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 an

d 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 ($\mu g \cdot L^{-1}$) of A component at any time (t), k_d is a deactivation rate constant of the a dsorbent ($L \cdot \mu g^{-1}\ h^{-1}$), 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 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 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 related using DKM.

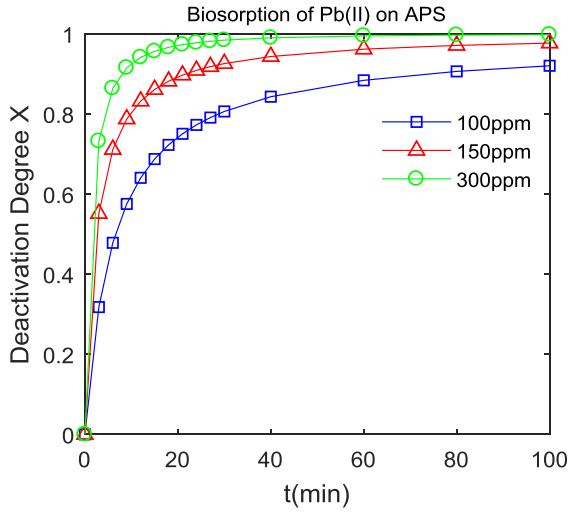
ion	Co mg/L	PSO			DKM, beta=1.5		
		$k_2 \times 10^{-4}$ g mg^{-1} min^{-1}	$q_e \times 10^2$ mg g^{-1}	R^2	k_A min^{-1}	k_d L mg^{-1} min^{-1}	R^2
Cd(II),	50	0.70	19.4	0.999	0.1313	0.3021	0.9989
	100	1.65	28.2	0.999	0.3521	1.2185	0.9996
	150	3.16	27.3	0.998	0.3840	2.0899	1.0000
Pb(II),	100	18.8	45.9	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

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

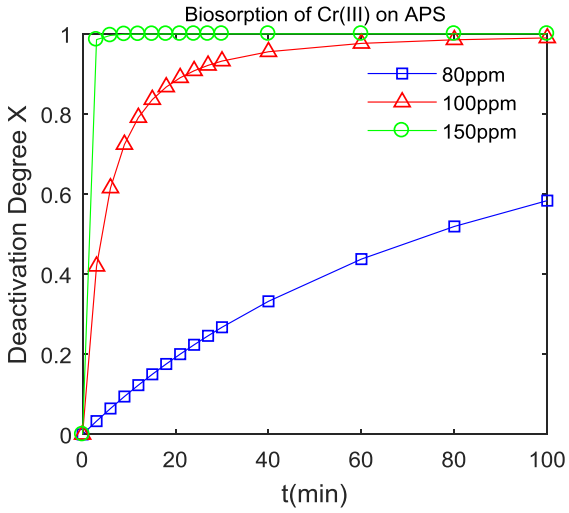
The concentration of adsorbates and deactivation of adsorbent calculated b

y Eq. (4) were shown in Fig. a-f. As shown in Figures, the experimental dat a agree well with the curves.

Kinetic conclusions can be obtained like above using DKM and these con clusions can't be obtained using PSO which assumes reaction order and conta ins the adsorption amount. Authors think that it may be more necessary to u se DKM than pseudo order models including the adsorption amount in adsorp tion kinetic studies.



a



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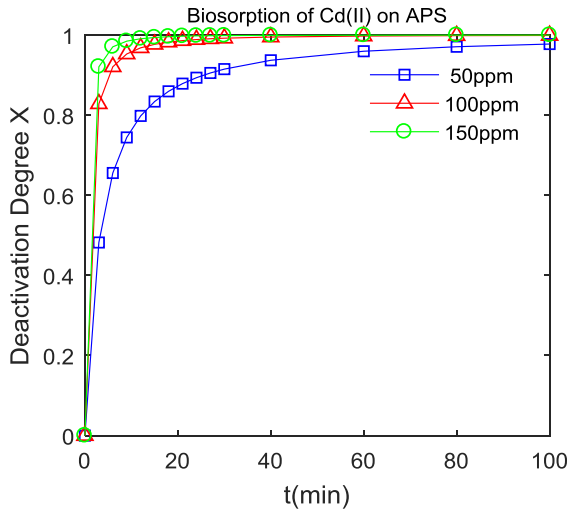

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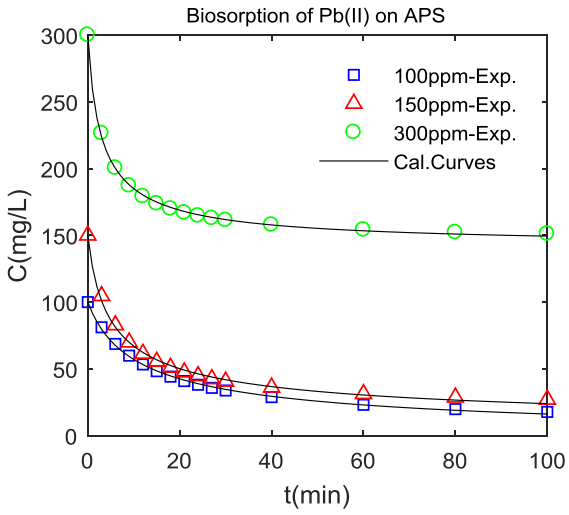

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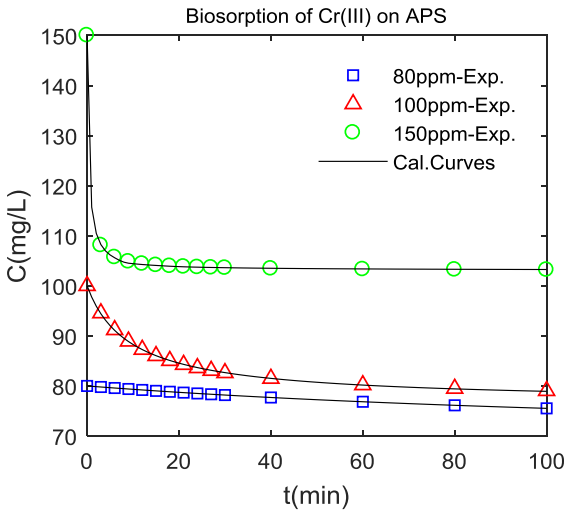
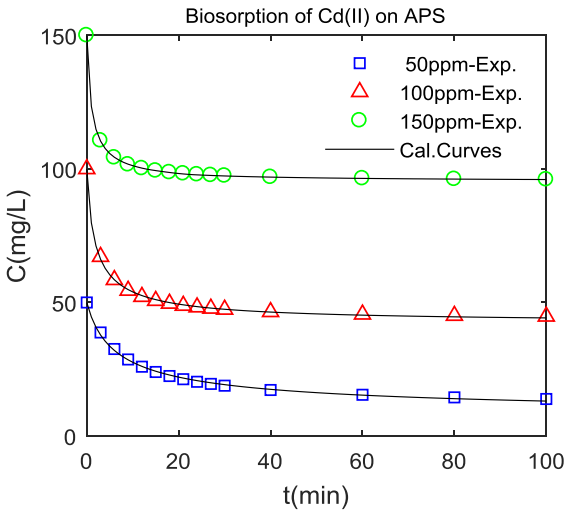

Biosorption of Cr(III) on APS
80ppm-Exp.
100ppm-Exp.
150ppm-Exp.
Cal.Curves
C(mg/L)
t(min)
150
140
130
120
110
100
90
80
70
0
20
40
60
80
100

e


Biosorption of Cd(II) on APS
50ppm-Exp.
100ppm-Exp.
150ppm-Exp.
Cal.Curves
C(mg/L)
t(min)
150
100
50
0
0
20
40
60
80
100

f

References

1. D. Zhang, C.T. Wang, Q.H. Bao, J. Zheng, D. Deng, Y.Q. Duan, L.Q. Shen The physicochemical characterization, equilibrium, and kinetics of heavy metal ions adsorption from aqueous solution by arrowhead plant (Sagittaria trifolia L.) stalk, J Food Biochem. 2018;42:e12448.
2. Ho, Y. S., McKay, G., 1999. Pseudo-second order model for sorp tion processes. Process Biochem. 34, 451–465.
3. Y.S. Hong, C.J. Kim, K.R. Sin, J.S. Pak, A New Adsorption Rate Equation in Batch System, Chemical Physics Letters, https://doi.org/10.1016/j.cplett.2018.06.010
4. Y.S. Hong, Kinetic reevaluation on "Synthesis of a novel nanosili ca-supported poly β-cyclodextrin sorbent and its properties for the removal of dyes from aqueous, Colloids and Surfaces A 545 (2018) 127–129 soluti on"
5. Y.S. Hong, Kinetic re-evaluation on "Comparative adsorption of P b(II), Cu(II) and Cd(II) on chitosan saturated montmorillonite: Kinetic, ther modynamic and equilibrium studies", Applied Clay Sci., https://doi.org/10.1016/j.clay.2018.01.030
6. Y.S. Hong, et al., Kinetic reevaluation on Adsorption of benzothio phene sulfone over clay mineral adsorbents in the frame of oxidative desul furization, viXra:1802.0287, http://viXra.org/abs/1802.0287
7. Y.S. Hong, et al., Evaluation of activation energies on As(V) sor ption onto magnetic separable poly p-phenylenediamine-thiourea-formaldehy de polymer [J.Hazard. Mater. 342 (2018) 335–346], viXra:1802.0308, http://vixra.org/abs/1802.0308
8. Y.S. Hong, Kinetic reevaluation of the competitive adsorption [J. Hazard. Mater. 326 (2017) 211–220] using deactivation kinetics model,viXra:1803.0381, http://vixra.org/abs/1803.0381
9. Y.S. Hong, Kinetic analysis on dyes adsorption by zeolite imidaz olate framework-9[New J. Chem. 2018, 42, 717-724] using deactivation ki netics model,viXra:1803.0382, http://vixra.org/abs/1803.0382
10. Y.S. Hong, Evaluation of activation energies on F- adsorption by hydrous ZrO2 decorated polyaniline nanofibres [J. Colloid Interf. Sci. 508

(2017) 342–358], viXra:1803.0383, http://vixra.org/abs/1803.0383

11. Y.S. Hong, Kinetic reevaluation on adsorption of Cu(II), Cd(II) a nd Pb(II) metal ions over functionalization of polyacrylonitrile/Na-Y-zeolite [Chem. Eng.J. 332 (2018) 727–736] using deactivation kinetics model, viX ra:1803.0398, http://vixra.org/abs/1803.0398

12. Y.S. Hong, Evaluation of activation energies for adsorption of dy es by modified activated carbons [J. Environ. Manage. 206 (2018) 170-177 and 383-397] using deactivation kinetics model, viXra:1803.0400, http://v ixra.org/abs/1803.0400

13. Y.S. Hong, et al., Kinetic reevaluation on uranium(VI) adsorption [Ind. Eng. Chem.Res. 2017, 56, 3251−3258 and 12745−12754] using deacti vation kinetics model, viXra:1803.0666, http://vixra.org/abs/1803.0666

14. Y.S. Hong, et al., Kinetic reevaluation on Adsorption of Co(II), Hg(II) and Ag(I) from fuel ethanol by silica gel supported sulfur-containin g PAMAM dendrimers[Fuel 199 (2017) 91–101 and 206 (2017) 80–88], vi Xra:1804.0023, http://vixra.org/abs/1804.0023

15. Y.S. Hong,, Evaluation reevaluation of activation energies on bio sorption of Pb (II) by extracellular polymeric substances [Scientific RepoRt s | 6:31575] using deactivation kinetics model, viXra:1804.0106, http://vixra. org/abs/1804.0106

16. Y.S. Hong, Evaluation reevaluation of activation energies on anion ic azo dye Congo Red adsorption over Cationic Modified Orange Peel Po wder [J. Mol. Liq. 220 (2016) 540–548] using deactivation kinetics model, viXra:1804.0107, http://vixra.org/abs/1804.0107

17. Y.S. Hong,, Evaluation reevaluation of activation energies on Acid Blue 193 adsorption over natural sepiolite [Colloids Surface A, 277(2006), 90–97] using deactivation kinetics model, viXra:1804.0124, http://vixra.org/ abs/1804.0124

18. Y.S. Hong, et al., Evaluation reevaluation of activation energies on Pb (II) adsorption over bael leaves (Aegle marmelos) [J. Hazard. Mate r., 173 502–509(2010)] usingdeactivation kinetics model, viXra:1804.0126, http://vixra.org/abs/1804.0126

19. Y.S. Hong, Z. F. Zhang, Z. P. Cai, X. H. Zhao and B. S. Liu, D

eactivation Kinetics Model of H2S Removal over Mesoporous LaFeO3/MCM- 41 Sorbent during Hot Coal Gas Desulfurization, Energy & Fuels, 2014, 28, 6012−6018.

20. Y.S. Hong, K.R. Sin, J.S. Pak, C.J. Kim and Bing-Si Liu, Kinetic Analysis of H_2S Removal over Mesoporous Cu−Mn Mixed Oxide/SBA- 15 and La−Mn Mixed Oxide/KIT6 Sorbents during Hot Coal Gas Desulfuriza tion Using the Deactivation Kinetics Model, Energy & Fuels, 2017, 31, 9874−9880.