Evaluation of activation energies on F$^-$ adsorption by hydrous ZrO$_2$ decorated polyaniline nanofibres [J. Colloid Interf. Sci. 508 (2017) 342–358]

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ABSTRACT

In this work, the F$^-$ adsorption on hydrous ZrO$_2$ decorated polyaniline nanofibres (HZrO2@PANI NFs) published by Parashar et al. [J. Colloid Interf. Sci. 508 (2017) 342–358] was reevaluated using deactivation kinetics model (DKM). As the result, the reaction order and the activation energies were newly calculated.

Keywords: Adsorption, Kinetics, Modeling, Deactivation Kinetics Model

Parashar et al. had published the paper entitled "Hydrous ZrO$_2$ decorated polyaniline nanofibres: Synthesis, characterization and application as an efficient adsorbent for water defluoridation" [1]. In the 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. Therefore, the activation energy can't be accurately calculated because both the rate constant and the adsorbed amount change with temperature. In recent researches [3-6] as like as them, although the adsorption experimental data with temperature were measured and the rate constants were estimated, the activation energy couldn't be calculated because PSO was used. One important

purpose of kinetic research is to calculate activation energy. In chemical kinetics the activation energy is the energy barrier, which must be overcome for a sufficient number of molecules to acquire enough kinetic energy for a reaction to occur appreciably. The activation energy can generally be achieved by supplying external energy.

In this work, the experimental data [1] was reevaluated kinetically using DKM and the activation energies were newly calculated.

The DKM [7] (Eq. (2)) is a kinetic model for heterogeneous reaction 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. The validity [8] 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 or random pore model 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. (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 ($mg \cdot L^{-1}$) of A component at any time (t), k_d is a deactivation rate constant of the adsorbent ($L \cdot mg^{-1} \cdot min^{-1}$), α is a reaction order of (1-X). The adsorption kinetic equation using 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 adsorbate. Eq. (3) were solved with ODE function of MATLAB, the kinetic parameters were calculated 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 adsorbate with time and X were automatically evaluated in the calculation process.

The parameters of PSO [1] 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 for F⁻ adsorption on $HZrO_2$@PANI NFs.

Condition*	PSO[1]				DKM, Eq. (4)		
	k_2 g mg^{-1} min^{-1}	q_e mg g^{-1}	R^2		k_A min^{-1}	k_d L mg^{-1} min^{-1}	R^2
5 (mg/L)	0.109	9.948	0.992		1.0712	0.5403	1.0000
10 (mg/L)	0.044	19.07	0.996		0.7327	0.3890	0.9997
15 (mg/L)	0.032	26.15	0.986		0.5837	0.3411	0.9986
20 (mg/L)	0.021	36.28	0.990		0.5886	0.3301	0.9991
15 (°C)	0.031	17.92	0.98		0.1133	0.0729	0.9949
25 (°C)	0.044	19.07	0.996		0.7327	0.3890	0.9997
35 (°C)	0.056	19.39	0.997		1.6256	0.8355	0.9962
45 (°C)	0.062	19.73	0.998		2.6319	1.3301	0.9931
*Condition: various C_0 at 25 °C, various T at 10 mg/L					78.567kJ/mol 2.8240E+13	72.718kJ/mol 1.5073E+12	

The following conclusions can be drawn from Table.

- The reaction orders were evaluated (Eq. (4)). If all reaction orders were equal to 1 or 2, some calculated adsorption rate constants were smaller than 0 or the correlation coefficients (R^2) were smaller than 0.95.

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$$\begin{cases} \dfrac{dC_A}{dt} = -k_A C_A (1 - X)^2 \\ \dfrac{dX}{dt} = k_d C_A (1 - X) \end{cases} \qquad (4)$$

- The calculated rate constants could quantitatively be compared on both adsorbate and adsorbent. With increasing F⁻ initial concentration, the adsorption rate constants of F⁻ and the deactivation rate constants of $HZrO_2$@PANI NFs become smaller except only F⁻ adsorption rate constant at C_0=20 (mg/L). Also rate constants of both adsorbate and adsorbent become larger with increasing temperature.

- The activation energies are newly calculated. The activation energy of F⁻ adsorption is 78.567 kJ/mol and the activation energy of $HZrO_2$@PANI NFs deactivation is 72.718kJ/mol , which are relatively high. In other words, it can be seen that F⁻

adsorption on HZrO$_2$@ PANI NFs is a difficult process.

Important kinetic conclusions can be obtained from Eq. (4) and can't be obtained from PSO which assumes reaction order and contains the adsorbed amount. The authors think that it may be more necessary to use DKM than pseudo order models including the adsorbed amount in adsorption kinetic studies.

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