Leaching of Lead and Zinc from a Low-Grade Oxide Ore in Citric Acid Media

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ABSTRACT: *Leaching of a low-grade lead and zinc oxide ore was studied by an organic reagent, citric acid. The quadratic mathematical models were developed for the relationship among the influential parameters and lead and zinc recoveries. Leaching rate was strongly affected by the interactive effects of factors. It was also found that the quadratic effects of stirring speed and linear effects of temperature have the most significance on the leaching rate of zinc and lead, respectively. It was found that the center level of influential factors was a good condition for getting higher zinc leaching rate, whilst, for the leaching of lead the extreme levels of factors were good. Additionally, the proposed models were optimized using the quadratic programming method to maximize recoveries. The highest recoveries of zinc and lead were achieved to be about 94 and 78 %, respectively.*

KEYWORDS: *Low- grade ore; Lead; Zinc; Recovery; Citric acid leaching.*

INTRODUCTION

Lead and zinc are produced mainly from sulfide ores and usually occur together in a variety of minerals. Zinc and lead sulfides ores have been continuously exploited and have gradually become depleted and low grade oxide ore have been developed as important sources of lead and zinc metals to meet future demands. Extraction of lead and zinc from oxidized ores is usually carried out by hydrometallurgical techniques. Much attention has been focused to develop the hydrometallurgical methods for the increment of the zinc recovery rate [1-7]. These studies indicate that the ores in nature have many impurities including silicon, iron, and calcium which influence the quality of the product. When H_2SO_4, HNO_3 or HCl are commonly applied as leaching agent, the undesired impurities especially iron can be considerably dissolved in the leaching reagent. Whereas, organic reagents have high selectivity and low dissolving capacity. This provides an advantage in leaching of metal oxide and carbonate compounds which include some impurities [8]. Recently, extensive research efforts were also carried out on recovery of lead from oxidized resources or other lead-bearing renewable resources using hydrometallurgical techniques [9-12]. The previous studies indicate that organic acids can be employed as beneficial leaching reagents. In addition, each ore has its own individual mineralogical and chemical composition and consequently its optimal leaching conditions are different from one type of ore to another. Thus, this work was aimed to investigate the leaching behavior leaching of zinc and lead using citric acid.

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EXPERIMENTAL SECTION

Materials

To conduct the leaching tests, the obtained oxide samples were prepared after two stages of laboratory comminution including crushing and milling such as 80% of particles were smaller than 150 microns. Thereafter, the composition of samples was characterized by XRF and the results showed that the sample contained 5.91%ZnO and 5.32% PbO, 24.77% SiO_2, 15.68% Fe_2O_3, 15.42% CaO and 15.76% BaO [13]. The phases of the representative sample were also detected by X-ray diffraction analysis, which the main phases of lead and zinc identified from the XRD pattern indicated smithsonite ($ZnCO_3$) and cerussite ($PbCO_3$).

Leaching experiments

Leaching experiments were conducted in a beaker of 500 mL which heated a hot plate, equipped with a digital controlled magnetic stirrer under different conditions including acid concentration of 0.25–1.25 M, temperature of 50–90°C, stirring speed of 200–600 rpm, liquid to the solid ratio of 10–30 mL/g and leaching time of 45–105 min. For each experiment, a 3 g sample was selected. Leaching solutions were prepared using distilled water and different concentration of citric acid, then based on the desired liquid to solid ratio, a definite volume of the solution was poured into the beaker at the required temperature. When the leaching process finished, the solution was filtered and the liquid phase was analyzed using AAS and recoveries were calculated by Eq. (1).

$$R = \frac{M_1}{M_0} \times 100 \quad (1)$$

Where *R* is the recovery percentage of lead and zinc; M_0 and M_1 correspond to lead and zinc contents of the sample before and after leaching.

RESULTS AND DISCUSSION

Influence of factors and their interactions

Response Surface Methodology (RSM) is the most important and efficient technique of DOE, which can be applied to develop, improve, model and optimize the processes and also to evaluate the relative significance of parameters even in the presence of complex interactions [14-17]. Among RSM designs, CCRD was employed to study the leaching behavior of zinc and lead and a series of 32 experiments (N= $2^{(5-1)} + 2 \times 5 + 6$) were designed and performed. To simplify the calculations and for uniform comparison, factors were studied with their codified values (Table 1). Then, data were analyzed using Design Expert software and were examined with various mathematical models and finally, the two quadratic models were suggested for the zinc and lead leaching rate (*Y*):

$$Y_{Zn} = +80.65 + 6.92\times A + 7.56\times B - 0.88\times C - 3.20\times D + 5.12\times E + 2.30\times A\times B + 3.87\times A\times C + 5.04\times A\times D - 3.20\times A\times E + 5.31\times B\times E + 4.97\times C\times D - 4.71\times C\times E - 4.15\times A^2 - 1.97\times B^2 - 8.92\times C^2 - 5.48\times D^2 \quad (2)$$

$$Y_{Pb} = +53.88 + 3.42\times A + 3.6\times B + 1.42\times C + 6.24\times D + 3.25\times E + 1.8\times A\times C - 2.11\times A\times E + 2.76\times B\times E + 2\times B^2 + 1.7\times C^2 - 1.85\times D^2 + 1.81\times E^2 \quad (3)$$

According to ANOVA, the *F*-value of models for zinc (165.65) and lead (28.13) were significant and the lack of fits was insignificant. In addition, the R^2 values of 0.9955 (for zinc) and 0.9547 (for lead) were obtained.

The effects of main factors on leaching of zinc and lead are illustrated in Fig. 1. It is observed that temperature (B) and L/S ratio (D) have the highest influence on the recoveries of Zn and Pb, respectively. Fig. 2(a–f) shows the 3D response surface plots for the relationship between two factors when the other two variables were fixed at their center levels for recovery of zinc and lead.

It is observed from Figs. 1 and 2 that zinc leaching rate increases meaningfully by increasing the acid concentration up to a certain value of citric acid concentration and thereafter become constant. It is also observed that increasing the leaching temperature increases the amounts of zinc and lead extracted. Also, the zinc leaching rate enhances with an increase in stirring speed up to zero levels (400 rpm), whereas above 400 rpm, the agitation has an insignificant influence. In addition, the effect of stirring speed on the lead recovery indicates that the agitation speed factor has the lowest influence on lead recovery. The effect of liquid/solid ratio on zinc recovery shows that zinc recovery increases with the increasing liquid/solid ratio to a certain amount, and with further increment reduces. It can also be observed that the recovery of lead rises quickly with increasing liquid/solid ratio and probably remains almost constant beyond a ratio of 25 (high factorial level). It is seen from

Table 1: CCRD matrix and measured and predicted values of recoveries of lead and zinc.

Factors			Low axial (-2)		Low factorial (-1)		Center (0)	High factorial (+1)	High axial (+2)
A: Acid concentration (mol/L)			0.25		0.5		0.75	1	1.25
B: Temperature (°C)			50		60		70	80	90
C: Stirring speed (rpm)			200		300		400	500	600
D: L/S (mL/g)			10		15		20	25	30
E: Leaching time (min)			45		60		75	90	105
Run	A	B	C	D	E	Zn recovery (%)		Pb recovery (%)	
						Actual	Predicted	Actual	Predicted
1	1	60	300	15	60	56.45	56.00	53.12	49.53
2	0.25	70	400	20	75	48.56	50.21	48.57	47.04
3	0.5	80	500	25	60	40.99	41.51	56.53	55.47
4	0.75	70	600	20	75	44.36	43.18	66.43	63.52
5	1.25	70	400	20	75	79.43	77.87	59.29	60.72
6	0.5	60	300	25	60	33.08	31.77	50.89	54.54
7	0.5	60	300	15	90	74.85	73.64	49.74	47.25
8	0.5	60	500	25	90	38.24	38.22	55.54	58.99
9	0.75	70	400	20	105	92.66	90.89	66.47	67.60
10	0.5	80	500	15	90	66.40	65.92	58.19	59.21
11	0.75	70	400	10	75	63.60	65.13	33.06	33.99
12	1	80	500	15	60	70.28	70.56	54.87	57.64
13	0.75	70	400	20	45	71.03	70.41	58.04	54.62
14	0.75	90	400	20	75	89.20	87.90	70.75	69.09
15	1	80	300	15	90	89.14	88.99	58.34	58.99
16	1	80	500	25	90	87.35	89.21	78.57	77.91
17	1	60	500	15	90	44.90	45.25	54.11	52.71
18	0.5	60	500	15	60	48.68	48.19	39.16	41.30
19	1	80	300	25	60	57.99	58.85	61.65	63.70
20	1	60	500	25	60	74.83	75.08	66.59	68.45
21	0.5	80	300	25	90	67.77	68.36	72.93	72.45
22	1	60	300	25	90	52.37	52.39	58.83	58.77
23	0.75	70	400	30	75	53.76	52.32	62.20	58.97
24	0.75	70	200	20	75	45.45	46.72	57.22	57.84
25	0.5	80	300	15	60	59.06	58.07	42.41	43.73
26	0.75	50	400	20	75	56.28	57.67	55.34	54.70
27	0.75	70	400	20	75	79.85*	80.65*	53.85*	53.88*

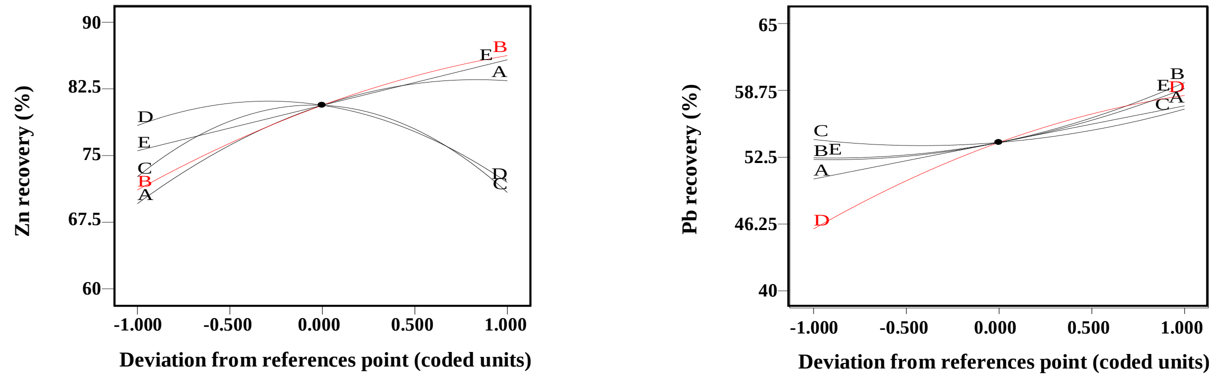

Fig. 1: The effect of acid concentration (A), temperature (B), stirring speed (C), liquid/solid (L/S) ratio (D) and leaching time (E) on recoveries of zinc and lead.

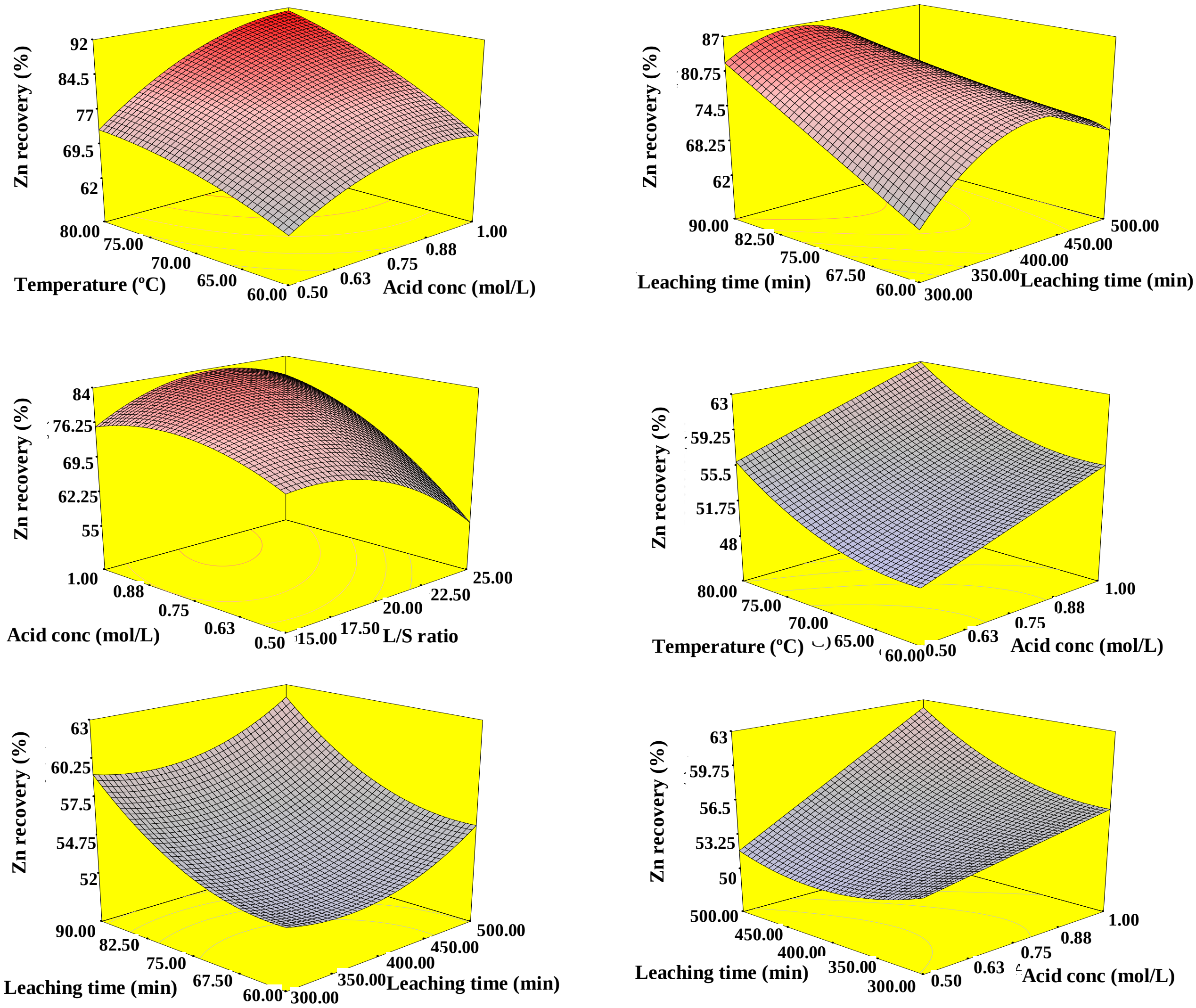

Fig. 2: Response surface plots for recovery of zinc: (a) acid concentration and temperature, (b) stirring speed and leaching time, (c) acid concentration and liquid/solid (L/S) ratio and for recovery of lead: (d) acid concentration and temperature, (e) stirring speed and leaching time, (f) temperature and acid concentration.

Table 2: The proposed levels of factors investigated and validation with laboratory experiments.

Factors	Citric acid (mol/L)	Temperature (°C)	Stirring speed (rpm)	L/S (mL/g)	Leaching time (min)	Zn recovery (%)
Model projections	0.99	79.66	412.74	20.61	81.76	94.44
Model validation	1	80	400	20	80	93.85
						Pb recovery (%)
Model projections	1	80	499.99	24.83	89.98	77.80
Model validation	1	80	500	25	90	77.98

Figs. 1 and 2 that recovery of zinc increases linearly with increasing leaching time, whilst there is an optimal value for acid concentration, agitation speed, L/S ratio and temperature and higher or lower values of these factors than the optimal amount have a negative effect on zinc leaching. Also, it can be seen that the center level of stirring speed, temperature and leaching time is not a good condition for getting higher lead leaching rate, but the extreme levels of these factors are good for the leaching of lead. In addition, the liquid/solid ratio has a significant effect on the leaching of lead whilst stirring speed has a trivial effect. Furthermore, it can be found from presented models and Figs. 1 and 2 that interactions among factors have very significant effects on the recoveries.

Optimization of process parameters

The optimal conditions of zinc and lead leaching rate was achieved using Design Expert software, which the results are presented in Table 2. It is found that the maximum recoveries of zinc and lead can be obtained 94.44 and 77.8 %, respectively. Also, three confirmation experiments were conducted at the predicted optimum conditions to confirm the validity of the model, which the average of three extra tests was reported in Table 2.

CONCLUSIONS

The following conclusions can be drawn from this work:

(1) This study demonstrates that zinc and lead can be successfully recovered from low grade lead and zinc oxide ores by citric acid leaching.

(2) The results showed that predicted values obtained using the model equations were in very good agreement with the observed values. It was found that the model could explain 99.55 and 99.47% of the variability in recovery of zinc and lead, respectively.

(3) It was found that influence degree of important terms on the zinc leaching was in the order of $C^2 > B > A > D^2 > E > BE > A^2 > AD > CD > CE > D > AC > AE > B^2 > AB > C$, whereas on the lead recovery was in the order of $D > B > A > E > BE > B^2 > D^2 > E^2 > C^2 > AE > AC > C$.

(4) Response surface plots showed that the recoveries of zinc and lead depended significantly on the interactions between factors.

(5) Under these conditions, the maximum recovery of zinc and lead were achieved about 94.5 and 77.8%, respectively.

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REFERENCES

[1] Abkhoshk E., Jorjani E., Al-Harahsheh M.S., Rashchi F., Naazeri M., Review of the Hydrometallurgical Processing of Non-sulfide Zinc Ores, *Hydrometallurgy*, **149**: 153-167 (2014).

[2] Dutra A.J.B., Paiva P.R.P., Tavares L.M., Alkaline Leaching of Zinc from Electric Arc Furnace Steel Dust, Miner Eng., **19**: 478–485 (2006).

[3] Santos F.M.F., Peina P.S., Porcaro A., Oliviera V.A., Silva C.A., Leão V.A., The Kinetics of Zinc Silicate Leaching in Sodium Hydroxide, *Hydrometallurgy*, **102**: 43–49 (2010).

[4] Rao Sh., Yang T., Zhang D., Liu W.F., Chen L., Hao Z., Xiao Q., Wen J.F., Leaching of Low Grade Zinc Oxide Ores in $NH_4Cl–NH_3$ Solutions with Nitrilotriacetic Acid as Complexing Agents, *Hydrometallurgy* ,**158**: 101–106 (2015).

[5] Larba R., Boukerche I., Alane N., Habbache N., Djerad S., Tifout L., Citric Acid as an Alternative Lixiviant for Zinc Oxide Dissolution, *Hydrometallurgy*, **134–135**: 117–123 (2013).

[6] Hursit M., Lacin O., Sarac H., Dissolution Kinetics of Smithsonite Ore as an Alternative Zinc Source with an Organic Leach Reagent, *J. Taiwan Inst Chem Eng.*, **40**: 6-12 (2009).

[7] Irannajad M., Meshkini M., Azadmehr A., Leaching of Zinc from Low Grade Oxide Ore Using Organic Acid, *Physicochem Probl Miner Process*., **49**: 547−555 (2013).

[8] Demir F., Lacin O., Donmez B., Leaching Kinetics of Calcined Magnesite in Citric Acid Solutions, *Ind Eng Chem Res.*, **45**: 1307-1311 (2006).

[9] Turan M.D., Altundoğan H.S., Tümen F., Recovery of Zinc and Lead from Zinc Plant Residue, *Hydrometallurgy*, **75**: 169-176 (2004).

[10] Behnajady B., Moghaddam J., Behnajady M.A., Rashchi F., Determination of the Optimum Conditions for the Leaching of Lead from Zinc Plant Residues in NaCl–H_2SO_4-$Ca(OH)_2$ Media by the Taguchi Method, *Ind. Eng. Chem. Res.*, **51**: 3887-3894 (2012).

[11] Zárate-Gutiérrez R., Lapidus G.T., Anglesite (PbSO4) Leaching in Citrate Solutions, *Hydrometallurgy*, **144-145**: 124-128 (2014).

[12] Feng Q., Wen S., Wang Y., Zhao W., Deng J., Investigation of Leaching Kinetics of Cerussite in Sodium Hydroxide Solutions, *Physicochem Probl. Miner Process*., **51**: 491−500 (2015).

[13] Azizi A., Seyed Ghasemi S.M., A Comparative Analysis of the Dissolution Kinetics of Lead from Low Grade Oxide ores in HCl, H_2SO_4, HNO_3 and Citric Acid Solutions, *Metall. Res. Technol.*, **114** (2017) 406. doi.org/10.1051/metal/2017014.

[14] Myers R.H., Montgomery D.C., Response Surface Methodology, New York, NY: John Wiley & Sons, Inc., (2002).

[15] Montgomery D.C., Design and Analysis of Experiments, 6th ed., John Wiley & Sons, Inc., New York, USA, 2005.

[16] Yousefi N., Pazouki M., Alikhani Hesari F., Alizadeh M., Statistical Evaluation of the Pertinent Parameters in Bio-Synthesis of Ag/MWf-CNT Composites Using Plackett-burman Design and Response Surface Methodology, *Iran. J. Chem. Chem. Eng. (IJCCE)*, **35**(2): 51-62 (2016).

[17] Zakeri A., Pazouki M., Vossoughi M., Use of Response Surface Methodology Analysis for Xanthan Biopolymer Production by Xanthomonas Campestris: Focus on Agitation Rate, Carbon Source, and Temperature, *Iran. J. Chem. Chem. Eng. (IJCCE)*, **36**(1): 173-183 (2017).