Evaluation reevaluation of activation energies on Acid Blue 193 adsorption over natural sepiolite [Colloids Surface A, 277(2006), 90–97] using deactivation kinetics model

*RyongBok Kim, CholSun Han, Yong-Son Hong**

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

Faculty of Building Materials, Pyongyang University of Architecture, Democratic People's Republic of Korea

Corresponding author. * E-mail address: yongsonhong77@yahoo.com

ABSTRACT

In this work, the Acid Blue 193 adsorption over natural sepiolite by Özcan et al. [Colloids Surface A, 277(2006), 90–97] was 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

Özcan et al. had published the paper entitled "Kinetics, isotherm and thermodynamic studies of adsorption of Acid Blue 193 from aqueous solutions onto natural sepiolite" [1]. In the adsorption kinetic study, their experimental data were analyzed using pseudo second order kinetic model (PSO [2], Eq. (1)).

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

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 sorption. 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 which is the thermodynamic quantity and assumed reaction order. Therefore, the activation energy can't be accurately calculated because both the rate constant and the adsorbed amount change with temperature. In recent researches [3-6] as like as them, although the adsorption experimental data with temperature were measured and the rate constants were estimated, the activation energy couldn't be calculated because PSO was used. One important purpose of kinetic research is to calculate activation energy. In chemical kinetics the activation energy is the energy barrier, which must be overcome for a sufficient number of molecules to acquire enough kinetic energy for a reaction to occur appreciably. The activation energy can generally be achieved by supplying external energy.

But, the activation energies were calculated by them [1] although PSO was used, this is a scientific mistakes.

In this work, the activation energies [1] was reevaluated using DKM.

The DKM [7] (Eq. (2)) is a kinetic model for heterogeneous reaction and used it for the kinetic analysis of H_2S removal over mesoporous $LaFeO_3$ /MCM-41 sorbent during hot coal gas desulfurization in a fixed-bed reactor. The validity [8] of DKM was verified through kinetic analysis for other experimental data. DKM has 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. The change of fractional conversion with time in solid phase was expressed as a deactivation rate, as shown in Eq. (2):

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

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

$$\begin{cases} \dfrac{dC_A}{dt} = -k_A C_A (1 - X) \\ \dfrac{dX}{dt} = k_d C_A (1 - X) \end{cases} \qquad (3)$$

where k_A is the apparent adsorption rate constant of adsorbate. Eq. (3) were solved with 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 the experimental data. The input data required for the nonlinear optimization were only the non-dimensionalized concentrations (C/C_0) of adsorbate with time and X were automatically evaluated in the calculation process.

The parameters of PSO [1] and kinetic parameters calculated by Eq. (3) were shown in Table. Activation energies 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).

The following conclusions can be drawn from Table.

- The reaction orders were evaluated (Eq. (4)). If all reaction orders were equal to

1 or 2, some calculated adsorption rate constants were smaller than 0 or the correlation coefficients (R^2) were smaller than 0.7.

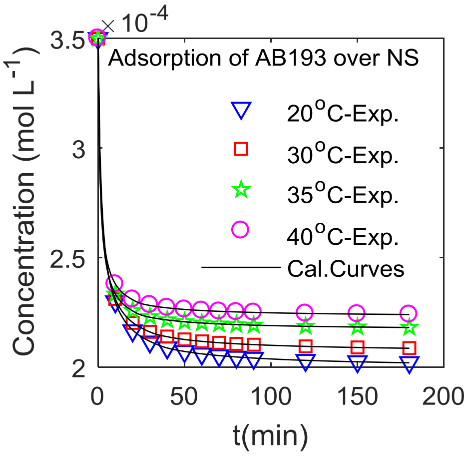
$$\begin{cases} \frac{dC_A}{dt} = -k_A C_A (1-X) \\ \frac{dX}{dt} = k_d C_A (1-X)^{1.5} \end{cases} \quad (4)$$

- The calculated rate constants could quantitatively be compared on both adsorbate a nd adsorbent. Also rate constants of both adsorbate and adsorbent become larger with in creasing temperature.
- The activation energies are newly calculated. The activation energies of AB193 ads orption is 17.280kJ/mol and the activation energy of natural sepiolite deactivation is 23.6 95kJ/mol.

Table. Kinetic parameters for AB193 adsorption onto natural sepiolite at various temperatures.

T(K)	PSO[1]			DKM, Eq beta=1.5;		
	$k_2 \times 10^3$ L mol^{-1} min^{-1}	$q_e \times 10^{-4}$ mol g^{-1}	R^2	k_A min^{-1}	k_d L mol^{-1} min^{-1}	R^2
293	2.69	1.50	0.999	0.2286	1.0566	1.0000
303	3.46	1.43	0.999	0.2640	1.2807	1.0000
308	5.40	1.33	0.999	0.3480	1.8157	1.0000
313	6.00	1.27	0.999	0.3440	1.8784	1.0000
E_a kJ/mol	32.41			17.280	23.695	

Calculated Reaction orders = 1, 1, 1, 1.5: Equation. (4)



The concentration of AB193 calculated by Eq. (4).

Important kinetic conclusions can be obtained from Eq. (4) and can't be obtained from PSO which assumes reaction order and contains the adsorbed amount. The author thinks that it may be more necessary to use DKM than pseudo order models including the adsorbed amount in adsorption kinetic studies.

References

[1] Özcan, A., Öncü, E. M., Özcan, A. S., Kinetics, isotherm and thermodynamic studies of adsorption of Acid Blue 193 from aqueous solutions onto natural sepiolite, Colloids Surface A, 277(2006), 90–97

[2] Y. S. Ho, G. McKay, Pseudo-second order model for sorption processes. Process Biochem. 34 (1999) 451–465.

[3] A. E. S. Choi, S. Roces, N. Dugos, M. W. Wan, Adsorption of benzothiophene sulfone over clay mineral adsorbents in the frame of oxidative desulfurization, Fuel. 205 (2017)153–160.

[4] T. T. Han, H. L. Bai, Y. Y. Liu, J. F. Ma, Synthesis of nanoporous cobalt/carbon materials by a carbonized zeolitic imidazolate framework-9 and adsorption of dyes, New J. Chem. 42 (2018) 717-724.

[5] B. Liu, N. Ge, B. Z. Peng, S.Y. Pan, Kinetic and isotherm studies on the adsorption of tenuazonic acid from fruit juice using inactivated LAB, J. Food Eng. 224 (2018) 45-52.

[6] Y. Luo, Z. Li, Y. H. Yuan, T.L. Yue, Bioadsorption of patulin from kiwi fruit juice onto a superior magnetic chitosan, J. Alloys Compd. 667 (2016) 101-108.

[7] Y. S. Hong, Z. F. Zhang, Z. P. Cai, X. H. Zhao, B. S. Liu, Deactivation Kinetics Model of H_2S Removal over Mesoporous $LaFeO_3$ /MCM-41 Sorbent during Hot Coal Gas Desulfurization, Energy Fuels. 28 (2014) 6012−6018.

[8] Y. S. Hong, K. R. Sin, J. S. Pak, C. J. Kim, B. S. Liu, Kinetic Analysis of H_2S 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 (2017) 9874−9880.