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Effects of Operation Conditions on the Apparent Rate Constant of Copper Removal in a Packed-Bed Electrolytic Reactor.

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ABSTRACT

The objectives of the present paper are to perform experimental work and formulate a mathematical model that describes the effect of the physical parameters which controls the reaction kinetics of the electrochemical removal of copper in a Packed-Bed Electrolytic Reactor. The reaction kinetics is intimately related to the optimum sizing of the reactor; as it enables the calculation of the residence time required to achieve a desired yield. The physical parameters under considerations were initial concentration of copper, intensity of the applied electric current, electrolyte flow rate and pH₀. The mathematical model was validated using the obtained experimental results. The adequacy of the model was verified using ANOVA analysis. R square of the obtained model is 94%.

Keywords: copper, electrolytic reactor.

Nomenclature

C: final concentration of copper ion, mg/dm³

C₀: the initial copper concentration, mg/ dm³

t: electrolysis time, min.

S_c: the total active cathode surface area, dm²

V_s: volume of the electrolyte solution being treated, dm³

k: the apparent first order reaction rate constant for copper electro-deposition at the cathode,

α: constant has the units of A⁻¹.

I: intensity of applied electric current, A.

k₀: factor similar to the frequency (or pre-exponential) factor in the well-known Arrhenius equation; it has the same units as k.

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INTRODUCTION

Previous manuscripts have shown that electrochemical techniques are widely applicable to removal of heavy metals from industrial wastewaters [1, 2]. For describing the removal process, the removal rate constant is an important parameter to be known; since it enables calculation of the size of the reactor via determining the residence time required to achieve a desired yield and the daily volume of the treated solution. Previous investigations indicate that a number of design and operating parameters affect the performance, i. e. the kinetics of the occurring process, of an electrolytic reactor.

Ruotolo and Gubulin [3] studied the kinetic and hydrodynamic behaviors of a fixed-bed electrochemical reactor. They reported that the curves describing the kinetics of the decrease in copper concentration in the electrolyte are linear up to the moment when they become exponential in time. In spite they did not introduce any rate expression; the presented data indicate that the slope of the linear portion, i.e. the rate of the deposition process, depends on the range of initial concentration of copper. They did not, however, consider the effect of current density on the deposition rate.

Basha et al. [4] investigated the kinetics of copper removal in a cylindrical-batch recirculation-electrochemical reactor when the pH was varied. They reported that at pH 0.64, 1.5 and 2 the removal rate was very fast during the initial 1h of electrolysis and afterwards the rate of removal of Cu is practically zero; but in general at higher pH removal rate is constant may be following zero order kinetics. The authors did not investigate the effects of the flow rate, the intensity of applied current and the initial concentration of copper on the rate of deposition.

Olufemi et al. [5] utilized optimization techniques to theoretically and practically optimize the fabrication and operation of suitable electrochemical cells with the possibility of totally removing copper from a $\text{CuSO}_4\text{-Na}_2\text{SO}_4$ wastewater at almost 100% current efficiency. They stated that the electrochemical removal of copper ions follows first order kinetics and the concentration at a particular time is given as:

$$\ln C_f = \ln C_o - kt (S_c / V_s) \quad (1)$$

They did not, however, consider the effects of flow rate and initial pH on k. Equation (1) indicates that the value of k is constant and independent of the applied current density. Additionally, the value of S_c might be difficult if not impossible to estimate for a packed bed electrode made of graphite particles. The equation, as well, does not reflect the effects of neither the initial concentration of metal nor the initial pH on k.

Khatab et al. [6] used packed-bed cathode, reported that the controlling regime of copper electrodeposition mostly was the electron-transfer regime and the removal of copper was found to follow first order kinetics and dependent on initial copper concentration, applied current density and supporting electrolyte concentration. But they did not neither indicate the effect of the initial pH on the value of the apparent reaction rate constant nor introduce a correlation reflecting the effect of over mentioned operating parameters on the rate constant.

Alebrahim et al. [7] reported that the electrochemical removal of copper, from monometallic solution, in the batch-circulated system followed a first order kinetic model and is affected by the following operational parameters: intensity of the applied electric current, initial copper concentration, time of electrolysis, the flow rate of the treated solution and the initial pH of the electrolyte.

The aim of this paper is not only to understand how some operating parameters affect the apparent rate constant of the electrochemical removal of copper from monometallic solution, but also to introduce a correlation for estimating this constant. It should be mentioned that the Microsoft Office Excel 2010 was used for constructing and curve fitting of the kinetic plots. Also, statistical and least square multivariate regression techniques were employed to find a model for predicting the apparent rate constant k.

EXPERIMENTAL

The experimental set up, batch-circulated reactor having a packed-bed cathode of graphite particles, and procedure were described elsewhere; Alebrahim et al. [7].

RESULTS AND DISCUSSION

Effect of electrolyte flow rate

Experiments were conducted at different electrolyte flow rates, keeping other operating parameters, i.e. intensity of applied current, pH₀ and C₀, at constant values. The effect of the flow rate (F. R.) on the removal of copper is shown in Figures (1 & 2), for two applied current intensities, in which the natural logarithm of copper concentration is plotted against time for different flow rate values. The results obtained from these runs revealed that the copper removal increased with an increase in the flow rate; similar observation was reported by Chu et al. [8] and Basha et al. [9]. The obtained straight lines mean that the decay of copper concentration is governed by a first order kinetic model with respect to the metal concentration represented by the equation

$$\ln \frac{C_t}{C_0} = -kt \tag{2}$$

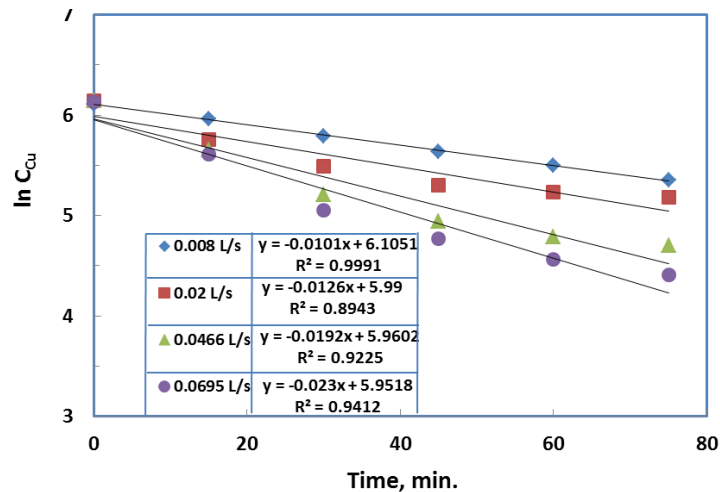


Figure (1) - Plot of ln C_{Cu} versus time for different flow rate values; under the experimental conditions: applied current: 4 A, pH₀: 2.55 & C₀ ~ 460 mg/ L.

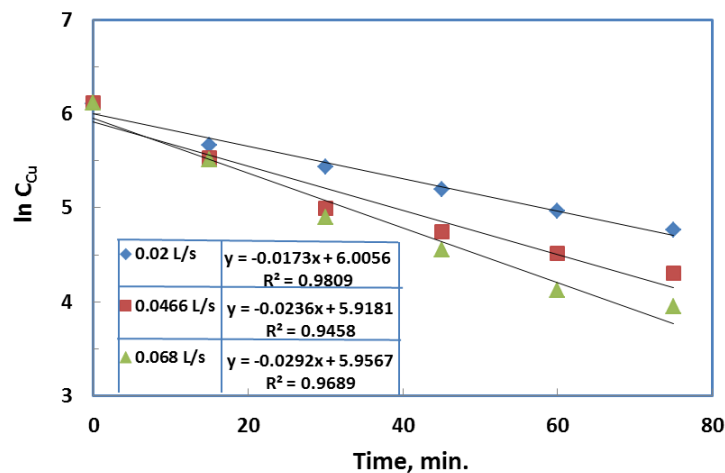
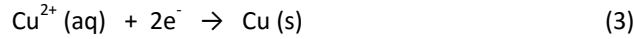


Figure (2) - Plot of ln C_{Cu} versus time for different flow rate values; under the experimental conditions: applied current: 5 A, pH₀: 2.55 & C₀ ~ 455 mg/ L.

The values of k were obtained from the slopes of the lines in Figures (1 & 2) and $\ln[k]$ were plotted against $\ln[F.R.]$ in Figures (3 & 4), respectively. Figures (3 & 4) show a linear relationship exists between $\ln[k]$ and $\ln[F.R.]$ in addition values of k increase with the increase of F.R. The increase of k ; i.e. increase of copper removal, might be explained according to what follows. In the electrochemical removal of copper from wastewaters, the reaction described by equation (3) is the desired reaction.



This desired reaction may be accompanied by secondary reactions resulting in loss of removal efficiency [1]. At a $\text{pH} < 7$ hydrogen and oxygen evolution at the cathode and anode, respectively, are the most important competitive reactions. Chen et al. [10] reported that hydrogen evolution occurs if the cathode current density is greater than the limiting value for copper deposition. On the other hand, Chu et al. [8] and Solisio et al. [11] reported the increase of limiting current with increasing flow rate. Consequently, if the difference between the applied current and the limiting current is narrowed, the discharge of hydrogen ions at the cathode will decrease leading to higher removal of copper. At low current densities these gases may dissolve in the electrolyte solution. However, at higher current densities gas bubbles are generated on the surfaces of the anode and cathode. Bubbles which cover the cathode surface reduce the available area for copper removal. Therefore, the increase of copper removal with an increase in flow rate is due to the ease of bubble detachment from the cathode surface [12].

It might be observed, from the two figures (3 & 4), that the slope of the line representing $\ln[k]$ versus $\ln[F.R.]$ increased with increasing applied current intensity from 4 to 5 A. The relation between k and F.R has the form

$$k = A_{F.R.} (F.R.)^{B_{F.R.}} \tag{4}$$

Values of $A_{F.R.}$ and $B_{F.R.}$ are given in Table (1) for two current intensities.

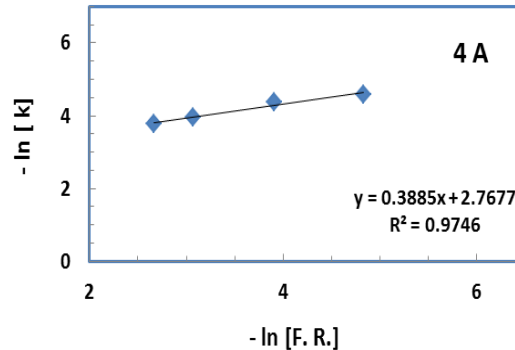


Figure (3) - Plot of $\ln[k]$ versus $\ln [F.R.]$ at current intensity of 4 A

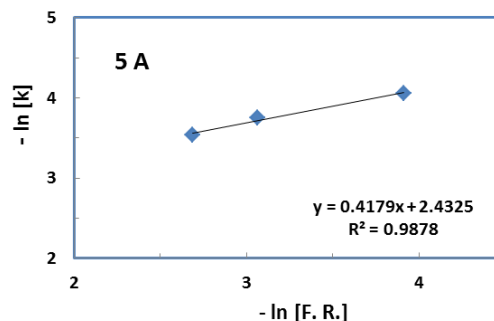


Figure (4) - Plot of $\ln[k]$ versus $\ln [F.R.]$ at current intensity of 5 A

Table (1) – Values of $A_{F,R}$ and $B_{F,R}$

| Current intensity, A | $A_{F,R}, \text{min.}^{-1}$ | $B_{F,R}$ |
|----------------------|-----------------------------|-----------|
| 4 | 0.0628 | 0.3885 |
| 5 | 0.0878 | 0.4179 |

Effect of initial metal concentration

The effect of initial Cu^{2+} ion concentration on the removal rate is shown in Figure (5). The removal process follows a first order kinetics. According to the presented results, the apparent rate constant decreased with an increase in initial copper concentration of the treated solution. This means that at constant values of other operating parameters (i.e. intensity of applied electric current, F. R. and initial pH), whenever the treated solution has larger initial concentration of copper ions, more time is needed to reach the same percent removal.

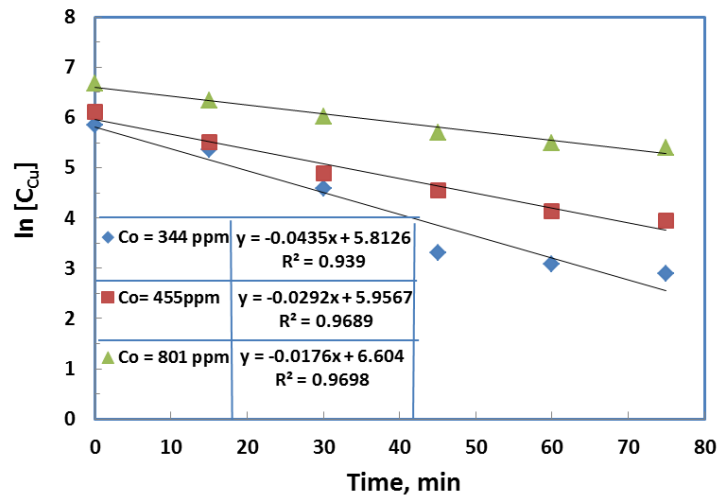


Figure (5) - Plot of $\ln C_{\text{Cu}}$ versus time for different initial Cu concentration; experimental conditions: applied current 5 A, $\text{pH}_o = 2.56$ & F. R. = 0.068 L/s

Using values of the apparent rate constant from Figure (5) a plot of $\ln[k]$ versus $\ln[C_o]$ was drawn in Figure (6). The straight line has a slope of -1.05 with a correlation coefficient of 0.9837. The relation between k and C_o is

$$k = 19.3018 * (C_o)^{-1.05021} \tag{5}$$

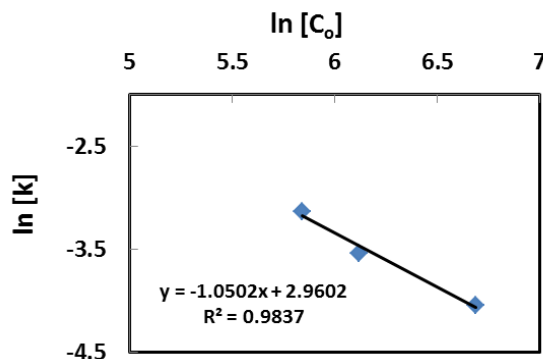


Figure (6) - Plot of $\ln [k]$ versus $\ln [C_o]$

Effect of initial pH (pH_o)

The effect of the initial pH of the treated solution on the kinetics of copper removal was investigated using different initial pH values by Alebrahim et al. [7]. Their experimental findings exhibited that the solution

pH₀ had a considerable effect on the copper removal rate; i.e. the removal rate increased with an increase of pH₀, as shown in Figure (7). The authors interpreted this behavior that the discharge of hydrogen ions was a strong competitor to the discharge of copper ions on the surface of the cathode when the acidity was high; and therefore limited the process of copper removal.

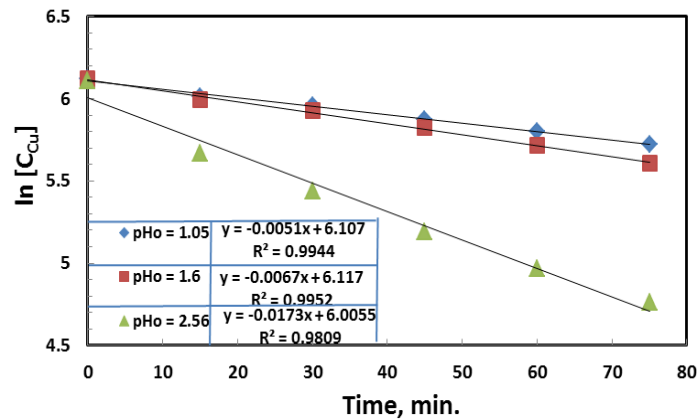


Figure (7) - Plot of $\ln C_{Cu}$ versus time for different initial pH values; experimental conditions: applied current = 5 A & F. R. = 0.02 L/s.

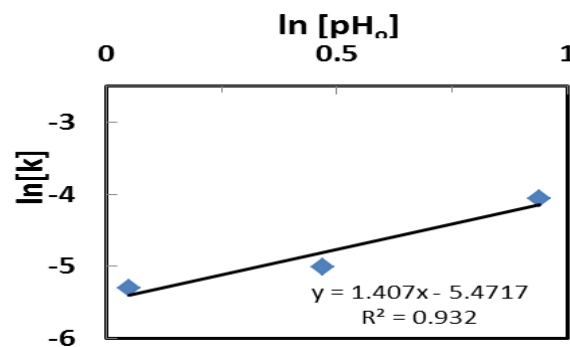


Figure (8) - Plot of $\ln [k]$ versus $\ln [pH_0]$

It might be observed from Figure (7) that the apparent rate constant increased with increasing the initial pH of treated solution. The increase in the rate of copper removal is due to the observation reported by Sarkar [12] that hydrogen bubbles are being smaller when they detach from the surface of the cathode as a result of an increase in pH, and, therefore, more surface is available for copper deposition.

Plotting of $\ln [k]$ against $\ln [pH_0]$ is shown in Figure (8). A straight line was obtained. The slope of the line is 1.407 with correlation coefficient of 0.932. The relation describing the effect of pH₀ on k is

$$k = 0.0042 * (pH_0)^{1.4067} \tag{6}$$

Effect of intensity of applied current

Figures (9) and (10) illustrate the effect of the intensity of electric current on the copper removal rate at two different values of flow rate. These figures reveal, as well, that the removal process follows a first order kinetics and the apparent rate constant, k, increase with an increase in the current intensity.

On plotting k versus the applied current intensity an exponential function was obtained a shown in Figures (11 & 12); and can be represented by equation (7).

$$k = k_0 e^{(\alpha I)} \tag{7}$$

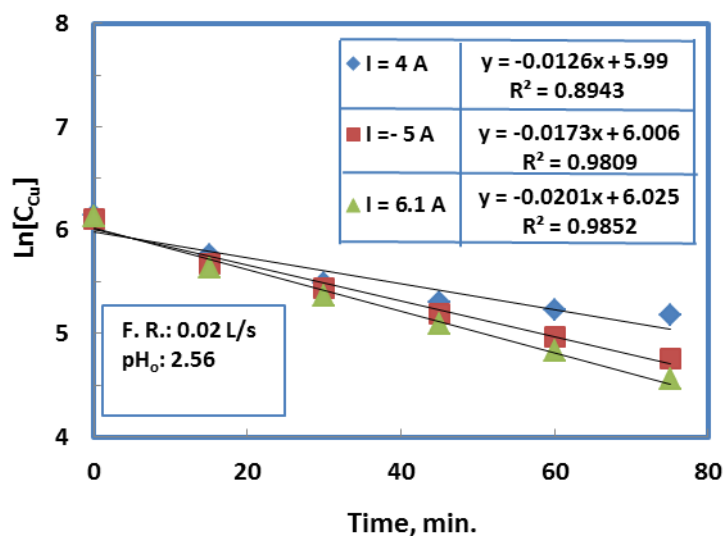


Figure (9) - Plot of $\ln[C_{Cu}]$ versus time for different values of current intensity

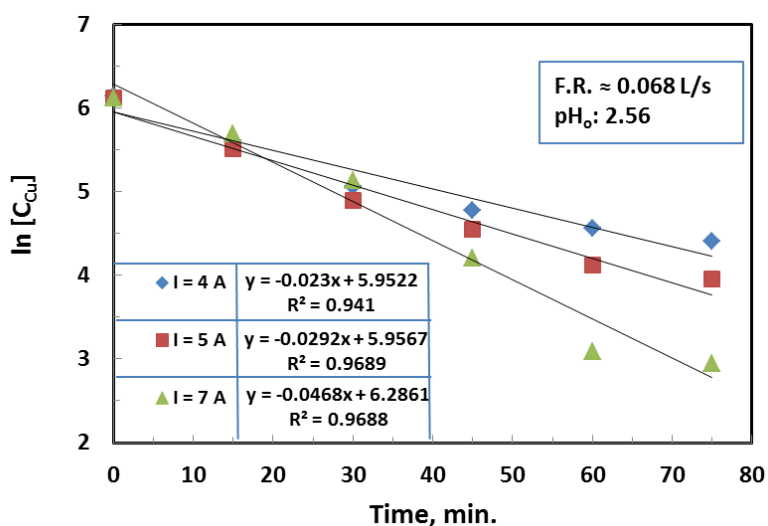


Figure (10) - Plot of $\ln[C_{Cu}]$ versus time for different values of current intensity

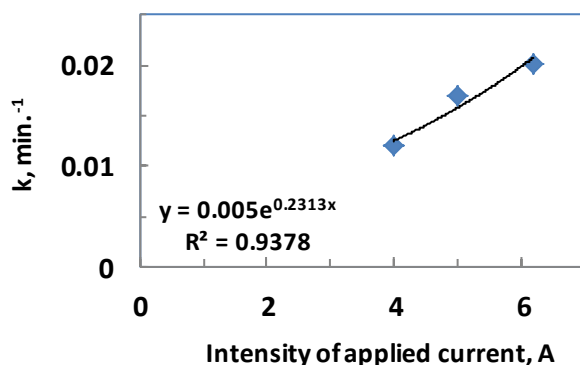


Figure (11) - Plot of k versus intensity of applied current; at the same operating parameters of Fig. (9).

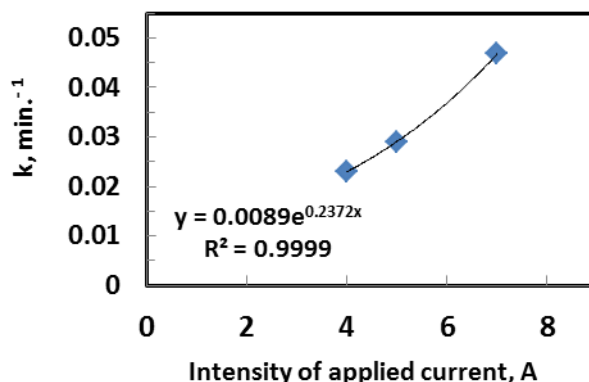


Figure (12) - Plot of k versus intensity of applied current; at the same operating parameters of Fig. (10).

Table (2) – Values of α and k_0 for two values of flow rate

| Flow rate, L/s | k_0 , min. ⁻¹ | α , A ⁻¹ |
|----------------|----------------------------|----------------------------|
| 0.02 | 0.005 | 0.2313 |
| 0.068 | 0.0089 | 0.2372 |

The values of α and k_0 are given in Table (2) for two different flow rates. The units of the pre-exponential factor k_0 are identical to those of the rate constant and will vary depending on the order of the reaction. If the reaction is first order it has the units time⁻¹, and for that reason it is often called the frequency factor. Most simply k_0 is the number of collisions (leading to a reaction or not) per unit time occurring with the proper orientation to react [13]. As shown in Table (2), k_0 increases with the increase in F. R. which means that more Cu^{2+} ions can contact the surface of the cathode and get reduced according to Eq. (3). On the other hand, $e^{(\alpha I)}$ is the probability that any given collision will result in a reaction. The values of α can be considered constant, within an acceptable error, and, therefore, k increases with an increase in current intensity.

Correlation for predicting k

To represent the influence of the operating parameters on the apparent rate constant of electrochemical removal of copper, a mathematical model must be proposed. Statistical and least square multivariate regression techniques are employed for modeling and analysis of problems in which a response of interest is influenced by several variables. Actually, it was reported by Khattab [6] that the rate of electrochemical removal of copper in the batch-circulated system, using a packed-bed cathode of graphite particles is affected by the following operating factor:

- Applied current density.
- Initial copper concentration.
- Time of electrolysis.
- The flow rate of the treated solution.
- Type and concentration of supporting electrolyte.
- Shape of current collector.

By neglecting the effects of items 5 and 6, the apparent rate constant can be assumed to be a function of (F.R.), (C_0), (pH_0) and (I); i.e.

$$k = f(\text{F.R.}, C_0, \text{pH}_0, I) \quad (7)$$

For estimating the relationships among dependent variable k and the independent variables (F.R.), (C_0), (pH_0) and (I), a suitable regression method must be used. It must be mentioned that, the resulting

correlation can only be used for electrolytic reactors similar to the one presented in this work when copper is to be removed.

Regression model

The Response Surface Methodology (RSM) technique employs multivariate regression least square in constructing the mathematical model that relates the response and specific controlling parameters. Analysis of variance (ANOVA) is used to test the adequacy of the proposed model and the significance of each controlling parameter. Kaminari et al. [14] used this technique to study the operational parameters involved in designing a particle bed reactor for the removal of lead from industrial wastewater. Cheng et al. [15] applied the response surface methodology for electrochemical destruction of cyanide. Also, Abouel-Fotouh et al. [16] used this technique to optimize conditions of biomass growth of algae under different conditions of nitrate starvation and salt stress.

In the current regression model, the response is the kinetic rates. The controlling parameters are (C_o), (l), flow rate (F.R.) and pH_o . The model takes the following form

$$k = b_o + b_1(F.R) + b_2C_o + b_3l + b_4pH_o + \epsilon \tag{8}$$

ϵ is the error which is the difference between the observed experimental and the model predictions. The regression model has been constructed by programming using Matlab platform.

Results of the model

The results of RSM and ANOVA are shown in Table 3. The table shows the coefficients of the correlation with their P-values. The P-values are less than 0.001 which indicate that each term of the correlation is significant. The F-test value of the model and its P-value are 42.2 and 7.824e-06, respectively. This implies that the model is significant. Coefficients b_1 , b_3 and b_4 of the independent parameters (F.R.), (l) and (pH_o), respectively, are positive which results in an increase in k with increasing their level, i.e. increase of Cu removal. On the contrary, the coefficient of (C_o) is negative, i.e. k decreases with increasing C_o .

Table 3. Value and P-value of each term coefficient

| Coefficient | Value | P-value |
|-------------|--------------|----------|
| b_o | -0.0218 | 5.71e-05 |
| b_1 | 0.322 | 5.04e-05 |
| b_2 | $-4.8e^{-5}$ | 0.00032 |
| b_3 | 0.0062 | 0.00152 |
| b_4 | 0.00093 | 0.00079 |

Figure (13) shows the normal probability of standardized residuals and the mean of model errors is equal to zero. The linear distribution of the residual indicates the model errors (ϵ) are normally distributed which indicates that the predictions of the model are not biased.

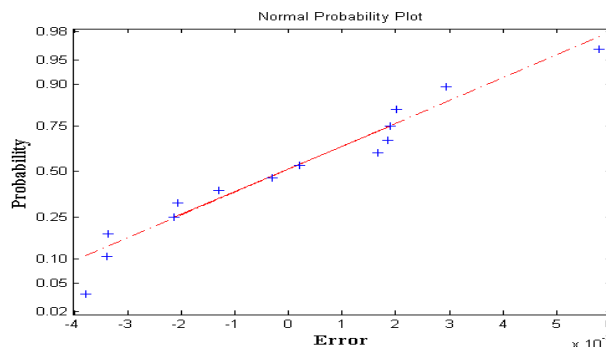


Figure (13) Normal probability plot of the error

Figure (14) shows a comparison between the observed data and correlation predictions. The figure shows a good agreement between them. It can be claimed that the present correlation well fits the experimental data and consequently we can use it to predict value of k .

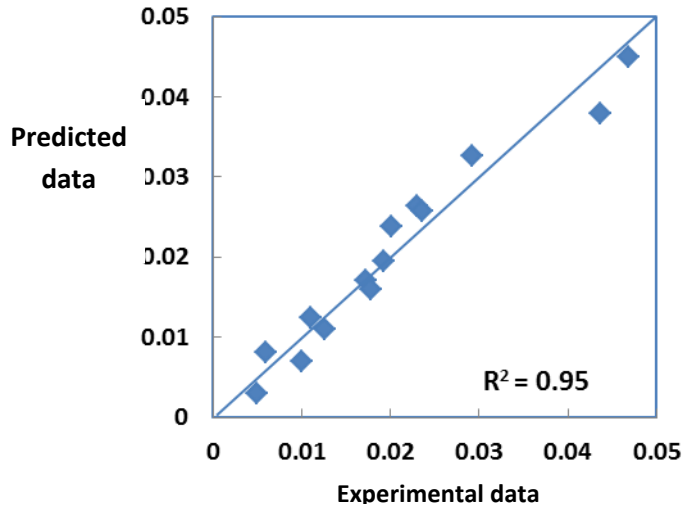


Figure (14) - Predicted versus the Experimental Data

Figure (15) shows a three-dimensional surface plot and contour lines at $I = 7$ A and $pH_0 = 2.56$ using (C_0) and $(F.R.)$ as the variables; the response is k . The contour plot shows contour lines of variable pairs that have the same value of k . The apparent rate constant k increased with increasing $(F.R.)$. Increased $(F.R.)$ simply means increased mass transfer; more explanation about the effect of $(F.R.)$ on electrolytic removal of copper was reported by Alebrahim et al. [7]. Increasing (C_0) , however, led to decreased value of k . At a specified electrolyte flow rate, i.e. a fixed mass transfer condition, k decreases with increasing (C_0) as the contour plot demonstrate. This behavior may be attributed to the development of some sort of polarization by which isolating barrier formed at the interface between cathode and electrolyte leading to decreased kinetics [17].

Figure (16), as well, shows a three-dimensional surface plot and contour lines at $pH_0 = 2.56$ and $C_0 = 570$ mg/L using (I) and $(F.R.)$ as the variables; the response is the apparent rate constant k . Generally, k increased with increasing the applied current which means the increase of reduction of Cu ions at the cathode surface.

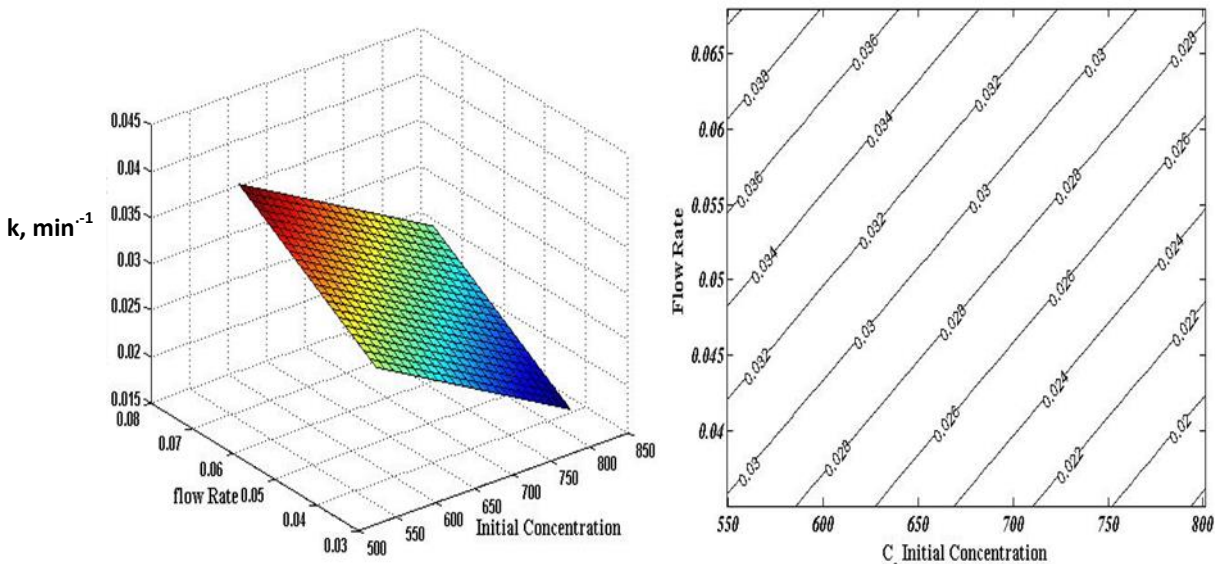


Figure (15) - Three-dimensional plot showing k as a function of (C_0) and $(F.R.)$ and contour plot illustrating the combined effect of (C_0) and $(F.R.)$ on k .

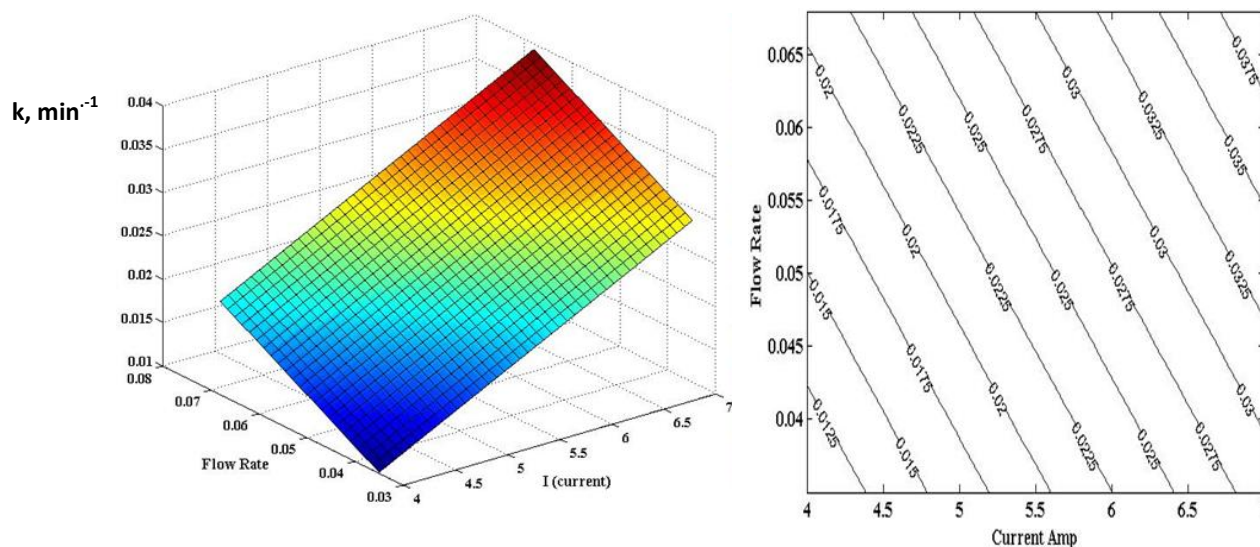


Figure (16) - Three-dimensional plot showing k as a function of (I) and (F.R.) and contour plot illustrating the combined effect of (I) and (F.R.) on k .

The resulted correlation was used to predict the data presented by Khattab et al. [6] as they used almost similar experimental set up for copper removal. Comparison between the predicted data and experimental is shown in Figure (17). The correlation could predict most values of k within $\pm 20\%$ deviation which may be considered satisfactory.

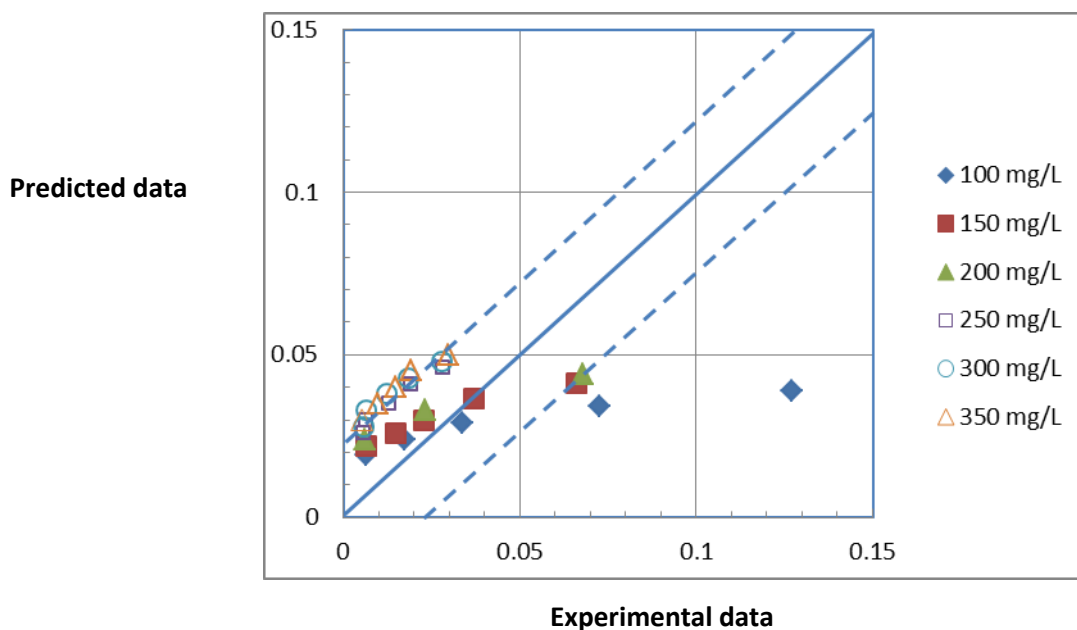


Figure (17)- Predicted versus the Experimental Data of Khattab et al. [6]

CONCLUSIONS

Removal of copper from CuSO_4 solution:

- The removal of copper ions followed first kinetics with respect to the copper concentration under all the experimental conditions reported in this work.

- The apparent rate constant, k , was found to be a function of (F.R.), (pH_0), (C_0)_{Cu} and (I). The relations correlating k with each of these operating parameters are:

- $k = A_{F.R.} (F.R.)^{B_{F.R.}}$; i.e. k increases with increasing F.R.
- $k = 0.0042 * (\text{pH}_0)^{1.4067}$; i.e. k increases with increasing pH_0 .
- $k = 19.3018 * (C_0)^{-1.05021}$; i.e. k decreases with increasing initial copper concentration C_0 .
- $k = k_0 e^{(aI)}$; i.e. k increases with increasing current intensity I .

The obtained statistical model has the form

$$k = -0.0218 + 0.322 (F.R.) - 4.8 * 10^{-5} C_0 + 0.0062 I + 0.00093 \text{pH}_0$$

The model could predict successfully the current experimental data where its F-test value and P-value are 42.2 and 7.824e-06, respectively. In addition, the model could predict the experimental values of k obtained using a similar experimental setup within $\pm 20\%$.

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