilization [4–7].

Nickel is a strategic metal due to its extensive application in the production of stainless steel, alloy, battery, and catalyst [8, 9]. Recently, by depletion of primary nickel resources, a lot of researches have been done on the extraction of nickel from secondary resources, including spent catalyst [10–12], waste battery [13, 14] alloys and other waste nickel scraps [15–18] and tailings [19, 20]. In addition, the kinetics of nickel leaching from nickel alloys has been studied in some recent researches [12, 21–23].

In the state of our knowledge, there is not enough information about nickel extraction from zinc plant residue and only one study has been performed on this waste [24]. In addition, there is not any detailed investigation about statistical optimization of nickel extraction from zinc plant residue.

Optimization of the process parameters in the leaching of zinc plant residue is of special importance. In classical experimental design, it is necessary to perform a large number of tests. Statistical design of experiments is a simple and systematic method to optimize a design for process performance, quality and cost of products. Statistics design of experiments can cover a larger area of experimental statistics and obtain unambiguous results at the minimum expense [25, 26]. Factorial design is a standard technique and widely used for studying a random response to a set of k possible factors [25, 26]. With the factorial design methodology, main effects, interaction effects and low-order interactions may be estimated [27, 28].

In this study, the most significant factors affecting the nickel extraction from zinc plant residue were studied. In order to obtain satisfactory nickel extraction at reasonable leaching times, parametric optimization and modeling of nickel extraction were investigated. A two-level factorial design was used to model the nickel extraction under different process conditions. In addition, the adequacy of the model was evaluated by analysis of variance.

MATERIALS AND METHODS

Material

The zinc plant residue used in the study came from Calcimin zinc plant in Iran. Table 1 shows the chemical composition of the sample. The chemical analysis was performed using X-ray diffractometer (Philips, Xunique II). As can be seen in Table 1, the concentration of nickel oxide was relatively high and the sample contained large amounts of cadmium and zinc. X-ray diffraction (XRD) analysis using Philips PW 1140 showed that the zinc-bearing minerals were the major components in the sample, and that cadmium, nickel and lead components were also present in the sample. Sulphuric acid (98%) was purchased from Merck (Germany) and used as leaching reagent. Leaching experiments were carried out in a 500 ml reactor equipped with a stirrer motor for mixing and a reflux condenser to prevent losses by evaporation.

Table 1. The chemical analysis of the sample

Component	ZnO	CdO	NiO	CuO	PbO	SO_3	CaO	Fe_2O_3	MgO	Al_2O_3	LOI$^{\times}$
Amount (%)	38.92	16.56	4.21	1.99	1.38	12.10	2.61	0.44	0.20	0.34	20.54

Loss on ignition (LOI) is the sample weight reduction after being ignited.

Method

The representative sample was crushed and milled to collect the desired faction for experiments. In the experiment, a 500 ml glass reactor fitted with an overhead stirrer was used. Temperature was controlled by water bath equipped with a thermostat. The reactor was fitted with a reflux condenser to prevent liquid loss by evaporation when the system was heated. In the experiments, after the desired temperature of the reactor content was reached, the reaction was initiated by adding the required volume of sample to 100 ml leaching solution based on the required solid-liquid ratio. The concentrations of nickel in leach liquors were determined by using Unicom atomic absorption spectrometry (AAS).

Experimental design

Factorial design is a useful tool for characterizing multivariable processes. It gives the possibility to separate the important factors from those which are not, and identifying any possible interactions between them [29]. By factorial design, the optimum leaching conditions having satisfactory nickel extraction can be achieved with minimum number of experiments. The Design Expert Software (version 8.0) was used for the design of experiments and data analysis. In this investigation, factorial design was applied to optimize the most important operating factors. In the leaching experiments, based on preliminary tests, reaction time (t), temperature (T), acid concentration (c), particle size (p), solid-liquid ratio (s/l) and stirring speed (ss) were chosen as the six factors to be investigated. These variables may affect the response of the dissolution system, and it is practically impossible to identify and control the small contributions from each one. Statistical design was carried out to determine which of these variables, and their interactions presented more significant effects. Two-level factorial designs are efficient and economical for the screening of variables [30, 31]. In this study, factorial design was used in order to estimate main factors as well as interaction effects. The variables and levels of our factorial design are given in Table 2.

Table 2. Control factors and their levels in leaching experiments

Control factor	Unit	Levels	
		Low level	High level
Reaction time	min.	10	40
Reaction temperature	°C	25	75
Acid concentration	%	5	10
Particle size	μm	75	250
Solid/liquid	g/l	50	200
Stirring speed	rpm	300	600

After evaluation of the results by design Expert Software 8.0, the desirability function was used for the optimization of the process. The desirability function gives the possibility to predict the optimum levels for the independent variables [28, 32].

RESULTS AND DISCUSSION

Analysis of the effects of main factors and their interaction

The experimental tests were carried out randomly to avoid systematic errors during the collection of extraction data. In order to recognize effective parameters of the nickel extraction, the experiment results were entered into Design-Expert 8 software. We have chosen factorial design to fit the results. The test conditions and their results are shown in Table 3.

Table 3. Screening test donditions and their results

Run	A: Time	B: Temperature	C: Acid Concentration	D: Particle Size	E: Solid/ /Liquid	F: Stirring speed	Extraction
	Minutes	°C	%	Micron	(w/w)	RPM	(%)
1	40	75	5	75	5	300	92
2	10	25	5	75	5	300	69
3	10	75	10	75	5	300	89
4	40	25	5	75	20	300	36
5	25	50	7.50	75	12.50	450	79
6	10	25	5	250	20	300	30
7	10	75	10	250	5	600	89
8	10	75	5	75	5	600	81
9	10	25	5	75	20	600	33
10	10	25	10	250	20	600	53
11	10	75	10	75	20	600	57
12	25	50	7.50	75	12.50	450	77
13	40	75	10	250	20	600	64
14	10	25	10	75	20	300	46
15	25	50	7.50	250	12.50	450	76
16	25	50	7.50	250	12.50	450	75
17	40	75	10	250	5	300	99
18	25	50	7.50	250	12.50	450	74
19	40	75	5	250	5	600	99
20	10	75	10	250	20	300	50
21	25	50	7.50	75	12.50	450	75
22	40	25	10	75	20	600	70
23	10	75	5	250	20	600	34
24	40	25	10	75	5	300	95
25	40	25	10	250	20	300	64
26	10	75	5	75	20	300	30
27	40	75	10	75	5	600	99
28	10	25	10	250	5	300	78
29	40	75	10	75	20	300	65
30	25	50	7.50	75	12.50	450	78
31	40	25	5	75	5	600	97
32	40	75	5	250	20	300	37
33	40	25	10	250	5	600	99
34	40	25	5	250	20	600	36
35	10	75	5	250	5	300	69
36	25	50	7.50	250	12.50	450	77
37	10	25	10	75	5	600	89
38	40	25	5	250	5	300	83
39	10	25	5	250	5	600	78
40	40	75	5	75	20	600	47

The experimental results can be examined by the analysis of variance (ANOVA). Important factors and the significance of their effects and interactions of the operating factors on the investigated variables during the nickel leaching tests can be estimated using ANOVA [27, 28, 33]. ANOVA is based on the partitioning of the total variability of data (SS_T) into its component parts related to the principal effects of each factor (SS_A, SS_B, ...), to their interactions (SS_{AB}, SS_{BC}, ..., SS_{ABC}, ...) and to the experimental error (SS_{ERR}) [28, 33, 34]:

$$SS_T = \sum_{i=1}^{n_i} (x_i - \bar{\bar{x}})^2 = SSA + SS_B + \ldots + SS_{AB} + SS_{BC} + \ldots + SS_{ABC} + \ldots + SS_{ERR} \quad (1)$$

where i refers to different experiments conditions examined in the design, n_i is the number of tests in each design, x_i are the dependent variables observed during the leaching tests (i.e., c nickel extraction), $\bar{\bar{x}}$ is the average of x_i, the capital letters indicate the investigated factor, and SS_k is the generic sum of squares. The experimental error contribution (SS_{ERR}) was evaluated by the replicates of the central point of each factorial design as [28, 33, 34]:

$$SS_{ERR} = \sum_{j=1}^{n_j} (x_i - \bar{x})^2 \quad (2)$$

Where x_j are the values of the investigated variables (nickel extraction) in the replicates obtained under the conditions chosen for the central point, n_j is the number of replicates and $\bar{x}$ is the average of x_j.

The sum of squares and the F test were used to estimate the effect of the factors. The experimental results were examined by the analysis of variance (ANOVA) to evaluate the significance of the main effects and interactions of the operating factors on the investigated parameters during the leaching tests (Table 4).

According to ANOVA analysis, solid liquid ratio, acid concentration and reaction time were the most significant factors affecting the nickel extraction in decreasing order under the investigated conditions. The predicted nickel extraction values against the actual values and normal plot of residual for nickel extraction are shown in Figure 1 (a and b). Figure 1a shows that the points follow a straight line, therefore the residuals follow a normal distribution. Figure 1b does not show significant differences between actual and predicted extraction.

The effects of important variables and their interactions are shown in Figure 2. In this section, our aim was as to maximize the nickel extraction and also to determine the most significant factors affecting the response. The results revealed that the reaction temperature, stirring speed and particle sizes did not significantly influence nickel extraction under the investigated conditions. It was also obvious that the reaction time, acid concentration and solid-liquid ratio influenced remarkably the nickel leaching. Reaction time and acid concentration positively affected nickel dissolution while nickel extraction decreased by increasing solid-liquid ratio. This conclusion is also proven by the ANOVA analysis shown in Table 4.

Temperature had a little positive effect on nickel extraction and the nickel extraction increased only a little when reaction temperature increased from 25 to 75°C. Nickel

Table 4. ANOVA for the nickel extraction

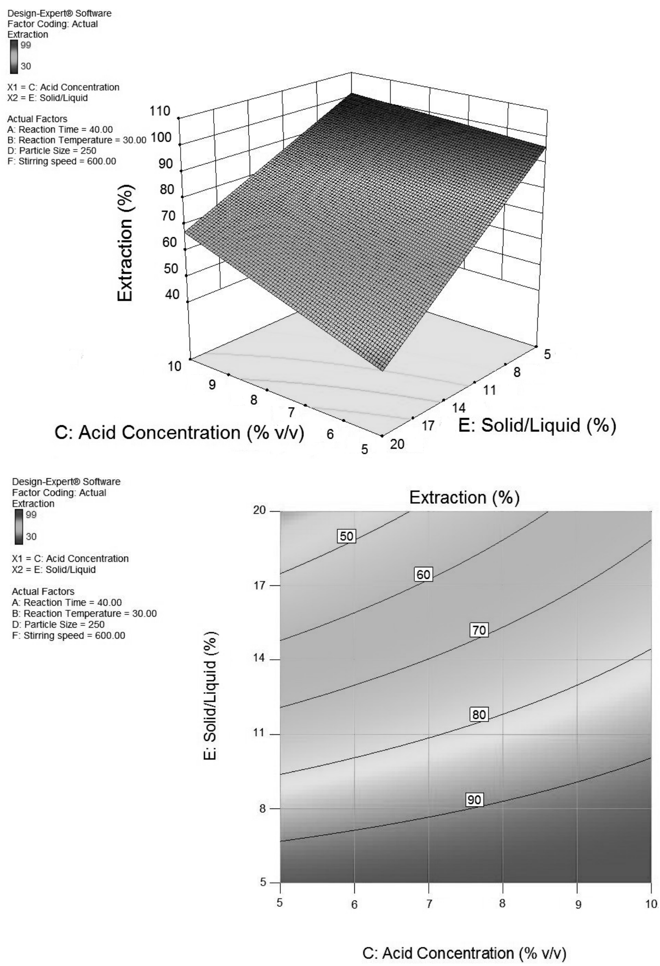
Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F
Model	17656.81	11	1605.16	233.64	< 0.0001
A-Reaction Time	1339.03	1	1339.03	194.90	< 0.0001
B-Reaction Temperature	63.28	1	63.28	9.21	0.0054
C-Acid Concentration	2032.03	1	2032.03	295.78	< 0.0001
D-Particle Size	34.03	1	34.03	4.95	0.0349
E-Solid/Liquid	13325.28	1	13325.28	1939.58	< 0.0001
F-Stirring speed	270.28	1	270.28	39.34	< 0.0001
AC	0.031	1	0.031	4.549E-003	0.9467
AE	38.28	1	38.28	5.57	0.0260
CE	427.78	1	427.78	62.27	< 0.0001
ACE	94.53	1	94.53	13.76	0.0010
ADE	26.28	1	26.28	3.83	0.0613
Residual	178.62	26	6.87	-	-
Pure Error	13.75	6	2.29	-	-
Cor Total	18350.40	39		-	-

extraction efficiency was not affected so much by a change in particle size, although the extraction increased slightly using smaller particle size. Under the experimental conditions, extracted nickel increased a little by increasing stirring speed from 300 to 600 rpm. Stirring speed positively affects nickel leaching rate but this effect is not one of the most important ones in relation to nickel extraction.

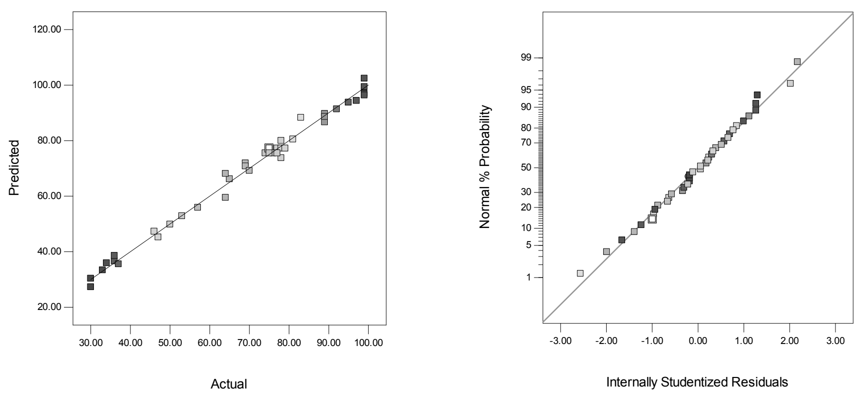
Reaction time positively influenced nickel extraction. Reaction time was significant in the first 20 minutes of extraction and then its importance decreased. Acid concentration was one of the most significant factors in nickel dissolution rate at each time. Solid-liquid ratio had a negative effect on nickel dissolution rate, and it was the most important factor which influenced nickel extraction yield. This effect was higher as compared to other factors such as acid concentrations and reaction time.

Process optimization

The goal of the optimization of nickel extraction was to find the levels of parameters, where nickel leaching rate could be maximized. In the optimization procedure, it is necessary to consider all the responses that may affect the nickel leaching yield. The optimization of nickel leaching was carried out by a multiple response method (desirability function) to optimize different combinations of the process parameters such as reaction time, acid concentration, solid-liquid ratio, particle size, temperature and stirring speed. The desirability function equation that describes the influence of the factors on the overall desirability was as follows:



a



b

Fig. 1. a: Predicted vs. actual values of nickel extraction %, b: Normal plot of residual for nickel extraction

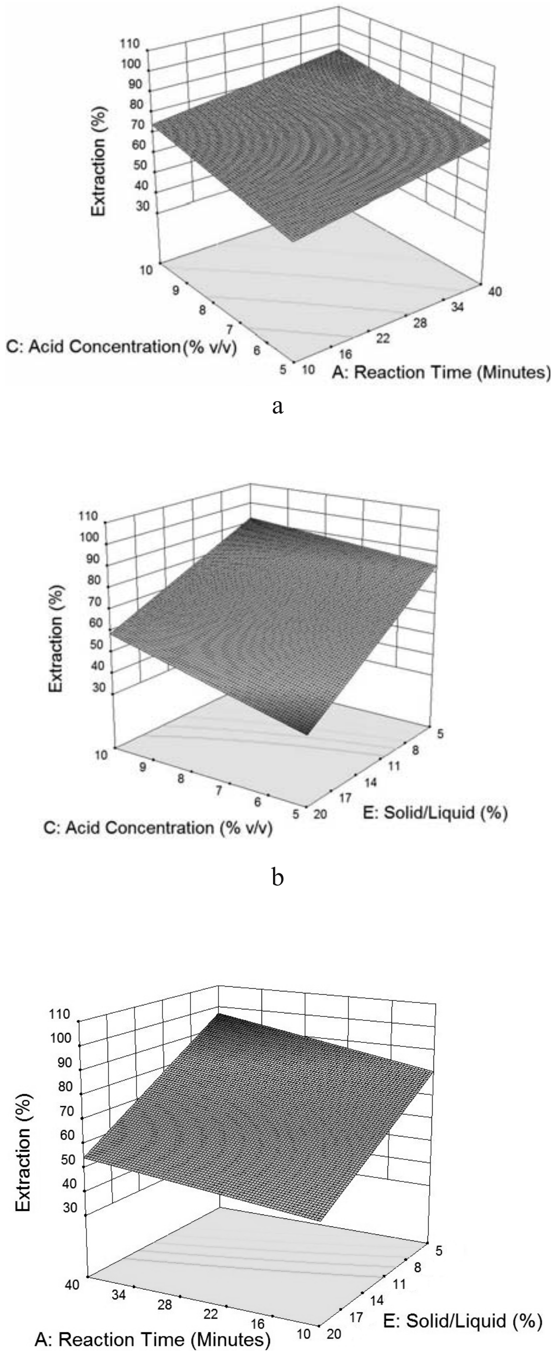
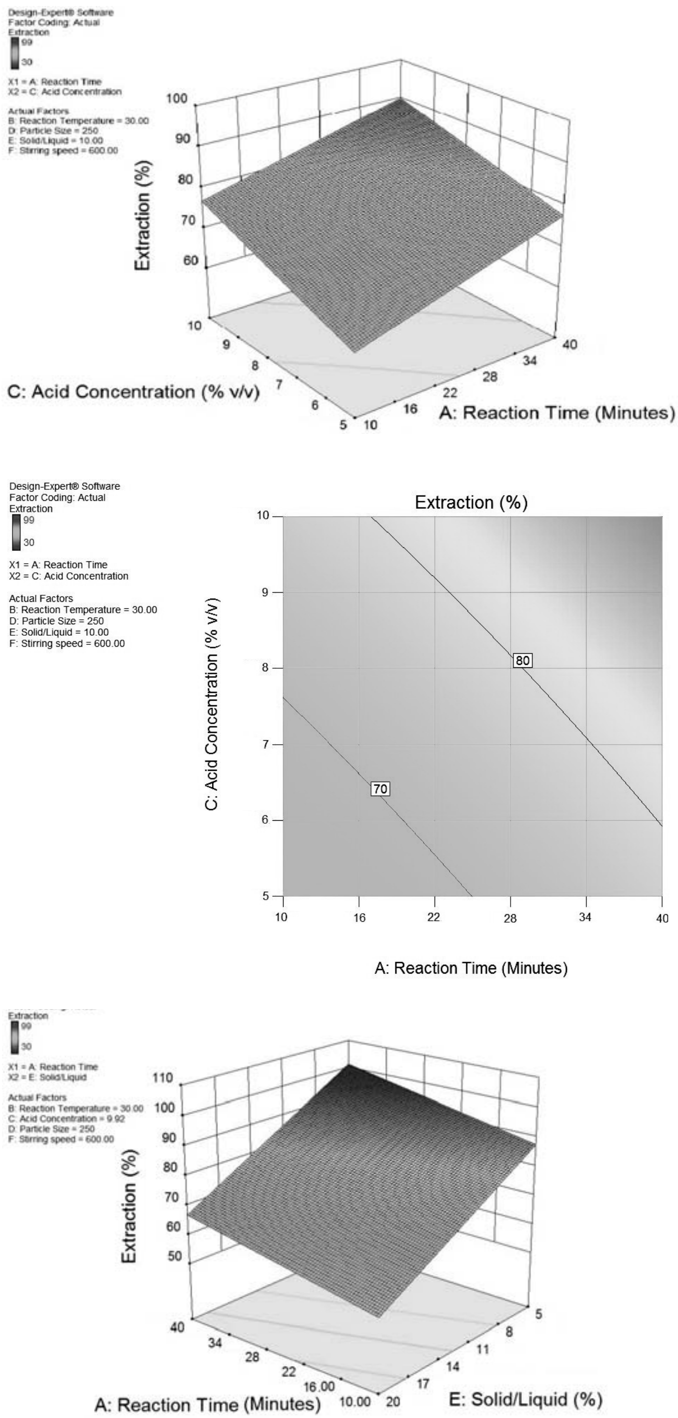
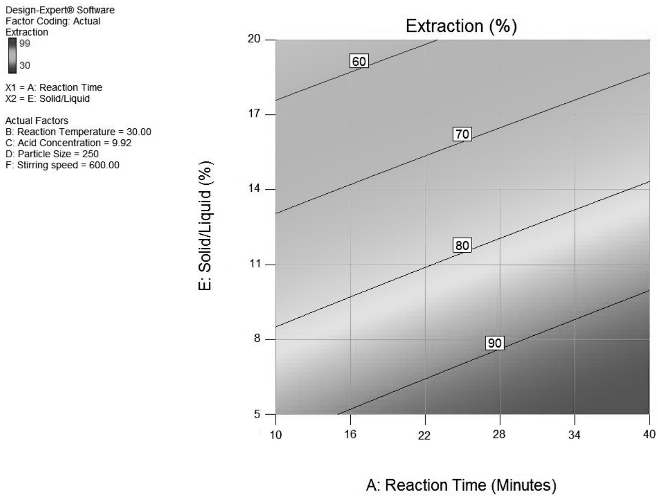


Fig. 2. The effects of Main variable interaction on the nickel extraction, a: acid concentration and reaction time, b: acid concentration and Solid/liquid ratio, c: Solid/liquid ratio and reaction time


Design-Expert® Software
Factor Coding: Actual
Extraction
99
30
X1 = A: Reaction Time
X2 = C: Acid Concentration
Actual Factors
B: Reaction Temperature = 30.00
D: Particle Size = 250
E: Solid/Liquid = 10.00
F: Stirring speed = 600.00
Extraction (%)
C: Acid Concentration (% v/v)
A: Reaction Time (Minutes)
80
70
Extraction
99
30
X1 = A: Reaction Time
X2 = E: Solid/Liquid
Actual Factors
B: Reaction Temperature = 30.00
C: Acid Concentration = 9.92
D: Particle Size = 250
F: Stirring speed = 600.00
Extraction (%)
A: Reaction Time (Minutes)
E: Solid/Liquid (%)

a



b

Fig. 3. 3D surface and contour plot for nickel extraction. (a) Influence of the acid concentration and solid-liquid ratio on the overall nickel extraction, (b) Influence of the acid concentration and reaction time on the overall nickel extraction, (c) Influence of the reaction time and solid-liquid ratio overall nickel extraction

Extraction = +57.58+1.119 × Reaction Time+0.0562 × Reaction Temperature + 2.639 × Acid Concentration -2.794 × Solid/Liquid+0.019 × Stirring speed-0.075 × Reaction Time × Acid Concentration-0.057 × Reaction Time × Solid/Liquid +0.042 × Acid Concentration × Solid/Liquid (3)

Table 5 shows several optimum conditions, and the expected results for nickel extraction. It is possible to extract 90% of the content by 9.9% (v/v) acid concentration at solid-liquid ratio of 0.10. Figure 3 shows the influence of the factors on the overall nickel extraction at optimum conditions. The study of these plots showed that higher than 90% nickel could be extracted at high amounts of acid concentration and low values of solid-liquid ratios.

In order to check the reliability of the results suggested by the model, four additional tests were conducted applying the optimum conditions to confirm the

Table 5. Optimum process conditions and their results

Number	Reaction Time (min)	Reaction Temperature (C)	Acid Concentration (V/V)%	Particle Size (micron)	Solid/ /Liquid	Stirring speed (RPM)	Extraction (%)
1	40.00	31.5	9.90	250	10.00	600	90
2	40.00	33.5	10	250	10.10	600	90
3	40.00	37.0	9.85	250	10.00	590	90

Table 6. Verification experiments at optimum conditions

Number	Reaction Time (min)	Reaction Temperature (C)	Acid Concentration (V/V)%	Particle Size (micron)	Solid/ /Liquid	Stirring speed (RPM)	Extraction (%)
Model	40.00	31.5	9.90	250	10.00	600	90
Experiment							91.5
Model	40.00	33.5	10.00	250	10.10	600	90
Experiment							93
Model	40.00	37.0	9.85	250	10.00	590	90
Experiment							92

agreement between model results and experiment results. As can be seen from Table 6, there was a good agreement between the predicted and the experimental values, so it we concluded that the effects of important variables on nickel extraction can be predicted properly by equation 3.

CONCLUSION

The results of this study showed that more than 90% of nickel can be extracted from hazardous waste. The effects of operating parameters such as reaction time, temperature, acid concentration, solid-liquid ratio, stirring speed and particle size on the nickel leaching were studied using factorial design. The results showed that the time, acid concentration and solid-liquid ratio were the main factors, and the interactions between these variables were found to be statistically significant. A model was developed by designing expert 8 software to predict nickel extraction. The process optimization was performed, and the experimental results were found to agree satisfactorily with the predicted values.

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