

Evaluation of activation energies for adsorption of dyes by modified activated carbons [J. Environ. Manage. 206 (2018) 170-177 and 383-397] using deactivation kinetics model

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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)).

$$\frac{dq}{dt} = k_2(q_e - q)^2 \quad (1)\text{-PSO}$$

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 consider 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):

$$\frac{dX}{dt} = k_d C_A (1 - X)^\alpha \quad (2) - \text{DKM}$$

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 ($\text{mg}\cdot\text{L}^{-1}$) of A component at any time (t), k_d is a deactivation rate constant of the adsorbent ($\text{L}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$), α is a reaction order of $(1-X)$. The adsorption kinetic equation used Eq. (2) in a batch system is given Eq. (3).

$$\begin{cases} \frac{dC_A}{dt} = -k_A C_A (1 - X) \\ \frac{dX}{dt} = k_d C_A (1 - X)^\alpha \end{cases} \quad (3)$$

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 ratio (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.

T(K)	PSO (Zbair et al., 2018)			DKM, Eq (3) $\alpha=1.5$		
	$k_2 \times 10^{-2}$ g mg ⁻¹ min ⁻¹	$q_e \times 10^2$ mg g ⁻¹	R ²	k_A min ⁻¹	k_d L mg ⁻¹ min ⁻¹	R ²
293	0.8	4.348	0.999	10.8196	24.7402	0.9999
303	1.0	4.545	0.999	19.3032	42.2574	1.0000
313	1.1	5.000	0.999	27.2077	52.1601	1.0000
Activation Energy →				35.943 kJ/mol	29.130kJ/mol	
Frequency Factor →				2.5×10^7	3.6×10^6	

Table 2. Kinetic parameters for the adsorption of RB onto magnetic CeO₂-AC at various temperatures.

T(K)	PSO (Tuzen et al. 2018)			DKM, Eq (3) $\alpha=1.0$		
	$k_2 \times 10^{-2}$ g mg ⁻¹ min ⁻¹	q_e mg g ⁻¹	R ²	k_A min ⁻¹	k_d L mg ⁻¹ min ⁻¹	R ²
293	2.5	2.74	0.993	0.0622	0.0731	1.0000
303	2.6	2.87	0.997	0.0712	0.0774	1.0000
318	2.8	2.99	0.990	0.0834	0.0840	0.9999
333	3.0	3.04	0.998	0.0923	0.0899	0.9998
Activation Energy →				8.0212 kJ/mol	4.2148kJ/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.

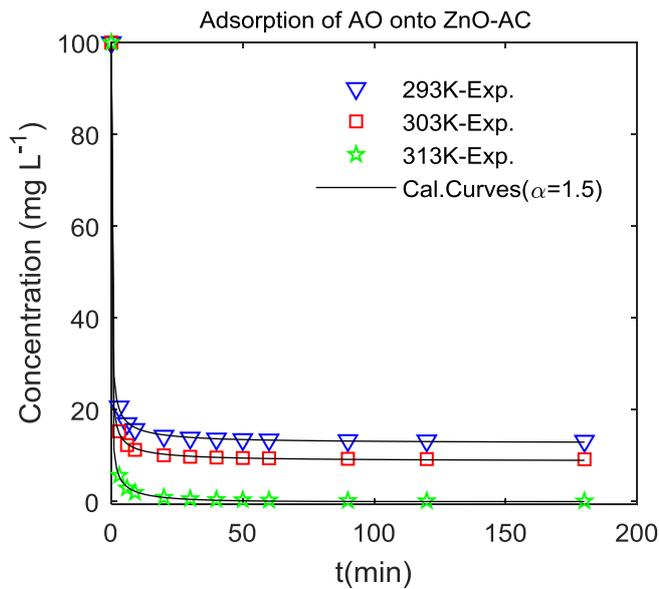


Fig. 1. AO concentration calculated by Eq. (3) on ZnO-AC.

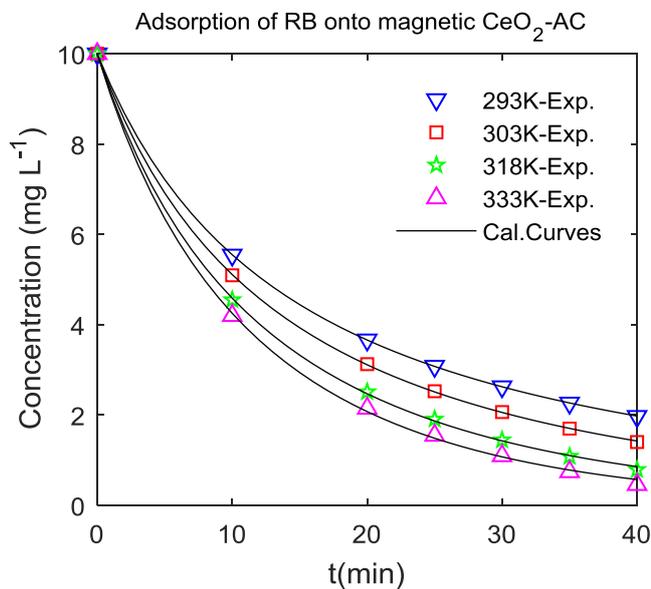


Fig. 2. RB concentration calculated by Eq. (3) onto magnetic CeO₂-AC

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 CeO₂-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 CeO₂-AC is 8.0212kJ/mol and the activation energy of magnetic CeO₂-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

- Choi, A. E. S., Roces, S., Dugos, N., Wan, M. W., 2017. Adsorption of benzothiophene sulfone over clay mineral adsorbents in the frame of oxidative desulfurization. *Fuel*. 205,153–160
- Eftekhari, S., Habibi-Yangjeh, A., Sohrabnezhad, Sh., 2010. Application of AIMCM-41 for competitive adsorption of methylene blue and rhodamine B: Thermodynamic and kinetic studies. *J. Hazard. Mater.* 178, 349–355.
- Liu B., Ge N., Peng, B. Z., Pan, S.Y., 2018. Kinetic and isotherm studies on the adsorption of tenuazonic acid from fruit juice using inactivated LAB. *J. Food Eng.* 224, 45-52.
- Luo, Y., Li Z., Yuan, Y. H., Yue, T.L., 2016. Bioadsorption of patulin from kiwi fruit juice onto a superior magnetic chitosan. *J. Alloys Compd.* 667, 101-108.
- Ho, Y. S., McKay, G., 1999. Pseudo-second order model for sorption processes. *Process Biochem.* 34, 451–465.
- Hong, Y. S., Zhang, Z. F., Cai, Z. P., Zhao, X. H., Liu, B. S., 2014. Deactivation Kinetics Model of H₂S Removal over Mesoporous LaFeO₃ /MCM-41 Sorbent during Hot Coal Gas Desulfurization. *Energy Fuels*. 28, 16012–6018.
- Hong, Y. S., Sin, K. R., Pak, J. S., Kim, C. J., Liu, B. S., 2017. Kinetic Analysis of H₂S Removal over Mesoporous Cu–Mn Mixed Oxide/SBA-15 and La–Mn Mixed Oxide/KIT-6 Sorbents during Hot Coal Gas Desulfurization Using the Deactivation Kinetics Model. *Energy Fuels*, 31, 9874–9880.

- Tuzen, M., Sari, A., Saleh, T. A., 2018. Response surface optimization, kinetic and thermodynamic studies for effective removal of rhodamine B by magnetic AC/CeO₂ nanocomposite, J. Environ. Manage. 206, 170-177.
- Zbair, M., Anfar, Z., Ahsaine, H. A., Alem, N. E., Ezahri, M. 2018. Acridine orange adsorption by zinc oxide/almond shell activated carbon composite: Operational factors, mechanism and performance optimization using central composite design and surface modeling. J. Environ. Manage. 206, 383-397.