Comment on ‘Removal of heavy metal ions by modified sawdust of walnut’ by Bulut, Y. and Tez, Z.

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In a recent publication Bulut and Tez [1], the section Results and Discussion, authors cited Low et al. [2] to mention that Ho and McKay reported that most of the sorption system followed a pseudo-second order kinetic model which can be expressed as:

\[ \frac{t}{q_t} = \frac{1}{k_{ps}q_e} + \frac{t}{q_e} \]  \hspace{1cm} (1)

where \( k_{ps} \) is the adsorption rate constant (g/mg min).

The equation that authors presented is not correct because units of all parameters are not compatible. Moreover Ho and McKay have not reported the equation for any sorption systems.

In fact, Ho and McKay [3] reported the pseudo-second order kinetic model. The peat-copper reaction may be represented in two ways [4]:

\[ 2P^- + Cu^{2+} \leftrightarrow CuP_2^2^- \]  \hspace{1cm} (2)

and

\[ 2HP + Cu^{2+} \leftrightarrow CuP_2 + 2H^+ \]  \hspace{1cm} (3)

where \( P^- \) and \( HP \) are polar sites on the peat surface.

A pseudo-second order rate expression based on sorption equilibrium capacity may be derived from Eqs. (2) and (3). If the pseudo-second order kinetic model holds true, the rate law for the reaction is expressed as:

\[ \frac{d(P)}{dt} = k\left[(P)_0 - (P)_t\right]^2 \]  \hspace{1cm} (4)

or

\[ \frac{d(HP)}{dt} = k\left[(HP)_0 - (HP)_t\right]^2 \]  \hspace{1cm} (5)

where \((P)_t\) and \((HP)_t\) are the number of active sites occupied on the sorbent at time \( t \), \((P)_0\) and \((HP)_0\) are the number of equilibrium sites available on the sorbent.

It is assumed that the sorption capacity is proportional to the number of active sites occupied on the sorbent, then the kinetic rate law can be rewritten as follows:

\[ \frac{dq_t}{dt} = k(q_e - q_t)^2 \]  \hspace{1cm} (6)

where \( k \) is the rate constant of sorption, \( (g/\text{mg} \text{min}) \), \( q_e \) is the amount of soluted sorbate sorbed at equilibrium, \( (\text{mg/g}) \), \( q_t \) is amount of soluted sorbate on the surface of the sorbent at any time, \( t \), \( (\text{mg/g}). \)

Separating the variables in Eq. (6) gives:

\[ \frac{dq_t}{(q_e - q_t)^2} = kdt \]  \hspace{1cm} (7)

Integrating this for the boundary conditions \( t = 0 \) to \( t = t \) and \( q_t = 0 \) to \( q_t = q_e \), gives:

\[ \frac{1}{(q_e - q_t)} = \frac{1}{q_e} + kt \]  \hspace{1cm} (8)

which is the integrated rate law for a pseudo-second order reaction.

Eq. (8) can be rearranged to obtain:

\[ \frac{t}{q_t} = \frac{1}{kq_e^2 + \frac{1}{q_e}t} \]  \hspace{1cm} (9)

The constants can be determined by plotting \( t/q_t \) against \( t \).

In addition, Eq. (9) can be rearranged to obtain:

\[ q_t = \frac{h}{t + kq_e^2t} \]  \hspace{1cm} (10)

where \( h \) can be regarded as the initial adsorption rate as \( q_t/t \) when \( t \to 0 \) [5], hence:

\[ h = kq_e^2 \]  \hspace{1cm} (11)

Thus, a plot of \( t/q_t \) against \( t \) of Eq. (9) should give a linear relationship with the slope of \( 1/q_e \) and intercept of \( 1/(kq_e^2) \).

The second order kinetic expression for the adsorption systems of divalent metal ions using sphagnum moss peat has been reported by Ho [5]. In order to distinguish kinetics equation based on adsorption capacity of solid from concentration of solution, Ho’s second order rate equation has been called pseudo-second order [5-14]. The earlier application of the pseudo-second order equation to the kinetic studies of competitive heavy metal adsorption by sphagnum moss peat was undertaken by Ho et al. [6]. The modified model has also been reported in following years. The most cited related papers were published in Water Research [7], Process Biochemistry [3] and Chemical Engineering Journal [8]. In addition, similar comments have also been published in Adsorption Science & Tech-
The pseudo-second order rate expression of Ho has been applied to the adsorption of metal ions, dyes and organic substances from aqueous solutions (Table 1). Moreover, discussion of the reaction order has been reported such as the comparison of chemisorption kinetic models [14] and pseudo-second order model [3]. Furthermore, Ho’s kinetic expression has also been applied to a multi-stage batch adsorption design [15, 16] and pseudo-isotherm studies [17]. Numerous applications of Ho’s kinetic expression have been reported in recent years. A list of pseudo-second order systems is given in Table 1.

Research papers conventionally include an introduction, a description of the objectives and procedures of the study, an account of the results and a discussion of the results and their implications. However, a paper’s contribution existed not only in its originality and creativity, but also in its continuity and development for the following researches. The reference section can play a key role to researchers that were interested in the paper’s statement and would like to follow the study or find useful information from the paper [67].

I suggest that Bulut and Tez cite Ho’s original pseudo-second order kinetic expression paper.

<table>
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<tr>
<th>Sorbent</th>
<th>Sorbate</th>
<th>References</th>
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</table>


67 Ho, Y.S. (2004), Citation review of Lagergren kinetic rate equation on adsorption reactions. Scientometrics, 59 (1), 171-177.