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A Statistical Method for Determining the Best Zinc Pregnant Solution for the Extraction by D2EHPA

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ABSTRACT

The application of D2EHPA in zinc solvent extraction has extensive background. To utilize more effectively, response surface methodology was used to optimize the concentration condition of zinc pregnant solution (ZPL) extracted by D2EHPA. In the current research, zinc, iron and manganese extraction along with separation factor of zinc-iron (Sf (Zn-Fe)) and zinc-manganese (Sf (Zn-Mn)) were considered as the response values. The optimal ZPL conditions extracted with 30% D2EHPA as the extraction solvent were as follows: Zn 21.96 g/L, Fe 382.57 ppm, Mn 1 g/L, Sf (Zn-Fe) 8.26 and Sf (Zn-Mn) 1529.82. In addition, it was found that the iron and manganese concentration were the most effective factors affecting the zinc and manganese extraction, respectively.

Keywords: D2EHPA; Response Surface Methodology; Pregnant Solution; Optimization

1. Introduction

The extraction of zinc sulfate with di-2-ethylhexyl phosphoric acid (D2EHPA) is a well-known route in zinc purification industry. According to the literatures, extraction of zinc increases from 10% to ca. 99% with increasing pH from 0.5 to 2.5 and increasing D2EHPA concentration from 5% to 40% (w/w) [1]. It is obvious that enhancement of extractant makes distribution coefficient increase; however, it is noteworthy that the high cost of the organic extractant limits the usage of D2EHPA to less than 30% (v/v or w/w) [2]; therefore, the best composition of D2EHPA in industrial zinc solvent extraction is 30% (v/v) dissolved in kerosene.

Mehdi Abad lead and Zinc mine located in Yazd, Iran with the fixed capacity of 200 M tons of sulfur and oxide ore is one of the greatest lead and zinc mines in the world. The investigations reveal that manganese and iron are the main and major impurities of Mehdi Abad ore, which consequently come to leach solution and associate with zinc ion. Therefore, evaluating the optimized concentration of impurities for solvent extraction process plays the significant role in the leaching and pre-concentration steps. These impurities have undesirable effect on the process. For instance, Mn^{2+} ions, oxidized anodically to MnO_4^- ions, depolarize the H^+ ions discharge and thus reduce the current efficiency for zinc deposition [3-7]. Furthermore the iron constitutes a severe impurity in zinc solution and must be removed before electrolysis [8]. Implementing iron (III) solvent extraction into the zinc roast-leach-electrowin flowsheet as a means of iron rejection has been under consideration for at least two decades [9].

Response surface methodology is used to reduce the number of assays necessary to optimize the process and to collect results more precise than those obtainable by traditional full factorial designs [10,11]. Accordingly, RSM has been increasingly employed to optimize solvent extraction process. However, there is little information that shows which concentration of ZPL can be optimally extracted by D2EHPA. Therefore, the optimization condition of ZPL in detail which is extracted optimally by 30% (v/v) D2EHPA is the aim of this report. In the present research, the best concentrations of iron, manganese and zinc concentration, which are significant factor in Mehdi Abad ore, were found. Furthermore, the interactions effects between ions and the most effective factors on extractions were investigated.

2. Experiment

2.1. Reagents

Analytical grade inorganic reagents used in the experiments have been illustrated in **Table 1**. The synthetic solutions were prepared with the chemicals at the target concentrations and are presented in **Table 2**. The extractant, D2EHPA, was provided from BDH in England. It was dissolved in the industrial kerosene from Tehran Refinery Company, Iran as the diluent. The metal ion concentrations in the solutions were analyzed by Perkin-Elmer AA300 model atomic absorption spectro-photometer.

2.2. Procedure of Extraction

The extraction experiments were carried out in mechanical agitated and thermostatic beakers. In each experiment, 50 mL of the solution containing various zinc, iron and manganese concentrations (see **Table 3**) and 50 mL of the extractant were agitated by a magnetic stirrer at a constant rate. The pH of the solution was adjusted to 2.5 by sulfuric acid and hydrogen hydroxide. After agitating the beakers for 10 min at equilibrium state, the organic phase was separated from the aqueous phase in a separator funnel. After separation, the concentrations of ions in the aqueous phase were analyzed by Perkin-Elmer AA300 model atomic absorption spectrophotometer. Concentration of metal ions calculation in the organic

Table 1. Inorganic reagents used in the experiments.

Solution/Application	Component	Supplier	Prepared Concentration
Aq. Feed	$MgSO_4 \cdot H_2O$	Fisher	See **Table 2**
Aq. Feed	$FeSO_4 \cdot 7H_2O$	Merck	See **Table 2**
Aq. Feed	$ZnSO_4 \cdot H_2O$	Merck	See **Table 2**
Aq. Feed	H_2O_2	Mojallali	3 cc per liter
pH adjusting	H_2SO_4	Mojallali	98%
pH adjusting	NaOH	Mojallali	36 %

Table 2. The coded values and corresponding actual values of the optimization parameters.

Factor	Name	Units	Type	Low Actual	High Actual
A	Zn	g/L	Numeric	15	60
B	Fe	ppm	Numeric	10	1000
C	Mn	g/L	Numeric	1	5

Table 3. The coded, experimental and predicted values for RSM design using D2EHPA as solvent.

	Factor 1	Factor 2	Factor 3	Resp. 1	Resp. 2	Resp. 3	Resp. 4	Resp. 5
Run	A: Zn g/L	B: Fe ppm	C: Mn g/L	%E Zn	%E Fe	%E Mn	Sf (Zn-Fe)	Sf (Zn-Mn)
1	38.8	150.25	2.20225	100	100	31.88784	0.258231	82874.33
2	13.1625	10.83	0.9145	100	100	78.13013	1.215394	3684.115
3	15.36	754.3	1.055	99.86784	100	64.52133	0.001002	415.5133
4	15	10	5	99.8432	98.6	61.98	9.041147	390.6007
5	23.765	155.4	0.959	99.91601	99.10553	38.18561	10.73688	1925.76
6	13.11	11.17	4.354	87.12433	99.99991	99.45361	6.06E-06	0.037175
7	40.65	45	2.946	92.61993	99.99978	66.05567	2.79E-05	6.449126
8	15.81	494.3	3.276	93.52309	99.98988	99.42643	0.001461	0.083297
9	44.65	561.9	0.6347	63.91937	99.61559	9.878683	0.006836	16.1617
10	44.65	561.9	0.6347	63.91937	99.61559	9.878683	0.006836	16.1617
11	24.07	750.1	4.921	81.79477	99.94267	17.57773	0.002577	21.06741
12	28.1	7.29	1.9926	87.16014	99.98601	75.27351	0.00095	2.229862
13	32.82	764.2	2.565	80.34735	99.91364	10.72125	0.003534	34.04499
14	15.02	733.8	0.921	99.9674	99.91823	55.23344	2.509152	2485.134
15	56.2	14.58	0.9963	93.58007	99.993	50.54702	0.00102	14.261
16	28.175	394.1	2.537	83.9929	99.92641	8.671659	0.003864	55.26286
17	13.1625	10.83	0.9145	100	100	100	ignored	ignored

phase was carried out according to the concentrations of ions in the aqueous phase.

2.3. Experimental Design of RSM

To determine the optimal combination of extraction variables for the extraction ions, response surface method (RSM) was used. **Table 2** shows the coded parameters and their levels, and **Table 3** illustrates the coded, experimental and predicted values. As seen in **Table 3**, three factors (*i.e.* concentrations of three ions) as the inputted data were used to model the extraction. The values for the extraction percent of zinc, iron, manganese (%E Zn, %E Fe and %E Mn), separation factor of zinc-iron (Sf (Zn-Fe)) and zinc-manganese (Sf (Zn-Mn)) in each trial were average of duplicates. Based on the experimental data, regression analysis was done and fitted into the quadratic model as shown in Equation (1).

$$Y = A_0 + \sum_{i=1}^{k} A_i X_i + \sum_{i=1}^{k} A_{ii} X_i^2 + \sum_{i=1}^{k=1} \sum_{j=i+1}^{k} Ai_j X_i X_j + e_i \quad (1)$$

where Y represents the response, X_i and X_j are variables, k is the number of independent variables (factors), A_0 is assigned as the constant coefficient, A_{ii} and A_{ij} are interaction coefficients of linear, quadratic and the second-order terms, respectively, and ei stands for the error. Design-Expert 7.0.1.0 (Trial version, Stat-Ease Inc., Minneanopolis, MN, USA) was used for the experimental design and regression analysis of the experimental data. The Student's t-test and Fischer's F-test were used to check the statistical significance of the regression coefficient, and determine the second-order model equation, respectively. The lack of fit, the coefficient of determination (R^2) and the F-test value obtained from the analysis of variance (ANOVA) were applied to evaluate the adequacy of the model.

3. Result and Discussion

If all the aforementioned variables are assumed to be measurable, the response surface will be expressed as Equation (2):

$$Y = f\left(X_1, X_2, X_3, \cdots, X_i\right) \quad (2)$$

where Y is candidate of responses and the X_i variables are called factors. To model using RSM, a total of 18 experimental runs are required. The results inserted to Design Expert software were used to fit a model to these results. The equations of models in terms of coded factors are obtained as Equations (3) to (5) for %E Zn, %E Mn, Sf (Zn-Fe) and Sf (Zn-Mn), respectively:

For %E Zn:

$$\begin{aligned} \%\text{E Zn} &= +81.43 - 12.09X_1 - 11.65X_2 + 6.14\,X_3 \\ &\quad - 8.97\,X_1X_2 + 12.83X_1X_3 - 3.66X_2X_3 \end{aligned} \quad (3)$$

The equation of model for iron extraction is not significant because p-value of model is less than 0.05. This is due to high extraction percent of iron (III) in any pH ranges, which reaches above 99%.

For %E Mn:

$$\begin{aligned} \%\text{E Mn} = &-19.31 - 27.09X_1 - 22.78X_2 - 58.09X_3 \\ &- 74.38X_1X_2 - 78.88X_1X_3 + 29.75X_2X_3 \\ &+ 94.90X_1^2 + 60.53X_2^2 - 43.60X_3^2 \end{aligned} \quad (4)$$

Selective extraction of A ion from B ion can be expressed by $\text{Sf}\left(\text{A-B}\right) = \text{D}_\text{A}/\text{D}_\text{B}$,
where $\text{D}_\text{A} = \left[\text{A}\right]_\text{organic} / \left[\text{B}\right]_\text{aqueous}$
and $\text{D}_\text{B} = \left[\text{B}\right]_\text{organic} / \left[\text{A}\right]_\text{aqueous}$. The equation of model for $\text{Sf}\left(\text{Zn-Fe}\right)$ is not presented in this study because it is not significant due to p-value less than 0.05. Nevertheless, $\text{Sf}\left(\text{Zn-Mn}\right)$ has been modeled using RSM as Equationn (5).

$$\begin{aligned} \text{Sf}\left(\text{Zn-Mn}\right) = &-560.69 - 1419.98X_1 \\ &- 387.08X_2 - 1014.53X_3 \end{aligned} \quad (5)$$

The result of analysis of variance (ANOVA) is illustrated in **Table 4-6**.

The results of this table reveal that the prediction models of the zinc and manganese extraction percent and separation factor of zinc-manganese are significant since the p-value is less than 0.05.

The result of **Table 4** indicated that the effect of ions concentration and their interactions on the zinc extraction are not significant. As observed in this table, iron concentration has the highest effect on zinc extraction. The reason for this effect is probably because of selective extraction of iron (III) ions (*i.e.*, among other species) by D2EHPA. **Table 5** illustrates the results of Mn extraction. The effect of all factors (variables) and their interactions except zinc concentration are significant on Mn extraction. As **Table 5**, manganese concentration has the highest effect on manganese extraction. In addition, **Table 6** displays that the results of $\text{Sf}\left(\text{Zn-Mn}\right)$, the zinc and manganese concentration are only significant factors. The high value of correlation coefficient (R^2) indicates that the model has been fitted very well. If this is a response surface design which is intended to be used for modeling the design space, then the R-squared values should be rather high (perhaps above 0.60) (Design Expert 7 Help). R^2 was found to be 0.904 for %E Zn, 0.991 for %E Mn and 0.627 for $\text{Sf}\left(\text{Zn-Mn}\right)$, as shown in **Figures 1** to **3**, which are acceptable statistically.

3.1. 3D Response Surface Plots

The 3D response surface plots simulated by Design-Expert software are graphical representations in order to understand the interaction effects of variables and the

Table 4. Analysis of variance (ANOVA) of developed models for zinc extraction.

Source	Sum of Squares	df	Mean Square	F-Value	p-value Prob > F	comment
Model	1841.69	6	306.95	11.04	0.0029	significant
A-Zn	79.98	1	79.98	2.88	0.1336	
B-Fe	151.85	1	151.85	5.46	0.052	
C-Mn	40.43	1	40.43	1.45	0.2669	
AB	38.9	1	38.9	1.4	0.2754	
AC	83.32	1	83.32	3	0.127	
BC	27.87	1	27.87	1	0.35	
Residual	194.54	7	27.79			
Lack of Fit	194.54	6	32.42			
Pure Error	0	1	0			
Cor Total	2036.23	13				

Table 5. Analysis of variance (ANOVA) of developed models for manganese extraction.

Source	Sum of Squares	df	Mean Square	F-Value	p-value Prob > F	
Model	14489.83	9	1609.981	50.42903	0.0009	significant
A-Zn	127.3896	1	127.3896	3.990193	0.1164	
B-Fe	357.9424	1	357.9424	11.21174	0.0286	significant
C-Mn	1330.366	1	1330.366	41.67074	0.0030	significant
AB	2234.237	1	2234.237	69.98246	0.0011	significant
AC	1478.275	1	1478.275	46.30365	0.0024	significant
BC	1176.359	1	1176.359	36.84678	0.0037	significant
A^2	2206.262	1	2206.262	69.1062	0.0011	significant
B^2	1087.321	1	1087.321	34.05789	0.0043	significant
C^2	2547.387	1	2547.387	79.79115	0.0009	significant
Residual	127.7027	4	31.92568			
Lack of Fit	127.7027	3	42.56757			
Pure Error	0	1	0			
Cor Total	14617.53	13				

Table 6. Analysis of variance (ANOVA) of developed models for separation factor of zinc and manganese.

Source	Sum of Squares	df	Mean Square	F-Value	p-value Prob > F	
Model	1.12E + 07	3	3.75E + 06	5.6	0.0162	significant
A-Zn	6.28E + 06	1	6.28E + 06	9.39	0.012	significant
B-Fe	7.73E + 05	1	7.73E + 05	1.15	0.3078	
C-Mn	7.40E + 06	1	7.40E + 06	11.06	0.0077	significant
Residual	6.69E + 06	10	6.69E + 05			
Lack of Fit	6.69E + 06	9	7.44E + 05			
Pure Error	0	1	0			
Cor Total	1.79E + 07	13				

relationship between the variables and responses. Three dimensional (3D) plots for the aforementioned responses were molded based on the model equations for zinc and manganese extraction and separation factor of zinc-manganese as Equations (3) to (5). These plots are shown in **Figures 4** to **6**. In these figures, two variables versus responses at the center level of third variable have constructed the plots.

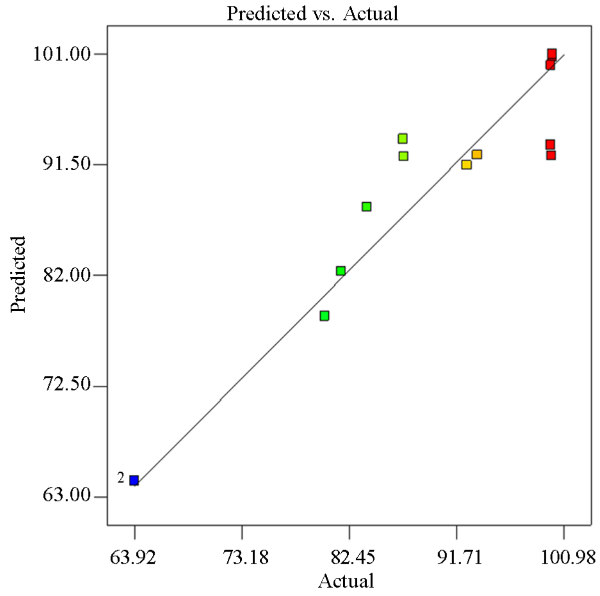

Figure 1. Relationship between predicted and actual (observed) values for zinc extraction.

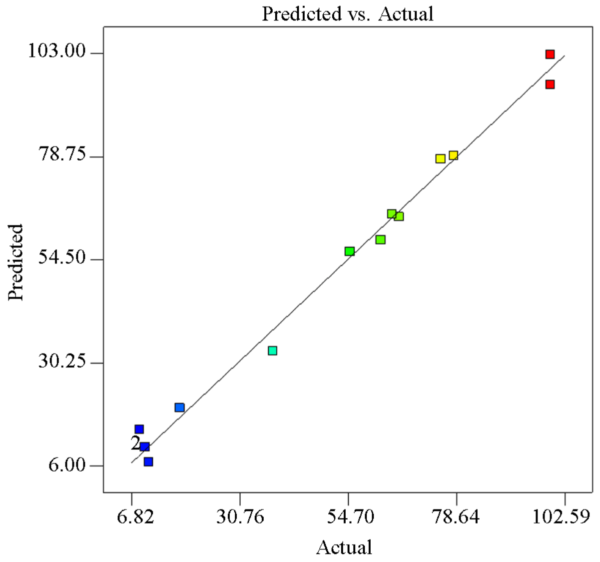

Figure 2. Relationship between predicted and actual (observed) values for manganese extraction

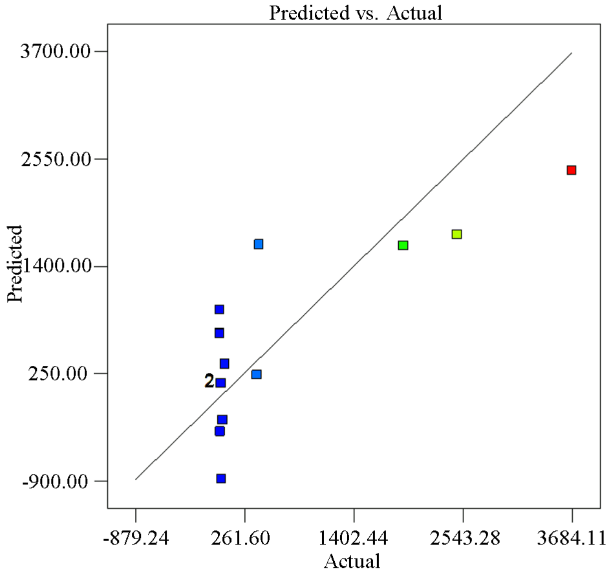

Figure 3. Relationship between predicted and actual (observed) values for separation factor of zinc and manganese.

Figure 4(a) shows the effect of manganese and iron concentration on zinc extraction at 40˚C and pH of 2.5. It expresses that increasing iron concentration in the aqueous feed decreases zinc extraction and enhancement of manganese concentration increases zinc ions extraction. **Figure 4(b)** demonstrates that at high levels of zinc and manganese concentrations, the zinc extraction decreases. Furthermore, in **Figure 4(c)**, enhancement of zinc and iron ions in the aqueous phase reduces zinc extraction. It is noteworthy that high concentration of ions in aqueous phase diminishes the capability of D2EHPA, which is related to specific capacity of extractant; moreover, **Figures 4(b)** and **(c)** justify this note.

Figure 5(a) shows considerable effect of iron concentration and invariable effect of manganese concentration on the manganese extraction. **Figure 5(b)** illustrates that enhancement of manganese ions in the aqueous phase increases its extraction. In addition, this figure shows that zinc ions have approximately invariable effect on manganese extraction. In **Figure 5(c)**, the effect of zinc and iron concentrations on manganese extraction is relative. As seen in this figure, the lowest manganese extraction has occurred at the middle levels of zinc and iron concentrations. Finally, all plots of **Figure 6** shows that higher amount of ions in the aqueous phase decreases separation factor of zinc-manganese.

3.2. Optimization by RSM

The aim of optimization is to have ZPL with the lowest impurities. Therefore, the highest zinc extraction, the lowest iron and manganese extraction and the highest values of separation factors were considered for optimizing by RSM. This optimization was carried out by DX7 software and the results of the process optimization with respect to the aforementioned aim were obtained as illustrated in **Table 7**. As seen in this table, the zinc, iron and manganese extraction percent at pH of 2 and temperature of 40˚C reached 93.72%, 99.20% and 11.18%, respectively. At this condition, it was found that Zn 21.22 g/L, Fe 376.08 ppm and Mn 1.00 g/L are extracted by 30% (v/v) D2EHPA dissolved in kerosene.

This result reveals that to extract more effectively by 30% D2EHPA, the best ZPL should be as the optimum condition of ions concentration. The desirability of this

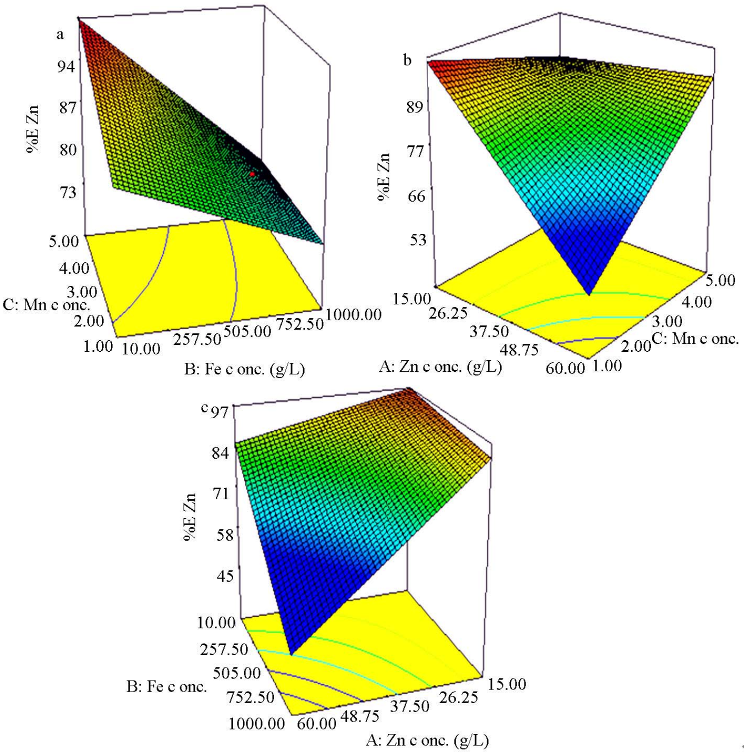

Figure 4. 3D response surface plots showing effect of two variables (factors) on zinc extraction at the center level of other variable. (a) Mn and Fe concentration (g/L and ppm, respectively). (b) Zn and Mn concentration (g/L). (c) Zn and Fe concentration (g/L and ppm, respectively).

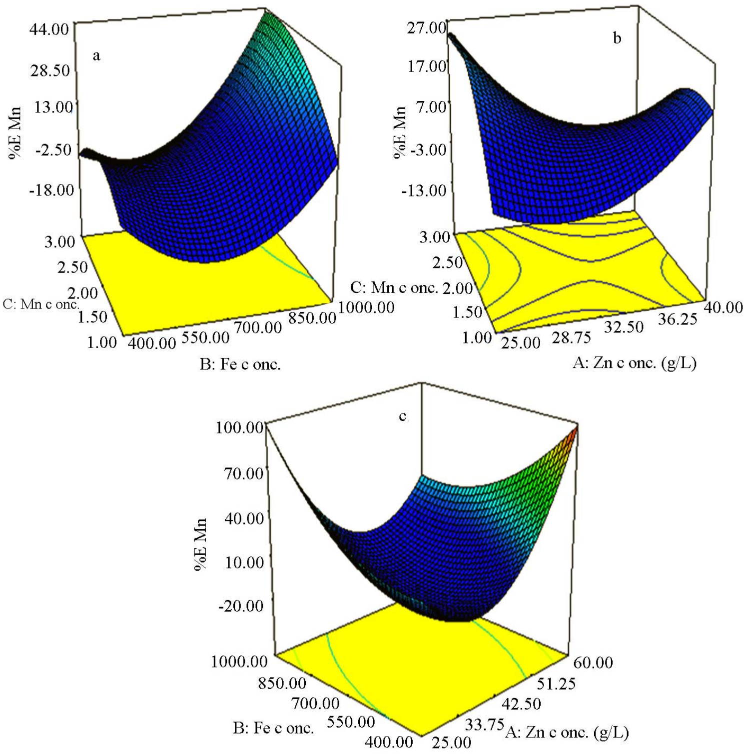

Figure 5. 3D response surface plots showing effect of two variables (factors) on manganese extraction at the center level of other variable. (a) Mn and Fe concentration (g/L and ppm, respectively). (b) Zn and Mn concentration (g/L). (c) Zn and Fe concentration (g/L and ppm, respectively).

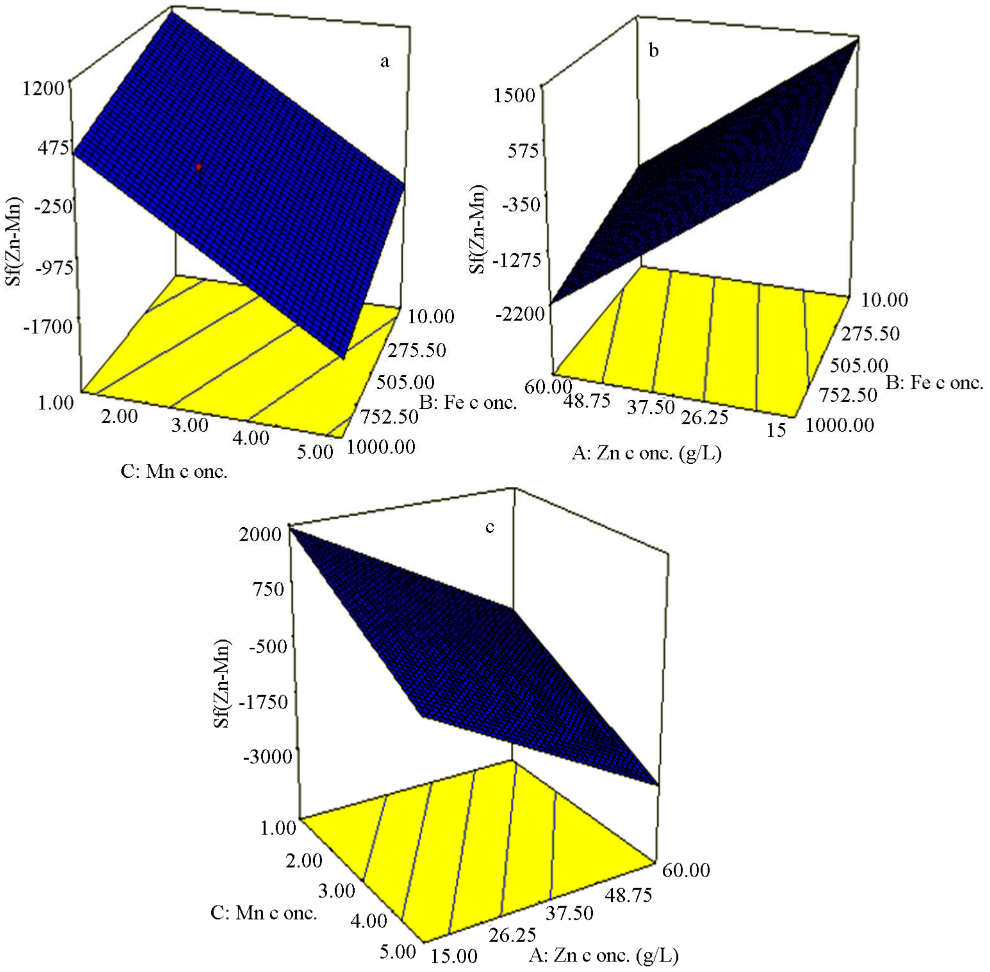

Figure 6. 3D response surface plots showing effect of two variables (factors) on separation factor of zinc-manganese at the center level of other variable. (a) Mn and Fe concentration (g/L and ppm, respectively). (b) Zn and Fe concentration (g/L and ppm, respectively) (c) Zn and Mn concentration (g/L).

Table 7. Results of process optimization and optimum levels of variable.

Name	Goal	Zn (g/L)	Fe (ppm)	Mn (g/L)	%E Zn	%E Fe	%E Mn	Sf (Zn-Fe)	Sf (Zn-Mn)
Zn	is in range	21.22	376.08	1	93.72	99.20	11.18	8.10	1582.39
Fe	is in range								
Mn	is in range								
E Zn	maximize								
E Fe	minimize								
E Mn	minimize								
Sf (Zn-Fe)	maximize								
Sf (Zn-Mn)	maximize								

optimum condition achieved 0.67, which is statistically acceptable. **Figure 7** shows the desirability of the optimum condition. As seen in this figure, at the optimum condition of iron concentration factor and the lowest levels of zinc and manganese concentration, the desirability of the model is high.

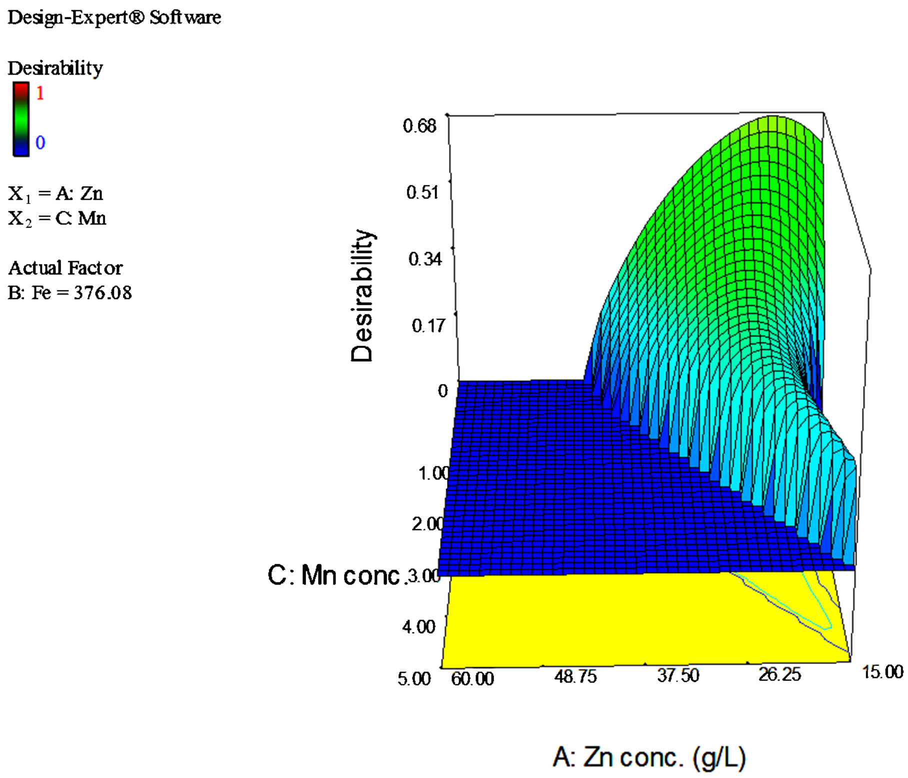

Figure 7. Response surface plot showing effect of ions concentration on desirability of optimum condition.

4. Conclusions

1) At the optimum condition, the zinc, iron and manganese extraction percent at pH of 2 and temperature of 40˚C reached 93.72%, 99.20% and 11.18%, respectively.

As a result, the best aqueous feed for extraction by 30%

2) As ANOVA tables indicate, iron extraction and $\mathrm{Sf}\left(\text{Zn-Fe}\right)$ are not significant responses to model.

3) Iron and manganese concentration had the highest effect on the zinc and manganese extraction, respectively.

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