

Kinetic reevaluation on uranium(VI) adsorption[Ind. Eng. Chem. Res. 2017, 56, 3251–3258 and 12745–12754] using deactivation

kinetics model

Kwang-Il Paek^a, Hong-Chol Jin^b, Yong-Son Hong^{*,c}

^a Faculty of Power Engineering, Kim Chaek university of technology, Pyongyang, Democratic People's Republic of Korea

^a Faculty of Thermal engineering, Kim Chaek university of technology, Pyongyang, Democratic People's Republic of Korea

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

Corresponding author. E-mail address *: hongyongson@126.com.

ABSTRACT

In this work, the adsorption of uranium (VI) on alkali-activated leather waste and mesoporous carbon were reevaluated using deactivation kinetics model (DKM). As the result, the reaction order were newly calculated and the rate constants quantitatively compared on both adsorbates and adsorbent.

Keywords: Adsorption, Kinetics, Modeling, Deactivation Kinetics Model

1. INTRODUCTION

Recently, Yan et al.(1) investigated the adsorption of uranium(VI) on alkali-activated leather waste. Zhao et al.(2) studied the adsorption of uranium(VI) on mesoporous carbon from sodium lignosulfonate by hydrothermal. In their kinetic studies of adsorption, a pseudo second order model (PSO) (3) was used to fit the experimental data. 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.

The experimental data of Yan et al.(1) and Zhao et al.(2) were re-evaluated kinetically using DKM.

The DKM (4) (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 (5) 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):

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

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 (mg 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 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 Yan et al. (1) and Zhao et al. (2) 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).

Table. Kinetic parameters

adsorbent	Ref.	PSO(1,2)			DKM, Eq (3)(In This work)		
		k_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
AALW	(1)	0.4×10 ⁻³	95.51	0.998	0.0268	0.0924	0.9996
		Condition: 0.05 g, 50 mL, 170 mg L ⁻¹ , pH=5			Calculated Reaction Order: 1, 1, 1, 1.5		
Carbon-LSs+ CTAB	(2)	4.533×10 ⁻⁵	134.1	0.9976	0.0063	0.0150	0.9999
		Condition: 0.04g, 50 mL, 140 mg/L, pH = 5.5			Calculated Reaction Order: 1, 1, 1, 1.5		

The following conclusions can be drawn from Table.

Firstly, The reaction orders were evaluated Eq. (4).

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

The 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 two type adsorption of uranium (VI) occur by same mechanisms.

The adsorbates concentration calculated by Eq. (4) were shown in Fig. 1 and 2. As shown in Fig. 1 and 2, the experimental data agree well with the calculated curves.

Secondly, The calculated rate constants were quantitatively compared on both adsorbate and adsorbent unlike PSO.

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.

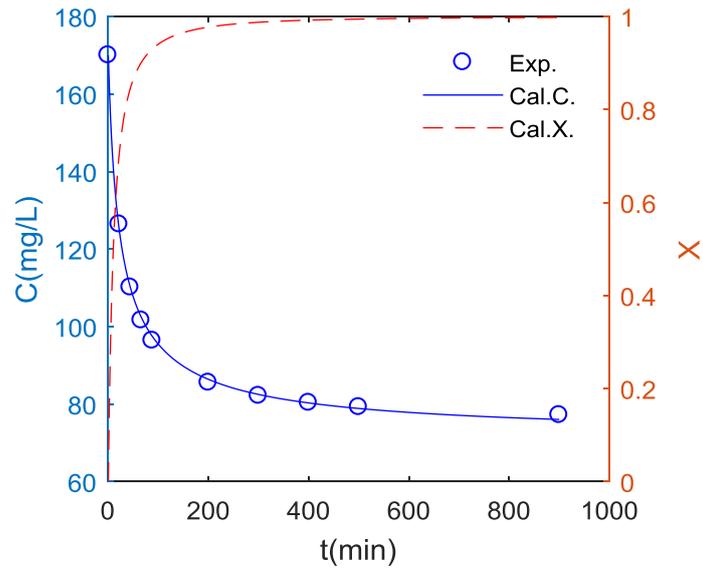


Fig. 1. The concentration of uranium (VI) and the deactivation degree of AALW calculated by Eq. (4).

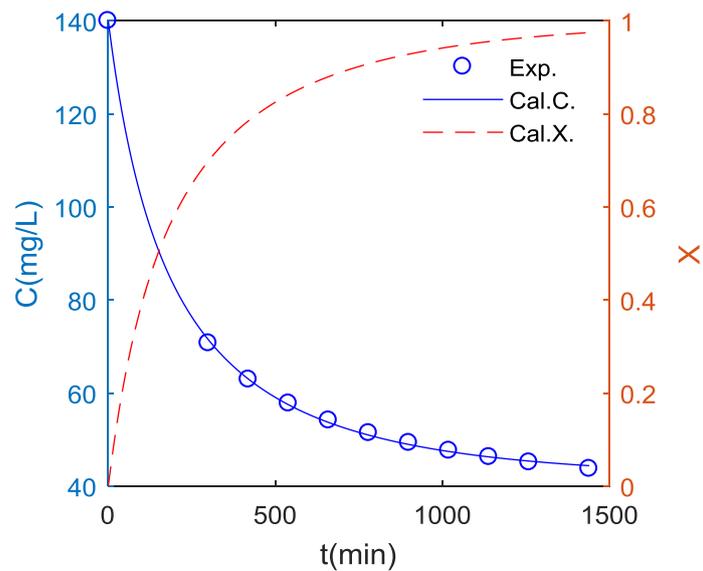


Fig. 2. The concentration of uranium (VI) and the deactivation degree of Carbon-LSs+CTAB calculated by Eq. (4).

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