Kinetic reevaluation on dyes adsorption by zeolite imidazolate framework-9 using deactivation kinetics model [New J. Chem. [2018, 42, 717-724]

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ABSTRACT

The dyes adsorption on zeolitic imidazolate framework-9 (ZIF-9) published at New J. Chem. [2018, 42, 717-724 by Han et al. was reevaluated using deactivation kinetics model (DKM). As the result, the reaction orders, the activation energies were newly evaluated and the adsorption rate constants of each component were calculated and compared.

Keywords: Adsorption Kinetics, Heterogeneous Reaction, Deactivation Kinetics Model

Recently, Han et al. published the paper entitled "Synthesis of nanoporous cobalt/carbon materials by a carbonized zeolitic imidazolate framework-9 and adsorption of dyes". [1] A lot of kinetic experiments had been carried out by them, but the more practical kinetic analysis couldn't be grained because pseudo-second order model (PSO, eq.1) [2] had been used.

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

where q and q_e are adsorption amount at any time(t) and at equilibrium, respectively, and k_2 is the adsorption rate constant. PSO that assumed reaction order and contained adsorption amount q_e is convenient in using, however, activation energy can't be calculated by using it. Because not only the adsorption rate constant but also the adsorption amount changes simultaneously according to the temperature. Also, the adsorption rate constants of each component on various adsorption conditions couldn't be compared because the adsorption amount changes. In strictly meaning, the adsorption amount q_e is not a kinetic quantity but a thermodynamic quantity.

In this work, the deactivation kinetics model (DKM) [3, 4] was used for kinetic reevaluation on the dyes adsorption by ZIF-9. [1]

In DKM, the change of fractional conversion with time in solid phase was expressed as a deactivation rate, as shown in eq. 2:

$$\frac{dX}{dt} = k_d C_{\mathrm{A}}(1 - X)^{\alpha} \qquad (2)$$

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 L^{-1}) of A component at any time (t), k_d 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. 2 in batch system is eq. 3.

$$\begin{cases} \dfrac{dC_{\mathrm{A}}}{dt} = -k_{\mathrm{A}} C_{\mathrm{A}}(1 - X) \\ \dfrac{dX}{dt} = k_d C_{\mathrm{A}}(1 - X) \end{cases} \qquad (3)$$

where k_{A} is the apparent adsorption rate constant of adsorbate. Eq. 3 were solved with ODE function of MATLAB, the kinetic parameters (reaction order and rate constant) 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 on various initial concentrations of twelve organic dyes were shown in Table 1. As shown in Table 1, the reaction orders were evaluated, they were 2, 1, 2 and 1, respectively, *i.e.* eq. 4.

$$\begin{cases} \dfrac{dC_{\mathrm{A}}}{dt} = -k_{\mathrm{A}} C_{\mathrm{A}}^2(1 - X) \\ \dfrac{dX}{dt} = k_d C_{\mathrm{A}}^2(1 - X) \end{cases} \qquad (4)$$

If all reaction orders were equal to 1 or 2, some calculated adsorption rate constants were smaller than 0 and the correlation coefficient (R^2) were smaller than 0.85. Also, the calculated rate constants could quantitatively be compared on both adsorbates and adsorbents unlike PSO.

Kinetic parameters calculated by eq. 4 on various adsorption conditions were shown in Table 2. As shown in Table 2, the rate constants of adsorbates and adsorbents were changed according to various adsorption conditions. Activation energies were calculated from the rate constants with temperature and Arrhenius equation. The calculated activation energies of MeG adsorption by Z9-600 and Z9-600 deactivation by MeG adsorption were E_A=8.8075 kJ/mol and E_d=9.1735kJ/mol, respectively.

The following kinetic conclusions can be drawn from Table 1 and 2.

- The practical reaction order, not the pseudo reaction order, had been determined.
- The rate constants had been quantitatively compared on both adsorbates and adsorbents.
- The activation energies had been newly evaluated.

These kinetic conclusions can't be obtained by PSO which contains the adsorption amount and assumes reaction order. We think that it may be more necessary to use DKM than pseudo order models in adsorption kinetic studies.

Table 1. Calculated kinetic parameters on various initial concentration of twelve organic dyes ⊗.

Dyes*	PSO[1]			Eq. 3[#]		
	k_2 g mg^{-1} h^{-1}	q_e mg g^{-1}	R^2	k_A L $mg^{-1}h^{-1}$	k_d $(L\ mg^{-1})^2$ h^{-1}	R^2
MeG (0.5)	0.127	14.3	0.999	0.5236	1.2609	0.9979
MeG (0.8)	0.066	23.1	0.999	0.4622	1.1055	0.9977
MeG (1.0)	0.023	29.5	0.999	0.2437	0.5797	0.9977
MeG (2.5)	0.012	72.9	0.999	0.2976	0.7123	0.9974
MeG (2.0)	0.024	58.2	0.999	0.4361	1.0364	0.9976
MaG (2.0)	0.136	61.6	0.994	1.6101	3.5233	0.9997
RO (2.0)	0.041	46.4	0.996	0.3932	1.1628	0.9976
CR (1.0)	0.006	50.2	0.997	0.2794	0.3754	0.9995
AR (1.0)	0.001	56.8	0.996	0.0514	0.0384	0.9999
OG (1.0)	0.004	34.0	0.994	0.0698	0.1506	0.9999
CV (1.0)	0.013	28.2	0.998	0.1337	0.3390	0.9984
AO (1.0)	0.029	23.9	0.998	0.1830	0.5397	0.9964
MO (1.0)	0.010	23.5	0.997	0.0708	0.2210	0.9984
MB (1.0)	0.001	62.6	0.996	0.0611	0.0222	1.0000
RHB (1.0)	0.006	30.3	0.997	0.0786	0.1904	0.9996
R6G (1.0)	0.009	27.6	0.995	0.0920	0.2423	0.9989

*: The data in parentheses are initial concentration of adsorbates ($\times 10^{-4}$mol L^{-1}).

[#]: Calculated orders on eq. 3 are 2, 1, 2 and 1, respectively, *i.e.* eq. 4.

⊗: Twelve organic dyes, *i.e.* cationic dyes: rhodamine 6G (R6G), rhodamine B (RHB), methylene green (MeG), malachite green (MaG), and crystal violet (CV), and anionic dyes: methyl blue (MB), methyl orange (MO), acid red 18 (AR), acid orange 7 (AO), orange G (OG), and congo red (CR), and neutral dye:rosaniline (RO).

Table 2. Various adsorption conditions, Experimental data and Calculated kinetic parameters

Various adsorption condition and Experimental data		k_A L $mg^{-1}h^{-1}$	k_d (L $mg^{-1})^2$ h^{-1}	R^2
MeG (2.0) Adsorption by Z9-600, Z9-700, Z9-800 and Z9-900 Experimental Data - Table S1.	Z9-600	0.4361	1.0364	0.9976
	Z9-700	0.5851	1.4259	0.9913
	Z9-800	0.4717	1.1679	0.9900
	Z9-900	0.4797	1.2199	0.9913
MeG (2.0) adsorption by Z9-600 at various ionic strength Experimental Data - Table S2.	Na^+(0.05)	0.4776	0.9191	0.9951
	Na^+(0.1)	0.5340	1.0397	0.9907
	Na^+(0.2)	0.5589	1.0747	0.9940
	Na^+(0.5)	0.6198	1.2048	0.9920
MeG (2.0) adsorption by Z9-600 at various temperature Experimental Data - Table S3.	20 ^oC	0.6955	1.6939	0.9893
	40 ^oC	0.7607	1.8134	0.9946
	60 ^oC	1.0804	2.5343	0.9992

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References

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Supplementary Information

In supplementary information, the experimental data for kinetic reevaluation were given. These experimental data were provided by Prof. Jian-Fang Ma who was corresponding author of the paper “Synthesis of nanoporous cobalt/carbon materials by a carbonized zeolitic imidazolate framework-9 and adsorption of dyes” [New J. Chem., 2018, 42, 717-724.].

Table S1. Experimental data of MeG adsorption by Z9-600, Z9-700, Z9-800 and Z9-900, *i.e.* Fig. 4 in *New J. Chem.*, 2018, **42**, 717-724.

Time	q_t (mg/g)		
(h)	Z9-700	Z9-800	Z9-900
2	46.86554	44.51065	44.5423
4	48.9229	47.46059	46.50471
6	50.68273	49.49263	47.89738
8	51.81586	50.48649	49.24574
10	53.1389	51.44237	49.99905
12	54.15175	52.22733	50.77768
24	55.9559	54.5569	52.89202
30	56.84055	55.31021	53.87322
48	57.18208	56.61426	55.4558
60	57.18209	56.77251	55.89893

Table S2. Experimental data of MeG adsorption by Z9-600 at various ionic strength, *i.e.* Fig. 12 in *New J. Chem.*, 2018, **42**, 717-724.

Time	q_t (mg/g)			
(h)	0.05 Na$^+$	0.1 Na$^+$	0.2 Na$^+$	0.5 Na$^+$
2	50.34738	53.22769	53.30365	55.15844
4	56.76635	57.48167	58.57049	58.81105
6	60.52657	59.84289	61.48878	61.62805
8	63.07136	62.29906	63.831	63.52082
10	64.48936	64.12853	65.49588	65.00845
12	66.29984	65.43891	66.81892	66.19222
24	69.16748	68.87628	69.65492	69.09151
30	69.85116	69.85749	70.4652	70.05373

48	71.29447	71.09823	71.46539	71.20585
60	71.57301	71.47172	71.77558	71.43374

Table S3. Experimental data of MeG adsorption by Z9-600 at various temperature, *i.e.* Fig. 13 in *New J. Chem.*, 2018, **42**, 717-724.

Time	q_t (mg/g)		
(h)	20 ^{o}C	40 ^{o}C	60 ^{o}C
1	40.000	41.61135	45.36524
2	46.87377	47.26435	51.29677
3	47.74422	49.73357	54.34166
4	49.76791	51.84157	55.58241
6	51.38083	53.8342	56.07618
8	52.60498	54.79686	56.77884
10	53.62007	55.64591	56.98775
12	54.70794	55.89279	57.06371
24	56.44674	57.23403	57.43593
30	57.23403	57.43403	57.43657
48	57.43403	57.4372	57.4372
60	57.43403	57.4372	57.4372