

Discussion

Evaluation of activation energies on As(V) sorption onto magnetic separable poly p-phenylenediamine-thiourea-formaldehyde polymer [J. Hazard. Mater. 342 (2018) 335–346]

Yong-Son Hong^{*}, Sok-Bong Pak, Yong-Uk Ryu, Sok-Jin Ri, Jong-Sob Kim, Jong-Hyok Yang

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

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

ABSTRACT

In this work, the As(V) sorption onto magnetic separable poly p-phenylenediamine-thiourea-formaldehyde polymer (MpPDTF) published by Elwakeel and Al-Bogami 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

Elwakeel and Al-Bogami had published the paper entitled “Influence of Mo(VI) immobilization and temperature on As(V) sorption onto magnetic separable poly p-phenylenediamine-thiourea-formaldehyde polymer” [1]. In the sorption kinetic study, their experimental data were analyzed using pseudo second order kinetic model (PSO [2], Eq. (1)).

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

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 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 this work, the experimental data [1] was reevaluated kinetically using DKM, the reaction order and the activation energies were newly calculated.

The DKM [7] (Eq. (2)) is a kinetic model for heterogeneous reaction and used it 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 [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):

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

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

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

where k_A is the apparent adsorption rate constant of sorbate. Eq. (3) were solved with ODE function of MATLAB, the kinetic parameters (rate constants and reaction orders) were calculated using the nonlinear least-squares fitting of the sorbate 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 sorbate 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. 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 newly calculated (Eq. (4) and Eq. (5)).

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

$$\begin{cases} \frac{dC_A}{dt} = -k_A C_A (1 - X)^{1.5} \\ \frac{dX}{dt} = k_d C_A^{1.5} (1 - X)^{1.5} \end{cases} \quad (5) - \text{on MpPDTF-Mo(VI)}$$

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, i.e. it can be seen that As(V) adsorption on MpPDTF and on MpPDTF-Mo(VI) occur in different mechanism. The As(V) concentration calculated by Eq. (4) and Eq. (5) were shown in Fig. 1 and 2. As shown in Fig. 1 and 2, the experimental data agree well with the calculated curves.

- Activation energies were newly calculated. The activation energies and frequency factors were calculated from the rate constants with temperature and the Arrhenius equation. Activation energy of As(V) adsorption on MpPDTF is 12.990 kJ mol⁻¹ and activation energy of MpPDTF deactivation is 23.262 kJ mol⁻¹. Also, activation energy of As(V) adsorption on MpPDTF-Mo(VI) is 34.716 kJ mol⁻¹ and activation energy of MpPDTF-Mo (VI) deactivation is 28.495 kJ mol⁻¹. It can be seen that activation energies on MpPDTF-Mo(VI) are higher than on MpPDTF, i.e. the energy barrier of MpPDTF-Mo(VI) is kinetically higher.

Important kinetic conclusions can be obtained from Eq. (3) 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 PSO including the adsorbed amount in adsorption kinetic studies.

References

- [1] K. Z. Elwakeel, A. S. Al-Bogami, Influence of Mo(VI) immobilization and temperature on As(V) sorption onto magnetic separable poly p-phenylenediamine-thiourea-formaldehyde polymer, *J. Hazard. Mater.* 342 (2018) 335–346.
- [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 H₂S Removal over Mesoporous LaFeO₃/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 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 (2017) 9874–9880.

Table.

Kinetic parameters for As(V) sorption on MpPDTF and MpPDTF-Mo(VI).

sorbent	PSO [1]				DKM, Eq. (3) [#]		
	T(K)	$k_2 \times 10^{-3}$ g mg ⁻¹ min ⁻¹	$q_e \times 10^2$ mg g ⁻¹	R ²	$k_A \times 10^{-2}$ min ⁻¹	$k_d \times 10^{-1}$ L mg ⁻¹ min ⁻¹	R ²
MpPDTF	298	0.37	0.4714	0.9978	0.44	0.370	0.9999
	308	0.64	0.4168	0.9996	0.60	0.568	0.9999
	318	0.866	0.3633	0.9997	0.61	0.666	0.9999
		Activation Energy (kJ mol ⁻¹) →			12.990	23.262	
	Frequency Factor →			0.8715	460.5386		
	#: Calculated Reaction orders = 1, 1, 1, 1.5 : Eq. (4)						
MpPDTF-Mo(VI)	T(K)	$k_2 \times 10^{-3}$ g mg ⁻¹ min ⁻¹	$q_e \times 10^2$ mg g ⁻¹	R ²	$k_A \times 10^{-2}$ min ⁻¹	$k_d \times 10^{-1}$ (L mg ⁻¹) ^{1.5} min ⁻¹	R ²
	298	0.60	1.0126	0.9998	3.30	0.769	0.9999
	308	0.68	1.1177	0.9999	4.80	1.029	0.9999
	318	0.878	1.2269	0.9999	7.98	1.588	0.9999
	Activation Energy (kJ mol ⁻¹) →				34.716	28.495	
	Frequency Factor →				39129	7399	
	#: Calculated Reaction orders = 1, 1.5, 1.5, 1.5 : Eq. (5)						
Condition: C ₀ : 200 mg As L ⁻¹ , 200 mg of sorbent, 200 mL of As (V) solution							

Figures captions

Figure 1: As(V) concentration calculated by Eq. (4) on MpPDTF.

Figure 2: As(V) concentration calculated by Eq. (5) on MpPDTF –Mo(VI) immobilization.

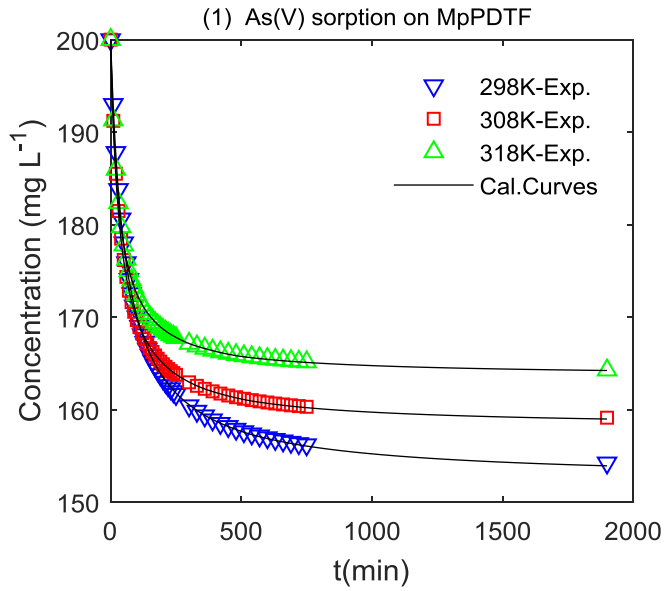


Fig. 1. As(V) concentration calculated by Eq. (4) on MpPDTF.

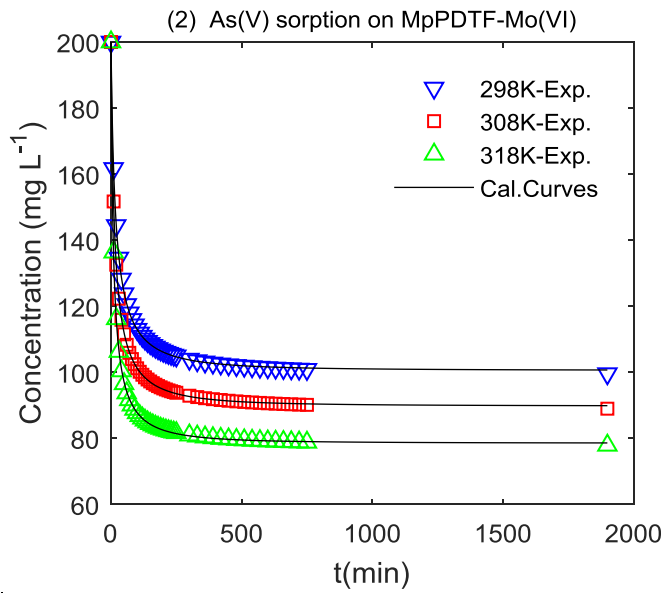


Fig. 2. As(V) concentration calculated by Eq. (5) on MpPDTF –Mo(VI) immobilization.