
Yong-Son Hong*, a, b, Wei-dong Chen**, a

a College of Management and Economics, Tianjin University, Tianjin 300072, People’s Republic of China

b Department of Physical Chemistry, Faculty of Chemistry, Kim Hyong Jik Normal University, Pyongyang, Democratic People’s Republic of Korea

Corresponding author. E-mail address*: yongsonhong77@yahoo.com,
**: chenweidong@tju.edu.cn

ABSTRACT

In this work, the acridine orange (AO) adsorption onto ZnO/almond shell activated carbon (ZnO-AC) and the rhodamine B (RB) onto magnetic CeO₂ – activated carbon (CeO₂ -AC) were reevaluated using deactivation kinetics model (DKM). As the result, the reaction order and the activation energies were newly calculated.

Keywords: Adsorption, Kinetics, Modeling, Deactivation Kinetics Model

1. INTRODUCTION

Recently, Zbair et al. (2018) investigated the adsorption of acridine by ZnO/almond shell activated carbon composites. Tuzen et al. (2018) studied the adsorption of rhodamine B on a magnetic AC/CeO₂ nanocomposite. In their kinetic studies of adsorption, a pseudo second order model (PSO) was used to fit the experimental data (Ho and McKay, 1999). The PSO model is represented by Eq. (1)).

\[
\frac{dq}{dt} = k_2 (q_e - q)^2
\]  

(1)-PSO

where \( q \) and \( q_e \) are the grams of solute adsorbed per gram of adsorbent at any time \( t \) and at equilibrium, respectively, and \( k_2 \) is the PSO rate constant of adsorption. The PSO was used in many previous studies for adsorption kinetics, the dominance of this model is simple and convenient to use. But the PSO involved the adsorbed amount \( q_e \), which is the thermodynamic equilibrium quantity and the exponent 2 is the assumed as reaction order. Therefore, the activation energy cannot be accurately calculated because both the rate constant and the adsorbed amount \( q_e \) change simultaneously according to temperature. In some researches (Eftekhari et al., 2010; Luo et al., 2016; Choi et al., 2017) as like as them, although the kinetic experimental data with temperature were measured and the rate
constants were estimated, the activation energy couldn’t be calculated when the PSO model was used. One important purpose of kinetic research is to calculate activation energy.

The experimental data of Zbair et al. 2018 and Tuzen et al. 2018 were re-evaluated kinetically using DKM and the activation energies were newly calculated.

The DKM (Hong et al., 2014) (Eq. (2)) is a kinetic model for heterogeneous reaction and was used for the kinetic analysis of H2S removal over mesoporous LaFeO3/MCM-41 sorbent during hot coal gas desulfurization in a fixed-bed reactor. The validity (Hong et al., 2017) of DKM was verified through kinetic analysis for other experimental data. DKM did not considered the detailed characteristic parameters of the solid sorbent in such a microscopic way as unreacted shrinking core model or random pore model but in a macroscopic way. According to DKM, the variation per unit surface area (pore structure, active surface area and others) of the adsorbent and the formation of adsorbed layer were popularly expressed in terms of deactivation rate, i.e. the change of fractional conversion with time in solid phase was expressed as shown in Eq. (2):

\[
\frac{dX}{dt} = k_d C_A (1 - X)^\alpha
\]

(2) - DKM

where \(X\) is the deactivation degree of adsorbent, i.e. fractional conversion of fresh adsorbent (0 \(\leq X \leq 1\), dimensionless). And \(C_A\) is the concentration (mg·L\(^{-1}\)) of A component at any time \((t)\), \(k_d\) is a deactivation rate constant of the adsorbent (L·mg\(^{-1}\)·min\(^{-1}\)), \(\alpha\) is a reaction order of \((1 - X)\). The adsorption kinetic equation used Eq. (2) in a batch system is given Eq. (3).

\[
\begin{align*}
\frac{dC_A}{dt} &= -k_A C_A (1 - X) \\
\frac{dX}{dt} &= k_d C_A (1 - X)^\alpha
\end{align*}
\]

(3)

where \(k_A\) is the apparent adsorption rate constant of A adsorbate. Eq. (3) was solved with the ODE function of Matlab, the kinetic parameters were calculated using the nonlinear least-squares fitting of the adsorbate concentration obtained by solving ordinary differential equations (Eq. (3)) to fit the experimental data. The input data required for the nonlinear optimization were only the dimensionless concentrations ration \((C/C_0)\) of the adsorbate with time and \(X\)-values were automatically evaluated in the calculation process.
2. Result and Discussion
The parameters of PSO estimated by Zbair et al., 2018 and Tuzen et al. 2018 and kinetic parameters calculated by Eq. (3) were shown in Table 1 and Table 2. Activation energies and frequency factors were calculated from the rate constants with temperature and the Arrhenius equation. The values calculated by Eq. (1) were used as the experimental data for Eq. (3).

**Table 1.** Kinetic parameters for the adsorption of AO onto ZnO-AC at various temperatures.

<table>
<thead>
<tr>
<th>T(K)</th>
<th>PSO (Zbair et al., 2018)</th>
<th>DKM, Eq (3) $\alpha=1.5$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k_2 \times 10^{-2}$ g mg$^{-1}$ min$^{-1}$</td>
<td>$q_e \times 10^{2}$ mg g$^{-1}$</td>
</tr>
<tr>
<td>293</td>
<td>0.8</td>
<td>4.348</td>
</tr>
<tr>
<td>303</td>
<td>1.0</td>
<td>4.545</td>
</tr>
<tr>
<td>313</td>
<td>1.1</td>
<td>5.000</td>
</tr>
</tbody>
</table>

Activation Energy → 35.943 kJ/mol; 29.130 kJ/mol

Frequency Factor → $2.5 \times 10^7$; $3.6 \times 10^6$

**Table 2.** Kinetic parameters for the adsorption of RB onto magnetic CeO$_2$-AC at various temperatures.

<table>
<thead>
<tr>
<th>T(K)</th>
<th>PSO (Tuzen et al. 2018)</th>
<th>DKM, Eq (3) $\alpha=1.0$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k_2 \times 10^{-2}$ g mg$^{-1}$ min$^{-1}$</td>
<td>$q_e$ mg g$^{-1}$</td>
</tr>
<tr>
<td>293</td>
<td>2.5</td>
<td>2.74</td>
</tr>
<tr>
<td>303</td>
<td>2.6</td>
<td>2.87</td>
</tr>
<tr>
<td>318</td>
<td>2.8</td>
<td>2.99</td>
</tr>
<tr>
<td>333</td>
<td>3.0</td>
<td>3.04</td>
</tr>
</tbody>
</table>

Activation Energy → 8.0212 kJ/mol; 4.2148 kJ/mol

Frequency Factor → 1.6996; 0.4126

The adsorbates concentration calculated by Eq. (3) were shown in Fig. 1 and 2. As shown in Fig. 1 and 2, the experimental data agree well with the calculated curves.
The following conclusions can be drawn from Tables.

- The reaction orders were evaluated. The reaction order related to the mechanism is an empirical quantity obtained from the experimental data and rate equation. By evaluating the reaction orders, we can see whether the reaction mechanisms are the same or different. From the Tables, it can be seen that the AO adsorption onto ZnO-AC ($\alpha=1.5$) and RB adsorption onto magnetic CeO$_2$-AC ($\alpha=1.0$) occur by different mechanisms.

- The calculated rate constants were quantitatively compared on both adsorbate and adsorbent unlike PSO. The rate constants of both adsorbate and adsorbent be
come larger with increasing temperature.

- The activation energies were newly calculated. The activation energy of AO adsorption onto ZnO-AC is 35.943kJ/mol, and the activation energy of ZnO-AC deactivation process is 29.130kJ/mol. Also, the activation energy of RB adsorption onto magnetic CeO$_2$-AC is 8.0212kJ/mol and the activation energy of magnetic CeO$_2$-AC deactivation process is 4.2148kJ/mol, which are very small.

Important kinetic conclusions can be obtained from Eq. (3) and cannot be obtained from PSO, which assumes a pseudo reaction order, and contains the adsorbed amount. The authors believe that the use of DKM rather than PSO should be used. Using DKM helps to better understand the adsorption kinetics, although further confirmation and refinement is required.

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**References**


