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ScienceDirect

Bioresource Technology 99 (2008) 3309–3312

BIORESOURCE TECHNOLOGY

Short Communication

Uncertainty of preset-order kinetic equations in description of biosorption data

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Received 23 February 2007; received in revised form 8 June 2007; accepted 10 June 2007
Available online 13 August 2007

Abstract

This study investigated uncertainty encountered in description of biosorption data by preset-order kinetic equations. It was shown that for a given set of biosorption data, the kinetic equations with the preset-order of first to fourth can all provide equally good fittings to the experimental data, indicated by comparable values of correlation coefficients (R). In the sense of chemistry, the reaction order of a biosorption process must be experimentally determined rather than preset to a fixed value. In this case, a generalized kinetic equation was proposed without any constrain on the reaction order. In order to statistically evaluate the curve fittings of biosorption data by various kinetic equations, a concept of the relative goodness of curve fitting was developed. Compared to all the preset-order kinetic equations studied, the generalized equation can offer the best prediction for experimental data obtained in various biosorption experiments.

Keywords: Biosorption kinetics; Reaction order; Curving fitting; Uncertainty

1. Introduction

So far, understanding of biosorption kinetics is much less than theoretical description of biosorption equilibrium. Within the scope of the literature review, two kinetic models, namely pseudo first- and second-order kinetics, have been widely used to describe biosorption data obtained under non-equilibrium conditions (Ho et al., 2000; Liu et al., 2003; Erdem and Ozverdi, 2006; Kiran et al., 2006; Rubin et al., 2006; Won et al., 2006). The pseudo first-order kinetic equation or the so-called Lagergren equation is expressed as follows:

$$\frac{dQ_t}{dt} = k_1'(Q_e - Q_t) \tag{1}$$

in which Q_t is the amount of adsorbate adsorbed at time t, Q_e is its value at equilibrium and k_1' is constant. It should be pointed out that Eq. (1) is indeed in line with the concept of linear driving force. Analogue to Eq. (1), the pseudo second-order kinetic equation has also been proposed to describe kinetic behaviors of biosorption as reviewed by Ho et al. (2000):

$$\frac{dQ_t}{dt} = k_2'(Q_e - Q_t)^2 \tag{2}$$

in which k_2' is constant. Eq. (2) has been widely used in analysis of biosorption data obtained from various experiments with different adsorbats and biosorbents.

As noted by Rudzinski and Plazinski (2006), in view of the large applicability of Eqs. (1) and (2), in the past decades it is surprising that no attempts were made to clearly explain their theoretical origins. These seem to indicate that there is lack of theoretical criteria for choosing Eqs. (1) and (2) to describe biosorption data. In most biosorption studies, Eqs. (1) and (2) have been commonly employed in parallel, and one is often claimed to be better than another according to marginal difference in correlation coefficient. However, the minor difference in correlation coefficient cannot offer a reasonable statistical evaluation of curve fitting of

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doi:10.1016/j.biortech.2007.06.026

biosorption data by various kinetic equations. Furthermore, in the sense of chemistry, the order of a chemical reaction needs to be determined by experiments and cannot be preset to a fixed integer, such as one or two, as commonly practiced in biosorption study. In fact, the order of a reaction is not necessarily an integer. Thus, this study attempted to address some fundamental questions arising from current biosorption study: (i) Is there uncertainty encountered in description of biosorption data using various preset-order kinetic equations?; (ii) How to reasonably determine the kinetic order of biosorption?; and (iii) How to more reasonably evaluate the goodness of curve fittings by different kinetic equations? It is expected that this study can offer some insights into biosorption kinetics.

2. Description of biosorption data by various preset-order kinetic equations

As discussed earlier, there is no reason to preset the kinetic order of biosorption to be the first or second. Thus, analogue to Eqs. (1) and (2), following four kinetic equations with a fixed order of 1.5–4 can be generated:

$$\frac{dQ_t}{dt} = k'_{1.5}(Q_e - Q_t)^{1.5} \tag{3}$$

$$\frac{dQ_t}{dt} = k'_{2.5}(Q_e - Q_t)^{2.5} \tag{4}$$

$$\frac{dQ_t}{dt} = k'_{3}(Q_e - Q_t)^{3} \tag{5}$$

$$\frac{dQ_t}{dt} = k'_{3.5}(Q_e - Q_t)^{3.5} \tag{6}$$

$$\frac{dQ_t}{dt} = k'_{4}(Q_e - Q_t)^{4} \tag{7}$$

in which $k'_{1.5}$, $k'_{2.5}$, k'_3, $k'_{3.5}$ and k'_4 are the rate constants. In this study, Eqs. (1)–(7) were used to fit four sets of biosorption data reported in the literature. For this purpose, a least squares-based method in Matlab 7.0 was employed to solve integrated Eqs. (1)–(7). Tables 1–4 show that Eqs. (1)–(7) all provided excellent curve fittings to biosorption data, indicated by very close correlation coefficients with a maximum difference of 0.05, while the corresponding rate constants determined were also summarized in these tables. It can be seen that the kinetic equations with a preset reaction order of 1–4, mathematically, are all equally good in describing a given set of the biosorption data. However, in the sense of chemistry, the reaction order should be unique for a given reaction. These seem to imply that there would be no theoretical basis for biosorption reaction to be restricted to first-, second- or other preset order as those commonly claimed and exercised in the literature (Ho et al., 2000; Liu et al., 2003; Erdem and Ozverdi, 2006; Kiran et al., 2006; Rubin et al., 2006; Won et al., 2006), and application of the preset-order kinetic equations would introduce uncertainty in description of biosorption data.

Table 1
Kinetic description of copper biosorption data from Gulnaz et al. (2005) using Eqs. (1)–(8)

Eq. no.	x	k'_x ($\mathrm{mg^{1-x}\ g^{x-1}\ min^{-1}}$)	Q_e ($\mathrm{mg\ g^{-1}}$)	R	f
1	1.0	0.07	73.8	0.995	0.24
3	1.5	1.04E−02	75.4	1.000	0.92
2	2.0	1.40E−03	78.4	0.995	0.25
4	2.5	1.74E−04	82.4	0.995	0.13
5	3.0	1.86E−05	86.8	0.990	0.088
6	3.5	1.87E−06	91.5	0.990	0.069
7	4.0	1.92E−07	96.1	0.985	0.059
8	*1.4*	*1.47E−02*	*75.0*	*1.000*	*1.00*

Table 2
Kinetic description of cadmium biosorption data from Lu et al. (2006) using Eqs. (1)–(8)

Eq. no.	x	k'_x ($\mathrm{mg^{1-x}\ g^{x-1}\ min^{-1}}$)	Q_e ($\mathrm{mg\ g^{-1}}$)	R	f
1	1.0	0.02	13.0	0.990	0.28
3	1.5	8.21E−03	13.4	0.995	0.69
2	2.0	2.16E−03	13.9	0.995	0.99
4	2.5	7.19E−04	14.6	0.995	0.92
5	3.0	1.71E−04	15.3	0.995	0.79
6	3.5	4.88E−05	16.0	0.995	0.65
7	4.0	1.27E−05	16.8	0.995	0.58
8	*2.1*	*1.78E−03*	*14.0*	*0.995*	*1.00*

Table 3
Kinetic description of biosorption data of reactive blue from Aksu (2001) using Eqs. (1)–(8)

Eq. no.	x	k'_x ($\mathrm{mg^{1-x}\ g^{x-1}\ min^{-1}}$)	Q_e ($\mathrm{mg\ g^{-1}}$)	R	f
1	1.0	1.65E−01	16.1	0.995	1.00
3	1.5	4.55E−02	17.1	0.995	0.71
2	2.0	1.05E−02	18.6	0.990	0.48
4	2.5	2.07E−03	20.4	0.990	0.37
5	3.0	3.63E−04	22.3	0.985	0.31
6	3.5	5.78E−05	24.4	0.985	0.27
7	4.0	8.50E−06	26.5	0.985	0.25
8	*1.0*	*1.65E−01*	*16.1*	*0.995*	*1.00*

Table 4
Kinetic description of biosorption data of Remazol Black B from Aksu and Tezer (2000) using Eqs. (1)–(8)

Eq. no.	x	k'_x ($\mathrm{mg^{1-x}\ g^{x-1}\ min^{-1}}$)	Q_e ($\mathrm{mg\ g^{-1}}$)	R	f
1	1.0	0.2	289.4	0.954	0.15
3	1.5	1.57E−02	294.1	0.975	0.27
2	2.0	1.16E−03	302.1	0.985	0.46
4	2.5	7.77E−05	312.8	0.990	0.69
5	3.0	4.82E−06	325.2	0.990	0.88
6	3.5	2.75E−07	337.6	0.995	1.00
7	4.0	2.19E−08	340.1	0.990	0.83
8	*3.5*	*2.75E−07*	*337.6*	*0.995*	*1.00*

3. Uncertainty incurred in kinetic description of biosorption data

It should be realized that for a given biosorption process, theoretically its reaction order must be unique, and can not vary in a large range. These seem to indicate that the description of biosorption data by a preset-order