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Evaluation of the Effective Parameters on Fe^{3+} Precipitation in the Bioleaching Process

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Abstract

Ferric ion is a strength oxidant and its precipitation is an undesired phenomenon in the bioleaching process. Previous studies showed that it considerably occurs in bioleaching operations even at optimum conditions. Although there have been many reports on the Fe^{3+} precipitation, no study has made a mathematical modeling of the affecting parameters. The aim of the present work is the development of a model that represents the impact of some parameters on the Fe3+ precipitation.The polynomial model was developed. The resulted model presents the positive effect of all parameters on minimization of Fe^{3+} precipitation; particularly, the effects of pH and iron concentration, which are more significant. The validation of model was confirmed using F-test($P<0.001$) and the coefficient of determination($R^2=96.84\%$). The optimum values of parameters were determinedas:pH=1.5,Temperature=35.5°C, iron concentration=20g/l,pulp density=15%(w/v).The non-linear nature of the modeled response for Fe^{3+} precipitation was explained by a second-order polynomial equation. Also it was observed that by increasing the considered parameters, precipitation rate was increased. The severity of the effects of the parameters at the studied range was as follows: pH and iron concentration> temperature> pulp density.

Keywords: *Uranium, Bioleaching, Ferric ion, Precipitation, Acidithibacillus ferrooxidans.*

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Introduction

In the first place, with the advancement of the industrialized world, metal consumption is rapidly increasing, second, the world wide reserves of high grade ores are close to depletion; yet, there exists a large reserve of metals in low and lean grade ores and other secondary sources [1]. Metal recovery which is deprived from low and lean grade ores using conventional techniques such as pyrometallurgy, etc. require high energy and capital inputs, which often, as we see in the world, result in the secondary environmental pollution. One of the best techniques which can be used is to utilize more efficient technologies such as biohydrometallurgy to recover metals [2]. As the development of bioleaching technology, and describe quantitatively, the processes underlying bioleaching have made great breakthroughs[3].

There are two major mechanisms involved in microbial metal solubilization of minerals. One is a direct mechanism that involves the physical contact of the organism with the insoluble mineral, where microorganisms oxidize the metal obtaining electrons directly from the reduced minerals. The second one, indirect mechanism, involves the ferric-ferrous cycle [4]. The oxidation of reduced metals is mediated by the ferric ion and this is formed by microbial oxidation of ferrous ion present in the system. Ferric ion acts as an oxidant and oxidizes metal, and then it is reduced to ferrous ion which, in turn, can be microbially oxidized. The three key reactions are:

- Gas (O_2 and CO_2) absorption from the gas phase into the liquid phase:

$$O_2(g) \rightarrow O_2(aq) \quad (1)$$

- Microbial oxidation of ferrous iron and/or sulphur species:

$$2Fe^{2+} + 0.5O_2 + 2H^+ \rightarrow Fe^{3+} + H_2O \quad (2)$$

$$S^0 + 1.5O_2 + 2H^+ \rightarrow H_2SO_4 \quad (3)$$

- Oxidative dissolution of the mineral [5]:

$$Men^+ + mFe^{3+} \rightarrow Me^{(n+m)+} + mFe^{2+} \quad (4)$$

The rate of the bacterial oxidation of ferrous ion is 10^6 times faster than the corresponding rate of chemical oxidation [6]. There are some undesirable reactions in this process, that result in ferric ion precipitation. Ferric ion is a strong oxidizer. If the ferric ion is removed from solution the system ability will be reduced. Several studies have been conducted in order to determine the manner and importance of ferric ion precipitation. Sandy Jones *et al.* investigated the structure and composition of the jarosites formed in the synthetic solution [7]. Their studies have shown that the K^+ facilitates the formation of jarosites more than NH_4^+. Botane et al. used a population balance approach for the studying rate of precipitation [8]. Their research was to measure and model the precipitation occurring during the bioleaching. Leahy and Schwarz focused on the inclusion of a basic model of jarosite precipitation with the associated removal of ferric ions from solution in the column bioleaching [9]. They showed that a higher inlet pH resulted in a higher colmn point, at which jarosite precipitation begins.

This has been concluded in the previous studies that some parameters play a role in the rate of oxidation of ferrous ion by *Acidithiobacillus ferrooxidans (A.ferrooxidans).*These factors include ferrous/ferric iron concentration, cell concentration, pH, temperature, and reactor type. pH and temperature have significant effects on the oxidation kinetics of iron by A.*ferrooxidans* [10]. The physicochemical parameters identified as significantly influencing the amount of ferric ion precipitation are pH, temperature and initial ferrous iron concentration [10]. In this study, the effects of some effective parameters were studied on the ferric ion precipitation during the bioleaching process.

Experimental

Ore

The ore sample was achieved from Khoshoumi mine that located in Yazd province, Iran. A representative sample was prepared by coning and quartering for chemical analysis.The composion of ore was as shown in Table 1.

Table 1. The composition of ore.

U(ppm)	V(ppm)	Mo(ppm)	Th(ppm)	Fe_2O_3(%)	SiO_2(%)
1315	150	102	22	4.63	54.691

Bacteria

A native strain of *A.ferrooxidans* was used in this study .*A.ferrooxidans* culture was maintained on modified culture medium. The composition of the culture medium was as shown in Table 2 [11].

Table 2. The composition of culture medium.

Components	**Concentration(g/l)**
Ammonium Sulfate[$(NH_4)_2SO_4$]	2
Di-Potassium Hydrogen Phosphate[K_2HPO_4]	0.5
Magnesiumchloride hexahydrate[$MgCl_2.6H_2O$]	0.5
Potassium chloride[KCl]	0.1
Calcium Nitrate Tetrahydrate[$Ca(NO_3)_2.4H_2O$]	0.01
Iron(II) Sulfate Heptahydrate[$FeSO_4.7H_2O$]	Variable

The cells were harvested from the exponential phase of growth. Cell growth was monitored through cell count which was determined according to ASTMD 4455-85. The enriched culture of *A.ferrooxidans* was subjected to a three-time adaptation on 5% (w/v) ore at

35˚C temperature and with a pH of 2.0 in the incubator shaker then the adapted cultures were used for bioleaching. This adapted culture was used as the inoculum to check leach ability.

Method

The bioleaching of uranium was carried out in 500 ml Erlenmeyer flasks containing 200 ml of leaching solution was inoculated with 10%(v/v) of enriched adapted culture with about 2×10^8 cells/ml. The aeration of the pulp in the flasks was achieved by agitation on a rotary shaker at a frequency of 150 rpm in order to prevent the solids from settling out of the pulp. The temperature of the rotary incubator shaker and the pH of each Erlenmeyer flasks were kept at the temperature and pH designed by Minitab® software for each run and it was monitored periodically and adjusted to the initial pH, till the pH got stabilized. 10N H_2SO_4 and 10N NaOH were used for the adjustment of pH. The decrease in the medium volume due to evaporation was compensated by adding distilled water. Total contents of each flask were filtered through Whatman No.1 filter paper. The filtrate was used for the analysis of soluble uranium, ferrous and ferric iron and ferric iron precipitation.

Optimization strategy

There are several factors such as pH, temperature, pulp density of ore and iron concentration which may affect the extraction process. In order to find the various conditions of ferric ion precipitation in bioleaching of uranium from ore samples and also to investigate the probable interaction between variables, the response surface methodology (RSM), based on rotatable face center central composite design (FCCD), was used. The design was made up of four factors at 5 levels with 8 axial points. In order to obtain an estimation of the experimental error, 5 replica at the center point were applied. The design was rotatable; this means that the design had points which were equidistant from the center. The variables and levels were as shown in Table 3.

This procedure leads to 31 experiments, where the experimental response data were analyzed by a regression procedure based on the RSM.

Table 3. Experimental variables and levels of the FCCD.

Factor	Level		
	Low	Center	High
pH	1.5	2	2.5
Temperature(ºC)	30	35	40
Iron Concentration(g/L)	0	10	20
pulp density(g/L)	0	7.5	15

The model that can be fitted to a composite design is an empirical function, determined from the statistical correlation suitability of the observed responses and the experimental factors. For this purpose, a second-order polynomial model equation is usually used [12]:

$$Y = a_0 + a_1x_1 + a_2x_2 + a_3x_3 + a_4x_4 + a_1\ x_1^2 + a_2\ x_2^2 + a_3\ x_3^2 + a_4\ x_4^2 + a_1\ x_1x_2 + a_1\ x_1x_3 + a_1\ x_1x_4 + a_2\ x_2x_3 + a_2\ x_2x_4 + a_3\ x_3x_4 \quad (5)$$

The Y is the predicted response. Here, response is the amount of ferric ion precipitation.

X_1, X_2, X_3 and X_4 are the independent variables or the experimental factors. The linear coefficients a_1–a_4 express the linear effect of each variable; the a11, a_{22}, a_{33} and a_{44} coefficients express the quadratic effects; a_{12}–a_{14}, a_{23}–a_{24} and a_{34}, coefficients express interactive effects between the variables and a0 is a constant corresponding to the central point of experimental variables. The statistical design, data analysis and various plots were obtained using Minitab® statistical software. This methodology, as a whole, proved to be quite adequate for the design and optimization of the reaction, and it helped to explain the importance of the factors, their interactions, and optimum values. Table 4 is the design table showing the randomized run order of the experiment, and the uncoded values of the different variables in the experimental design for the determination of the modeled response (Eq. (5)).

Table 4. Central Composite design of four independent variables.

Number	pH	Temperature(^{o}C)	Iron Concentration(g/L)	Pulp density(w/v%)
1	2.25	37.5	15	3.75
2	1.75	32.5	15	11.25
3	2.25	32.5	5	3.75
4	1.75	32.5	15	3.75
5	1.75	32.5	5	11.25
6	1.75	37.5	15	11.25
7	2.25	32.5	15	11.25
8	2.25	32.5	15	3.75
9	2.00	35.0	10	7.50
10	1.75	37.5	15	3.75
11	2.00	35.0	10	15.00
12	2.00	35.0	10	7.50
13	2.00	35.0	10	7.50
14	2.00	35.0	10	7.50
15	2.25	37.5	15	11.25
16	2.00	35.0	10	7.50
17	2.00	30.0	10	7.50
18	2.00	35.0	10	0.00
19	2.25	37.5	5	3.75
20	2.00	40.0	10	7.50
21	2.00	35.0	10	7.50
22	2.00	35.0	20	7.50
23	2.50	35.0	10	7.50
24	1.75	37.5	5	11.25
25	2.00	35.0	0	7.50
26	2.00	35.0	10	7.50
27	1.50	35.0	10	7.50
28	2.25	37.5	5	11.25
29	2.25	32.5	5	11.25
30	1.75	37.5	5	3.75
31	1.75	32.5	5	3.75

Results and discussion

In order to obtain optimum factor, the effects of different parameters such as pH, temperature, pulp density of ore and iron concentration were analyzed (Table 5). Response surface methodology including face-center central composite approach was utilized to find the optimum values of effective variables involved in the system.

In Table 5 the P values show that the factors affect the response in the following order: pH and iron concentration>Temperature>PD.

Table 5. Estimated regression coefficients for quadratic response (Eq.(5)).

Term	**coefficient**	**Standard Error coefficient**	**T**	**P**
Constant	798.929	66.63	11.991	0.000
Ph	559.833	35.98	15.558	0.000
Temp	141.65	35.98	3.937	0.001
[$FeSO_4.7H_2O$]	372.625	35.98	10.356	0.000
PD	102.583	35.98	2.851	0.012
pH×pH	43.691	32.96	1.325	0.204
Temp×Temp	106.028	32.96	3.216	0.005
[$FeSO_4.7H_2O$]×[$FeSO_4.7H_2O$]	-29.559	32.96	-0.897	0.383
PD×PD	-71.997	32.96	-2.184	0.044
Temp×pH	141.125	44.07	3.202	0.006
pH×[$FeSO_4.7H_2O$]	407.875	44.07	9.255	0.000
pH×PD	39.500	44.07	0.896	0.383
Temp×[$FeSO_4.7H_2O$]	50.562	44.07	1.147	0.268
Temp×PD	3.438	44.07	0.078	0.939
[$FeSO_4.7H_2O$]×PD	-0.562	44.07	-0.013	0.99

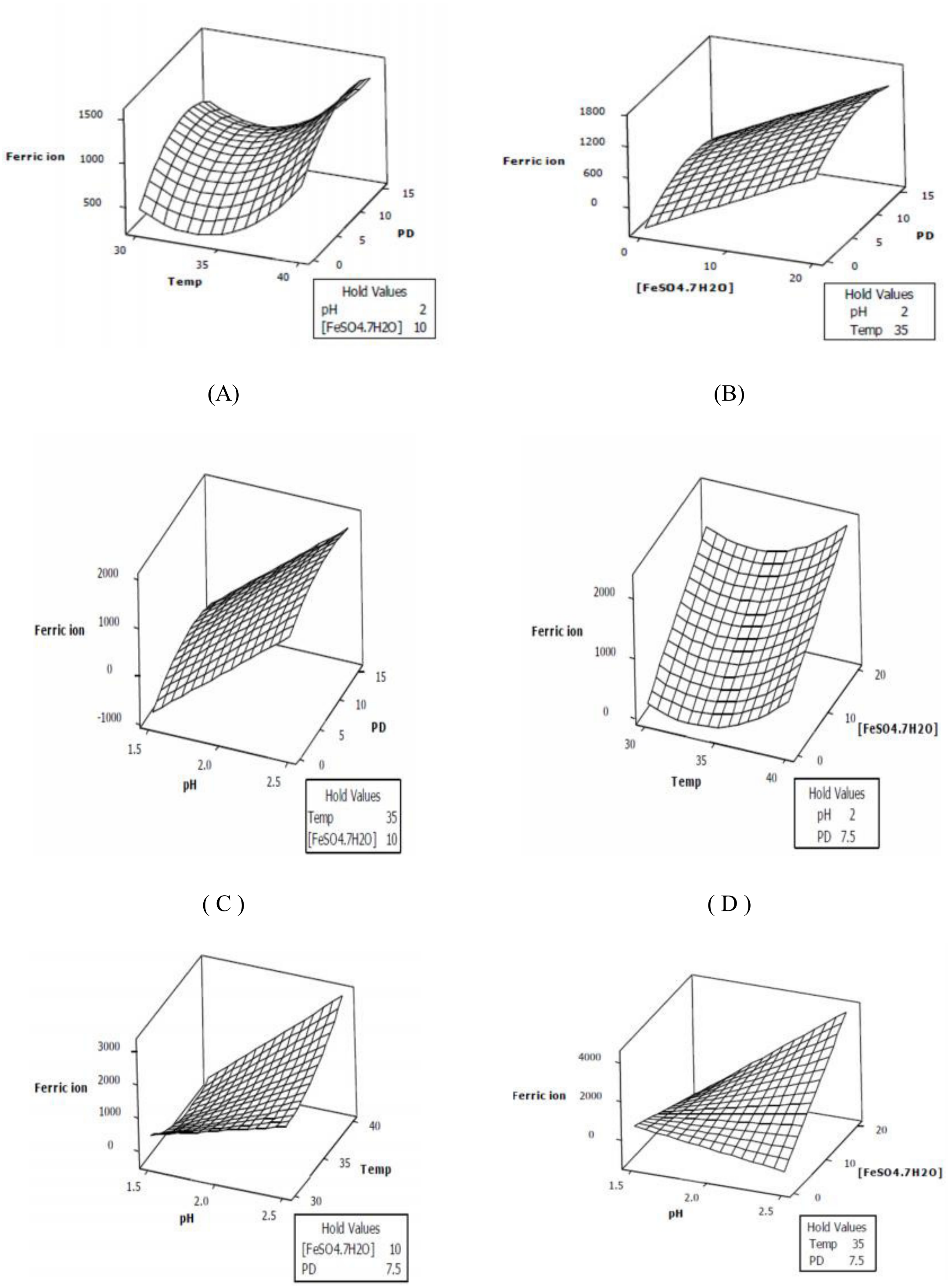
The results show that all the parameters have positive effect on the ferric ion precipitation. The estimated value of the determination coefficient (R^2), expressed as a percentage, indicates that the model fits 96.84% of the experimental raw data. The quality of the regression, estimated by the analysis of variance (ANOVA), is shown in Table 6.

Table 6. Analysis of variance for result.

Source	DF[a]	MSS[b]	F-value	P-value
Regression	8	1886140	63.67	0.000
Linear	4	2897105	97.8	0.000
Square	2	260122	8.78	0.002
Interaction	2	1490226	50.31	0.000
Residual Error	22	29622		
Lack-of-Fit	16	40697	450.82	0.000
Pure Error	6	90		
Total	30			

[a]Degree of freedom
[b]Mean sum of square

The 3D plots were drawn to illustrate the main and interactive effects of the independent variables on the dependent one. The optimum values of the variable were obtained as the response is minimized using the RSM technique. The best response range can be obtained by analyzing the response surface plots. The response surfaces based on these coefficient is shown in Fig.1 with two variables kept at middle level and the other two within the experimental range. In general, exploration of the response surfaces indicated a complex interaction between the variables.



(A) (B)

(C) (D)

(E) (F)

Figure 1. (A)-(F) Different three dimensional surface plots. The units used in these figures are g/L for concentrations (PD, Iron Concentration) ,^{o}C for temperature (Temp).

Figure 1.a shows the effect of temperature and pulp density on ferric ion precipitation, while other variable (pH and iron concentration) were fixed at their middle level. It was observed that the ferric ion precipitation was less at lower level. Figure 1.b shows the effect of pulp density and iron concentration on ferric ion precipitation, while other variable (pH and temperature) were fixed at their middle level. Figure 1.c shows the effect of pulp density and pH on ferric ion precipitation, while other variable (iron concentration and temperature) were fixed at their middle level. It was observed that the ferric ion precipitation was less at lower level. Figure 1.d shows the effect temperature and iron concentration on ferric ion precipitation, while other variable (pulp density and pH) were fixed at their middle level. It was observed that while the temperature increased, first the amount of ferric ion increased and then decreased and it was maximum at higher level. Figure 1.e shows the effect temperature and pH on ferric ion precipitation, while other variable (iron concentration and pH) were fixed at their middle level. It was observed that the ferric ion precipitation was less at lower level. Figure1.f shows the effect of pH and iron concentration on ferric ion precipitation, while other variables (temperature and pulp density) were fixed at its middle level. It was observed that the ferric ion precipitation was less at lower level.

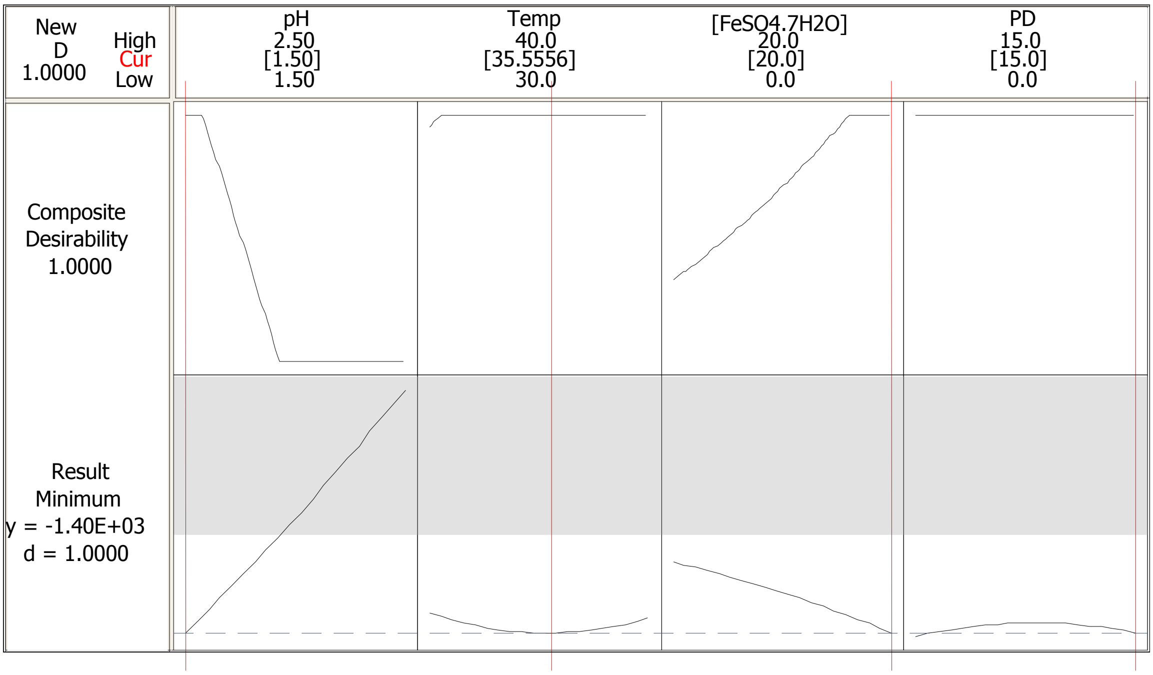


Figure 2. The optimization plot.

With the assumption of the pulp density is at the highest amount of its range, the optimum values of experimental conditions are obtained. Figure 2 shows the optimization plot.

Figure 3 shows the plot of residuals (difference between the observed and fitted values) versus the randomized run order, which presents a completely random pattern and it does not show any systematic effects or unusual observations.

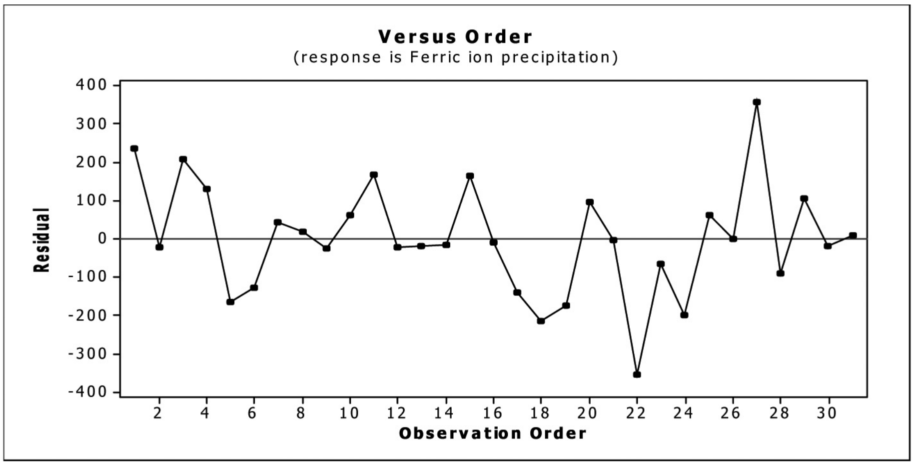


Figure 3. Residual vs. randomized order of experimental runs according to generated designs in Table 2.

Figure 4, the plot of residuals versus fitted values, also confirms a reasonable random distribution of the residuals around the zero line. The residual plot in Figure 4 shows an equal scatter of the residual against fitted value of the model indicating that the variance was independent from the ferric ion precipitation, thus supporting the adequacy of the model in various conditions. This indicates that the model was well fitted with the experimental results. Since the residuals from the fitted model are equally distributed, all the major assumptions of the model have been validated. The residual values obtained for center point also illustrate the precision of the measurements.

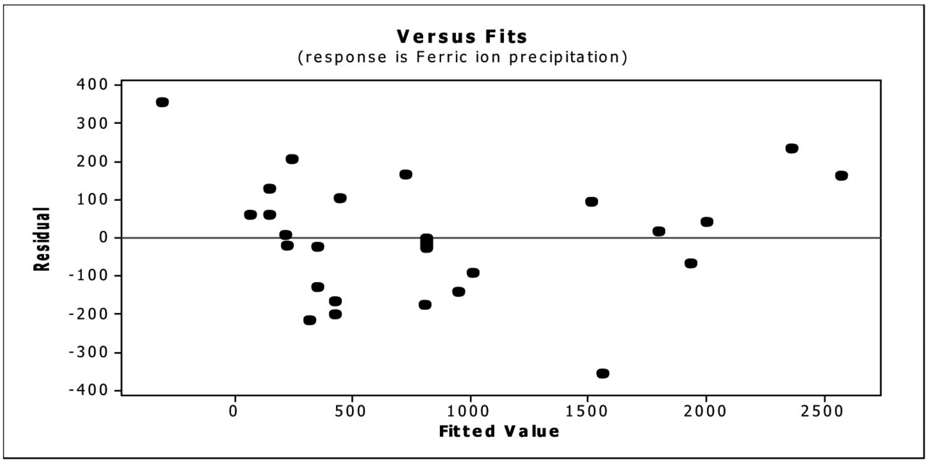


Figure 4. Residual vs. fitted experimental values.

By constructing a normal probability plot of the residual, a check was made for the normality assumption, as given in Figure 5. The normality assumption was satisfied as the residuals plot approximated along a straight line. The linear trend of the normal plot confirms the fairly normal character of the residuals.

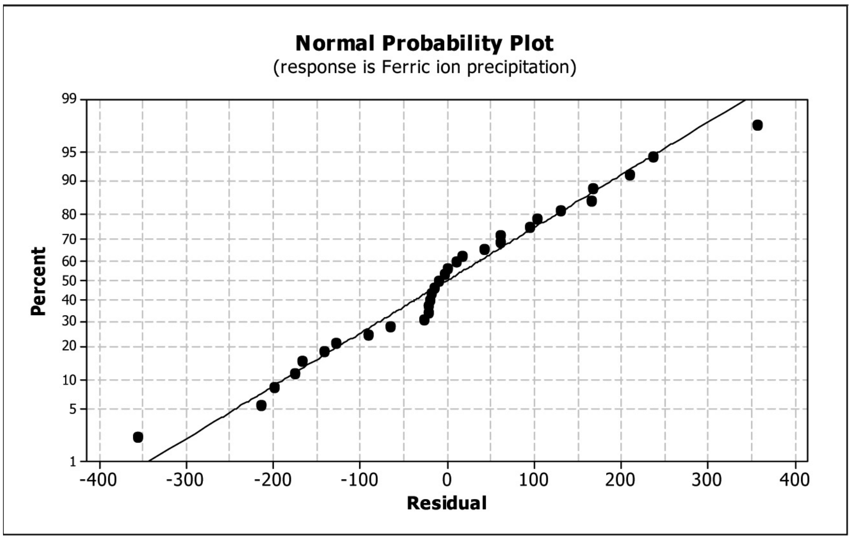


Figure 5. Normal probability of the residuals.

Conclusion

In this study, response surface methodology and central composite design were used to investigate the effects of pulp density, iron concentration, temperature and pH on ferric ion precipitation during uranium bioleaching experiments. A model was developed to describe the correlation between ferric ion precipitation and the four variables by applying Minitab® software. Using RSM, it was possible to determine the optimal experimental conditions via effective parameters such as pH, temperature, iron concentration and pulp density of ore. The non-linear nature of the modeled response for this system was explained by a second-order polynomial equation(Eq(5)).

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