Response Surface Methodology for the Evaluation of Magnetite Partitioning Behavior in Polyethylene Glycol-Based Aqueous Biphasic System

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Abstract

Response surface methodology in the framework of central composite design has successfully applied to polyethylene glycol (PEG)-based aqueous two-phase system in order to evaluate its efficiency in extracting Fe from iron ores with respect to PEG molecular weight, PEG concentration and salt concentration factors. Furthermore, ANOVA and multiple regression analysis have provided a second-order polynomial equation that is highly capable of predicting the experimental results. The PEG molecular weight and weight percent of the salt in the feed had a major and minor effects on the iron ion partition coefficient, respectively.

Keywords Iron ion · Aqueous two-phase system · Response surface methodology · Polyethylene glycol · Zinc sulfate

1 Introduction

Iron is one of the most precious metals that can provide industrial and civil development due to its wide range of applications. For example, it can be employed in constructing and manufacture of machine parts and vehicles (Mazumdar 2001), building structures (Emsley 2011) and ship hulls (Townsin 2003). Also, iron is an imperative material for appliance and surgical equipment (Cornell and Schwertmann 2003). Furthermore, when it is used in its stainless formulation, it can be applied in electrical (Callister and Rethwisch 2011) and steel (Emsley 2011) industries. That is why iron production has been accelerated.

One of the solutions of responding to the high level of worldwide demand for iron is its extraction from mines that are rich in it. In this respect, Iran is a great supplier, which has a large sector (12th place) of the world iron's reservoirs (http://www.iraninternationalmagazine.com/issue_74/texts_p/iran's%20mining%20sector%20statistics.htm). Specifically, Central Iran, mainly Bafq District, is so rich in iron (Sadeghi et al. 2013), and Chadormalu and Golgohar iron ore suppliers are the largest iron ore mines of Iran, which provide more than 80% of iron ore (Walter and Forciniti 1994).

One of these alternative treatments is using aqueous two-phase systems (ATPSs). ATPSs are liquid–liquid extraction systems that have been proposed for metal separation. ATPSs were first introduced in 1896 by Beijerinck, who reported that turbid solutions would form if aqueous gelatin and agar solutions or aqueous gelatin and starch solutions be mixed (Albertsson 1986). The unique feature of such system is that both phases are commonly consisted of over 80% water, but they are immiscible and their properties differ, significantly (Madeira et al. 2011, 2012, 2014). Consequently, many researchers have attempted to investigate metal partition coefficient and extraction yield of ATPSs (Bulgariu and Bulgariu 2011, 2013; Bulgariu et al. 2007; Chen et al. 2009; da

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Rocha Patrício et al. 2011; de Lemos et al. 2013; Smolik et al. 2007).

Though ATPSs have demonstrated favorable characteristics, most industries and commercial applications have neglected its application. The principal underlying reason can regress back to our limited knowledge about the mechanism of metal and macromolecule equilibrium partitioning phenomenon. It, in turn, has restricted theoretical prediction of experimental trends. So that industries are not capable of pre-evaluation of the relevant industrial parameters and adjusting their production streams in accordance to this technique. However, this theoretical gap might be filled with appropriate theoretical modeling investigations.

Response surface methodology (RSM) has been used as a mathematical tool by many researchers to optimize and analyze effectiveness of several variables on partitioning of biomolecules in ATPSs (Alcântara et al. 2011; Aydoğan et al. 2011; Dembczyński et al. 2013; Silva et al. 2009), and RSM is a commonly utilized approach for generation of approximate models founded on experimental observations (El-Taweel and Gouda 2011). Also, Hill and Hunter (Hill and Hunter 1966) and Bezerra et al. (Bezerra et al. 2008) have published reviews about RSM and its application for optimization of analytical methods, respectively.

Though theoretical studies have been attempting to realize partitioning mechanisms of biomolecules in ATPS procedure, the findings are still insufficient and further investigations are essential. Moreover, to the best of our knowledge, no study has undertaken analysis and understanding of metal ions partitioning in ATPS process by the means of RSM. Therefore, this work aims to study partitioning of iron ions using an ATPS formed by a polyethylene glycol (PEG) (2000, 4000 and 6000 g mol⁻¹), zinc sulfate and water, at 298 K. Further, the impact of different parameters, such as molecular weight (MW), salt concentration and polymer concentration, is illustrated by RSM.

2 Experiments

2.1 Materials

Several PEG materials with average molecular weights of 2000, 4000 and 6000 g mol⁻¹ and zinc sulfate (anhydrous GR > 99% for analysis) were obtained from Merck (Darmstadt, Germany). Hydrochloric acid (95–97% HCl; GR > 95.0% for analysis), Na₂CO₃ and K₂CO₃ were retrieved from Rankem (New Delhi, India), and potassium thiocyanate was purchased from Sigma-Aldrich, Germany. All throughout the experiments, deionized water was used for solution preparation. The other materials were of analytical grades.

2.2 Apparatus and Procedure

The effects of several experimental parameters on partition behavior of magnetite in ATPSs were investigated by first preparing to leachate iron from iron concentrate. In the next step, two aqueous phase systems of PEG and zinc sulfate salt in presence of Fe ion and potassium thiocyanate (da Rocha Patrício et al. 2011) were prepared as the extracting agents, according to the experimental design. It is noteworthy that in our previous work (Shahrokhi et al. 2017) we determined the two-phase region of this ATPS, in addition to the ranges of PEG and salt concentrations in that two-phase region. Then, Fe ion partition coefficient was calculated and the obtained data were implemented in RSM software to extract a RSM model. Finally, through the model, the relationships between input and output variables were identified. Figure 1 summarizes the flow diagram of the applied procedure, in this study.

2.2.1 Leachate Iron from the Iron Concentrate

Magnetite concentrate sample of 0.25 g was weighted and inserted in a platinum crucible. Then, sodium potassium carbonate was added as a mixture fusion and the mixture was fused in a muffle furnace, at 950 °C for about half an hour. After taking it out of the furnace and cooling it, the crucible was inserted in a glass beaker. Then, HCl 1:1 was added to the crucible. When all the sample was dissolved in acid, the crucible was removed and diluted in a 250-mL volumetric flask. Flame atomic absorption spectrometer (FAAS) (Australia, VARIAN AA100) with 248.3 nm wavelength, 1.5 mg L⁻¹ sensitivity check and air-acetylene flame flux of 1.5 L min⁻¹ was employed to measure concentration of main metals in the obtained solution, which resulted in a 0.2 absorption peak, at 248.3 nm. Table 1 reports concentration of the main metals in the final solution.

2.2.2 Preparation of the Two-Phase System

A solution containing 50% w/w stock PEG solution, 30% w/w zinc sulfate and potassium thiocyanate, as the extractor agent (da Rocha Patrício et al. 2011), was prepared. Then, iron ion solution of 30 mg L⁻¹ concentration was poured in a graduated centrifuge tube and centrifuged (Thermo Scientific, Heraeus Megafuge 11R).

2.2.3 Experimental and Optimization of Iron Extraction from Ore Leachate

In this study, Design Expert 7 (Stat-Ease Inc., Minneapolis, MN, USA) software was employed to carry out regression

Fig. 1 Flow diagram of the procedure applied to analysis of iron partitioning **Table 1** Component concentration on ore sample

Component	Fe%	FeO%	Fe ₂ O ₃ %	Si ₂ O%	Al ₂ O ₃ %	MgO%	S%	P%	L.o. ^a
Sample	67.47	22.45	71.52	1.51	0.77	5.18	0.10	0.029	1.35

^aL.o.I loss on ignition

and graphical analysis of the generated data. Table 2 presents the factors and levels employed in this approach. Furthermore, one of the major responses, i.e., partition coefficient, was selected as the response. Then, in the second stage, RSM was used to investigate the impacts of three major factors including polymer concentration, salt concentration and polymer MW on the response. Based on

this method, a quadratic model (Eq. 1) was utilized to describe each variable response:

$$Y = \beta_0 + \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^k \beta_{ii} x_i^2 + \sum_{i=1}^{k-1} \sum_{j=2}^k \beta_{ij} x_i x_j + \varepsilon \quad (1)$$

In Eq. 1, Y is the predicted response (i.e., Fe ion partition coefficient); x_i and x_j are input variables affecting the

Table 2 Levels and factors regarding two-level fractional factorial study of iron ion partitioning

Factor	Range and level		
	– 1	0	+ 1
PEG MW	2000	4000	6000
Salt concentration	15	20	25
PEG concentration	25	32.5	40

response (the factors in Table 2); and k is the partition coefficient. As an outcome, squared effects are represented by x_i^2 , x_j^2 to x_k^2 and mutual interactions between the case effects are concerned with $x_i x_j$, $x_i x_k$ and $x_j x_k$ -containing terms. Also, β_0 stands for the intercept, while β_i ($i = 1, 2, \dots, k$), β_{ii} ($i = 1, 2, \dots, k$) and β_{ij} ($i = 1, 2, \dots, k; j = 1, 2, \dots, k$) are the linear, squared and interaction effects coefficients, respectively. ε refers to random error. (Aksu and Gönen 2006; Göksungur et al. 2005).

It should be noted that all experimental data were analyzed by analysis of variance (ANOVA) as embedded in Design Expert Software. Within this analysis tool, fitting quality of the model was confirmed through determining root-mean-squared deviation (R^2). Moreover, the final subset of variables was chosen on the basis of the respective p value at 95% level of confidence.

The related response, i.e., partition coefficient K , can be calculated as a function of equilibrium Fe ion concentration (the solute) in the two phases, following Eq. 2:

$$K = \frac{[\text{Fe concentration}]_{\text{top}}}{[\text{Fe concentration}]_{\text{bottom}}} \quad (2)$$

3 Results and Discussion

3.1 Fitting the Model and Statistical Analysis

ANOVA analysis gave significant terms of the model for each response while their significances were evaluated according to the calculated probability levels for them being below 5%. Also, regression analysis (R^2 and adjusted- R^2 determination coefficients) approved correlation of the results and their adequacies. The results of statistical analysis of the quadratic model (ANOVA) are summarized in Table 3. These results demonstrate statistical significance of this regression ($F = 34.65$, $p < 0.0001$). Also, the obtained determination fitting value of R^2 ($= 0.9303$) implied that the model is successful in explaining 93.03% of the experimental variables. In addition, adjusted R^2 value of 0.9054 declared high significance of the generated model.

As the model was statistically verified, the regression equation was employed to partition Fe ion as a function of PEG and ZnSO_4 concentrations and also PEG MW. Fitting of the experimental data and application of multiple regression analysis provided a second-order full polynomial equation, in the framework of CCD design. This acquired equation, which shows an empirical relationship between iron ion partition (Y) and the independent variables, as shown in Eq. 3:

$$K = + 1.46665 - 0.015300X_1 - 6.06000E - 003X_2 - 3.35013E - 004X_3 + 2.32500E - 006X_1 * X_3 + 0.000000180 X_3^2 \quad (3)$$

Here, as aforementioned, K is the percentage of Fe ion partition coefficient, i.e., the response. In addition, X_1 , X_2 and X_3 are polymer concentration, salt concentration and PEG MW values, respectively.

It can be observed that Fe partition coefficient would decrease upon MW increase. Meantime, changes in PEG concentration would result in increased volume of the upper phase with elevated PEG concentration. This volume change has negative impact on Fe ion partitioning since K equals to ratio of iron ion concentration in the upper phase to the lower phase concentration. As an outcome, it will decrease if PEG concentration increases. On the other hand, it was inferred from the results that ZnSO_4 concentration poses the smallest impact on Fe ion partitioning, while higher ZnSO_4 weight percent reduces Fe ion partition coefficient.

Findings revealed that increasing PEG MW would decrease Fe partition. The reason is attributed to more hydrophobicity of the polymer-rich phase, when PEG MW is higher. Intensified hydrophobicity can facilitate entrance of the complexes to the top phase. It means that if higher MW PEG polymers be used in the ATPS process, then improved partition of Fe ion (magnetite partition) can be guaranteed. This finding is also supported by other researches on ATPS application to gold (Zheng et al. 2015) and gallium (Chen et al. 2009) extraction.

Figures 2 and 3 display contour and 3D surface plots to elucidate the main and interactive effects of the independent variables on the dependent variable.

3.2 Optimum Conditions and Model Verification

Table 4 reports the optimum conditions for Fe ions partition, which are determined based on RSM.

Figure 4 shows Fe ion partition coefficient. In this figure, maximum Fe ion partition is marked with a triangle sign.

Table 3 Analysis of variance (ANOVA) for response surface quadratic model

Source of variation	SS	df	Mean square	F value	p value
Model	0.31000	5	0.061	37.36	< 0.0001
PEG MW	0.02000	1	0.020	12.37	0.0034
PEG concentration	0.00918	1	0.00918	5.61	0.0328
Salt concentration	0.22000	1	0.22	136.87	< 0.0001
PEG concentration * MW	0.00973	1	0.00973	5.94	0.0287
[MW] ²	0.04300	1	0.043	26.01	0.0002
Residual	0.02300	14	0.00163		
Lack of feed	0.01600	9	0.00181	1.39	0.3763
R^2	0.9303				
R^2_{adj}	0.90540				

%CV 17.92

Fig. 2 Contour plot of iron ion partition: **a** polymer concentration and MW; **b** salt concentration and polymer MW; and **c** salt concentration and polymer concentration

Fig. 3 Response surface plots for the effect of **a** polymer concentration and MW; **b** salt concentration and polymer MW; and **c** salt concentration and polymer concentration

Table 4 Optimum conditions for Fe partition

Polymer concentration	Salt concentration	MW	Desirability
26.50	16.00	2000	1

Fig. 4 Maximum partition coefficient of Fe ion in ATPS

4 Conclusion

Extensive use of iron in technology and industry has made it a very important metal in survival and improvement of modern life quality. Therefore, promotion of its extraction from iron ores is an essential objective. In this respect, response surface methodology was used to collect maximum experimental data for minimum number of experiments and evaluate effectiveness of different variables on separation of Fe through ATPS approach. In order to

prepare the separation phases, zinc sulfate and polyethylene glycol were used. The modeling results verified that the applied ATPS method has the potency of extracting Fe ion and identified the impacts of PEG MW, salt concentration and PEG concentration on Fe ion partition among the two phases. According to the results, PEG MW can affect iron partitioning, noticeably, while its optimum value is 2000 g/mol. Meanwhile, it was revealed that higher PEG concentration poses unfavorable impacts on Fe partition.

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