Kinetic reevaluation of the competitive adsorption [J. Hazard. Mater. 326 (2017) 211–220] using deactivation kinetics model

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ABSTRACT

In this discussion, the competitive adsorption published by Fan et al. were reevaluated kinetically using deactivation kinetics model. As the result, kinetic conclusions could be obtained as following. First, single component adsorption and binary component adsorption occur in different mechanisms. Second, the adsorption rate of one component can be calculated how times faster than the other in competitive system.

Keywords: Adsorption Kinetic, Heterogeneous Reaction, Deactivation Kinetics Model

It can be said that the adsorption process is one of heterogeneous reaction process. The models of adsorption kinetics have been greatly improved but used "pseudo" term in many case. The pseudo order kinetic models [10-12] involve the adsorption amount which is a thermodynamic quantity. Therefore, the activation energy can't be calculated and the reaction rate constants can't be compared in the competitive adsorption using the pseudo order kinetic models. The rate constants, activation energies and reaction mechanism must be discussed in kinetic studies. Furthermore, it is doubtful whether the pseudo order kinetic models which had been proposed for single adsorption can be used on competitive adsorption system. In many of the kinetic analysis on competitive adsorptions, the kinetic models for single component adsorption are used ignoring the interaction between adsorbates and adsorbent [1-5]. The competitive adsorptions are more complex than the single system and those should be considered.

In this discussion, the competitive adsorption published by Fan et al. [1] was reevaluated kinetically using deactivation kinetics model (DKM).

The DKM had proposed in 2014 [6] 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. In 2017 [7], 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) [8] or random pore model (RPM) [9] 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):

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

where X is deactivation degree of adsorbent ($0 \leqq X \leqq 1$, dimensionless), C_A is concentration (mg·L^{-1}) of A component at any time (min), k_d is a deactivation rate constant of the adsorbent (L·mg^{-1}·min^{-1}), α is a reaction order of (1-X). Single and binary adsorption kinetic equations used Eq. (1) (DKM) in batch system are Eq. (2) (Sin.Eq.) and Eq. (3) (Bin.Eq.).

$$\begin{cases} \dfrac{dC_A}{dt} = -k_A C_A (1 - X) \\ \dfrac{dX}{dt} = k_d C_A (1 - X) \end{cases} \qquad \text{(2) – Sin.Eq.}$$

$$\begin{cases} \dfrac{dC_A}{dt} = -k_A C_A (1 - X) \\ \dfrac{dC_B}{dt} = -k_B C_B (1 - X) \\ \dfrac{dX}{dt} = k_d (C_A + C_B)(1 - X) \end{cases} \qquad \text{(3)- Bin.Eq.}$$

where k_A and k_B are apparent adsorption rate constants of A and B (min^{-1}). If C_B=0 in the initial state (t=0), Bin.Eq. is equal to Sin.Eq.. The Sin.Eq. and Bin.Eq. were solved with ODE function of MATLAB, the kinetic parameters were calculated using the nonlinear least-squares fitting of the adsorbates concentration obtained by solving ordinary differential equations (Sin.Eq. or Bin.Eq.) 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 pseudo-second order model (PSO) estimated by them [1] and kinetic parameters by Sin.Eq. and Bin.Eq. were shown in Table 1 and Table 2. As the experimental data for Sin.Eq. and Bin.Eq., the values calculated by PSO [1] were used.

Table 1. Parameters calculated for single adsorption of Cu (II) and Pb (II) on two adsorbents.

Kinetic Model →	PSO [1]	DKM, Sin. Eq.* [this

					work]		
Adsorbent	Metal ion	$k_2 \times 10^{-2}$ mg g^{-1} min^{-1}	q_e mg g^{-1}	R^2	k_A L mg^{-1} min^{-1}	k_d L mg^{-1} min^{-1}	R^2
Chitosan/$CoFe_2O_4$	Cu(II)	0.773	57.143	0.999	0.0855	0.2780	0.9940
	Pb(II)	0.646	71.942	0.999	0.1179	0.2889	0.9951
TEPA# modified chitosan/$CoFe_2O_4$	Cu(II)	1.067	132.100	0.999	0.7227	0.7070	0.9988
	Pb(II)	0.554	151.515	0.999	0.5994	0.4521	0.9994
#: tetraethylenepentamine Condition: V=25mL, M=25mg, C_0=200mgL^{-1}, T=303 K, pH=5.0					*: $dC_A/dt = k_A C_A^2(1-X)$ in Sin.Eq.		

Table 2. Parameters calculated for binary adsorption of Cu (II) and Pb (II) on two adsorbents.

Kinetic Model →		PSO [1]			DKM, Bin. Eq.* [this work]			
Adsorbent	Metal ion	$k_2 \times 10^{-2}$ mg g^{-1} min^{-1}	q_e mg g^{-1}	R^2	$k_A{}^{\#}$ min^{-1}	$k_B{}^{\#\#}$ min^{-1}	k_d L mg^{-1} min^{-1}	R^2
Chitosan/$CoFe_2O_4$	Cu(II)	1.014	40.323	0.999	0.2802	0.9270	1.7394	0.9604
	Pb(II)	0.872	52.631	0.999				0.9995
TEPA modified chitosan/$CoFe_2O_4$	Cu(II)	1.457	95.785	0.999	0.2381	0.6117	1.0561	0.9902
	Pb(II)	0.760	105.153	0.999				0.9988
Condition: V=25mL, M=25mg, C_0=200mgL^{-1}, T=303 K, pH=5.0					# A = Cu(II), ##: B = Pb(II) *: $dX/dt = k_d(C_A+C_B)(1-X)^{1.5}$ in Bin.Eq.			

The following conclusions can be drawn from Tables 1 and 2.

- 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 single component adsorption and binary component adsorption occur in different mechanisms. Because reaction order of C_A in single system and reaction order of (1-X) in binary system are difference. If all reaction orders were equal to 1, the correlation coefficient became smaller than 0.88 or some calculated adsorption rate constants became smaller than 0.

- In binary system, the adsorption rate of one component can be calculated how times faster than the other component. From the Tables, it can be seen that the Pb^{2+} adsorption rates are 3.30 and 2.57 times faster than Cu^{2+} on the two adsorbents, respectively. While, the deactivation rate constant of Chitosan/$CoFe_2O_4$ is bigger than TEPA modified chitosan/$CoFe_2O_4$, in other words, it can be seen that the senescence rate of Chitosan/$CoFe_2O_4$ is faster.
- If there are adsorption experiment data on temperature, the activation energies can be calculated using DKM.

Kinetic conclusions can be obtained like above and these conclusions can't be obtained by pseudo order kinetic models containing the adsorption amount. Although small correlation coefficients calculated by Sin.Eq. and Bin.Eq. are smaller than PSO. But I think that it is better to use Bin.Eq. than pseudo order models for single adsorption in kinetic studies of competitive adsorption.

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