Determination methods of Langmuirian sorption kinetic coefficient

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ABSTRACT

The Langmuirian kinetic coefficient \( k_{ads} \) was determined by several methods. The study of Pb\(^{2+} \) sorption kinetic using Caulerpa lentillifera showed that \( k_{ads} \) was about 0.074, 1.49, 0.223, and 8.15 m\(^3\)/(mol*min) for method A, B, C, and D, respectively. Method A (direct method) gave the best fit while method C (Extended geometric method) seem to have very good prediction compared with the other approximation method (method B and D).

1. INTRODUCTION

Sorption kinetic is very important in sorption study. Generally, sorption kinetics were represented by pseudo first and pseudo second order models while kinetic rate coefficients in these models are dependent with process parameters such as initial sorbate concentration and sorbent dose. Rate coefficient of Langmuirian kinetic model is independent with both sorbate concentration and sorbent dose which is better in prediction of kinetic profile than the two models. Hence, determination of the Langmuirian kinetic coefficient is very important. This work summarized methods in determination of the coefficient. Pb\(^{2+} \) and Caulerpa lentillifera were selected as sorbate and sorbents, respectively, to evaluate efficiency of each determination method.

2. LANGMUIRIAN KINETIC AND DETERMINATION OF ITS COEFFICIENT

Langmuirian kinetic model as shown in Eq. (1)

\[
\frac{dq_t}{dt} = k_{ads} C_t (q_{max} - q_t) - k_{des} q_t
\]

This equation could be solved by integrating from \( t = 0 \) to \( t = t \) and \( q_t = 0 \) to \( q_t = q_t \) using partial fraction integration technique results in the exact solution as:

\[
q_t = \frac{2q_{max}bC_o}{\alpha(1 - e^{kt})} \left(1 - e^{k_{ads}b \beta t} \right)
\]

where \( \alpha \) and \( \beta \) are dimensionless parameters which defined as \( \alpha = q_{max} bX_o + bC_o + 1 \) and

\[
\beta = \sqrt{(q_{max}bX_o + bC_o + 1)^2 - 4q_{max}b^2C_oX_o},
\]

\( q_{max} \) is maximum sorption, \( b \) is affinity constant (\( b = k_{ads}/k_{des} \)), \( C_o \) is initial sorbate concentration in liquid phase, \( X_o \) is sorbent dose, \( t \) is contact time, \( q_t \) and \( C_t \) is sorption capacity and sorbate concentration in liquid phase at time \( t \), respectively. \( k_{ads} \) can be obtained using following techniques:

**Method A:** This method can be achieved by rearranging Eq. (2) into linear from as follows:

\[
\frac{b}{\beta} \ln \left[ \frac{q_t (\alpha - \beta) - 2q_{max}bC_o}{q_t (\alpha + \beta) - 2q_{max}bC_o} \right] = k_{ads}t
\]

\( k_{ads} \) can be obtained by plotting the left hand side of Eq.(3) as y-axis and \( t \) as x-axis and find the slope using linear regression technique. Then \( k_{des} \) can also be obtained using the relationship \( k_{des} = b/k_{ads} \).

**Method B:** This method is to determine \( k_{ads} \) from pseudo first or pseudo second order kinetic model as follow:

Oral presentation
Determination of \( k_{\text{ads}} \) and \( k_{\text{des}} \) could be achieved from slope and intercept, respectively, of the plot between \( k_1 \) and \( C_o \) when the sorption kinetic data fit with pseudo first order [1]. In case of pseudo second order, Azizian reported that \( k_2 \) is a complex function of \( C_o \) as \( k_2 = -\gamma / 2q_e \) [1]. This could be rearranged and written into Eq. (4) according to format of this work.

\[
k_2 = k_{\text{ads}}X_0 (\alpha + \beta) / (\alpha - \beta)
\]

Hence, \( k_{\text{ads}} \) can be determined from a slope of the plot between \( k_2 \) against \( X_0(\alpha + \beta)/(\alpha - \beta) \) when the sorption kinetic data fit with pseudo second order.

**Method C:** This method was called as extended geometric method [2] which could be express in Eq. (5).

\[
k_{\text{ads}} \approx \frac{k_i}{C_0 \left(1 - \frac{t_L}{2t_e}\right) - q_{\text{max}}X_0k_iX_0 \left(\frac{1 - k_iX_0}{3}\right)}
\]

where \( k_i = q_L/q_{\text{max}}t_L \), \( t_L \) is a initial time that relationship between \( q_t/q_{\text{max}} \) and \( t \) is linear (min), \( q_e \) is sorption capacity at \( t_L \), and \( t_e \) is equilibrium time.

**Method D:** This method applied limit theorem to Eq. (1) by taking limit at \( t \to 0 \) to the both side of the equation resulted in:

\[
h = k_{\text{ads}}q_{\text{max}}C_o
\]

where \( h \) is initial sorption rate which equal to \( q_tk_1 \) and \( q_e^2k_2 \) when the sorption kinetic data fit with pseudo first and second order, respectively. \( k_{\text{ads}} \) can be obtained from slope of the plot between \( h \) and \( q_{\text{max}}C_o \).

### 3. DISCUSSION AND CONCLUSION

The experiment was performed by mixing 0.5 g of sorbent in 30 mL of the synthetic Pb\(^{2+}\) solution with \( C_o \) varied from 0 – 10 mM. The pH was chemically controlled to 5 using CH\(_3\)COONH\(_4/\)CH\(_3\)COOH buffer system. The mixtures were mixed vigorously for 0 – 60 min at 21 ± 2°C. Suspended solids were separated out with GF/C filter. Pb\(^{2+}\) was then measured by AAS.

The kinetic results were well fit with the pseudo second order kinetic model. The \( q_t \) predicted by the pseudo second order model was used for calculating the sorption isotherm. The isotherm was found to follow the Langmuir isotherm. The \( q_{\text{max}} \) and \( b \) were about 0.165 mol/kg and 3.30 m\(^3\)/mol, respectively. The results shows that \( k_{\text{ads}} \) was equal to 0.074, 1.49, 0.223, and 8.15 m\(^3\)/(mol*min) for method A, B, C, and D, respectively. The model predictions compared with the experimental data are shown in Fig. 1. It was found that method A gave the best fit followed by method C, B, and D, respectively. This might because the method A is a direct method in determination of \( k_{\text{ads}} \) without approximation whilst the other are approximation method. This indicated that method C is the best approximation method in determination \( k_{\text{ads}} \) since it gave the value of the coefficient very close to the direct method.

### 4. REFERENCES


![Fig. 1 Experimental data vs. Model prediction](image-url)