Linear and Non-linear Regression Analysis for the Kinetics of \([\text{AuCl}_4^{-}]\) Removal by \(p\)-Hydroxybenzoate intercalated Mg/Al-Hydrotalcite

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Abstract. The best fit equations of linear and non-linear forms of the two widely used kinetic models, namely pseudo-first-order (PFO) and pseudo-second-order (PSO) equations, were compared in this study. The experimental kinetics of \([\text{AuCl}_4^{-}]\) removal by \(p\)-hydroxybenzoate intercalated Mg/Al-hydrotalcite was used for this research. \(R^2\) coefficient was employed as error analysis methods to determine the best-fitting equations. The results show that the non-linear form was better at best-fitting than the linear form. The experimental kinetics may have been distorted by linearization of the linear kinetic equations, and thus, the non-linear forms of kinetic equations should be primarily used to obtain the adsorption parameters.

Introduction

Sorption processes are proved to be an effective method for uptake of metal ions from solution [1-3]. Hydrotalcite potentially have high capability for adsorption. Hydrotalcite adsorption ability is supported by their high anion exchange and surface area [4,5]. In order to enhance the effectiveness of their adsorption capability, many researchers have modified hydrotalcite by various ways. There are some hydrotalcite modification techniques, but surfaces and galleries modifications were more often conducted. Many different anions can be intercalated into the interlayer space. In order to enhance the effectiveness of their adsorption capability, \(p\)-hydroxybenzoate was chosen as modifier for hydrotalcite [6].

The nature of sorption process will depend on physical or chemical characteristics of the adsorbent systems and also on the system conditions. Adsorption kinetics is an important parameter to describe the characteristics of an interaction between adsorbent and adsorbate, which in turn controls the resident time in the adsorbent-solution interface. The accuracy of the model for estimating it is generally a function of a number of independent parameters. The mathematical simplicity of applying the model and its wide use in various data adsorption will have implications for its popularity.

In recent years, the linear forms of the PFO and PSO equations were widely used to determine the most fitted kinetic model for the adsorption process. When using the linear form, experimental adsorption kinetics should be linearized for the linear least-squares regression to estimate the model.
parameters. It has been reported that transformations of non-linear equations to linear forms implicitly alter their error structure in the measurement of model parameters [7-11]. As a result, one may obtain different kinetic parameters when using different forms of model equations for a given adsorption process. However, recently a nonlinear optimization model has been developed for the adsorption kinetics model. A number of researchers have conducted studies on the accuracy of the application of linear and non-linear regression models to explain the adsorption kinetics parameters.

Currently, however, there are few studies comparing the linear and non-linear forms of the PFO and PSO models in estimating the kinetic parameters for the adsorption of metal ions on hydrotalcite. Thus, in this study, the non-linear forms of the PFO and PSO equations were used to fit the experimental kinetic data for the adsorption of [AuCl₄]⁻ onto p-hydroxybenzoate intercalated Mg/Al-hydrotalcite, and a comparative analysis between the linear and non-linear method in determining the kinetic parameters was conducted.

Methods

1.1. Materials

All chemicals - Mg(NO₃)₂•6H₂O, Al(NO₃)₃• 9H₂O, NaOH, and HCl were purchased from Merck Co. Inc., Germany, NH₃•H₂O and p-hydroxybenzoic acid were purchased from Sigma-Aldrich and nitrogen sufficiently high purity (99.99%) was purchased from CV Perkasa (Indonesia) - are of analytical grade and used as received without further purification. [AuCl₄]⁻ solution (HAuCl₄) was prepared by dissolving of gold (99.99%) in aqua regia solution. Gold (99.99%) were purchase from PT. ANTAM Indonesia. The p-hydroxybenzoate intercalated Mg/Al-hydrotalcite was prepared by co-assembly process [6]. Absorption spectra were obtained using a Atomic Absorption Spectroscopy.

1.2. Batch equilibrium and kinetic studies

Into a series of flasks containing 10 mL of [AuCl₄]⁻ 100 mg/L solutions at optimum pH obtained from the above experiment, 10 mg of p-hydroxybenzoate intercalated Mg/Al-hydrotalcite was added. The flasks were then subjected to continuous stirring at contact times 0, 10, 20, 30, 60, 90, 120, 150, 200, 250, 300 and 350 min. At each selected contact time, a sample from the respective flask was immediately taken, filtered through a Whatman 42 filter and the remaining concentration of [AuCl₄]⁻ in the filtrate was analyzed by AAS.

Results and Discussions

The ability of p-hydroxybenzoate intercalated Mg/Al-hydrotalcite to remove [AuCl₄]⁻ was carried out at temperature 25 °C and initial medium acidity equivalent to pH 3. To describe adsorption data obtained under non-equilibrium conditions, two kinetic models, namely the pseudo-first-order (PFO) and the pseudo-second-order (PSO) were used [12-17]. The kinetic rate equations following PFO can be represented as

\[ \frac{dq}{dt} = k_1(q_e - q_t) \]  

Where \( k_1 \) is the rate constant.

Integrating Eq. (1) for boundary conditions \( t = 0 \) and \( t = t \) and \( q_t = 0 \) and \( q_e = q_e \), gives [16]:

\[ \log(q_e - q_t) = \log(q_e) - \frac{k_1}{2,303} t \]  

(2)

The constants can be determined experimentally by plotting of \( \log(q_e - q_t) \) against \( t \).

Likewise, the reductive adsorption of [AuCl₄]⁻ following PSO kinetics can be represented as

\[ \frac{dq}{dt} = K_2(q_e - q_t)^2 \]  

(3)

Where \( k_2 \) is the rate constant.

Integrating Eq. (3) for boundary conditions \( t = 0 \) and \( t = t \) and \( q_t = 0 \) and \( q_e = q_e \), gives [17]:

\[ \log(q_e - q_t) = \log(q_e) - \frac{k_2}{2,303} t \]  

(4)
\[ q_t = \frac{k_q q_e^2 t}{1 + k_q q_e t} \]  

Eq. (4) can be linearized to at least five different linear forms as shown in Table 1. Table 1 also shows the non-linear form of Eq.

**Table 1. Linear and non-linear of pseudo-first-order and pseudo-second-order equations**

| Kinetic model       | Non-linear | Linear | Type |
|---------------------|------------|--------|------|
| Pseudo-first-order  | \[ q_t = q_e (1 - e^{-k_e t}) \] | \[ \log(q_e - q_t) = \log(q_e) - \frac{k_1}{2,303} t \] | PFO |
| Pseudo-second-order | \[ \frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \] | \[ \frac{t}{q_t} = \frac{1}{q_e} + \frac{1}{k_2 q_e^2} t \] | PSO-1 |
|                     | \[ \frac{1}{q_t} = \frac{1}{q_e} + \frac{1}{k_2 q_e^2} t \] | \[ q_t = q_e - \frac{1}{k_2 q_e} t \] | PSO-2 |
|                     | \[ q_t = k_2 q_e^2 - k_2 q_e q_t \] | \[ q_t = k_2 q_e^2 - k_2 q_e q_t \] | PSO-3 |

Data analysis from experimental [AuCl\(_4\)]\(^-\) removal by p-hydroxybenzoate intercalated Mg/Al-hydrotalcite aims to determine adsorption kinetics of [AuCl\(_4\)]\(^-\) removal process. The analysis was performed by matching [AuCl\(_4\)]\(^-\) data removal to PFO and PSO kinetics models. Data matching was carried out through linear and non-linear models. Linear model matching was done by determining the \(R^2\) coefficient which can be obtained automatically from Microsoft® Excel software by plotting according to the Table 1. While non-linear model matching was done using the solver add-in feature available in Microsoft® Excel software. Determination of \(R^2\) coefficient for non-linear model was done using Eq. (5).

\[ R^2 = 1 - \frac{\sum (q_{t_{\text{calc}}} - q_{t_{\text{exp}}})^2}{\sum (q_{t_{\text{calc}}} - q_{t_{\text{exp}}})^2 + \sum (q_{t_{\text{calc}}} - q_{t_{\text{exp}}})^2} \]

\(q_{t_{\text{exp}}}\) and \(q_{t_{\text{calc}}}\) are amount of adsorbate which was adsorbed by the experimental and the adsorbate which was adsorbed by the calculation, respectively.

Study of the removal kinetics of [AuCl\(_4\)]\(^-\) by linear model was studied by plotting the graph as shown in Fig. 1, while non-linear model of the two kinetics is presented in Fig. 2.
Figure 1. Experimental data and the fitted linear (a) PFO, (b) PSO-1, (c) PSO-2, (d) PSO-3, (e) PSO-4, and (f) PSO-5
Fig. 1 shows that matching result of [AuCl₄]⁻ removal by p-hydroxybenzoate intercalated Mg/Al-hydrotalcite using linear model produces a double result where the $R^2$ coefficient of the PFO kinetics was greater than $R^2$ coefficient of PSO-1, PSO-4, and PSO-5, but smaller when compared to $R^2$ coefficient of PSO-2 and PSO-3. This can lead to errors in drawing conclusions, whether following PFO or PSO kinetics. The difference in matching results depends on how the kinetics equation was transformed into a linear form, which would have an impact on changing the error distribution so that the model parameter deviates [18]. In addition, the linear method which was based on the assumption that the scatter vertical points around the line were following the Gaussian distribution and the error distribution of each value on the X axis had a uniform value [19]. This rarely occurred or even practically could be said to be impossible in kinetics, as it was known that all adsorption kinetics models are non-linear. The linear method emphasized the distribution of errors only along the y-axis, each of the types of a kinetic model would produce different parameter values even with the same experimental data. Therefore, the linear method was not appropriate in predicting the suitability of a kinetics model for experimental data specifically and was unable to provide a good basic understanding of kinetics in the adsorption system so that it can produce wrong conclusions.

| Table 2. Kinetic parameters obtained by using the linear and non-linear methods. |
|---------------------------------|--------|-----------------|-----------------|---|
| Kinetic model                  | Eq.    | $k_1 \times 10^2$ (min⁻¹) | $k_2 \times 10^4$ (g.mg⁻¹.min⁻¹) | $R^2$ |
| Linear pseudo-first-order      |        |                  |                           |   |
| Linear PFO                    | 5      | 1.0364           |                               | 0.9593 |
| Linear pseudo-second-order    |        |                  |                           |   |
| Linear PSO-1                  | 6      | 50               |                               | 0.7505 |
| Linear PSO-2                  | 7      | 3.2778           |                               | 0.9596 |
| Linear PSO-3                  | 8      | 7.0453           |                               | 0.9662 |
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Linear PSO
-4 9 5.0772 0.8459
Linear PSO-5 10 4.7574 0.8459

Linear pseudo-first-order

Non-linear PFO 11 1.9871 0.9474
Non-linear pseudo-second-order

Non-linear PSO 12 2.4938 0.9710

In non-linear form, Fig. 2 and Table 2 show that PSO kinetic model with $R^2$ coefficient value of 0.9710 gets a more appropriate result than the PFO kinetic model which has an $R^2$ coefficient value of 0.9474. The use of non-linear models avoids the transformation process into linear form so that each experimental data has the same error structure. The matching results show that the removal rate of $[\text{AuCl}_4]^{-}$ by $p$-hydroxybenzoate intercalated Mg/Al-hydrotalcite follows the pseudo-second-order kinetics model, where $[\text{AuCl}_4]^{-}$ removal rate constant was $2.4938 \times 10^{-4}$ g.mg$^{-1}$ .minute$^{-1}$.

4. Conclusion
The removal rate of $[\text{AuCl}_4]^{-}$ by $p$-hydroxybenzoate intercalated Mg/Al-hydrotalcite was found to be well represented by the pseudo-first-order and pseudo-second-order kinetic. The matching results show that the removal rate of $[\text{AuCl}_4]^{-}$ by $p$-hydroxybenzoate intercalated Mg/Al-hydrotalcite follows the pseudo-second-order kinetics model, where $[\text{AuCl}_4]^{-}$ removal rate constant was $2.4938 \times 10^{-4}$ g.mg$^{-1}$ .min$^{-1}$. This study shows that the bestfitting non-linear forms of the pseudo-first-order and pseudo-second-order kinetic models were superior to the linear forms. The model parameters may be distorted when the non-linear equations were transformed to linear forms. Therefore, the non-linear method should be primarily adopted to obtain the adsorption parameters.

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