Kinetic reevaluation on heavy metal ions adsorption by arrowhead plant (Sagittaria trifolia L.) stalkusing using deactivation kinetics model

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ABSTRACT

The heavy metal ions adsorption from aqueous solution by arrowhead plant (Sagittaria trifolia L.) [J Food Biochem. 2018;42:e12448] stalk was reevaluated using deactivation kinetics model (DKM). As the result, the reaction orders were newly evaluated and the adsorption rate constants of each component were calculated and compared.

Keywords: Adsorption Kinetics, Heterogeneous Reaction, Deactivation Kinetics Model

Zhang et al. published the paper entitled "The physicochemical characterization, equilibrium, and kinetics of heavy metal ions adsorption from aqueous solution by arrowhead plant (Sagittaria trifolia L.) stalk" [1].

In their adsorption kinetic study, their experimental data were analyzed using pseudo second order kinetic model (PSO) [2], Eq. (1)).

$$\frac{dq}{dt} = k_2(q_e - q)^2 \qquad \text{(1)-PSO}$$

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 sorption. 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 which is the thermodynamic quantity and assumed reaction order.

Recently, the deficiencies and cause of previous adsorption kinetic models

were revealed, new adsorption rate equation [3] using deactivation kinetics model (DKM) has been proposed and its validities were verified by kinetic a nalysis of various experimental data. Also, many of experiment date were kin etically reevaluated by it [4-18].

In this work, the experimental data of [J Food Biochem. 2018;42:e12448] was reevaluated kinetically using DKM.

The DKM [19] (Eq. (2)) is a kinetic model for heterogeneous reaction an d 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. T he validity [20] of DKM was verified through kinetic analysis for other expe rimental data. DKM has 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. The change of fracti onal conversion with time in solid phase was expressed as a deactivation rate, as shown in Eq. (2):

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

where X is the deactivation degree of adsorbent, i.e. fractional conversion of fresh adsorbent ($0 \leqq X \leqq 1$, dimensionless). And C_A is concentration ($\mu g\ L^{-1}$) of A component at any time (t), k_d is a deactivation rate constant of the a dsorbent ($L\ \mu g^{-1}\ h^{-1}$), α is a reaction order of (1-X). The adsorption kinetic eq uation used Eq. (2) in batch system is Eq. (3).

$$\begin{cases} \dfrac{dC_A}{dt} = -k_A C_A (1 - X) \\ \dfrac{dX}{dt} = k_d C_A (1 - X) \end{cases} \qquad (3)$$

where k_A is the apparent adsorption rate constant of A adsorbate. Eq. (3) were solved with ODE function of MATLAB, the kinetic parameters were cal culated using the nonlinear least-squares fitting of the adsorbate concentration obtained by solving ordinary differential equations (Eq. (3)) to the experime ntal data. The input data required for the nonlinear optimization were only th

e non-dimensionalized concentrations (C/C_0) of the adsorbates with time and X were automatically evaluated in the calculation process.

The parameters of PSO estimated by Zhang et al., 2018 and kinetic parameters calculated by Eq. (3) were shown in Table. Activation energies and frequency factors were calculated from the rate constants with temperature and the Arrhenius equation. The values calculated by Eq. (1) were used as the experimental data for Eq. (3).

Table. Kinetic parameters reevaluated using DKM.

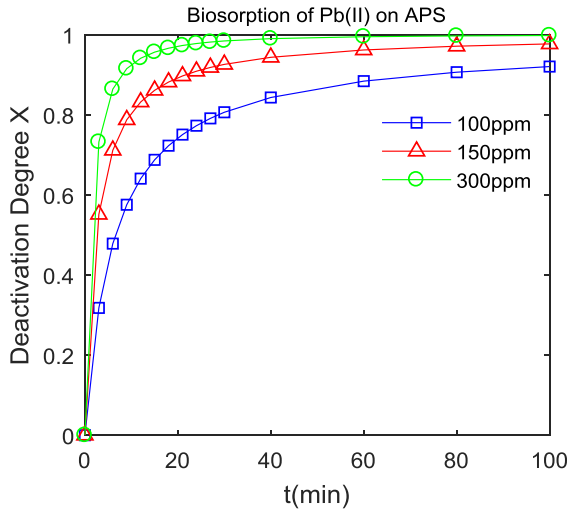
ion	Co mg/L	PSO			DKM, beta=1.5		
		$k_2 \times 10^{-4}$ g mg^{-1} min^{-1}	$q_e \times 10^2$ mg g^{-1}	R^2	k_A min^{-1}	k_d L mg^{-1} min^{-1}	R^2
Cd(II),	50	0.70	19.4	0.999	0.1313	0.3021	0.9989
	100	1.65	28.2	0.999	0.3521	1.2185	0.9996
	150	3.16	27.3	0.998	0.3840	2.0899	1.0000
Pb(II),	100	18.8	45.9	0.998	0.0924	0.1582	0.9994
	150	27.6	64.9	1.000	0.2025	0.4086	0.9985
	300	39.7	76.9	0.999	0.1949	0.7387	0.9996
Cr(III)	80	0.01	5.98	0.999	0.0009	0.0114	1.0000
	100	0.09	11.5	0.999	0.0252	0.2151	0.9999
	150	1.17	23.5	0.999	0.9779	6.1651	0.9999

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

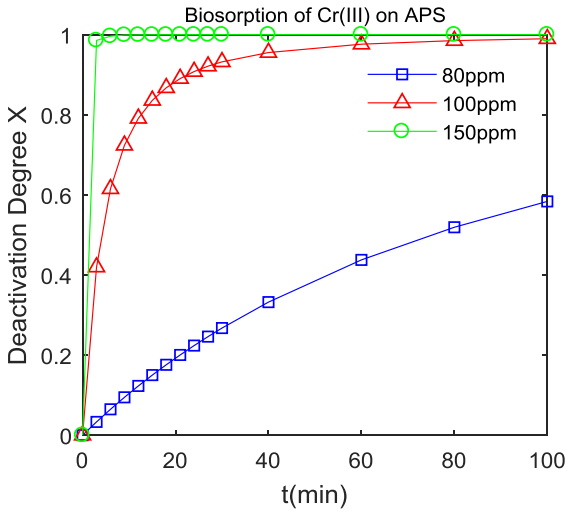
The concentration of adsorbates and deactivation of adsorbent calculated by Eq. (4) were shown in Fig. a-f. As shown in Figures, the experimental data agree well with the curves.

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. Authors think that it may be more necessary to use DKM than pseudo order models including the adsorption amount in adsorp

tion kinetic studies.



a



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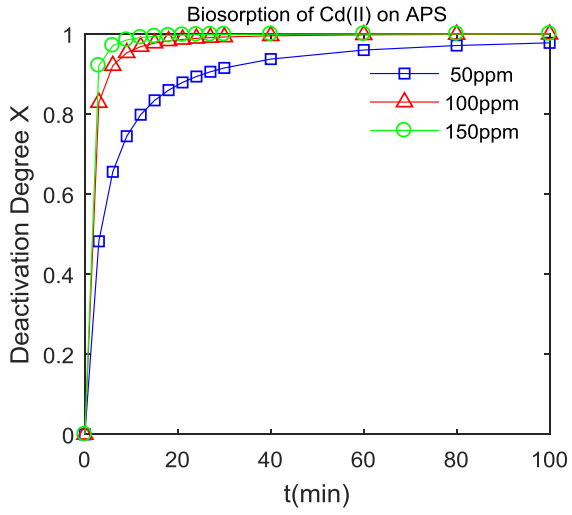

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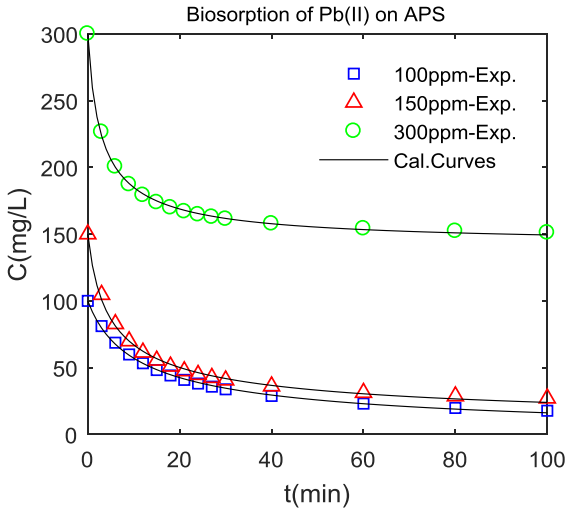

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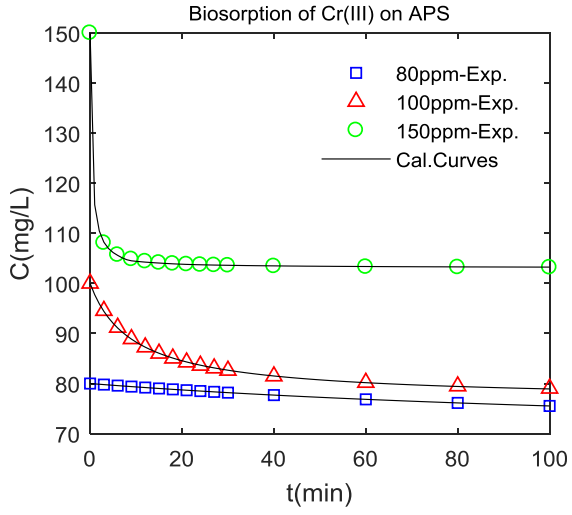

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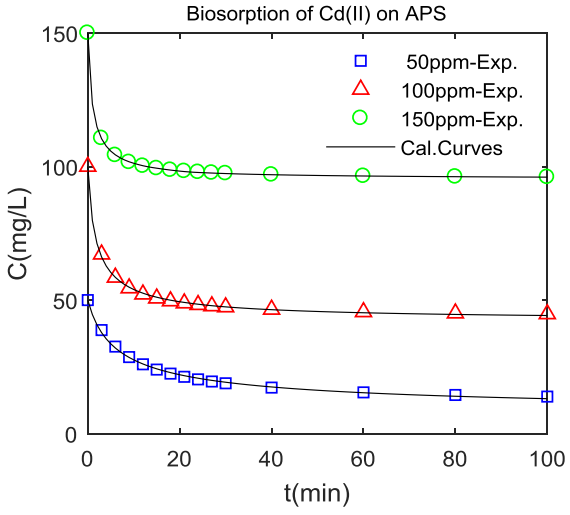

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