

Kinetic reevaluation on Adsorption of Co(II), Hg(II) and Ag(I) from fuel ethanol by silica gel supported sulfur-containing PAMAM dendrimers[Fuel 199 (2017) 91–101 and 206 (2017) 80–88]

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In our letter, the adsorption of Co(II), Hg(II) and Ag(I) from fuel ethanol by silica gel supported sulfur-containing PAMAM dendrimers [Fuel 199 (2017) 91–101 and 206 (2017) 80–88] were reevaluated using deactivation kinetics model (DKM). As the result, the reaction orders newly were estimated and the calculated rate constants were quantitatively compared on both adsorbate and adsorbents.

Recently, the adsorption of Co(II), Hg(II) and Ag(I) from fuel ethanol on silica gel supported sulfur-containing PAMAM dendrimers were reported by Song et al.[1,2]. In adsorption kinetics study, their experiment data were analyzed using pseudo-second-order kinetic model (PSO) [3].

The PSO was 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. It can also be said that the adsorption process is one of heterogeneous reaction process.

The experiment data published by Song et al. [1, 2] were reevaluated kinetically using deactivation kinetics model (DKM), a kinetic model for heterogeneous reaction. The DKM had proposed in 2014 [4] 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 [5], 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) [6] or random pore model (RPM)[7] 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 ($\text{mol} \cdot \text{L}^{-1}$) of A component at any time(min), k_d is a deactivation rate constant of the adsorbent ($\text{L} \cdot \text{mmol}^{-1} \cdot \text{min}^{-1}$), α is the reaction order of (1-X).

The adsorption kinetic equation used Eq. (1) in batch system is Eq. (2).

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

where k_A is apparent adsorption rate constant of A (min^{-1}). Eq. (2) was solved with ODE function of MATLAB and the kinetic parameters (reaction orders and rate constants) 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 parameters of PSO estimated by them [1, 2] and kinetic parameters calculated by Eq. (2) were shown in Table.

Table. Calculated parameters

Ion	Adsorbent	PSO[1, 2]			DKM, Eq. (2)*, [this work]		
		k_2 mmol $\text{g}^{-1} \text{min}^{-1}$	q_e mmol g^{-1}	R^2	k_A L mmol^{-1} min^{-1}	k_d $\text{L}^{0.5} \text{mmol}^{-0.5}$ min^{-1}	R^2
Co(II)[1]	SiO ₂ -G0.5	0.58	0.25	1.000	0.0487	0.1176	1.0000
	SiO ₂ -G1.0	0.15	0.44	0.999	0.0398	0.0394	0.9999
	SiO ₂ -G1.5	0.72	0.26	1.000	0.0661	0.1515	1.0000
	SiO ₂ -G2.0	0.07	0.50	0.999	0.0236	0.0176	0.9999
	SiO ₂ -G2.5	0.16	0.34	0.998	0.0247	0.0381	0.9999
	SiO ₂ -G3.0	0.09	0.34	0.999	0.0137	0.0210	0.9999
Hg(II)[2]	SiO ₂ -G0.0	0.1491	0.54	0.9993	0.0609	0.0387	0.9998
	SiO ₂ -G1.0	0.1604	0.58	0.9996	0.0764	0.0401	0.9998
	SiO ₂ -G2.0	0.1083	0.63	0.9991	0.0598	0.0234	0.9997
Ag(I)[2]	SiO ₂ -G0.0	0.0594	0.47	0.9989	0.0175	0.0149	0.9999
	SiO ₂ -G1.0	0.0872	0.52	0.9993	0.0321	0.0221	0.9998
	SiO ₂ -G2.0	0.0528	0.51	0.9994	0.0183	0.0130	0.9999

Condition: 25 mg adsorbent and 20 mL of 1 mmol L⁻¹ metal ion solution

*: reaction orders $\alpha=2, \beta=2, \gamma=0.5, \lambda=2$

The following conclusions could be drawn from Table.

- The reaction orders were evaluated (Eq. (3)). If all reaction orders were equal to 1 or 2, some calculated adsorption rate constants became smaller than 0.

$$\begin{cases} \frac{dC_A}{dt} = -k_A C_A^2 (1 - X)^2 \\ \frac{dX}{dt} = k_d C_A^{0.5} (1 - X)^2 \end{cases} \quad (3)$$

- The calculated rate constants could quantitatively be compared on both adsorbate and adsorbents unlike PSO.
- Also, the activation energy can be calculated if the experiment data with temperature had been given. The activation energy can't be accurately calculated with the PSO in which both the rate constant and the adsorption amount change with temperature.

Kinetic conclusions could be obtained like above using DKM and these conclusions couldn't be obtained using PSO. In our view, it may be more necessary to use DKM than pseudo order models including the adsorption amount in adsorption kinetic studies.

References

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