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"Gheorghe Asachi" Technical University of Iasi, Romania

OPTIMIZATION OF CADMIUM DISSOLUTION FROM A HAZARDOUS WASTE BY STATISTICAL DESIGN OF EXPERIMENTS

Mahdi Gharabaghi[1*], Mehdi Irannajad[2], Amir Reza Azadmehr[2]

[1]*University of Tehran, College of Engineering, School of Mining Engineering, Tehran, Iran*
[2]*Amirkabir University of Technology, Department of Mining and Metallurgical Engineering, Hafez Ave., Tehran, Iran*

Abstract

Cadmium leaching experiments from hazardous waste containing 16.5 wt% CdO were conducted using H_2SO_4. Dominant experimental and process parameters were determined by factorial design. Six controlling factors were considered, i.e. solid-liquid ratio, acid concentration, reaction time, particle size, stirring speed and temperature. Analysis of variance (ANOVA) was used to identify main effects and their interactions. An empirical model, based upon experimental results, was developed to optimize the cadmium extraction by the process. The optimisation study showed that leaching time, solid-liquid ratio and acid concentration were the main factors affecting cadmium extraction. It was found that 91% of cadmium could be extracted under the optimum conditions. Verification experiments showed that the predicted values were in good agreement with the experimental values.

Key words: cadmium, factorial designed experiments, hazardous waste, leaching, optimization

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1. Introduction

Cadmium is a toxic heavy metal which is found as a minor constituent of most zinc ores. Cadmium is usually produced and recovered from both primarily and secondary resources such as base metals concentrates, spent Ni–Cd batteries, electrical arc furnace dust, cadmium containing alloys, solar cells, fluorescent materials (Butterman and Plachy, 2002; Freitas and Rosalém, 2005; Habashi, 1997; Safarzadeh et al., 2007; Zazouli et al., 2014). Cadmium extraction from various resources has been reviewed in the literature Safarzadeh et al. (2007).

Although cadmium is a toxic metal, it has wide applications in various industries such as pigments, plating, plastic stabilizing, electronics, and ceramics industries. Cadmium applications are increasing in some industries like nickel–cadmium batteries and cadmium telluride solar panels while other cadmium related industries are decreasing their consumptions (Butterman and Plachy, 2002; Kirk-Othmer, 2007; Safarzadeh et al., 2007).

The presences of cadmium ions in wastes have advers effects on human and aquatic lives. Cadmium recycling from wastes can decrease its unfavorable environmental impacts. Zinc plant residue is considered a hazardous waste which is produced in hydrometallurgical zinc production and the content of zinc, cadmium and nickel is very high in this waste. The disposal of this waste causes both environmental pollution and of resources loss. In addition, cadmium compounds are highly toxic and carcinogenic in nature (Altundoğan et al., 1998; Bulgariu et al., 2013; Safarzadeh et al., 2008; Safarzadeh et al., 2009; Turan et al., 2004). Several studies have been performed on extraction of cadmium from zinc plant residue (Gouvea and Morais, 2007; Safarzadeh et al., 2008; Safarzadeh et al., 2009; Shahsavari., 2001). Gouvea and Morais (2007) extracted zinc and cadmium from a waste

* Author to whom all correspondence should be addressed: e-mail: gharabaghi@ut.ac.ir; m.gharabaghi@gmail.com;

using leaching and cementation. Safarzadeh et al. (2009) studied cadmium extraction and its leaching kinetics from zinc plant residue. Shahsavari (2003) used this waste for cadmium extraction. Gharabaghi and co-workers investigated kinetics of cadmium extraction from zinc plant residue (Gharabaghi et al., 2011; Gharabaghi et al., 2012).

By using this waste as cadmium secondary resource, it is possible to decrease its environmental impact and produce marketable concentrates. The information about recovery of cadmium from this waste is scarce (Gharabaghi et al., 2011; Gouvea and Morais, 2007; Safarzadeh et al., 2009; Shahsavari., 2001). Although previous studies have dealt with the cadmium extraction, the present study presents an in-depth analysis of the process by planning experiments using statistical design expert software.

Optimization of main variables in leaching of zinc plant residue is of special importance. In the classical experimental design, a lot of tests must be done for process optimization. Process optimization by statistical method is a simple and systematic method for improving a 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 (Lee et al., 2006; Myers et al., 2009). The 2^k factorial design is a standard technique and widely used for studying a random response to a set of *k* possible factors (Lee et al., 2006; Myers et al., 2009). With the factorial design methodology major interaction effects and low-order interactions may be estimated (Box et al., 1978; Montgomery, 2008)

In this study, the most significant factors affecting cadmium extraction from zinc plant residue were studied. Process parameters which maximize cadmium extraction were identified by statistical design of experiment. Parametric optimization and modelling of cadmium extraction were also investigated.

Two-level factorial design was used to determine the optimum process conditions. For this purpose, the simultaneous effects of six control factors including of time, acid concentration, temperature, S/L ratio, stirring speed and particle size for cadmium leaching were optimized using factorial design. In addition, the adequacy of the model was evaluated by analysis of variance.

2. Experimental

The zinc plant residue sample was from Calcimin zinc plant in Zanjan, Iran. The sample has high concentrations of cadmium and zinc (Table 1). According to XRD analysis, zinc-bearing minerals were the major components in the sample. The sample also contains cadmium, nickel and lead components. Sulfuric acid (Merck, Germany) and distilled water were used in the dissolution tests experiments. Leaching tests were perfoormed in a 500 mL reactor equipped with a stirrer motor and reflux condenser to prevent losses by evaporation. Cadmium concentrations in solutions were determined by Atomic Absorption Spectrophotometer [AAS 300] of Unicom.

Leaching experiments were performed using a fractional factorial design (2^{6-1}) and the Design Expert 8 (DX8) statistical software was used. For increasing process accuracy 8 centre points were considered in this study. Factorial design can be applied to identify important factors from those, which are not, and identifying any possible interactions between them (Özgüney et al., 2007; Paterakis et al., 2002). Six factors were investigated, and their levels are shown in Table 2. Statistically design was carried out to determine which of these variables, and their interactions presented more significant effects.

Analysis of variance (ANOVA) was used to identify the significance of the process factors and their interactions on the cadmium extraction. ANOVA provides statistical results and diagnostic checking tests which enable researchers to evaluate adequacy of the models (Bose, 2009; Box et al., 1978; Ghafari et al., 2009; Montgomery, 2008).

ANOVA is based on the partitioning of the total variability of data (SS_T) into its components 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}) (Eq. 1) (Bose, 2009; Montgomery, 2008; Pagnanelli et al., 2004).

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 [×]
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.

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

$$SS_T = \sum_{i=1}^{n} (x_i - \overline{\overline{x}})^2 = SS_A + SS_B + ... + SS_{AB} + SS_{BC} + ... + SS_{ABC} + ... + SS_{ERR} \quad (1)$$

In Eq. (1), i refers to the different experimental 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., cadmium extraction), $\overline{\overline{x}}$ 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 (Eq. 2) (Bose, 2009; Montgomery, 2008; Pagnanelli et al., 2004).

$$SS_{ERR} = \sum_{j=1}^{n} (x_j - \overline{x})^2 \quad (2)$$

where x_j are the values of the investigated variables (cadmium extraction) in the replicates obtained under the conditions chosen for the central point, n_j is the number of replicates and $\overline{x}$ is the average of x_j. The sum of squares and the F test used to estimate the effect of the factors.

3. Results and discussion

3.1. Results analysis and effects of variables on cadmium extraction

Leaching experiments were carried out randomly to avoid systematic errors. Table 3 shows the experimental plan and results of cadmium extraction. ANOVA was used to analyses of the results of experiments and to study the effects of individual process variables as well as their combined interactive effects on cadmium extraction. The ANOVA results in Table 4 showed that the effects of solid liquid ratio, acid concentration and reaction time and their interaction were statistically significant whilst all other variables and interactions were statistically insignificant compared to significant factors.

Fig. 1 (a, b) shows the predicted cadmium extraction values against the actual values and normal plot of residual for cadmium extraction. As it can be seen in Fig. 1a, the residuals have a normal distribution because the points follow a straight line. Fig. 1b shows that the predicted values match the experimental values reasonably well and therefore, the results can be predicted by statistical model.

The effects of the parameters on the cadmium extraction under investigated conditions showed that the temperature, stirring speed and particle size had no significant effects on cadmium extraction. Cadmium extraction decreased significantly by increasing solid-liquid ratio. Based on Table 4, it may be concluded that the solid-liquid ratio was the most important variable in cadmium dissolution rate.

Acid concentration had positive effects on cadmium extraction, and its effect was maximum during the early stages of leaching and diminished during the process though it was the second significant factors at each time. Reaction time positively influenced cadmium leaching rate, but its effect was not as high as solid-liquid ratio or acid concentration. Cadmium extraction increased slightly by increasing temperature and stirring speed and decreasing particle size.

The interactions of important factors on the cadmium extraction are shown in Fig. 2. The effects of reaction time and solid-liquid ratio on cadmium extraction at the center level other variables are shown in Fig. 2a and 2b. It is obvious that the cadmium extraction depended more on the solid-liquid ratio rather than on leaching time. A maximum cadmium extraction was obtained with the minimum level of solid liquid ratio at the maximum reaction time. The effects of solid-liquid ratio and acid concentration are shown in Fig. 2c and 2d. The form of these plots is similar to the Fig. 2a and 2b, however the cadmium extraction in these conditions was lower. Fig. 2e and 2f show effects of leaching time and acid concentration on the results. Both factors had significant effects on cadmium leaching rate and higher extractions were obtained at the higher acid concentration levels. As described before, the response function representing cadmium extraction can be expressed as a function of operating parameters. The relationship between response and operating parameters was obtained (Eq. 3).

Extraction = +78.86+ 0.46 × Reaction Time + 0.041 × Reaction Temperature +0.53 × Acid Concentration -3.56 × Solid/Liquid +0.016 × Stirring speed -0.020 × Reaction Time × Solid/Liquid +0.15× Acid Concentration × Solid/Liquid +1.90E-003 × Reaction Time × Acid Concentration × Solid/Liquid (3)

The cadmium extraction at any condition in the interval of our experiment design can be calculated from Eq. (3).

3.2. Process optimization

The main aim of this study was to maximize cadmium extraction in the leaching process. Graphical optimization can display the area of feasible cadmium extraction in parameters space and it is possible to determine the regions that do fit the optimization criteria (Mason et al., 2003). In order to find optimum condition for process variables, we have used graphical optimization option in design expert software. Three desirable experimental condition suggested by the software are given in Table 5. Maximum cadmium recovery was reached to 91.50% using 10% acid concentration, solid-liquid ratio of 10%, 600 rpm stirring speed at 25 °C. The optimum particle size was chosen < 250 µ because of economical point of view. The effects of main factors on the cadmium extraction at optimum condition are shown in Fig. 3. These contours showed that higher than 90% cadmium could be extracted at optimum conditions.

The most desirable experimental conditions deduced from the software were selected to be verified. Table 6 shows the verification results of the software. The predicted cadmium extractions were 91.5, 90.5 and 89.2% while the experimental data were 95.75, 92.61 and 91.3% respectively. The experimental result showed good agreement with the value obtained from the model (Table 6).

After leaching process, leaching residue was characterized. XRD pattern of leaching residue is shown in Fig. 4. After leaching process, gypsum and lead oxide amounts in the leaching residues increased markedly, and cadmium quantity decreased significantly. It was conluded that cadmium compounds dissolved in the leaching system and Fe_2O_3 intensity slightly increased.

Table 3. Experimental design matrix and cadmium extraction results

Run	*A:Reaction time*	*B:Reaction temperature*	*C:Acid concentration*	*D:Particle size*	*E:Solid-Liquid*	*F:Stirring speed*	*Extraction*
	Minutes	°C	%	Micron	g/L	RPM	(%)
1	40	75	5	75	5	300	95
2	10	25	5	75	5	300	74
3	10	75	10	75	5	300	92
4	40	25	5	75	20	300	41
5	25	50	7.5	75	12.5	450	83
6	10	25	5	250	20	300	35
7	10	75	10	250	5	600	91
8	10	75	5	75	5	600	84
9	10	25	5	75	20	600	37
10	10	25	10	250	20	600	57
11	10	75	10	75	20	600	60
12	25	50	7.5	75	12.5	450	81
13	40	75	10	250	20	600	67
14	10	25	10	75	20	300	51
15	25	50	7.5	250	12.5	450	79
16	25	50	7.5	250	12.5	450	78
17	40	75	10	250	5	300	99
18	25	50	7.5	250	12.5	450	79
19	40	75	5	250	5	600	99
20	10	75	10	250	20	300	54
21	25	50	7.5	75	12.5	450	77
22	40	25	10	75	20	600	76
23	10	75	5	250	20	600	39
24	40	25	10	75	5	300	97
25	40	25	10	250	20	300	69
26	10	75	5	75	20	300	37
27	40	75	10	75	5	600	99
28	10	25	10	250	5	300	81
29	40	75	10	75	20	300	70
30	25	50	7.5	75	12.5	450	83
31	40	25	5	75	5	600	99
32	40	75	5	250	20	300	43
33	40	25	10	250	5	600	99
34	40	25	5	250	20	600	41
35	10	75	5	250	5	300	71
36	25	50	7.5	250	12.5	450	82
37	10	25	10	75	5	600	93
38	40	25	5	250	5	300	86
39	10	25	5	250	5	600	82
40	40	75	5	75	20	600	51

Table 4. ANOVA Table for Experimental design

Source	*Sum of Squares*	*df (Degree of freedom)*	*Mean Square*	*F Value*	*p-value Prob > F*
Model	15612.81	10	1561.28	199.64	< 0.0001
A-Reaction Time	1164.03	1	1164.03	148.84	< 0.0001

B-Reaction Temperature	34.03	1	34.03	4.35	0.0466
C-Acid Concentration	1815.03	1	1815.03	232.08	< 0.0001
D-Particle Size	57.78	1	57.78	7.39	0.0113
E-Solid/Liquid	11742.78	1	11742.78	1501.52	< 0.0001
F-Stirring speed	195.03	1	195.03	24.94	< 0.0001
AE	9.03	1	9.03	1.15	0.2921
CE	442.53	1	442.53	56.59	< 0.0001
ACE	124.03	1	124.03	15.86	0.0005
ADE	26.28	1	26.28	3.36	0.0778
Curvature	561.01	2	280.51	35.87	< 0.0001
Residual	211.16	27	7.82		
Lack of Fit	178.16	21	8.48	1.54	0.309
Pure Error	33	6	5.5		
Cor Total	16384.98	39			
Adj R-Squared	0.97				
Pred R-Squared	0.95				

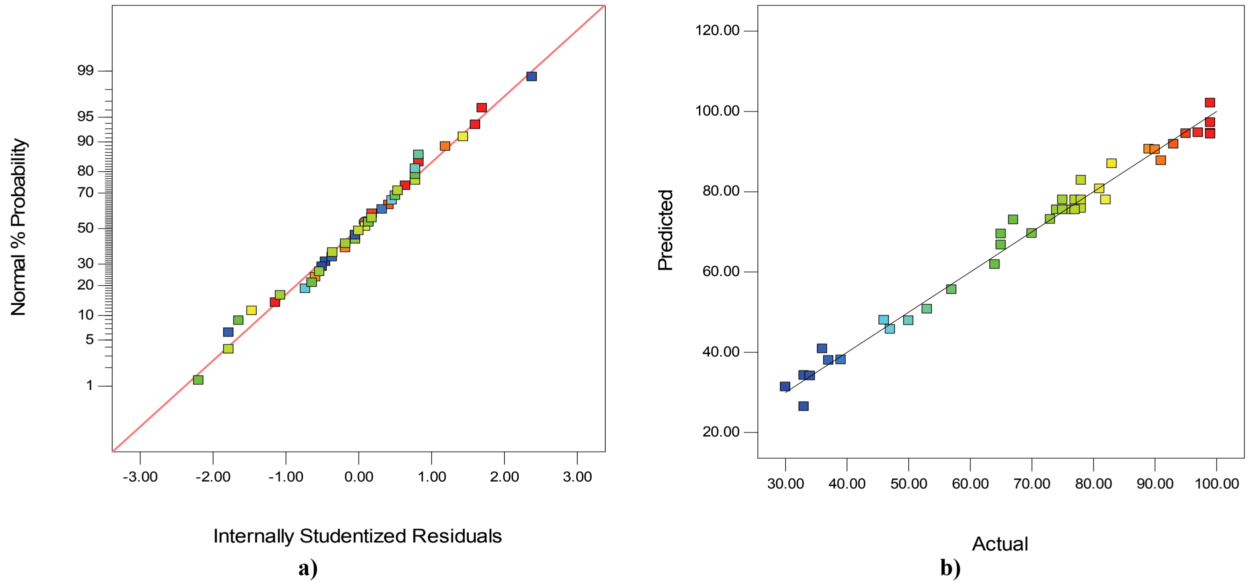
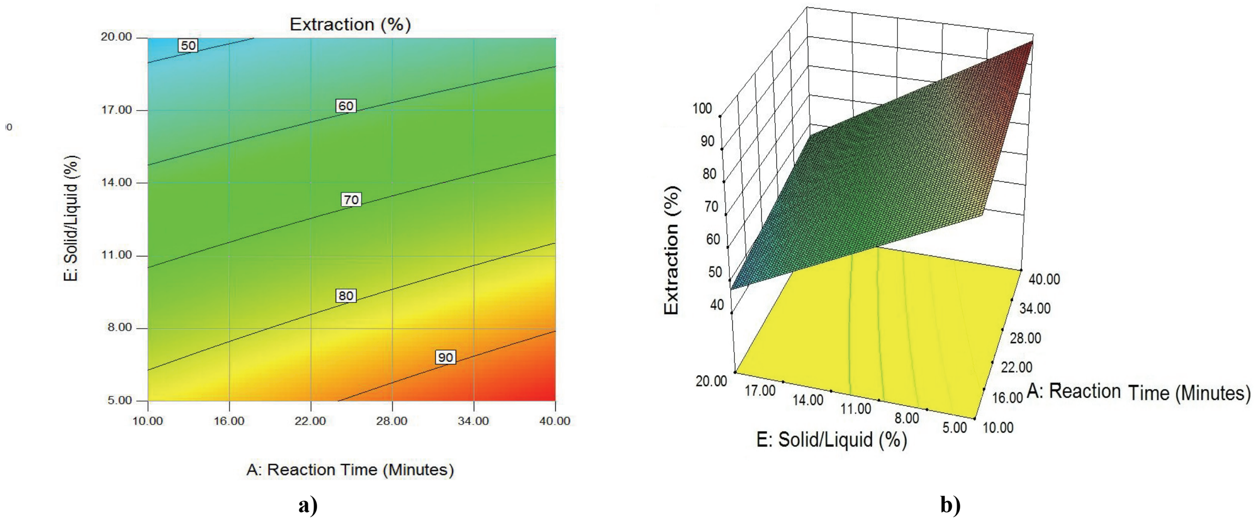


Fig. 1. a) Normal plot of residual for cadmium extraction,%; b) Relation between experimental and predicted cadmium extraction



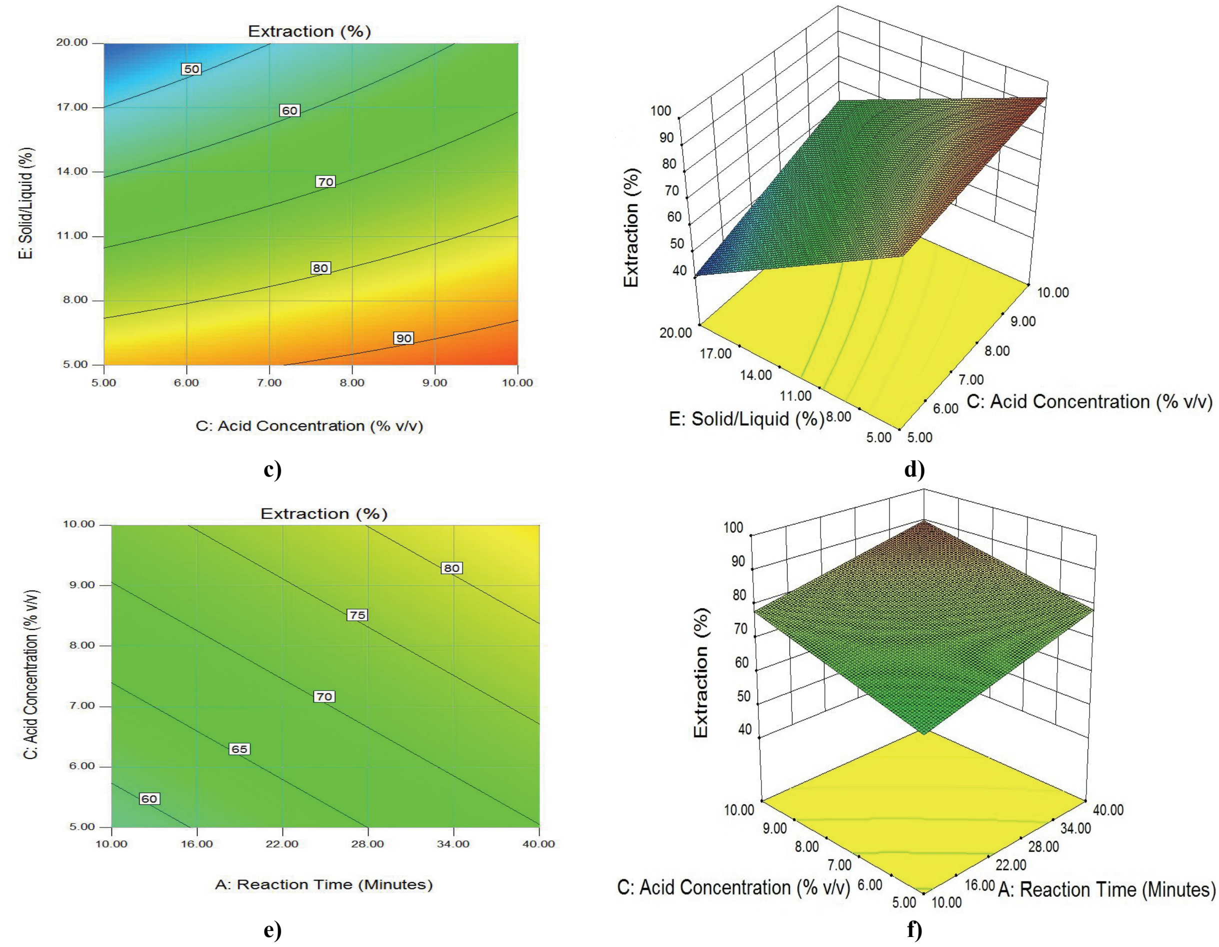
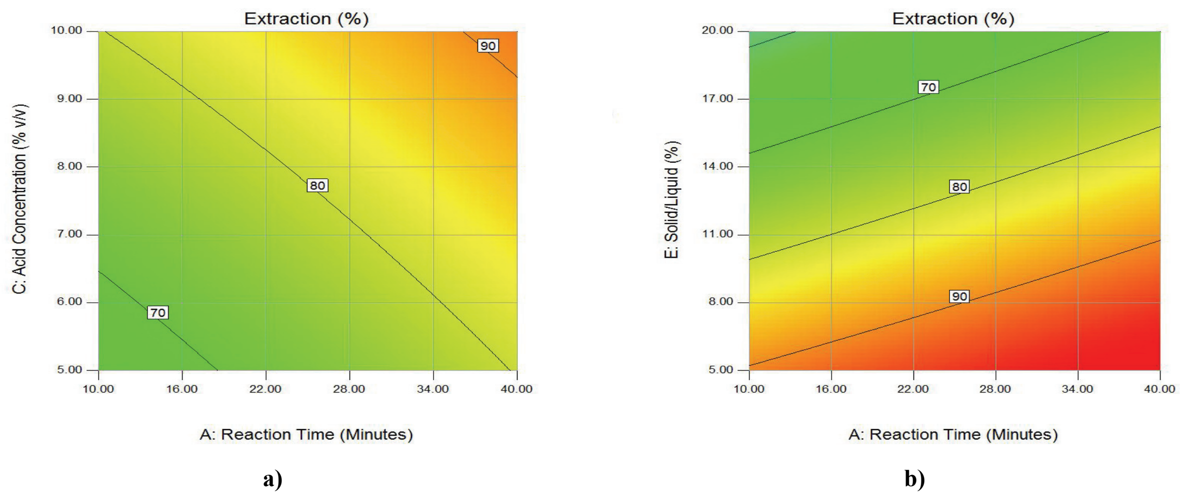
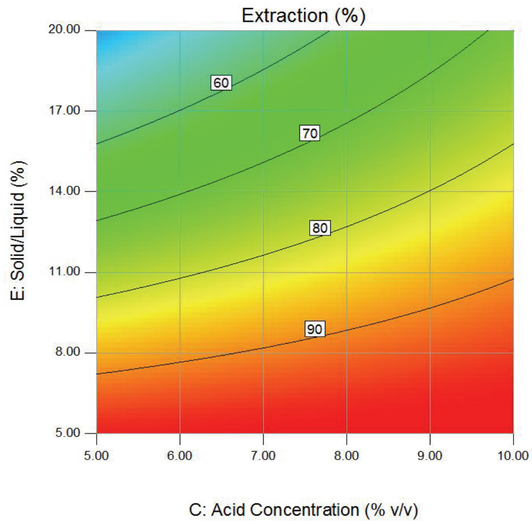


Fig. 2. Effects of various parameters and their interaction on the cadmium extraction, a, b) effects of the leaching time and solid-liquid ratio on the cadmium recovery (reaction temperature=25 °C, acid concentration= 7.5 % (v/v), stirring speed=600 rpm), c, d) Influence of solid-liquid ratio and acid concentration on the cadmium extraction (reaction time=40 min, reaction temperature=25 °C, stirring speed=500 rpm), e, f) effects of the reaction time and acid concentration on the overall cadmium extraction (reaction temperature=25 °C, stirring speed=600 rpm, solid-liquid ratio: 10%)

Table 5. Several optimum conditions suggested by software

Number	*Reaction Time*	*Reaction Temperature*	*Acid Concentration*	*Particle Size*	*Solid-Liquid*	*Stirring speed*	*Extraction*	*Desirability*
1	40	25	10	250	10	600	91.51	1
2	40	25	9.67	250	10	600	90.51	0.97
3	40	25	9.0	250	10	600	89.21	0.944





c)

Fig. 3. Optimization of cadmium leaching process, (a) Influence of the acid concentration and reaction time on the overall cadmium extraction (reaction temperature=25 °C, solid liquid ratio= 10 %, stirring speed=600 rpm), (b) Influence of the reaction time and solid-liquid ratio overall cadmium extraction (reaction temperature=25 °C, acid concentration= 10 %(v/v), stirring speed=600 rpm), (c) Influence of the acid concentration and solid-liquid ratio on the overall cadmium extraction (reaction time=40 min, reaction temperature=25 °C, stirring speed=600 rpm)

Table 6. Some optimum conditions predicted by the model and their verification experiments

Number	*Reaction Time (min)*	*Reaction Temperature (C)*	*Acid Concentration (V/V)%*	*Particle Size (micron)*	*Solid/Liquid*	*Stirring speed (RPM)*	*Extraction (%)*
Model	40.00	25	10.0	250	10.00	600	91.51
Experiment							95.75
Model	40.00	25	9.67	250	10.00	600	90.51
Experiment							93.79
Model	40.00	25	9.0	250	10.00	590	89.21
Experiment							92

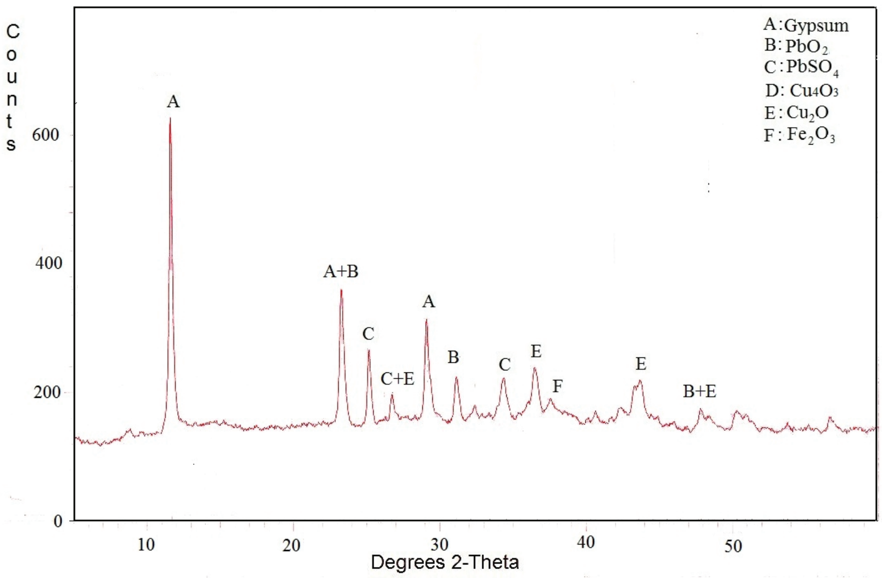


Fig. 4. XRD graph of head sample

4. Conclusions

The leaching method was used as an effective way to recycle hazardous waste as cadmium secondary resource. The effects of operating parameters on cadmium extraction were optimized using factorial design. The results showed that the leaching time, solid-liquid ratio and acid concentration were statistically significant. A model equation was derived to correlate the process variables with the cadmium extraction yield. Process optimization was performed, and its results showed that more than 91% cadmium could be extracted at optimum conditions. The experimental data have a good agreement with the predicted values. The results of this study indicated that extraction of cadmium from this waste could be technically feasible and an effective way for managing this waste.

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