# Factorial Design for the Analysis of Packed-bed Sorption of Copper using Eggshell as a Biosorbent

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**Abstract**

Bench-scale column packed eggshell was utilized as a biosorption media for the removal of copper ions from aqueous solution. The sorbent used within the column was an eggshell and Ottawa sand mixture. The factorial design technique was employed to evaluate the influence of operating variables such as pH, influent flow rate, and copper influent concentration on the performance of the column. The break-through time was considered as a measure of the column performance. The maximum break-through time of 150 min was achieved at the operating condition of 2.5 ml/min influent flow rate, a pH of 5.0, and a copper concentration of 30 mg/l. The results of the factorial design showed that the main parameters resulted from influent flow rate and influent copper concentration having a strong influence on the break-through time, while the other binary interaction parameters had only slight effects. In addition to column studies, batch sorption tests were carried out to develop the equilibrium isotherms for the considered sorbent-sorbate system.

**Keywords:** Eggshell, Sorption, Packed-bed, Copper, Factorial design.

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## 1. Introduction

Contamination of wastewater by heavy metals is a very serious environmental problem [1,2]. The source of environmental pollution by heavy metals is mainly industry, i.e., metallurgical, electroplating, and metal finishing industries, tanneries, chemical manufacturing, mine drainage, and battery manufacturing [3]. Copper, lead, cadmium, chromium and mercury are among the toxic metals that present potential danger to human health [4]. These metals are dangerous as they are non-biodegradable and tend to accumulate in living organisms, causing various diseases and disorders [5]. Thus, removal of heavy metals from industrial wastewater is of primary importance [6].

Some of the conventional techniques for removal of metals from industrial wastewater include adsorption [1], sedimentation [7], electrochemical processes [8], ion exchange [9], biological operations [10], cementation [11], coagulation / flocculation [7], filtration and membrane processes [11], chemical precipitation and solvent extraction [12,13]. Recently, the use of non-living biomaterials as metal-binding compounds has been gaining advantage as these compounds require minimum care and maintenance and can be obtained more cheaply. Several studies have shown that non-living plant biomass materials are effective for the removal of trace metals from the environment [14-16]. Biomaterials with animal origin as waste, such as animal bones [17, 18] and chicken feathers [19], have been used for removal of heavy metals. The unique ability of these materials to bind metals has been attributed to the presence of various functional groups, which can attract and sequester metal ions. It has been demonstrated [16] that carboxyl groups found on the cell walls of dead algal biomass are potentially responsible for copper binding. This phenomenon has spurred interest in other natural materials that may contain similar functional groups.

In this work, eggshell was tested for its ability to remove copper from aqueous solution. Eggshell has a cellulosic structure and contains amino acids; thus, it is expected to be a good biosorbent candidate. Large amounts of eggshells are produced in some countries, such as the United States, in which 120,000 tons of waste eggshells

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are generated and disposed in landfills annually [20]. This also represents a serious problem for egg processing industries due to stricter environmental regulations and high landfill costs [21]. Therefore, this paper aims to present eggshells as porous adsorbents since it is feasible to grind the eggshell agro waste in the preparation of fine powders, which might pave the way for available materials [22]. Packed-bed operation will be implemented and important parameters that might affect this sorption process will be considered. Copper was selected as a model metal for this sorption process. Factorial design analysis will be implemented in order to attain this goal. The effect of sorbent concentration and equilibrium isotherm will be considered.

## 2. Two-Level Experimental Factorial Design

Factorial design is a statistical technique used to screen variables, to estimate the main effects and interaction effects of different variables, and to develop an empirical model for a given process. It is used because of its ability to gain a large amount of information from a minimum number of data points.

The first step in a factorial design test involves determination of an experimental outcome to be tested. The experimental outcome is the variable that the operating factors will influence and represents a measure of process performance; this is often referred to as the response variable. The experimental outcome for this work was chosen to be the column break-through time. Traditionally, in two-level factorial design the response variable is two at two levels of each operating variable in the process. These operating variables are represented as +1 or -1 depending upon their magnitude. The “high” operating variables are deemed positive ones (+1) and the “low” operating variables deemed negative ones (-1). This is also designated as a $2^3$ design. Through the use of factorial design, the operating variables influencing the column break-through time can be quantified. In this work, the break-through time is defined as the time at which the effluence copper concentration from the top of the column reaches 1 mg/l. This is the permissible level of copper [23].

## 3. Materials and Methods

*3.1. Biosorbent*

In this work, eggshell from chicken eggs was used as a new biosorbent for heavy metals. White chicken eggs were obtained from a Madison, Wisconsin farm. They were cracked and the yolks removed. The remaining eggshells were rinsed with water, while the yolks were discarded. It was noted that membrane did remain on the interior side of the eggshells. After the yolks were rinsed, they were dried using a vacuum drier. After drying, the shells were crushed using a mortar and pestle. Then, they were crushed to an average diameter of 0.8 mm (as determined from the sieve trays). The eggshell density and porosity were measured and found to be 1.31 g/cm$^3$ and 0.3837, respectively. The eggshells were mixed with Ottawa sand, as a supporting media, to produce a 50-wt% mixture of each. A mixture of both constituents of eggshell and Ottawa sands was achieved by manual mixing until a homogeneous mixture was observed. Ottawa sand was used as immobilizing media to support the eggshell particles. The control test showed negligible copper uptake by this type of sand.

*3.2. Packed-column test*

A column made of plexiglas was used for the packed-bed sorption test. The length and the inner diameter of the column were 32 and 1.8 cm, respectively. The column was packed with equal weights of eggshell and Ottawa sand mixture. The two ends of the column were held with a circular metal screen followed by filter papers.

Copper solution, at a given concentration and pH, was prepared, maintained in a flask, and then pumped through the column by a peristaltic pump at a certain flow rate. Samples were collected from the top of the column until the effluent concentration became almost the same as that of the influent.

Copper solutions were prepared using copper sulphate, $CuSO_4.7H_2O$ (analytical grade, Sigma). To maintain the pH consistency through the column, the solutions were made in buffer solutions at pHs 3 and 5. The buffer solutions were created from potassium hydrogen phalate with the addition of 0.1 M NaOH of HCl to reach a pH of 3 or 5. The concentration of copper was measured using Inductivity Plasma Mass Spectrometer; ICP-MS (model 7500a, Aglient Technologies Company, Japan). Several standards and a blank were used for standardization of the ICP. The copper solutions for running the trials were created to be 60 and 30 mg/l. The experimental set up is shown in Figure 1.

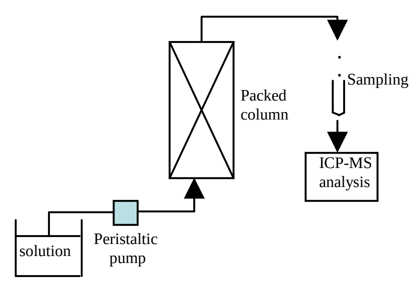


**Figure 1. Experimental setup for the packed bed operation**

Before running each trial, the column was pre-run with the same pH and flow rate of the next trial. This was to minimize possible channelling and allowed the column to settle before starting the test. The flow rates used for the experimentation were 2.5 and 5.0 ml/min. Table 1 shows the list of the trials and conditions along with their respective operating factors that would affect the break-through time. This table represents the conventional two-level factorial design (i.e., $2^3$ design), where the lower and higher levels are designated by -1 and +1, respectively.

**Table 1. Two-level factorial design for the packed-bed sorption of copper by eggshell**

| Trial # | Flow rate (ml/min), $x_1$ 2.5(-1)/5.0(+1) | pH, $X_2$ 3(-1)/5(+1) | Copper concentration (mg/l), $X_3$ 30(-1)/60(+1) | Break-through time, Y(h) |
|---|---|---|---|---|
| 1 | +1 | +1 | +1 | 35.0 |
| 2 | +1 | +1 | -1 | 66.0 |
| 3 | +1 | -1 | +1 | 32.0 |
| 4 | +1 | -1 | -1 | 42.0 |
| 5 | -1 | +1 | +1 | 97.0 |
| 6 | -1 | +1 | -1 | 150.0 |
| 7 | -1 | -1 | +1 | 64.0 |
| 8 | -1 | -1 | -1 | 125.0 |

At the beginning of the tests, there was no information about the characteristics of the break-through curve. Therefore, for trial # 1 the samples were taken every minute. This was determined to be more efficient. To facilitate easier data collection and testing for remaining trials, if the flow rate was 2.5 ml/min the samples were taken every 5 minutes, and for 5 ml/min they were taken every 3 minutes. These sampling intervals were found sufficient to describe the break-through curve.

*3.3. Batch sorption test*

Batch tests were done to develop the isotherm equilibrium curve for the system under consideration. The batch trials consisted of adding different amounts of eggshell-sand mix sorbent, in the range of 0.3165–7.163 g, to small vials each containing 20 ml of 50 mg/l copper solution at pH 5. This would also indicate the effect of the amount of sorbent in this sorption process. The vials were then allowed to reach equilibrium with the aqueous mixture over a three-day period with various mixing to ensure that equilibrium had occurred. These samples were then filtered and the concentration of copper in the residual was measured using the ICP.

## 4. Results and Discussion

*4.1. Break-through curves*

A typical break-through curve, i.e., effluent concentration versus time, for the case of 60 mg/l influent copper concentration at pH 5 and 5 ml/min influent flow rate, is shown in Figure 2. Break-through curves for the other cases shown in Table 1 were also obtained and are similar in shape, but different in characteristics. In this case (Figure 2), steady-state was attained almost after 120 minutes of the operation, while about 35 minutes were required for the break-through time to be attained. In the case of lower flow rate (data not shown), a longer period was required to attain steady-state. This also gives a longer break-through time, i.e., in the case of a lower flow rate, which is expected because of the better opportunity of sorbent exposure to sorbate. It was also noted that a lower pH value (pH 3) resulted in a shorter break-through time than a higher pH value (pH 5). This is due to the fact that sorption uptake of heavy metals by biological materials increases with an increase in solution pH. It was also noted (data not shown) that the decrease in the influent concentration resulted in a delay in the occurrence of the break-through. These are normal trends that could be obtained by any metal packed-sorption system.

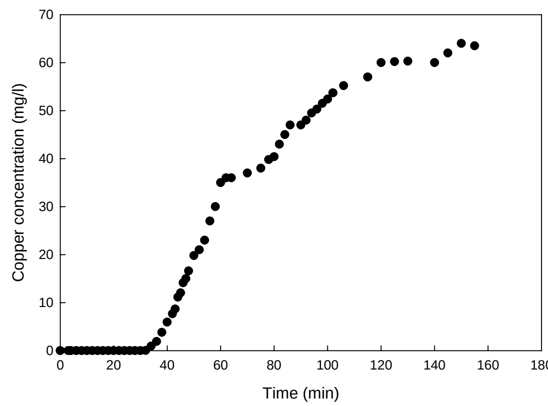


**Figure 2. Break-through curve for the packed-bed sorption of copper using eggshell Influent copper concentration: 60 mg/l; pH: 5; influent flow rate: 5 ml/min.**

*4.2. $2^3$ factorial model*

In the factorial design analysis, the operating variables flow rate, pH, and copper concentration were designated as $X_1$, $X_2$, and $X_3$, while the break-through time, as a response variable, was designated as $Y$. A $2^3$ complete factorial design was performed with the values of these operating variables shown in Table 1. As mentioned previously, this results in eight tests with all possible combinations of $X_1$, $X_2$, and $X_3$. The break-through time, $Y$, was measured for each of these tests as shown in Table 1. These tests were performed randomly to avoid any time trend or other types of influences on the experiments. The factorial design yielded results pertaining to the main operating parameters and interaction parameters. Furthermore, since replicate runs were not produced, a standard deviation was estimated based on the sampling interval. Similar analysis outlined in this work has been previously applied for packed-bed sorption of copper using spent animal bones, in which the effect of such operating variables, port location, flow rate, and copper concentration on the response variable break-through time was determined using the complete factorial design model [17].

The complete factorial model that can be used to fit the data in Table 2 is:

$$E(Y) = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 + \beta_{123} X_1 X_2 X_3$$
(1)

where the parameters $\beta_i$ are responsible for the influence of the operating variable $X_i$ on the response $Y$, while $\beta_{ij}$ and $\beta_{ijk}$ are responsible for possible interactions among the operating variables $i$, $j$, and $k$ and the effect of this interaction on the response. Values of the parameter displayed in Eq. (1) can be obtained from the least square estimates:

$$\underline{\beta} = \left(\underline{X}^T \underline{X}\right)^{-1} \underline{X}^T \underline{Y}$$
(2)

The matrix $\underline{X}$ represents the matrix of the operating variables at different runs. The elements of the columns of $\underline{X}$ associated with the interaction terms $X_1 X_2$, $X_1X_2X_3$ are the products of the corresponding elements in the columns associated with $X_1$, $X_2$, and $X_3$. The matrix $\underline{X}^T\underline{X}$ is an 8 × 8-symmetrical-square matrix with diagonal elements each equal to 8, and off-diagonal elements each equal to zero. Therefore, $(\underline{X}^T\underline{X})^{-1}$ is also 8 × 8-symmetrical-square matrix with diagonal elements each equal to 1/8, and off-diagonal elements each equal to zero. Because $\underline{X}^T\underline{X}$ is a diagonal matrix, each of the parameter estimates in Eq. (2) can be calculated independently of the other parameters. That is, the parameter estimates are mutually uncorrelated. Further, since the variances of the parameter estimates, $V(\hat{\beta})$, are the diagonal elements of $(\underline{X}^T\underline{X})^{-1}\sigma^2$ [24], where $\sigma^2$ is the estimate of pure error variance, it is clear that a $2^3$ design produces parameter estimate equal variances, namely $\sigma^2/8$.

Using the experimental data listed in Table 1, the matrix $(\underline{X}^T\underline{X})^{-1}$ $X^TY$ was calculated and accordingly, the parameters in Eq. (1) were estimated and resulted in the following model:

$$\hat{Y} = 76.3 - 32.6X_1 + 10.6X_2 - 19.4X_3 - 3.8X_1X_2 + 9.2X_1X_3 - 1.7X_2X_3 - 3.6X_1X_2X_3$$
(3)

It is obvious that interactions exist among the operating variables and that the parameters do not operate independently on the response (they are not additive).

**Table 2. Calculations and results for main effects and interaction effects**

| Main operating variables | | | | Factor interactions | | | |
|---|---|---|---|---|---|---|---|
| Y(h) | $X_1$ | $X_2$ | $X_3$ | $X_1X_2$ | $X_1X_3$ | $X_2X_3$ | $X_1X_2X_3$ |
| 35.0 | +1 | +1 | +1 | +1 | +1 | +1 | +1 |
| 66.0 | +1 | +1 | -1 | +1 | -1 | -1 | -1 |
| 32.0 | +1 | -1 | +1 | -1 | +1 | -1 | -1 |
| 42.0 | +1 | -1 | -1 | -1 | -1 | +1 | +1 |
| 97.0 | -1 | +1 | +1 | -1 | -1 | +1 | -1 |
| 150.0 | -1 | +1 | -1 | -1 | +1 | -1 | +1 |
| 64.0 | -1 | -1 | +1 | +1 | -1 | -1 | +1 |
| 125.0 | -1 | -1 | -1 | +1 | +1 | +1 | -1 |
| $^a\sum_+$ | 175 | 348 | 228 | 290 | 342 | 334 | 269 |
| $^a\sum_-$ | 436 | 263 | 383 | 321 | 269 | 312 | 320 |
| Difference effect | -65.25 | 21.25 | -38.75 | -7.75 | 18.25 | 5.50 | -12.75 |

$^a\sum_+$ corresponds to the sums of the responses at high $X_i$, while $^a\sum_-$ corresponds to sums of the responses at low $X_i$

*4.3. Estimation of main effects and interaction effects*

One of the features of factorial design analysis is the direct estimation of the main effects and interaction effects. The main effect can be estimated from the difference between the average high- and low-factor-level responses:

$$\text{Main effect of } X_i = \frac{\sum\{\text{Response at high } X_i\} - \sum\{\text{Response at low } X_i\}}{\{\text{Half the number of factorial runs}\}}$$
(4)

In this case, all the data in the experiment (Table 1) should be used to estimate each main effect and interaction effect, and each of these can be estimated independently of the other effects. This feature of $2^n$ effect is referred to as *hidden replication*, giving maximum information per experimental run [24]. A summary of the calculation procedure for the main effect of each term in Eq. (3) is shown in Table 2.

Thus, according to the calculations displayed in Table 2, the effect of increasing the flow rate from 2.5 to 5.0 ml/min over all levels of influent copper concentrations and solution pH is to decrease the break-through time to 65.25 minutes. Also, the solution pH effects increase the break-through time to 21.25 minutes, while the metal concentration effect decreases the break-through time to 38.75 minutes. It can be concluded that the influence of feed flow rate is greater than that of metal concentration followed by solution pH.

The effect of factor interactions can be similarly calculated. These factors measure any possible interactions in the system. It is seen that the values of these effects (Table 2) are significant compared to the effect of the operating variables; therefore, their influence on the response cannot be neglected.

*4.4. Assessment of significance of main effects*

The influence of each term in Eq. (3) on the response can be assessed by giving a confidence interval for each parameter. Accordingly, if the confidence interval for a given parameter contains the point zero, it means that the term associated with such parameter is not important and can be excluded from the model. The confidence interval for the least squares parameter estimates is given by [25]:

$$\hat{\beta}_i \pm t_{\nu,\alpha}\left[V\left(\hat{\beta}_i\right)\right]^{1/2} \quad (5)$$

where $t_{\nu,\alpha}$ is a student's statistics, $\nu$ is the degrees of freedom associated with the pure variance, $\sigma^2$, and $\alpha$ is the probability limit. In this work, an estimate of pooled variance, based on sampling intervals of 3 and 5 minutes for high and low flow rates, of 17 was obtained with corresponding $t_{\nu,\alpha}$ of 1.95 at 95% confidence level. Since $V(\hat{\beta})$ of each of the parameter estimates in Eq. (3) is $\sigma^2/2^3$, then the 95% confidence internal for each parameter, according to Eq. (5) is $\hat{\beta}_i \pm 8.04$. Therefore, the 95% confidence intervals are:

| | | | |
|---|---|---|---|
| $X_1$ flow rate | -32.6 ± 8.04 | or | -41 to -24.4 |
| $X_2$ pH | 10.6 ± 8.04 | or | 2.56 to 18.64 |
| $X_3$ copper concentration | -19.4 ± 8.04 | or | -27.44 to -11.36 |
| $X_1X_2$ factor interaction | -3.8 ± 8.04 | or | -11.84 to 4.24 |
| $X_1X_3$ factor interaction | 9.2 ± 8.04 | or | 1.16 to 17.24 |
| $X_2X_3$ factor interaction | -1.7 ± 8.04 | or | -4.5 to 6.34 |
| $X_1X_2X_3$ factor interaction | -3.6 ± 8.04 | or | -11.64 to 4.4 |

It is seen that the 95% confidence interval for the parameters associated with such interactions, $X_1X_2$, $X_2X_3$ and $X_1X_2X_3$, passes through the zero point. Thus, at 95% confidence level these interactions are insignificant and do not have important effects on the response variable $Y$. However, the effect of each main variable, influent flow rate, solution pH, and copper concentration on the response variable cannot be neglected over the operating conditions tested in this work. Therefore, at 95% confidence level, Eq. (3) can be simplified as:

$$\hat{Y} = 76.3 - 32.6X_1 + 10.6X_2 - 19.4X_3 + 9.2X_1X_3 \quad (6)$$

Comparison between experimental and predicted values using this approximate model is displayed in Table 3. It is seen that the model predicts most of the experimental data reasonably well with an $R^2$ value of 0.9815 and Sum Square of Residual $\left(SSR = \sqrt{\sum (Y - \hat{Y})^2 / (n-1)}\right)$ of 5.933.

**Table 3. Comparison between experimental and predicted values for break-through time using Equation 6**

| Trial # | Experimental Break-through time, Y(h) | Predicted Break-through time, $\hat{Y}$ (h) |
|---|---|---|
| 1 | 35.0 | 44.1 |
| 2 | 66.0 | 64.5 |
| 3 | 32.0 | 22.9 |
| 4 | 42.0 | 43.3 |
| 5 | 97.0 | 90.9 |
| 6 | 150.0 | 148.1 |
| 7 | 64.0 | 69.7 |
| 8 | 125.0 | 126.9 |

*4.5. Effect of sorbent concentration*

The effect of the amount of eggshell addition on the removal of copper ions from aqueous solutions was investigated in batch-test experiments. Different amounts of eggshell in the range 0.3165-7.163 g were added to 20 ml of a metal solution of 52 mg/l initial copper concentration, as previously mentioned. The results are expressed as amount of adsorbent added versus residual copper concentration remaining in the solution and are shown in Figure 3. As expected, the clay residual concentration of Cu ions decreased with an increase in the amount of clay added. A maximum of 96% removal of copper ion was achieved when 7.163 g of eggshell was used.

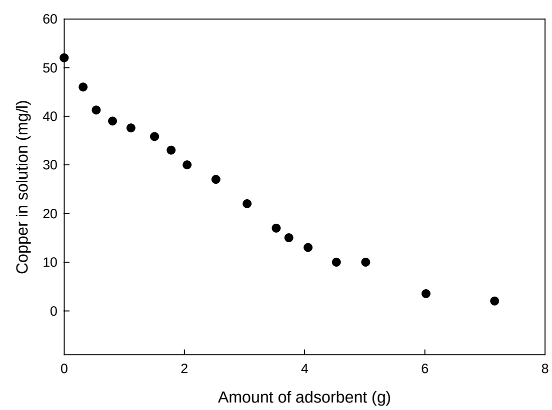


**Figure 3. Effect of sorbent dosage on copper removal by eggshell Initial copper concentration: 52 mg/l; pH: 5.0.**

*4.6. Equilibrium isotherm*

The equilibrium isotherm for sorption of copper by eggshell can be obtained from the results of Figure 3. An isotherm is a relationship between equilibrium metal concentration in solution, $C_e$ (mg/l), i.e., residual concentration, and equilibrium metal concentration in the sorbent, $q_e$ (mg/g), i.e., metal uptake. Such an equilibrium relationship can be represented by different models, the most famous being the Langmuir and Freundlich. These are described below in linearized forms:

*Langmuir isotherm model:*

$$\frac{1}{q_e} = \left(\frac{b}{q_m}\right)\frac{1}{C_e} + \frac{1}{q_m}$$

where $q_m$ (mg Cu/g sorbent) and $b$ (l/mg) are the characteristic Langmuir parameters where $q_m$ represents the maximum sorbent capacity while $b$ is a parameter related to the energy of adsorption.

*The Freundlich isotherm*:

$$\ln q_e = \ln k_f + (1/n)\ln C_e$$

In this case $k_f$ and $1/n$ are the characteristic parameters of this model where $k_f$ is a parameter responsible for the relative maximum sorption of the sorbent and $1/n$ is normally related to the sorption intensity.

The experimental equilibrium isotherm data (Table 4) were attempted with both of the models, but it was found that the data better follow the Freundlich representation, with $R^2$ and SSR values of 0.976 and 0.0148, respectively, as shown in Figure 4. The equilibrium data did not lie on the straight line of the Langmuir model, which would indicate the heterogeneous nature of the sorption sites. Normally, the parameters $k_f$ and $1/n$, can be obtained from the plot ln$q$ versus ln$C$; the intercept and the slope of the resulting straight line were used for the determination of $k_f$ and $1/n$, respectively. According to Figure 4, these parameters were found to be 0.223 and 0.138, respectively. These values of $k_f$ and $1/n$ are comparable to the other reported values in the literature for the sorption of copper ion by other sorbents [18, 26, 27].

**Table 4. Equilibrium isotherm data used for fitting of Freundlich model**

| Copper concentration, Ce (ppm) | Copper uptake Experimental, $q_e$ (mg/g) |
|---|---|
| 0.0400 | 0.1390 |
| 0.0700 | 0.1605 |
| 0.2000 | 0.1670 |
| 0.2000 | 0.1840 |
| 0.2600 | 0.1910 |
| 0.3000 | 0.1968 |
| 0.3400 | 0.1970 |
| 0.4400 | 0.1957 |
| 0.5400 | 0.1964 |
| 0.6000 | 0.2130 |
| 0.6700 | 0.2110 |
| 0.7164 | 0.2120 |

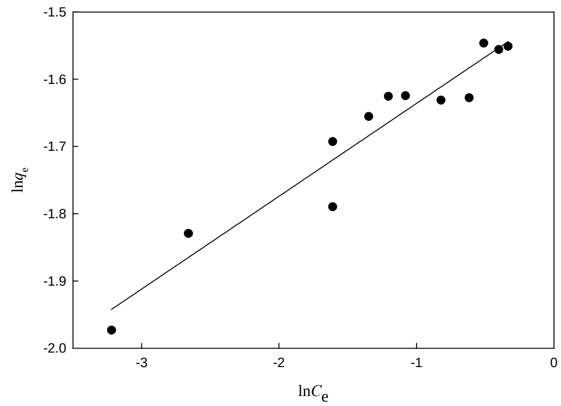


**Figure 4. Freundlich equilibrium isotherm for batch sorption of copper using eggshell**

## 5. Conclusions

The factorial design is a useful tool in determining the operating variables that significantly influence the column's break-through time. It also reduces the guesswork that would have would have gone into determining which factors actually affected the column breakthrough time. At 95% confidence level, the factorial design showed that all three variables tested in this work, flow rate, solution pH, and copper concentration, have significant effects on the break-through time during the backed bed sorption of copper by eggshell. Also, all possible interactions between these variables, except interaction between flow rate and copper concentration, are insignificant and do not affect the value of the break-through time within the range of the operating conditions tested in this work.

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