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

Article *in* Journal of Environmental Chemical Engineering · June 2014

Talal Shahwan
Birzeit University

Journal of Environmental Chemical Engineering 2 (2014) 1001–1006

Contents lists available at ScienceDirect

Journal of Environmental Chemical Engineering

journal homepage: www.elsevier.com/locate/jece

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

ARTICLE INFO

Article history:
Received 28 January 2014
Accepted 25 March 2014

Keywords:
Kinetics
Second order
Sorption
Material balance

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.

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:

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

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:

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

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).

2213-3437/$ - see front matter © 2014 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.jece.2014.03.020

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:

$$-\frac{dC}{dt} = k_2C^2 \tag{3}$$

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:

$$\frac{1}{C} - \frac{1}{C_0} = k_2t \tag{4}$$

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

Table 4
Values of Q obtained from experiment, values of Q predicted by Eq. (11), and the Chi-test values for the sorption systems of MO-nano iron and MB-zeolite.

Time (min)	Q_{exp}(mg g^{-1})	Q_{model}(mg g^{-1})	$(Q_{exp}-Q_{model})^2/Q_{model}$
MO-nano iron			
5	7.7	7.7	0.000000
30	22.2	24.8	0.276164
60	33.0	31.9	0.034515
120	39.7	37.2	0.164984
210	42.7	40.1	0.161973
300	43.9	41.4	0.150180
360	44.2	41.9	0.130729
		χ^2	0.918545
MB-zeolite			
5	14.0	13.9	0.000263
10	15.5	15.5	0.000000
30	16.4	16.8	0.008850
60	17.3	17.1	0.001584
120	17.6	17.3	0.004667
240	18.1	17.4	0.027560
420	17.8	17.4	0.007144
960	18.0	17.5	0.015666
1440	18.4	17.5	0.047937
		χ^2	0.113671

terms of Q and C_0 as:

$$\frac{1}{C_0 - Q(m/v)} - \frac{1}{C_0} = k_2 t \tag{6}$$

This equation can be rearranged to yield:

$$\frac{m}{V}Q = \frac{C_0^2 k_2 t}{C_0 k_2 t + 1} \tag{7}$$

Noticing that multiplying V/m with C_0 yields the amount of solute that would be sorbed if the sorption reaction goes to completion and denoting this value by Q_m, the above equation can then be rearranged to give:

$$Q = \frac{Q_m C_0 k_2 t}{C_0 k_2 t + 1} \tag{8}$$

This equation can be linearized in the following form:

$$\frac{t}{Q} = \frac{1}{Q_m C_0 k_2} + \frac{1}{Q_m} t \tag{9}$$

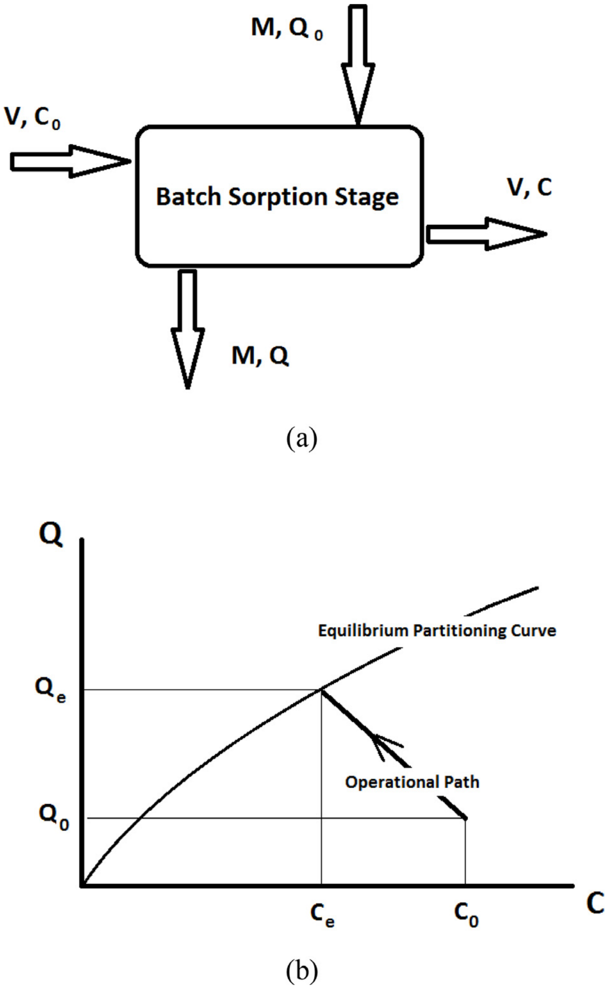
With this formulation, plotting t/Q vs. t should yield a linear plot with the rate constant being obtained from the intercept. Notice that the unit of k_2 will depend on the unit of concentration. Hence the unit of k_2 will be L min^{-1} mg if the concentration is expressed in terms of mg L^{-1}, and L min^{-1} mol if the concentration unit is mol L^{-1}. It is notable that Eqs. (8) and (9) look similar to the corresponding equations suggested by Ho, which are given by [2,3]:

$$Q = \frac{Q_e^2 k_2 t}{Q_e k_2 t + 1} \quad \text{and} \quad \frac{t}{Q} = \frac{1}{Q_e^2 k_2} + \frac{1}{Q_e} t$$

However the differences between the two equations include the interpretation of Q_m (vs. Q_e), the unit of k_2 and its method of determination.

In order to illustrate the applicability of Eq. (9), sorption data obtained from different sorption systems were used. These include data corresponding to sorption of Co^{2+} on a composite of nano iron and bentonite [4], sorption of methyl orange on 'greener' nano iron [5], and sorption of methylene blue on clinoptilolite (unpublished data). The obtained results of k_2, Q_m in addition to the linear correlation coefficients are given in Table 1, and the corresponding linear fits are shown in Figs. 2(a), 3(a), and 4(a).

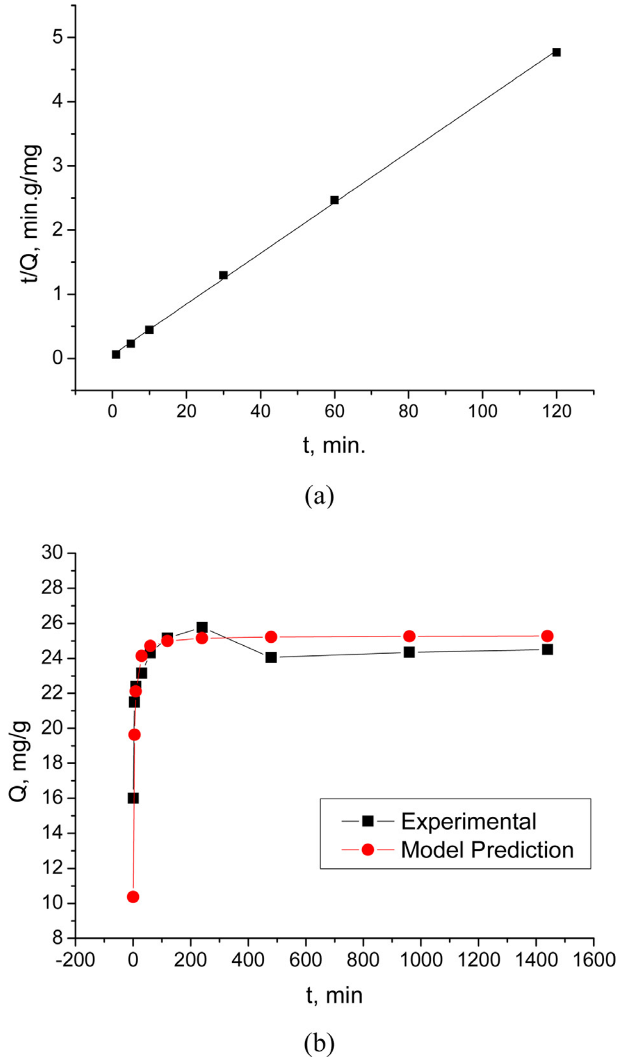
It is necessary to note that the data used in the plots correspond to the pre-equilibrium stage of sorption, as kinetic analysis pertains fundamentally to variation of concentration with time, which occurs during the initial period of the experiment. The linear correlation coefficients, provided in Table 1, indicate excellent correlation between



(a)

(b)

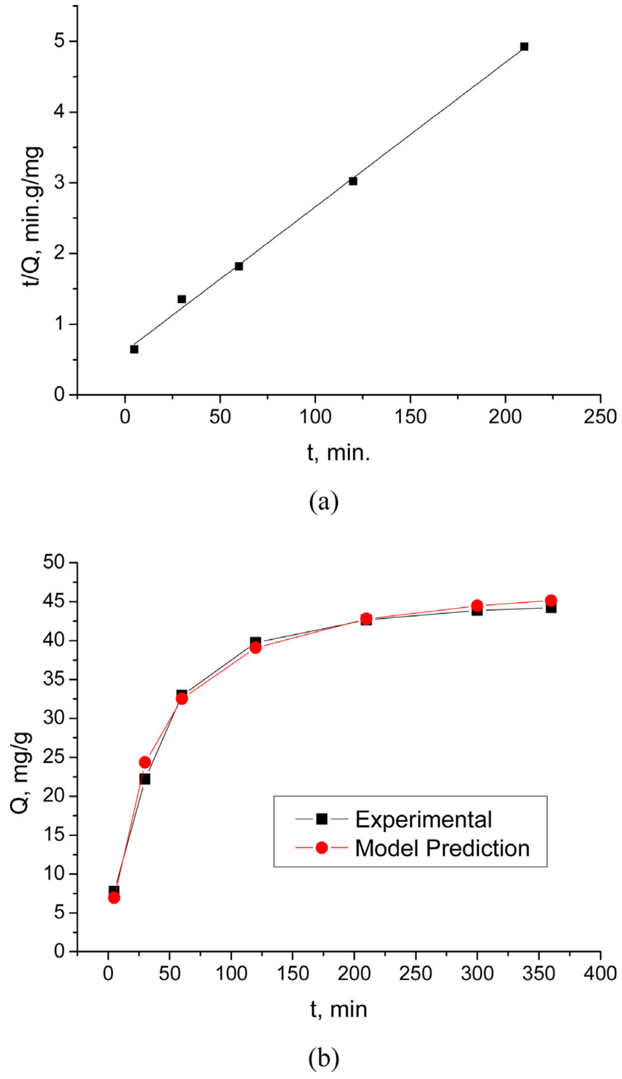
Fig. 1. (a) A typical schematic representation of inlet and outlet sorbate concentrations in a single stage batch sorption unit. C_0 and Q_0 are the initial sorbate concentrations, C and Q are the sorbate concentrations at equilibrium, V is the volume of the solution, and M is the mass of the sorbent. (b) A typical isotherm and an operational path in a single stage batch sorption operation. The slope of the operational line stands for the $(-V/M)$ ratio.



(a)

(b)

Fig. 2. (a) Linear plot of Co-nZVI/bentonite sorption data obtained using Eq. (9) and (b) comparison of the experimental values of Q with the Q values predicted by Eq. (9).



(a)

(b)

Fig. 3. (a) Linear plot of MO-nano iron sorption data obtained using Eq. (9) and (b) comparison of the experimental values of Q with Q values predicted by Eq. (9).

the sorption data and Eq. (9) in all cases. However, linear correlation by itself might be misleading in certain cases. Hence, in order to check this result, the obtained values of k_2 and Q_m were inserted in Eq. (8) which was in turn used to obtain the model prediction. Figs. 2(b), 3(b), and 4(b) show a comparison of the experimental data and data predicted using Eq. (8). According to the results, the best correlation is obtained for MO sorption on nano iron, and the worst is seen in the case of Co^{2+} sorption on nZVI–bentonite composite. On the overall, although very close results are obtained in MO sorption case, the figures do not display the outstanding correlation reflected by the linear plots and linear correlation coefficients, in particular, during the early stages of sorption.

As another means of checking the results, the experimental and model values of Q_m were compared, as provided in Table 1. The experimental value of Q_m is defined by C_0V/m, and any convenient fit should provide a Q_m value with little departure from its experimental value. The results show close values in the cases of MO sorption on nano iron, and MB sorption on zeolite. However, a large difference is seen in the case of Co^{2+} sorption on nZVI–bentonite composite. The Q_m check confirms that Eq. (9) is appropriate for correlating the sorption data of MO and MB. The Co^{2+} data, however, could not be accounted for although its correlation is high and shows nice linear fit.

For further assessment of the difference between experimental values and predicted values, Chi-square values were calculated using the equation [3]:

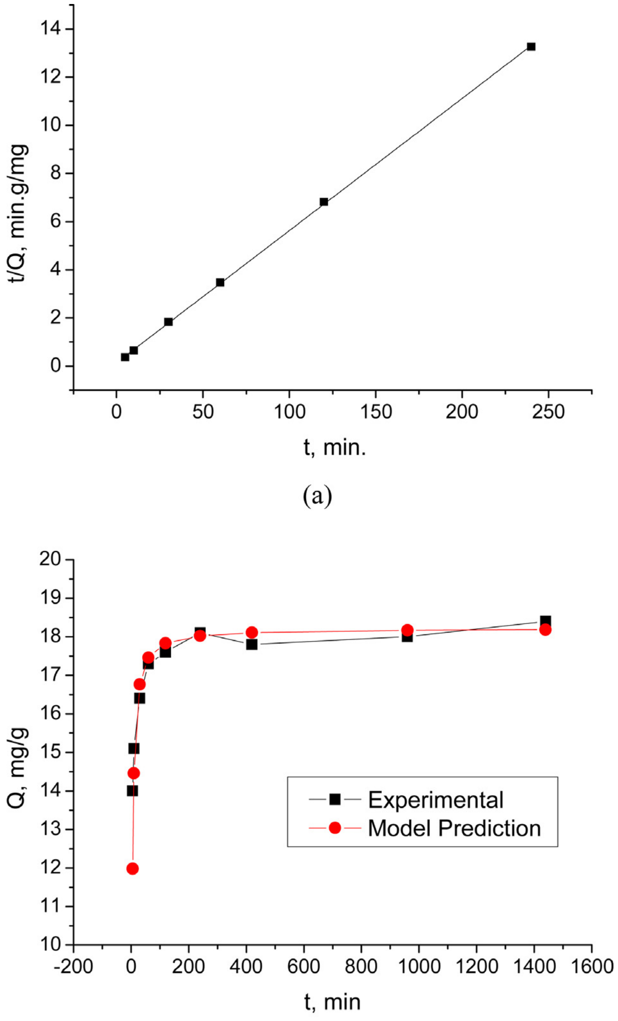
$$\chi^2 = \sum_{1}^{n} \frac{(Q_{\mathrm{exp}} - Q_{\mathrm{model}})^2}{Q_{\mathrm{model}}} \tag{10}$$

The smaller the value of χ^2 the smaller is the difference between experimental and predicted values. As reflected by the values given in Table 2, except for Co^{2+} sorption case, the values of χ^2 are less than 1.0 indicating very small discrepancies. This confirms the adequacy of Eq. (9) to MO and MB sorption data, but raises further concern about the adequacy of the same equation to describing the sorption data of Co^{2+} in spite of the high correlation coefficient of the linear fit.

Given the discrepancy in the data of Co^{2+}, Eq. (8) was linearized in another form and used to test the sorption data of the three systems. The new linear form is expressed as:

$$\frac{1}{Q} = \frac{1}{Q_m} + \frac{1}{Q_m C_0 k_2}\left(\frac{1}{t}\right) \tag{11}$$

Plotting $1/Q$ vs. $1/t$ should yield a linear plot, with Q_m being again an adjustable parameter. It is evident from the linear regression plots in Fig. 5 that, unlike MO and MB sorption data, the data of Co^{2+} does not yield a linear plot. This is confusing at the first glance as both of



(a)

(b)

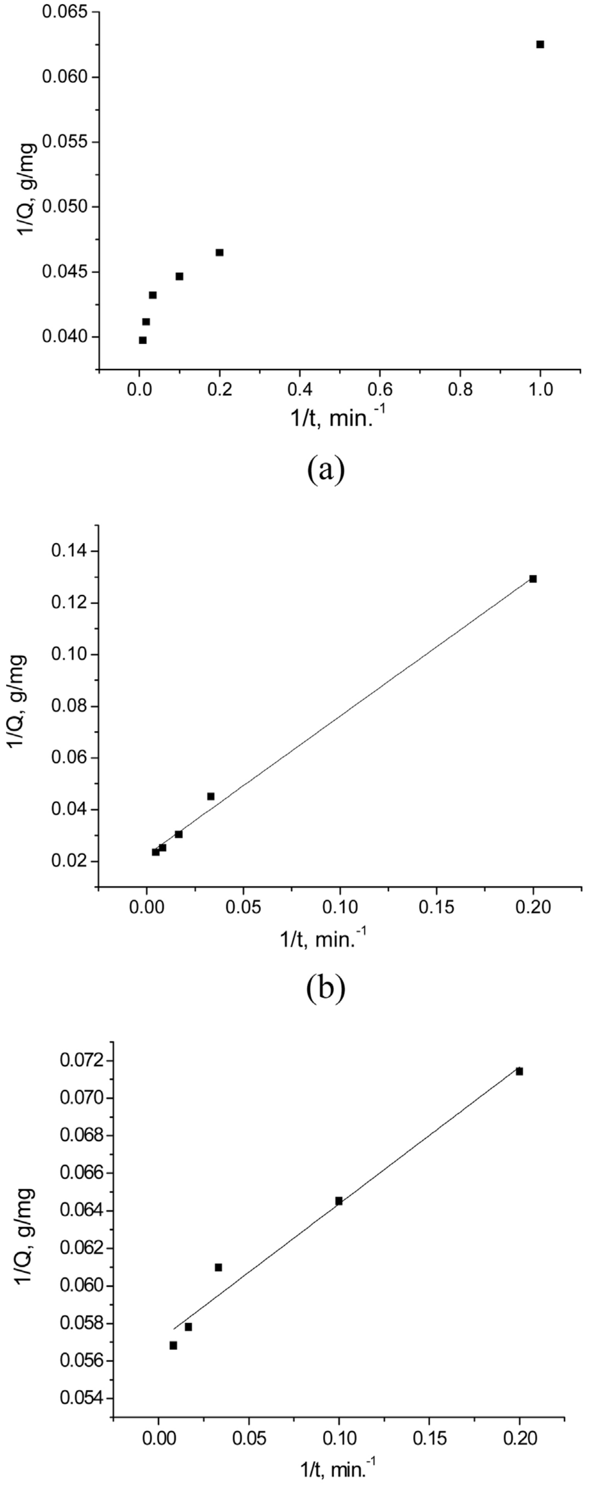
Fig. 4. (a) Linear plot of MB-zeolite sorption data obtained using Eq. (9) and (b) comparison of the experimental values of Q with Q values predicted by Eq. (9).

Eqs. (9) and (11) originate from the same equation. After trying many sets of kinetic data, the most probable explanation for the confusion seems to stem from errors due to linearization. Such errors have been reported to accompany different linear forms of Langmuir isotherm [8,9]. In Eq. (9), the existence of the variable t in both the x- and y-coordinates seems to falsely contribute to the linearization of the plot even if the x and y data are not changing linearly. The regression results provided in Tables 2 and 4 show that the model predictions of MO and MB regression came out to be close regardless of whether Eq. (9) or Eq. (11) is used. Notice that the data of Co^{2+} sorption are not included in Tables 3 and 4 as it was decided based on Fig. 5(a) that the pseudo second equation derived in this study does not apply properly to Co^{2+} case.

From the above discussion it is evident that Eq. (11) gave better results than Eq. (9). For more convenient results, nonlinear forms should be preferred. If linear forms are to be used, the results should be checked and verified by model predictions.

Conclusions

A pseudo second order equation can be obtained by combining the mass balance equation with second order rate derivative. When testing for the correlation of the sorption data with the equation, the adequacy of the equation should not be linked solely to the linear correlation coefficient. This is because linearizing non-linear equations generate/create errors as evidenced by plotting t/Q vs t. Model prediction check, such as Chi-test are useful in verifying the results. On the overall, it is more convenient to apply Eq. (11) to the tested kinetic data.



(a)

(b)

(c)

Fig. 5. Linear plot of obtained using Eq. (11) for the sorption system of (a) Co-nZVI/bentonite, (b) MO-nano iron, and (c) MB-zeolite.

Conflict of interest

None.

Acknowledgment

The kinetic experiments of methylene blue sorption on zeolite (clinoptilolite) are part of a study that was performed by Sevgi Gemicioglu under the supervision of the author at Izmir Institute of Technology.

References

[1] K.V. Kumar, S. Sivanesan, Pseudo second order kinetics and pseudo isotherms for malachite green onto activated carbon: comparison of linear and non-linear regression methods, Journal of Hazardous Materials 136 (2006) 721–6. http://dx.doi.org/10.1016/j.jhazmat.2006.01.003, 16488537.

[2] Y.-S. Ho, A.E. Ofomaja, Kinetic studies of copper ion adsorption on palm kernel fibre, Journal of Hazardous Materials 137 (2006) 1796–802. http://dx.doi.org/10.1016/j.jhazmat.2006.05.023, 16875778.

[3] Y.-S. Ho, A.E. Ofomaja, Pseudo-second-order model for lead ion sorption from aqueous solutions onto palm kernel fiber, Journal of Hazardous Materials 129 (2006) 137–42. http://dx.doi.org/10.1016/j.jhazmat.2005.08.020, 16188379.

[4] T. Shahwan, Ç. Üzüm, A.E. Eroğlu, I. Lieberwirth, Synthesis and characterization of bentonite/iron nanoparticles and their application as adsorbent of cobalt ions, Applied Clay Science 47 (2010) 257–62. http://dx.doi.org/10.1016/j.clay.2009.10.019.

[5] T. Shahwan, Sirriah S. Abu, M. Nairat, E. Boyacı, A.E. Eroğlu, T.B. Scott, et al, Green synthesis of iron nanoparticles and their application as a Fenton-like catalyst for the degradation of aqueous cationic and anionic dyes, Chemical Engineering Journal 172 (2011) 258–66. http://dx.doi.org/10.1016/j.cej.2011.05.103.

[6] F.M.M. Morel, J.G.. Hering, Principles and Applications of Aquatic Chemistry, New York, Wiley, 1993.

[7] S. Azizian, Kinetic models of sorption: a theoretical analysis, Journal of Colloid and Interface Science 276 (2004) 47–52. http://dx.doi.org/10.1016/j.jcis.2004.03.048, 15219428.

[8] C.H. Bolster, G.M. Hornberger, On the use of linearized Langmuir equations, Soil Science Society of America Journal 71 (2007) 1796–806. http://dx.doi.org/10.2136/sssaj2006.0304.

[9] N.J. Nnaji, N.O. Obi-Egbedi, M.A. Nnabugwu, Kinetics and thermodynamics of aluminium corrosion inhibition by *Anthocleista djalonensis* leaf extract in hydrochloric acid solution, International Journal of Chemical Sciences 10 (2012) 182–94.