Kinetic reevaluation on adsorption of Cu(II), Cd(II) and Pb(II) metal ions over functionalization of polyacrylonitrile/Na-Y-zeolite[Chem. Eng. J. 332 (2018) 727–736] using deactivation kinetics model

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ABSTRACT

In this work, the adsorption of of Cu(II), Cd(II) and Pb(II) metal ions over functionalization of polyacrylonitrile/Na-Y-zeolite [Chem. Eng. J. 332 (2018) 727–736] was reevaluated using deactivation kinetics model (DKM). As the result, the reaction orders were newly calculated and rate constants were quantitatively compared on both adsorbates and adsorbent.

Keywords: Adsorption Kinetic, Heterogeneous Reaction, Deactivation Kinetics Model

Recently, Elwakeel et al. (2018) investigated the adsorption of Cu(II), Cd(II) and Pb(II) metal ions by polyacrylonitrile/Na-Y-zeolite[1]. In their kinetic studies of adsorption, a pseudo second order model (PSO) was used to fit the experimental data[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 a mount which is the thermodynamic quantity and assumed reaction order. Therefore, the calculated rate constants can't be compared. It can be said that the adsorption process is one of heterogeneous reaction process.

In this work, the experiment data published by Elwakeel 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 sorbentin 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 wi th 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≦X≦1, dimensionless), CA is concentration (mg•L-1) of A component at any time (min), kd is a deactivation rate constant of the adsorbent (L•mg-1•min-1), α is a reaction order of (1-X).

The adsorption kinetic equation using eq. 1 in batch system is eq. 2.

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

where k_A is the apparent adsorption rate constant of adsorbate. Eq. 2 were solved with ODE function of MATLAB, the kinetic parameters (reaction order and rate constant) were calculated using the nonlinear least-squares fitting of the adsorbate concentration obtained by solving ordinary differential equations (eq. 2) to the experimental data. The input data required for the nonlinear optimization were only the non-dimensionalized concentrations (C/C_0) of adsorbate with time and X were automatically evaluated in the calculation process.

Kinetic parameters calculated by DKM were shown in Table. Also the calculated concentration of adsorbates and deactivation degree of adsorbent were shown in Fig. 1 and 2.

Table. Kinetic parameters

T(K)	PSO (Chem. Eng. J. 332 (2018) 727–736)			DKM, Eq (This work)		
	k_2 g mmol^{-1} min^{-1}	q_e mmol g^{-1}	R^2	k_A min^{-1}	k_d L mg^{-1} min^{-1}	R^2
Cu(II)	0.492	0.561	0.991	0.2748	0.3950	0.9997
Cd(II)	0.932	0.365	0.990	0.3202	0.2655	0.9996
Pb(II)	2.411	0.173	0.999	0.4294	0.6162	0.9997
$\frac{dq}{dt} = k_2 (q_e - q)^2$ (1)-PSO				Calculated Reaction orders = 1, 1, 0.5, 1.5 : i.e.		

	$\begin{cases} \frac{dC_A}{dt} = -k_A C_A (1-X) \\ \frac{dX}{dt} = k_d C_A^{0.5} (1-X)^{1.5} \end{cases}$ (3)

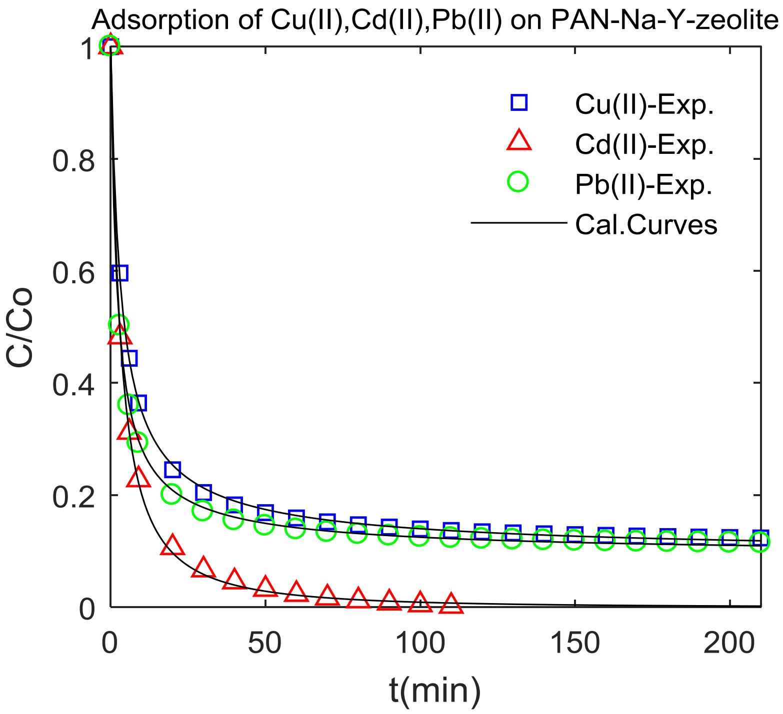

Fig. 1 Concentration of Adsorbates

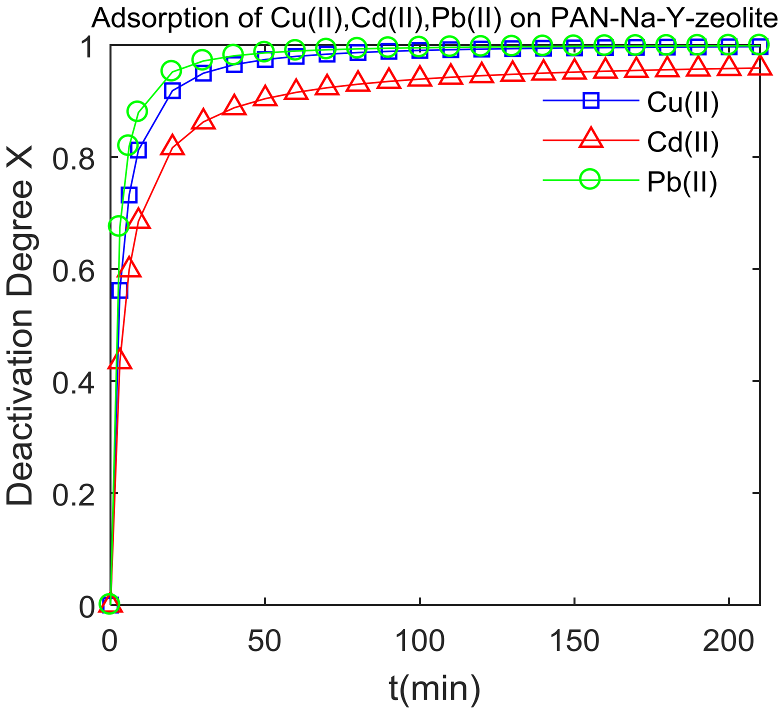

Fig. 2 Deactivation Degree of Adsorbent

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. The reaction order related to the mechanism is an empirical quantity obtained from the experimental data and rate equation.
- The calculated rate constants could quantitatively be compared on both adsorbates and adsorbent unlike PSO.

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