

Determination of the Optimum Conditions of the Dissolution of Chalcopyrite Concentrate in Aqueous Solutions Saturated with Chlorine Gas

Hakan Temur

Ahmet Yartaşı

M. Muhtar Kocakerim

Atatürk University, Engineering Faculty
Department of Chemical Engineering
Erzurum, TURKEY
mkerim@atauni.edu.tr

Abstract: The present work aims an experimental design based on the of Taguchi approach to optimize the dissolution of chalcopyrite concentrate in aqueous solutions saturated with chlorine gas. The ranges of experimental parameters were between 16-45 °C for reaction temperature, 0.05-0.20 g.mL⁻¹ for solid-to-liquid ratio, 30-120 min for reaction time, 0.027-0.4 mol.L⁻¹ for [Fe³⁺] and 0.025-0.4 mol.L⁻¹ for [Cu²⁺].

The optimum conditions were found to be as follows: Reaction temperature (°C); 45, solid-to-liquid ratio(g.mL⁻¹); 0.05, [Fe³⁺](mol.L⁻¹); 0.2, [Cu²⁺] (mol.L⁻¹); 0,025 and reaction time(min); 120. Under these conditions, the dissolution percentage of copper from chalcopyrite concentrate in aqueous solutions saturated with chlorine was 68.44 %.

Keywords: Chalcopyrite, optimization, Taguchi method, chlorination.

Introduction

Chalcopyrite, being one of the most abundant copper ores in the world is the most important are used in production of the copper by pyrometallurgical methods. Recently, in production of copper and its compounds hydrometallurgical process have taken the place of classical metallurgical processes¹. Important features of chlorination are high reactivity of chlorine, high volatilities of metal chlorides and solubility of most metal chlorides in water. Chlorination of metal sulphides offers the additional prospect of recovering sulphur in the nonpolluting elemental form².

The high reactivity of gaseous chlorine as an oxidizing agent in leaching processes have been caused a number of studies on the extraction of metal sulphides by chlorine leaching. Bayrakçeken et al.³ studied the kinetics of the chlorination of pyrite in aqueous suspensions and found that the rate controlling step was the chemical reaction between chlorine and pyrite for the temperature range 13-35 °C, and the diffusion of chlorine through the fluid film for the temperature range 40-60 °C with the activation energies respectively 36.7 kJ.mol⁻¹ and 3.7 kJ.mol⁻¹. Çolak et al.¹ examined the kinetics of dissolution of chalcopyrite in aqueous solutions saturated by chlorine gas and determined that the diffusion of the reactants through product layer was the rate controlling step with an activation energy of 9.81 kJ.mol⁻¹.

Reactions of copper sulfide minerals with chlorine in an aqueous medium were studied by Groves and Smith and determined that when the dissolution process was complete, the reaction products(copper, iron and sulfur) were in their highest oxidation states and stoichiometric amount of chlorine was consumed.⁴

In an study carried out by Ekmekyapar et. al.⁵, they investigated the dissolution kinetics of an oxidized copper ore in water saturated by chlorine, and found that the dissolution process proceeded in two stages and was controlled by diffusion through the ash layer in each stage. The authors determined that the activation energies for the first and second stages were 27.15 and 20.21 kJ.mol⁻¹, respectively.

Chalcopyrite can be dissolved with various leaching agents such as hydrochloric acid⁶, chloride/hypochloride media⁷, ferric chloride^{8,9}, acidic Cl⁻ solutions¹⁰, CCl₄ saturated with chlorine¹¹ and H₂SO₄-NaCl-O₂¹².

In addition to these, oxide and sulphide ores of base metal minerals were examined by various

chlorinating agents such as Cl_2 , HCl , $\text{Cl}_2\text{-O}_2$, FeCl_2 and O_2 and CuCl_2 .²

The optimization of leaching conditions of the ores is important in industrial processes and some researcher have been interested in these topics by using various techniques¹³⁻²⁰.

As a technique, Taguchi's Orthogonal Array (OA) analysis is used to produce the best parameters for the optimum design process, with the least number of experiments. In recent years, Taguchi method has been used to determine optimum parameters because of its advantages. The main advantages of this method over other statistical experimental design methods are that the parameters affecting an experiment can be investigated as controlling and not controlling, and that the method can be applied to experimental design involving a large number of design factors¹⁸.

In this study, determination of the optimum conditions of the dissolution of chalcopyrite concentrate in aqueous solutions saturated with chlorine gas was investigated by using Taguchi experimental design method. Reaction temperature, solid-to-liquid ratio, reaction time, $[\text{Fe}^{3+}]$, $[\text{Cu}^{2+}]$ and $[\text{H}^+]$ were chosen as parameters.

Materials and Methods

The chalcopyrite concentrate used in this study was provided from Çayeli, Rize in Turkey and sieved by using a 75 μm ASTM standard sieve. Chemical analysis of concentrate gave a composition of 24.02 % Cu, 29.36 % Fe, 36.55 % S, 2.19 % Zn, 0.19 % Pb, 0.1 % Al_2O_3 , 0.9 % moisture and 6.69 % other components. X-ray diffractogram of chalcopyrite concentrate obtained by Rigaku DMAX 2000 Series X-ray diffractometer is given in Figure 1. It is seen that the chalcopyrite concentrate contains CuFeS_2 , FeS_2 , ZnS , Cu_2S , CuS and very small amount of Al_2O_3 and SiO_2 . Also, SEM photogram of the concentrate is shown in Figure 2.

Dissolution experiments were carried out two stages. In the first stage, 7.0 g chalcopyrite was added to 200 mL of distilled water saturated with chlorine gas and the mixture was stirred at ambient temperature for two hours. At the end of the experiment, the mixture was filtered and determined that 17.99 % of Fe and 13.66 % of Cu in the ore were dissolved. At the second stage, 3.5 g chalcopyrite was added to 100 mL of the filtrate saturated with chlorine gas and the mixture was stirred under the same conditions of the first stage. After the second stage experiment, the mixture was filtered and Cu and Fe analysis were done in the filtrate. It was seen that 65 % of Fe and 60 % of Cu in the ore were dissolved. This means that Cu^{2+} and/or Fe^{3+} are effective parameters in this dissolution system. Because of this fact, Cu^{2+} and Fe^{3+} concentrations were taken as parameters. The other parameters chosen for this study were reaction temperature, solid to liquid ratio, reaction time and $[\text{H}^+]$.

Dissolution experiments were carried out in 250 mL a jacketed glass reactor at atmospheric pressure. The reactor contents were mixed by a mechanical stirrer with tachometer and its temperature was controlled by a constant temperature circulator. The reactor was fitted with a cooler to prevent the volume reduction of the solution by the evaporation.

In the experiments, 100 mL- distilled water was saturated previously with Cl_2 at the desired experimental temperature. After the sample was added to the reactor, during the desired time period, Cl_2 was passed through the reaction mixture, and the mixture was stirred at a fixed speed. At the end of dissolution period, the amounts of Cu^{2+} passing to the solution during the reaction were determined the volumetric method²¹.

In this study, Taguchi method was used to optimize the dissolution of chalcopyrite concentrate in water saturated by chlorine. The application of Taguchi Method to optimize of a process by using multiple performance characteristics includes eight steps, which make up Robust Design cycle view of planning and performing the experiments and analysing and verifying the experimental result²²:

- identify the main function, side effects, and failure modes,
- identify noise factors and the testing conditions for evaluating the quality loss,
- identify the quality characteristics to be observed and the objective function to be optimized,
- identify the control factors and their alternate levels,
- design the matrix experiment and define the data analysis procedure,
- conduct the matrix experiment,
- analyze the data, determine optimum levels for the control factors, and predict performance under these levels,
- conduct the verification(also called confirmation)experiment and plan future action.

Performance characteristics chosen as the optimization criteria are divided by three categories, the larger-the-better, the smaller-the-better and the nominal-the-best. The first two of them were calculated by using Equation 1 and 2.

$$\text{Larger-the-better SNL} = -10\text{Log}_{10} \left(\frac{1}{n} \sum_{i=1}^n \frac{1}{Y_i^2} \right) \quad (1)$$

$$\text{Smaller-the-better } SNS = -10 \log_{10} \left(\frac{1}{n} \sum_{i=1}^n Y_i^2 \right) \quad (2)$$

where SNL and SNS are performance characteristics, n number of repetition done for an experimental combination, and Y_i performance value of i^{th} experiment²².

In Taguchi method, the experiment corresponding to optimum working conditions might not be found in randomized experimental plan table. In such cases; the performance value for optimum conditions can be predicted by using the balanced characteristic of OA. For this purpose; an additive model can be used as follows²³.

$$Y_i = \mu + X_i + e_i \quad (3)$$

where μ is the overall mean of performance value, X_i the fixed effect of the parameter level combination used in i^{th} experiment, and e_i the random error in i^{th} experiment.

If experimental results are in percentage (%), before evaluating Eq 3 Ω transformations of percentage values should be applied first using the Eq. 4 by which values of interest are also later determined by carrying out reverse transformation by using the same equation²⁴:

$$\Omega(db) = -10 \log_{10} \left(\frac{1}{P} - 1 \right)$$

(4)

Where $\Omega(db)$ is the decibel value of percentage value subject to omega transformation and P the percentage of the product obtained experimentally.

Because Eq. 3 is a point estimation, which is calculated by using experimental data in order to determine whether the additive model is adequate or not, the confidence limits for the prediction error must be evaluated²². The prediction error is the difference between the observed Y_i and the predicted \hat{Y}_i . The confidence limits for the prediction error, Se , is

$$Se = \pm 2 \sqrt{\left[\frac{1}{n_o} \right] \sigma_e^2 + \left[\frac{1}{n_r} \right] \sigma_e^2} \quad (5)$$

$$\sigma_e^2 = \frac{\text{sum of squares due to error}}{\text{degrees of freedom for error}} \quad (6)$$

$$\frac{1}{n_o} = \frac{1}{n} + \left[\frac{1}{n_{A_i}} - \frac{1}{n} \right] + \left[\frac{1}{n_{B_i}} - \frac{1}{n} \right] + \left[\frac{1}{n_{C_i}} - \frac{1}{n} \right] \dots \quad (7)$$

where s is the two-standard-deviation confidence limit, n the number of rows in the matrix experiment, n_r the number of repetition in confirmation experiment and $n_{A_i}, n_{B_i}, n_{C_i}, \dots$ are the replication number for parameter level A_i, B_i, C_i, \dots . If the prediction error is outside these limits, it should be suspected of the possibility that the additive model is not adequate. Otherwise, it can be considered that the additive model to be adequate.

A verification experiment is a powerful tool for detecting the presence of interactions among the control parameters. If the predicted response under the optimum conditions does not match the observed response, then it implies that the interactions are important. If the predicted response matches the observed response, then it implies that the interactions are probably not important and that the additive model is a good approximation²².

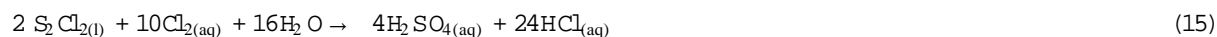
Experimental parameters used in this study and their levels are seen in Table 1. The orthogonal array (OA) was chosen as the most suitable to make up the experimental design, $L_{16}(5^4)$, with five parameters each four values given Table 2^{18,22}. Each experiment was repeated twice under the same conditions at different times, to determine the effects of noise sources on process.

Results and Discussions

Dissolution reactions

When chalcopyrite concentrate is added into solution obtained by dissolution of chalcopyrite concentrate in water saturated with chlorine, the reactions taking place in the medium can be written as follows¹;





Statistical analysis

The collected data were analysed by an IBM compatible PC using a program prepared by taking into account Tagushi approach. In order to see effective parameters and their confidence levels on dissolution process, the analysis of variance was performed. A statistical analysis of variance (ANOVA) was performed to see whether process parameters are statistically significant or not. F-test is a tool to see which process parameters have a significant effect on the dissolution value. The F value for each process parameter is simply a ratio of mean of the squared deviations to the mean of squared error. Usually, the larger the F value, the greater the effect on the dissolution value due to the change of the process parameter. With the performance characteristics and ANOVA analyses, the optimal combination of process parameters can be predicted¹⁸. The results of variance analysis were given in Table 3.

To obtain optimal dissolution performance, the larger-the-better performance characteristic (Eq. 1) has been taken for dissolution of Cu.

The order of graphs in Figure 3-7 is according to the degrees of the influences of parameters on the performance characteristics. The optimal level of a process parameter is the level with the highest SN value calculated by Eq.1. At first sight it can be difficult and complicated to deduce the experimental conditions for the graphs given in Figure 3-7. We'll try to explain it with an example.

Let's see how Figure 4 is obtained. Figure 4 shows the variation of performance characteristics with solid-to-liquid ratio. Let's try to determine the experimental conditions for the first datum point. The level 1 is 0.05 g.mL⁻¹ for this parameter in this point. Now, let's go to Table 2 and find the experiments for which the level in the column B is 1. It seen in Table 2 that the level is 1 for the experiment with 1, 5, 9 and 13 numbers. The first datum point in Figure 4 is arithmetical average of performance characteristics for these experiments. All the points in Figure 4 graph and other graphs are established by the same way. In each graph, the numerical value of maximum point is correspond to the best value for that parameter. These values are seen to be A4 (45°C), B1(0.05 g.mL⁻¹), C3(0.2M), D1(0.025M) and E4(120 min). Therefore, for these process A4, B1, C3, D1 and E4 condition were taken as optimum dissolution conditions and the dissolution fraction under these conditions was found to be 68.44 %.

If the experimental plan given in Table 2 is studied carefully together with parameter values given as A4(45 °C), B1(0.05 g.mL⁻¹), C3(0.2M), D1(0.025M) and E4(120 min), it can be seen that experiments corresponding to optimum conditions A4(45°C), B1(0.05g.mL⁻¹), C3(0.2M), D1(0.025M) and E4(120 min) have not been carried out during the experimental work. Thus it should be noted that the dissolution percentages in Table 4 are predicted results obtained by using Eqs. 3-4 and observed results for same conditions. Also, the results in Table 4 are confidence limits of predictions. In order to test the predicted results, confirmation experiments were carried out twice at the same working conditions. The fact that the dissolution percentages from confirmation experiments are within the calculated confidence intervals calculated from Eqs.5-7 (see Table 4) shows that the experimental results are within ± 5 % in error. This case states that there is a good agreement between the predicted values and experimental values, and the interactive effects of the parameters are indeed negligible. It may be concluded that the additive model is adequate for describing the dependence of this dissolution process on the various parameters¹⁸.

Conclusion

The major conclusions from the present work are:

1-The effective parameters on dissolution of chalcopyrite concentrate in aqueous solutions saturated with chlorine gas are solid-to-liquid ratio, reaction time, $[\text{Fe}^{3+}]$, reaction temperature and $[\text{Cu}^{2+}]$, respectively.

2-The optimum conditions are 45 °C for reaction temperature, 0.05 g. mL⁻¹ for solid-to-liquid ratio, 120 min. for reaction time, 0.2 M for $[\text{Fe}^{3+}]$ and 0.025 M for $[\text{Cu}^{2+}]$. Under these conditions given in Table 4, it can be seen that the dissolution of 68.44 % is just for Cu.

3-The predicted and observed dissolution values are very close to each other, it may be concluded that the additive model is adequate for describing the dependence of the dissolution process on the examined parameters.

4-Since optimum conditions determined by Taguchi method in laboratory environment is reproducible in real production environments as well, the findings of the present study may be very useful for processing in industrial scale.

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Parameters		Levels			
		1	2	3	4
A	Reaction temperature (°C)	16	25	35	45
B	Solid-to-liquid ratio (g.mL ⁻¹)	0.05	0.1	0.15	0.2
C	[Fe ³⁺] (mol.L ⁻¹)	0.027	0.1	0.2	0.4
D	[Cu ²⁺] (mol.L ⁻¹)	0.025	0.1	0.2	0.4
E	Reaction time (min)	30	60	90	120

Table1.Parameters and their values corresponding to their levels studied in experiments.

Experiment No	Quantities and their levels					Conversion fraction of copper		
	A	B	C	D	E	Experiment(I) Cu %	Experiment(II) Cu %	Average Cu %
1	1	1	1	1	1	34.65	39.88	37.27
2	1	2	2	2	2	31.75	23.01	27.38
3	1	3	3	3	3	30.45	25.73	28.09
4	1	4	4	4	4	16.22	20.17	18.20
5	2	1	2	3	4	48.11	41.70	44.91
6	2	2	1	4	3	33.65	36.33	34.99
7	2	3	4	1	2	25.73	22.12	23.93
8	2	4	3	2	1	18.61	23.33	20.97
9	3	1	3	4	2	56.62	54.23	55.43
10	3	2	4	3	1	18.78	20.18	19.48
11	3	3	1	2	4	38.63	37.09	37.86
12	3	4	2	1	3	30.85	34.65	32.75
13	4	1	4	2	3	47.79	43.14	45.47
14	4	2	3	1	4	56.75	49.62	53.19
15	4	3	2	4	1	24.68	29.38	27.03
16	4	4	1	3	2	29.54	26.52	28.03

Table 2. L₁₆ (4⁵) Experimental plan table and results of experiments

Parameters		Degrees of freedom	Sum of squares	Mean of squares	F
A	Reaction temperature (°C)	3	568.9250	189.6417	17.17
B	Solid-to-liquid ratio (g.mL ⁻¹)	3	1929.8293	643.2764	58.26
C	[Fe ³⁺] (mol.L ⁻¹)	3	653.2051	217.7350	19.72
D	[Cu ²⁺] (mol.L ⁻¹)	3	181.0988	60.3663	5.47
E	Reaction time (min)	3	657.5962	219.1987	19.85
Error		16	176.6779	11.0424	

Table 3. Results of the analysis of variance for the chlorination of chalcopyrite concentrate

Parameters		Value	Level
A	Reaction temperature (°C)	45	4
B	Solid-to-liquid ratio (g.mL ⁻¹)	0.05	1
C	[Fe ³⁺] (mol.L ⁻¹)	0.2	3
D	[Cu ²⁺] (mol.L ⁻¹)	0.025	1
E	Reaction time (min)	120	4
Observed dissolved quantity for Cu (%)		67.86	
Predicted dissolved quantity for Cu (%)		65.19	
Confidence limits of prediction for Cu (%)		60.21-70.17	

Table 4. Optimum working conditions and alternative working conditions for two different experimental conditions, observed and predicted dissolved quantities of Cu

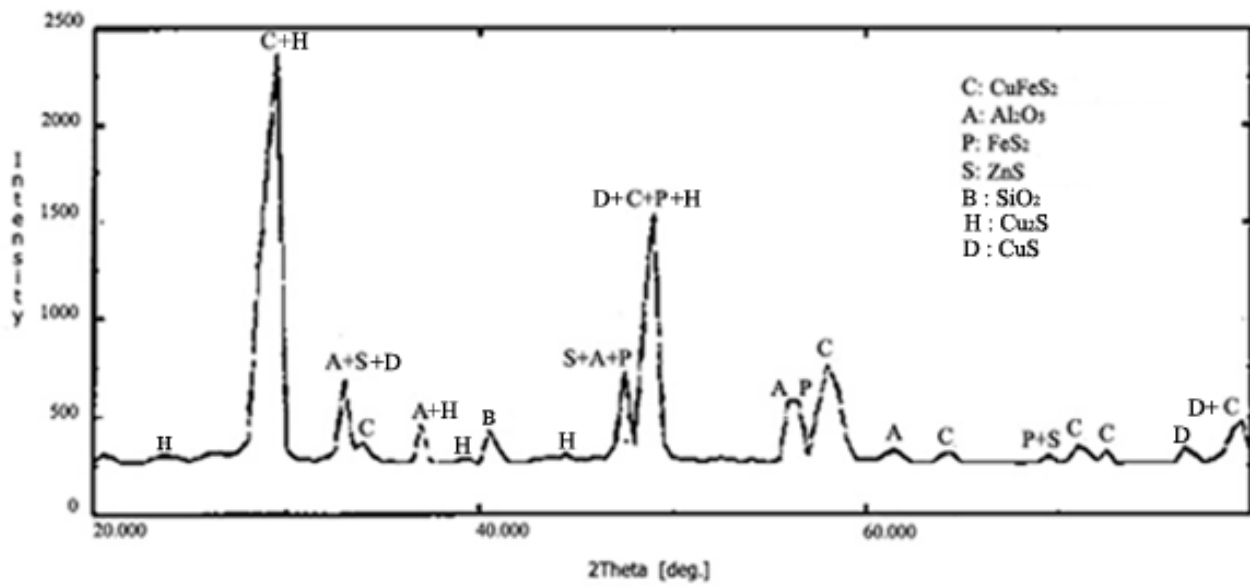


Figure 1. X-Ray diffractogram of the chalcopyrite concentrate



Figure 2. SEM photograph of the chalcopyrite concentrate

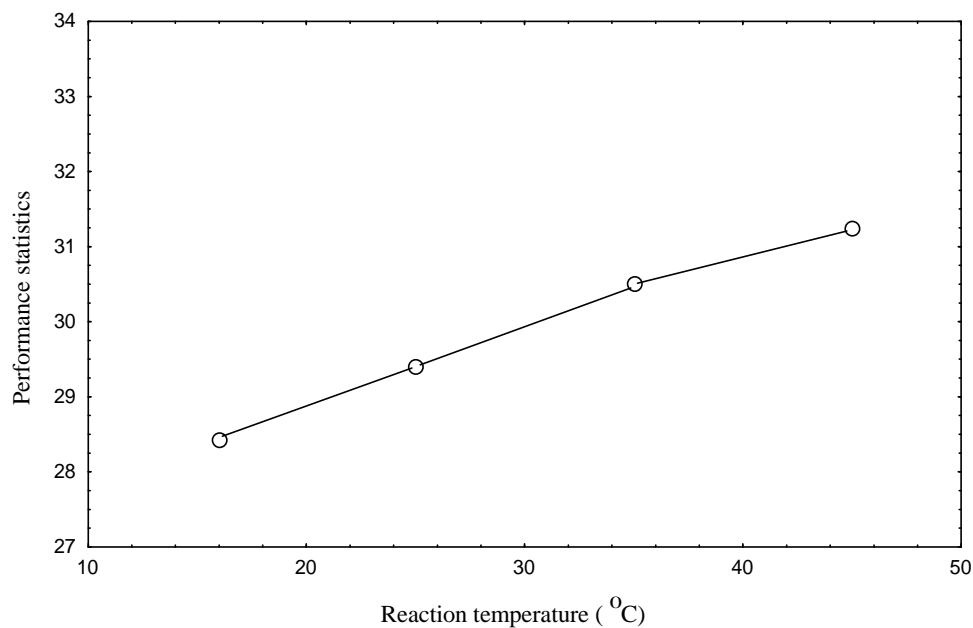


Figure 3. The effect of reaction temperature on performance statistics

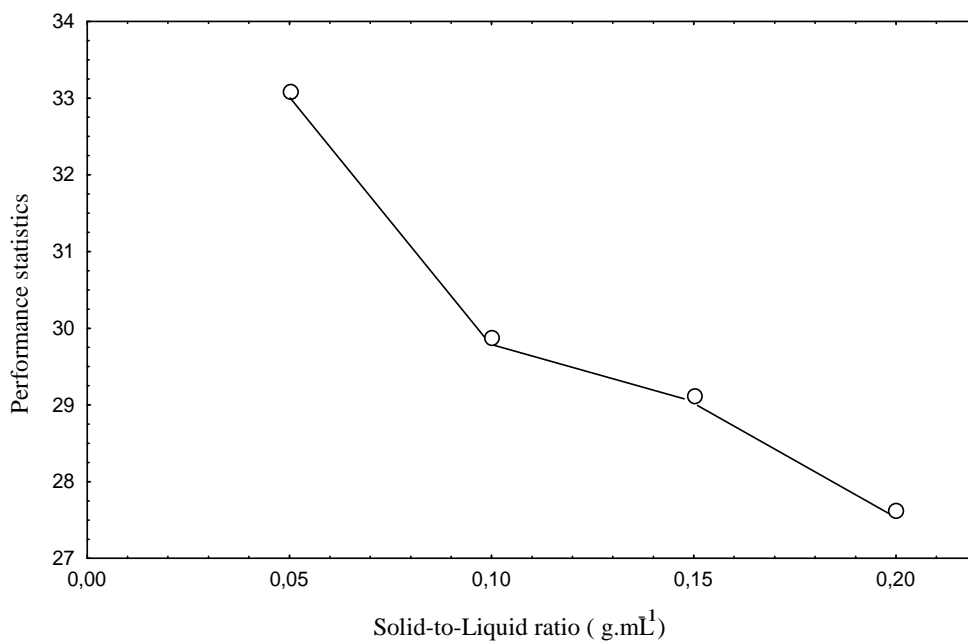


Figure 4. The effect of solid-to-liquid ratio on performance statistics

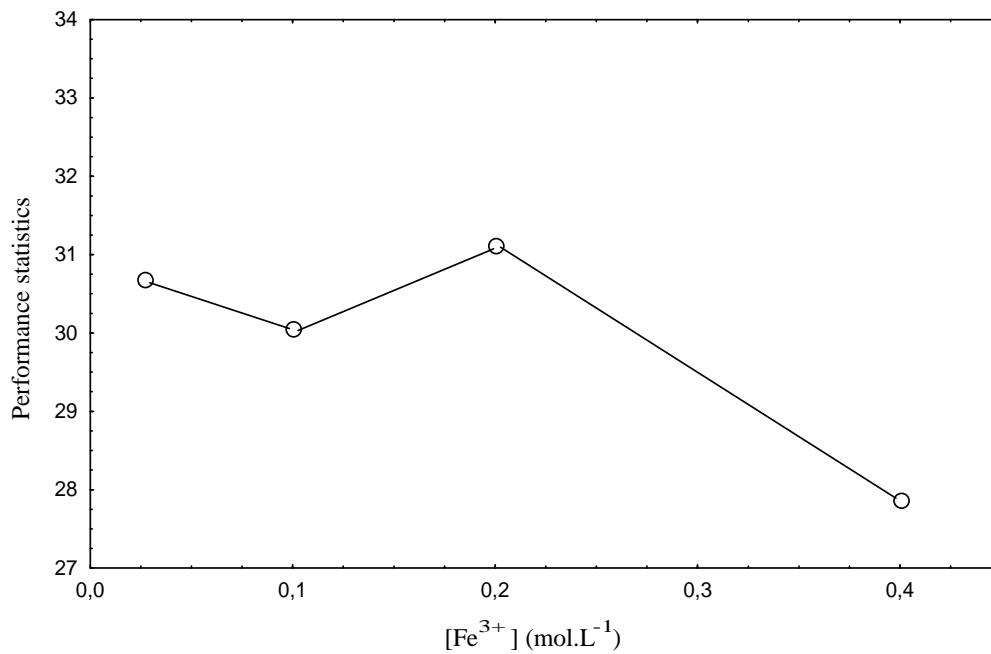


Figure 5. The effect of [Fe³⁺] on performance statistics

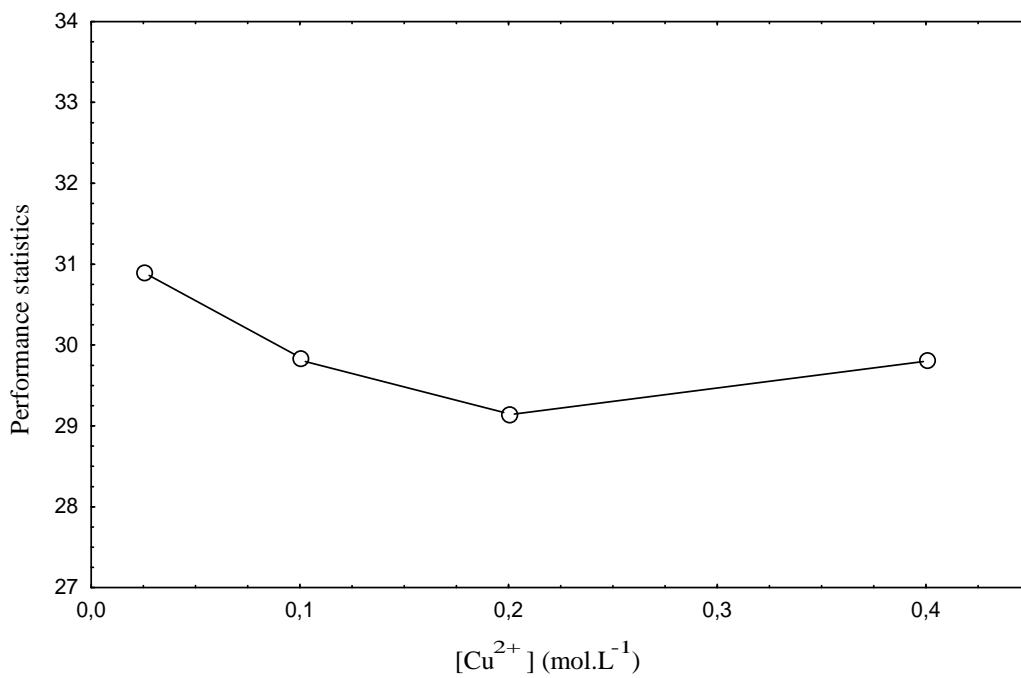


Figure 6. The effect of [Cu²⁺] on performance statistics

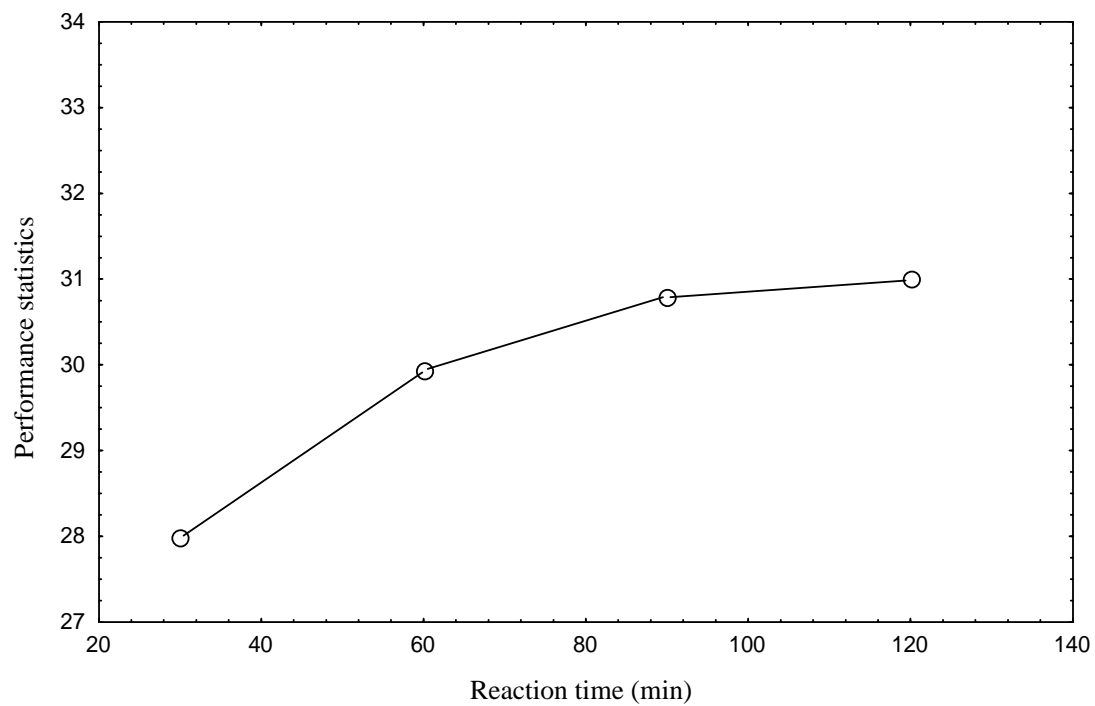


Figure 7. The effect of reaction time on performance statistics