Short communication

Sorption kinetics: Obtaining a pseudo-second order rate equation based on a mass balance approach

Talal Shahwan

Chemistry Department, Birzeit University, Ramallah, West Bank, Palestine

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ABSTRACT

Various formulations of pseudo second-order rate equations have been widely used in elucidating the rate constants of a wide variety of sorption systems. In this paper, it is shown that a new formulation can be obtained by making use of the mass balance equation of a single stage batch-type system. Two linear forms of the equation were then used to analyze different sets of kinetic data. It is shown that the adequacy of kinetic models should not be linked solely to linear correlation coefficients.

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Introduction

The obtained rate constants in sorption studies are usually phenomenological, i.e. they are 'observed' values that depend on the set of experimental parameters like initial concentration, volume of solution, mass of sorbent, pH and others. The kinetic aspect of the sorption process is usually tested using various formulations of first and second rate equations. In most cases, the pseudo first-order analysis of sorption data is carried out using Lagergren's equation. On the other hand, pseudo second-order analysis can be performed using several formulations that have been developed over the past decades. Four of these formulations, which include Sobkowsk and Czerwinski, Ritchie, Blanachard et al., and Ho equations were revised and discussed by Kumar and Sivanesan [1]. Among these four formulations, Ho's equation [2,3] has been intensively used during the last decade to test for the correlation of the sorption data for pseudo second order kinetic mechanisms. Furthermore, in our recent publications other formulations of the pseudo first-order and second-order rate equations have been used to analyze the sorption data on nano iron based materials [4,5]. The corresponding two equations were formulated by considering the driving force of solute removal to be proportional to the difference between its concentration at any time prior to equilibrium and its concentration at equilibrium.

In this paper, it is shown that a pseudo second-order formulation can be obtained by integrating the mass balance equation into the related rate derivative. Three sets of kinetic data were subsequently analyzed to test the new formulation.

Derivation and discussion

In a batch system, as defined by Morel and Hering [6], the sorption reaction can be simply represented as:

$$C_{(aq)} \rightarrow Q_{(s)} \qquad (1)$$

where $C_{(aq)}$ stands for the solute concentration in solution (mg L^{-1}) and $Q_{(s)}$ (mg g^{-1}) stands for the adsorbed solute concentration. In this equation, the role of sorption sites as a reactant is ignored, so that the given reaction becomes a special case of a more general reaction:

$$C_{(aq)} + s \rightarrow Q_{(s)} \qquad (2)$$

Here s represents the sorption sites. In this way, sorption is operationally considered to take place on the surface, whether the surface is external or internal. This is in line with the nature of sorption as a two dimensional interaction, although it can be tricky from a kinetic perspective, as the accessibility to surface sites is usually easier than that to internal sites due to diffusion barriers. In the reaction as written, the sorption sites are presumed to be of equivalent energy and negligible forces of interaction with each other. Including the sorption sites as a reactant is particularly important at higher loadings because they can affect the sorption process both thermodynamically and kinetically. Thermodynamically, for a sorbent surface possessing a certain sorption capacity, the energy barrier against sorption is usually expected to increase as loading is increased, the thing that affects the driving force of sorption. Kinetically, at lower loadings the rate of sorption is normally determined by the sorbate concentration in solution, but with increased loading, the rate of uptake becomes increasingly controlled by the availability of the sorption sites.

In his derivation of pseudo first and second order rate equation based on a surface coverage approach, Azizian [7], showed that the first order rate equation is associated with high initial solute concentration, while the second order rate equation is associated with low

E-mail address: tshahwan@birzeit.edu (T. Shahwan).

Table 1
Results of kinetic analysis performed using Eq. (9) for different sorption systems.

Sorption system	Slope	Intercept	R^2	k_2(L mg^{-1} min^{-1})	$Q_m$exp.(mg g^{-1})	$Q_m$model (mg g^{-1})
Co^{2+} ions and nZVI/bentonite	0.03953	0.05688	0.9995	0.00695	80.0	25.3
Methyl orange and nano iron	0.02043	0.6159	0.9973	0.00066	50.0	49.0
Methylene blue and zeolite	0.05488	0.14307	0.9998	0.00384	20.0	18.2

Table 2
Values of Q obtained from experiment, values of Q predicted by Eq. (9), and the Chi-test values for the three sorption systems.

Time (min)	Q_{exp}(mg g^{-1})	Q_{model}(mg g^{-1})	$(Q_{exp} - Q_{model})^2/Q_{model}$
Co-nZVI/bentonite			
1	16.0	10.4	3.057085
5	21.5	19.6	0.176855
10	22.4	22.1	0.003786
30	23.1	24.1	0.040405
60	24.3	24.7	0.006405
120	25.2	25.0	0.001163
240	25.8	25.1	0.015235
480	24.0	25.2	0.054603
960	24.3	25.3	0.03301
1440	24.5	25.3	0.023149
		χ^2	3.411696
MO-nano iron			
5	7.7	6.9	0.092995
30	22.2	24.4	0.190564
60	33.0	32.5	0.005943
120	39.7	39.1	0.010406
210	42.7	42.8	0.000334
300	43.9	44.5	0.007624
360	44.2	45.1	0.018221
		χ^2	0.326088
MB-zeolite			
5	14.0	12.0	0.340501
10	15.5	14.5	0.075466
30	16.4	16.8	0.007935
60	17.3	17.5	0.001505
120	17.6	17.8	0.003044
240	18.1	18.0	0.000317
420	17.8	18.1	0.00523
960	18.0	18.2	0.001604
1440	18.4	18.2	0.002492
		χ^2	0.438093

Table 3
Results of kinetic analysis performed using Eq. (11) for the sorption systems of MO-nano iron and MB-zeolite.

Sorption system	Slope	Intercept	R^2	k_2(L mg^{-1} min^{-1})	$Q_m$exp.(mg g^{-1})	$Q_m$model(mg g^{-1})
Methyl orange and nano iron	0.5375	0.02237	0.9952	0.00083	50.0	44.7
Methylene blue and zeolite	0.0729	0.05708	0.9694	0.00783	20.0	17.5

solute concentrations. For the sake of derivation in this work, Azizian result could justify assuming that the concentration of the solute is much smaller than the concentration of the sorption sites such that the latter is assumed to be almost constant, and the observed rate constant can then be taken equivalent to $k[s]$. Under this *pseudo* condition Eq. (1) becomes justified, and can form a basis for the derivation of a pseudo second order rate equation.

In light of the above, the rate of removal of the solute from solution can be represented by pseudo second order rate kinetics as:

$$-\frac{dC}{dt} = k_2 C^2 \tag{3}$$

Here k_2 represents the 'observed' rate constant for the reaction. Integrating Eq. (3) using the boundary conditions: $C = C_0$ at $t = 0$, and $C = C$

at $t = t$ gives the well known second order integrated rate equation:

$$\frac{1}{C} - \frac{1}{C_0} = k_2 t \tag{4}$$

A single-stage batch operation of sorption and the associated typical mass balance curve are represented in Fig. 1. The concentration of the solute in solution is related to that on the solid phase by the well known equation:

$$m(Q - Q_0) = (C_0 - C)V \tag{5}$$

C_0 stands for the initial solute concentration in solution (mg L^{-1}), Q_0 is the initial solute concentration on the solid (mg g^{-1}), m is the mass of the sorbent (g), and V is the solution volume (L). If none of the particular sorbate species is initially present on the solid then Q_0 can be eliminated, and the above rate equation might be rewritten in