

Kinetic reevaluation on Adsorption of benzothiophene sulfone over clay mineral adsorbents in the frame of oxidative desulfurization

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ABSTRACT

In this communication, the adsorption of benzothiophene sulfone (BTO) over clay mineral adsorbents [Fuel 205 (2017) 153–160] was reevaluated using deactivation kinetics model (DKM). As the result, the reaction order and the activation energies were newly calculated.

Keywords: Adsorption, Kinetics, Modeling

Jia et al. published the paper entitled “Bromate Adsorption on Three Variable Charge Soils: Kinetics and Thermodynamics” [1].

In adsorption kinetics study, their experiment data were analyzed using pseudo-second-order kinetic model (PSO) [2]. PSO used in many previous studies for adsorption kinetics, the dominance of this model are simple and convenient to use. But the PSO involved the adsorption amount which is the thermodynamic quantity and assumed reaction order. Therefore, the calculated rate constants can't be compared and furthermore, the activation energy can't be calculated. One important purpose of kinetic research is to calculate activation energy, however, they did not evaluate it. It can also be said that the adsorption process is one of heterogeneous reaction process.

In this communication, the experiment data published by Choi et al. [1] was reevaluated kinetically using DKM which was a kinetic model for heterogeneous reaction.

The DKM had proposed in 2014 [3] 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. In 2017 [4], the validity 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 (SCM) [5] or random pore model (RPM)[6] 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 (1):

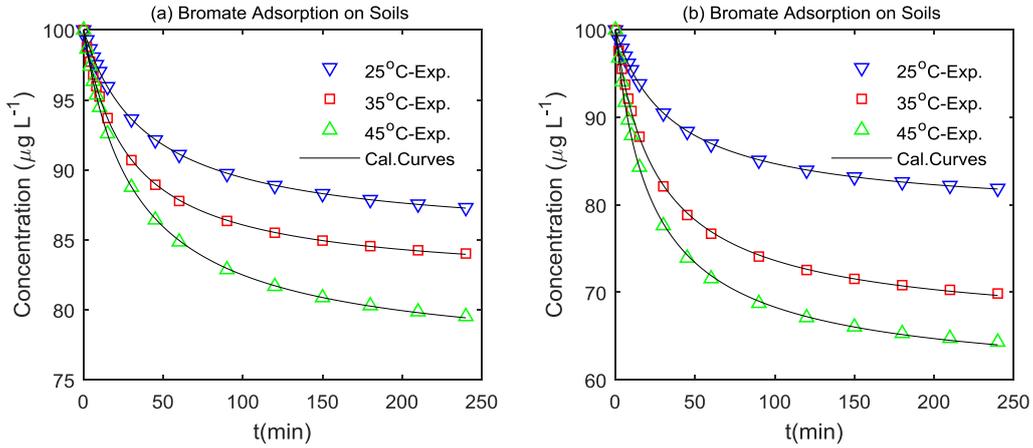
$$\frac{dX}{dt} = k_d C_A (1 - X)^\alpha \quad (1)$$

where X is deactivation degree of adsorbent ($0 \leq X \leq 1$, dimensionless), C_A is concentration ($\text{mg} \cdot \text{L}^{-1}$) of A component at any time(min), 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. (1) in batch system is Eq. (2).

$$\begin{cases} \frac{dC_A}{dt} = -k_A C_A (1 - X) \\ \frac{dX}{dt} = k_d C_A (1 - X)^\alpha \end{cases} \quad (2)$$

where k_A is apparent adsorption rate constants of A (min^{-1}). Eq. (2) was solved with ODE function of MATLAB and the kinetic parameters were calculated using the nonlinear least-squares fitting of the adsorbates concentration obtained by solving Eq. 2 to the experimental data. The input data required for the nonlinear optimization were only the non-dimensionalized concentrations (C/C_0) of the adsorbates with time and X was automatically evaluated in the calculation process.

The concentration of adsorbates calculated by Eq. (2) were shown in Fig. a-c. As shown in Figures, the experimental data agree well with the curves calculated by Eq. (2).



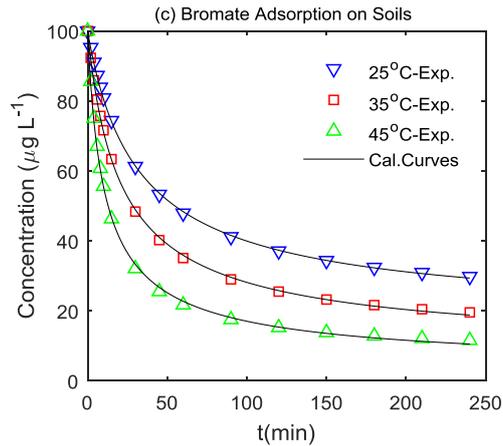


Fig. Concentration of adsorbates calculated by Eq. (2) at 25, 40 and 55°C.

(a-, b-, c-)

The parameters of PSO estimated by them [1] and kinetic parameters calculated by Eq. (2) were shown in Table.

Table. Estimated kinetic parameters

Soil sample site	T(°C)	PSO[1]			DKM, Eq. 2 $\alpha=1.5$, $\alpha=2$		
		k_2 $\text{g mg}^{-1} \text{min}^{-1}$	q_e mg g^{-1}	R^2	k_A min^{-1}	k_d $\text{L mg}^{-1} \text{min}^{-1}$	R^2
Activated Clay	25	0.0273	4.0051	0.9999	0.0705	0.0449	0.9977
	40	0.0081	4.4437	0.9991	0.0295	0.0170	0.9995
	55	0.0312	4.7545	0.9999	0.1315	0.0698	0.9997
	Activation Energy \rightarrow Frequency Factor \rightarrow				23.541kJ/mol 6.4210×10^2	16.358kJ/mol 2.2480×10^0	
Bentonite	25	0.0037	2.1733	0.9792	0.0028	0.0036	0.9974
	40	0.0023	3.7306	0.9959	0.0058	0.0042	0.9992
	55	0.0062	4.3621	0.9994	0.0218	0.0129	0.9994
	Activation Energy \rightarrow Frequency Factor \rightarrow				80.546 kJ/mol 3.3338×10^{11}	49.847 kJ/mol 1.6726×10^9	
Kaolinite	25	0.0176	1.7436	0.9999	0.0074	0.0112	0.9945
	40	0.0054	2.9389	0.9989	0.0077	0.0069	0.9975
	55	0.0116	3.8295	0.9999	0.0283	0.0190	0.9981
	Activation Energy \rightarrow Frequency Factor \rightarrow				52.285 kJ/mol 8.7687×10^6	20.175kJ/mol 3.0177×10^1	

The following conclusions can be drawn from Table.

- The reaction order was evaluated $\alpha= 1.5$. If all reaction orders were equal to 1, the correlation coefficient became smaller than 0.8 and some calculated adsorption rate constants became smaller than 0.
- The activation energies were newly calculated. The activation energies of bromate adsorption on three variable charge soils are 27.484, 45.399 and 51.006 kJ/mol, the activation energies of adsorbents deactivation are 9.1699, 19.556 and 44.954 kJ/mol, respectively.

Kinetic conclusions can be obtained like above using DKM and these conclusions can't be obtained using PSO which assumes reaction order and contains the adsorption amount. Author thinks that it may be more necessary to use DKM than pseudo order models including the adsorption amount in adsorption kinetic studies.

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