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Common mistake in adsorption papers: The Blanchard et al.'s pseudo-second order kinetics model equation

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ABSTRACT

In the last decades, the removal of organic and inorganic pollutants from aqueous solutions by adsorption has been extensively investigated. The most used equations to describe and model the adsorption kinetics are the pseudo-first order and pseudo-second order models. Despite some citation inconsistencies in the literature, the pseudo-first order equation was indisputably proposed by Lagergren (Kungliga Svenska Vetenskapsakademiens Handlingar, Vol. 24, No. 4, pp. 1–39, 1898). However, the pseudo-second order model continues to be erroneously cited as the Ho's pseudo-second order equation. This model was developed in 1984 by Blanchard et al. (Water Research, Vol. 18, No. 12, pp. 1501-1507, 1984) and only a linearized expression was proposed by Ho. Therefore, the nonlinear form of the pseudo-second order equation, which may be linearized in 6 various forms, was not originally reported and applied by Ho, but initially proposed by Blanchard et al. In a word, to be scientifically honest, the original work by Blanchard et al. should be cited for the pseudo-second order kinetics equation model.

1. Introduction

Adsorption is one of the important mass transfer unit operations for gas separation and water treatment. Adsorption is time-dependent process. For design and evaluation of adsorbent, it is necessary to know the rate of adsorption. Several adsorption kinetic mechanistic equations have been used to describe the uptake of adsorptive on adsorbents, but simplest models are commonly preferred. The pseudo-first order and pseudo-second order equations, which are based on the sorption at vacant adsorbent surface sites, are the commonly employed lumped kinetic models.

Notwithstanding some citation irregularities in the literature, the pseudo-first order kinetics model was incontrovertibly proposed by Lagergren (S. Lagergren, About the theory of so-called adsorption of soluble substances, Kungliga Svenska Vetenskapsakademiens Handlingar, Vol. 24, No. 4, pp. 1–39, 1898). Nevertheless, the pseudo-second order kinetics equation remains to be mistakenly cited as the Ho's pseudo-second order model.

This report aims to correct a common citation error in adsorption papers, which cited the pseudo-second order model as an expression firstly proposed and applied by Ho, but the equation was originally reported by Blanchard et al. [1].

2. Background

In 1984, Blanchard et al. [1] proposed a second-order rate equation for the removal of divalent metallic ions from aqueous solution using NH_4^+ fixed zeolite particles (Eq. (1)).

$$\frac{dn}{dt} = K(n_0 - n)^2 \quad (1)$$

where n is the amount of divalent metal ions fixed or the amount of NH_4^+ released at each instant, n_0 is the exchange capacity and K is the rate constant.
Integration of Eq. (1) gives:

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$$\frac{1}{(n_0 - n)} - \alpha = Kt \quad (2)$$

By plotting $1/(n_0 - n)$ as a function of time, a straight line must be obtained, the slope of which gives the rate constant K and the intercept leads to the exchange capacity.

Table 1 - Linear forms of the Blachard et al.'s pseudo-second order kinetics model equation.

Type	Linear form	Plot
Type 1	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$	$\frac{t}{q_t}$ $vs. t$
Type 2	$\frac{1}{q_t} = \frac{1}{q_e} + \frac{1}{k_2 q_e^2} \frac{1}{t}$	$\frac{1}{q_t}$ $vs.$ $\frac{1}{t}$
Type 3	$q_t = q_e - \frac{1}{k_2 q_e} \frac{q_t}{t}$	q_t $vs.$ $\frac{q_t}{t}$
Type 4	$\frac{q_t}{t} = k_2 q_e^2 - k_2 q_e q_t$	$\frac{q_t}{t}$ $vs. q_t$
Type 5	$\frac{1}{t} = -k_2 q_e + k_2 q_e^2 \frac{1}{q_t}$	$\frac{1}{t}$ $vs. \frac{1}{q_t}$
Type 6	$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t$	$\frac{1}{q_e - q_t}$ $vs. t$

After rearranging, Eq. (2) becomes:

$$n = \frac{n_0 Kt + \alpha n_0 - 1}{Kt + \alpha} \quad (3)$$

Considering the boundary condition of n = 0 for t = 0, it follows that $\alpha = 1/n_0$.

Eq. (3) can be rearranged to:

$$n = \frac{n_0^2 Kt}{1 + n_0 Kt} \quad (4)$$

By supposing $q_t = n$, $q_e = n_0$ and $k_2 = K$, the non-linearized form of pseudo-second order expression can be obtained as follows:

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \quad (5)$$

where q_t (mg/g) and q_e (mg/g) are the amount of adsorbate adsorbed at any time t (min) and at equilibrium, respectively, and k_2 (g/mg·min) is the rate constant of the pseudo-second order equation.

The pseudo-second order expression (Eq. (5)) can be linearized to 6 different linear forms as shown in Table 1 [2]. Expression of type 6 was previously reported by Blanchard et al. (Eq. (2)) [1]. A type 1 linear expression, as shown in Table 1, was formerly applied by Ho [3,4].

Eq. (5) is the mathematical form of the pseudo-second order kinetics equation proposed by Blanchard et al. [1]. Thus, this equation was not originally reported by Ho [2] or first applied by Ho et al. [3] who just proposed a linear form of the Blanchard et al.'s pseudo-second order kinetics model equation, which may be linearized in 6 different expressions.

Undoubtedly, only the linear form (type 1) might have been reported by Ho [3] and Ho et al. [4] for, respectively, the adsorption of heavy metals and dyes from waste streams by peat. In a word, the original paper by Blanchard et al. [1] should be cited for the expression of the pseudo-second order equation.

3. Conclusion

This report was presented in order to stop the propagation of the citation error of the pseudo-second order kinetics equation wrongly called Ho's pseudo-second order model. The pseudo-second order equation was not proposed by Ho, it was originally reported by Blanchard et al. [1]. Ho [2,3] has just proposed a linearized form of the pseudo-second order equation, which may be presented in 5 other linear forms. In conclusion, to be scientifically honest, the original work by Blanchard et al. [1] should be cited for the pseudo-second order kinetics model equation.

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