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Kinetic Analysis of the Adsorption of the Brominated Flame Retardant 4-bromodiphenyl Ether onto Biochar-immobilized *Sphingomonas* sp.

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ABSTRACT

4-bromophenyl phenyl ether or 4-bromodiphenyl ether (4-BDE) is a less brominated PBDE, which are brominated flame retardants (BFRs), that has come into importance when it was detected as the main pollutant in Sungai Buah, a tributary to the Sungai Semenyih that have recently caused the pollution of drinking waters in the Semenyih Water Treatment Plant, Putrajaya Selangor that led to water shortage for many days to affecting many areas. 4-BDE is also a recalcitrant priority pollutant where it is barely degraded at all. Many of the PBDE can cause developmental neurotoxicity. The absorption kinetics data of biosorption isotherm on the biosorption of 4-BDE onto Biochar-immobilized *Sphingomonas* sp. were analyzed using three models—pseudo-1st, pseudo-2nd and Elovich, and fitted using non-linear regression. The Elovich model was the poorest in fitting the curve based on visual observation followed by the pseudo-1st order. Statistical analysis based on root-mean-square error (RMSE), adjusted coefficient of determination (adjR^2), bias factor (BF), accuracy factor (AF), corrected AICc (Akaike Information Criterion), Bayesian Information Criterion (BIC) and Hannan–Quinn information criterion (HQC) that showed that the pseudo-1ST order model is the best model. Kinetic analysis using the pseudo-1st order model at 400 mg/L 4-BDE gave a value of equilibrium sorption capacity q_e of 31.89 mg g^{-1} (95% confidence interval from 30.37 to 33.42) and a value of the pseudo-1st-order rate constant, k_1 of 0.22 (95% confidence interval from 0.019 to 0.025). Further analysis is needed to provide proof for the chemisorption mechanism usually tied to this kinetic.

INTRODUCTION

Brominated flame retardants (BFRs) which include 4-Bromophenyl phenyl ether (4-BE) happen to be consistently included with a range of customer and commercial items for many years. They have turn into an international top priority environmental pollutant and is also found in the tissues of virtually everyone examined up to now (USEPA 1980a; Tabak et al. 1981; Costa and Giordano 2007; Bierla et al. 2010; Chen and Hale 2010; Liu et al. 2012). In other areas around the globe, 4-Bromophenyl phenyl ether has been discovered in raw drinking water, in mineral water, and in river water (USEPA 1980b). The absolute maximum allowable limit to safeguard freshwater aquatic life recommended by the United States Environmental Protection Agency (USEPA) is 6.2 µg/L.

The concentration which induces 50% lethality (LC50) on the aquatic organism Daphnia magna (Water flea) is 0.36 mg/L/48 hr (USEPA 1980a). 4-BDE is another recalcitrant top priority pollutant in which a research making use of activated sludge microorganisms has demonstrated that it must be not appreciably degraded in the least (Tabak et al. 1981) as well as

in an additional research under aerobic conditions has demonstrated that its degradation takes place at a really low concentration (Chen et al. 2010).

In order to understand the mechanism of biosorption of 4-BDE, the correct assignment of the kinetics and isotherms of biosorption is of utmost importance. Resorting to the linearization of an obviously nonlinear curve disrupts the error structure of the data. This makes it extra difficult to estimate the uncertainty of the parameters of the kinetics, which are commonly shown in the form of a 95% confidence interval range [1]. In addition, the introduction of error into the independent variable is also a result of the linearization process. In addition, alteration of the weight placed on each data point can occur that normally leads to differences in the fitted parameter values between linear and nonlinear versions of the kinetics model [2]. In some instances, authors reported the best kinetics without resorting into nonlinear regression.

In this study, the published data from a 4-BDE biosorption experiment onto Biochar-immobilized *Sphingomonas* sp. [3] is remodelled with several more kinetic models and then regressed using nonlinear regression method and assessment of the best mode was carried out using various error function analysis. The reason for this modelling study is that there was no modelling exercise for the kinetics carried out in the original work published above.

METHODS

Data acquisition and fitting

Data from Figure **1** from a published work [4] were digitized using the software Webplotdigitizer 2.5 [5]. Digitization using this software has been acknowledged for its reliability [6,7]. The data were then nonlinearly regressed using the curve-fitting software CurveExpert Professional software (Version 1.6) using several models (**Table 1**).

Table 1. Kinetic models utilized in this study.

Model	Equation	Reference
Pseudo-1st order	$q_t = q_e(1 - e^{-K_1 t})$	[8]
Pseudo-2nd order	$q_t = \frac{K_2 {q_e}^2 t}{(1 + K_2 q_e t)}$	[9]
Elovich	$q_t = \frac{1}{\beta ln\alpha\beta} + \frac{1}{\beta lnt}$	[10]

Statistical analysis

Commonly used statistical discriminatory methods such as corrected AICc (Akaike Information Criterion), Bayesian Information Criterion (BIC), Hannan and Quinn's Criterion (HQ), Root-Mean-Square Error (RMSE), bias factor (BF), accuracy factor (AF) and adjusted coefficient of determination (R^2).

The RMSE was calculated according to **Eq. (1)**, [1], and a smaller number of parameters is expected to give a smaller RMSE value. n is the number of experimental data, Ob_i and Pd_i are the experimental and predicted data, while p is the number of parameters.

$$RMSE = \sqrt{\frac{\sum_{i=1}^{n}(Pd_i - Ob_i)^2}{n - p}} \quad \textbf{(Eqn. 1)}$$

As R^2 or the coefficient of determination ignores the number of the parameter in a model, the adjusted R^2 is utilized to overcome this issue. In the equation (**Eqns. 2** and **3**), the total variance of the y-variable is denoted by S_y^2 while RMS is the Residual Mean Square.

$$Adjusted\left(R^2\right) = 1 - \frac{RMS}{s_y^2} \quad \textbf{(Eqn. 2)}$$

$$Adjusted\left(R^2\right) = 1 - \frac{\left(1 - R^2\right)(n-1)}{(n - p - 1)} \quad \textbf{(Eqn. 3)}$$

The Akaike Information Criterion (AIC) is based on information theory. It balances between the goodness of fit of a particular model and the complexity of a model [11]. To handle data having a high number of parameters or a smaller number of values corrected Akaike information criterion (AICc) is utilized [12]. The AICc is calculated as follows (**Eqn. 4**), where p signifies the quantity of parameters and n signify the quantity of data points. A model with a smaller value of AICc is deemed likely more correct [12].

$$AICc = 2p + n\ln\left(\frac{RSS}{n}\right) + 2(p+1) + \frac{2(p+1)(p+2)}{n-p-2} \quad \textbf{(Eqn. 4)}$$

Aside from AICc, Bayesian Information Criterion (BIC) (**Eqn. 5**) is another statistical method that is based on information theory. This error function penalizes the number of parameters more strongly than AIC [13].

$$BIC = n.\ln\frac{RSS}{n} + k.\ln(n) \quad \textbf{(Eqn. 5)}$$

A further error function method based on the information theory is the Hannan–Quinn information criterion (HQC) (**Eqn. 6**). The HQC is strongly consistent unlike AIC due to the ln ln n term in the equation [12];

$$HQC = n \times ln\frac{RSS}{n} + 2 \times k \times ln(\ln n) \quad \textbf{(Eqn. 6)}$$

Further error function analysis that originates from the work of Ross [14] is the Accuracy Factor (AF) and Bias Factor (BF). These error functions test the statistical evaluation of models for the goodness-of-fit but do not penalize for a number of the parameter (**Eqns. 7 and 8**).

$$\text{Bias factor} = 10^{\left(\sum_{i=1}^{n}\log\frac{(Pd_i/Ob_i)}{n}\right)} \quad \textbf{(Eqn. 7)}$$

$$\text{Accuracy factor} = 10^{\left(\sum_{i=1}^{n}\log\frac{|(Pd_i/Ob_i)|}{n}\right)} \quad \textbf{(Eqn. 8)}$$

RESULTS AND DISCUSSION

The absorption kinetics data of biosorption isotherm experiment from a published work [4] on the biosorption of 4-BDE onto Biochar-immobilized *Sphingomonas* sp. were analyzed using three models—pseudo-1st, pseudo-2nd and Elovich, and fitted using non-linear regression. The Elovich model was the poorest in fitting the curve based on visual observation followed by Pseudo-2nd order (**Figs. 1-3**). Statistical analysis based on root-mean-square error (RMSE), adjusted coefficient of determination (adjR^2), bias factor (BF), accuracy factor (AF), corrected AICc (Akaike Information Criterion), Bayesian Information Criterion (BIC) and Hannan–Quinn information criterion (HQC) that showed that the pseudo-first-order model is the best (**Table 2**).

Kinetic analysis using the pseudo-1st order model at 400 mg/L 4-BDE gave a value of equilibrium sorption capacity q_e of 31.89 mg g^{-1} (95% confidence interval from 30.37 to 33.42) and a value of the pseudo-1st-order rate constant, k_1 of 0.22 (95% confidence interval from 0.019 to 0.025). In the original published work, the pseudo-1st order model at 400 mg/L 4-BDE gave a value of equilibrium sorption capacity q_e of 31.3 mg g^{-1} and value of the pseudo-1st-order rate constant, k_1 of 1.732. Further analysis is needed to provide proof for the mechanism usually tied to this kinetic. In the works originally published, there was no modelling works carried out.

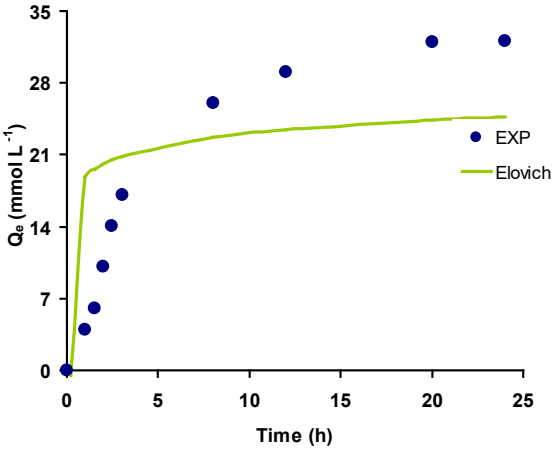

Fig. 1. Kinetics of on the biosorption of 4-BDE onto Biochar-immobilized *Sphingomonas* sp. modelled using the Elovich model.

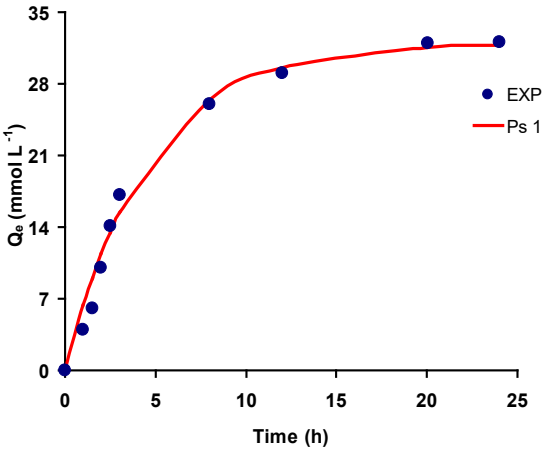

Fig. 2. Kinetics of on the biosorption of 4-BDE onto Biochar-immobilized *Sphingomonas* sp. modelled using the pseudo-1st order model.

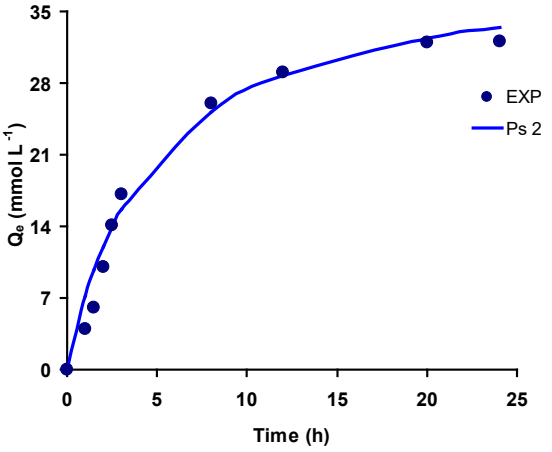

Fig. 3. Kinetics of on the biosorption of 4-BDE onto Biochar-immobilized *Sphingomonas* sp. modelled using the pseudo-2nd order model.

Table 2. Error function analysis of regressed models.

Model	p	RMSE	*adR*^{2}	AICc	BIC	HQC	AF	BF
Pseudo-1st order	**2**	1.347	0.982	19.39	12.93	11.46	1.093	1.048
Pseudo-2nd order	**2**	1.725	0.970	27.30	20.85	19.38	1.115	1.060
Elovich	**2**	7.940	-0.229	76.16	69.71	68.24	1.526	1.286

Note:
RMSE Root mean Square Error
p no of parameters
adR^2 Adjusted Coefficient of determination
BF Bias factor
AF Accuracy factor
AICc Adjusted Akaike Information Criterion

In order to investigate the mechanism of sorption and possible rate-controlling steps, for instance, chemical reaction and mass transport processes, kinetic models have been used to analyze experimental data. These kinetic models integrated the pseudo-1st order equation, the pseudo-2nd order equation as well as the Elovich equation. The concentration of the adsorbate is set at a saturation level in the pseudo first-order reaction. This results in its level to be constant, and the adsorbate is adsorbed at a constant rate, due to the rate being dependent on a single concentration of the adsorbate. When film diffusion controls the rate, there is an inverse relationship between rate and particle size, the distribution coefficient and the film thickness. In this situation, the label physisorption is given as the rate-limiting step is diffusion and is independent on the level of both reactant (physical exchange).

In the event the reaction is govern by a pseudo second order reaction, chemical reaction controls the rate-controlling step, and when this happen the process is called chemisorption. Under this circumstances, the sorption kinetics matches to a reversible second order reaction at low adsorbate/adsorbent ratios, and at higher sorbate/sorbent ratios, two competitive reversible second order reactions will occur [15]. However, to confirm the mechanism is chemisorption, further proofs should be provided such as the evaluation results of the activation energies by repeating the experiment at various temperatures and also by checking out the process rates dependences to the sizes of the adsorbent particle [16].

The pseudo-1st order model has been called the Lagergren model [17] in honour of its developer [8]. In general, pseudo-1st order means physisorption is involved as the main mechanism instead of chemisorption. Physisorption (or physical adsorption) is adsorption in which the forces involved are intermolecular forces (van der Waals forces) . The model has been utilized to explain the mechanism of adsorption but several researchers have expressed cautions in using either the pseudo-1st (PFO) or pseudo-2nd models (PSO) in explaining the mechanism of adsorption [2,18,19]. In the original published work on the biosorption of 4-BDE onto Biochar-immobilized *Sphingomonas* sp. [4], the authors reported that the pseudo-1st order is the best model and is likely to use a linearization form as the linearized pseudo-1st order equation is mentioned.

Examples of PFO models include studies on the removal of copper (II) from water and copper plating industry wastewater by adsorption onto peanut hull carbon [20], removal of two basic dyes; methylene blue and Victoria blue from aqueous solutions using the dried roots of water hyacinth (*Eichhornia crassipes*) [21], removal of patulin from apple juice using carbon beads that are Ca-alginate-activated [22], the use of spent black tea for the removal of nitrobenzene from aqueous media [23] and the removal of the methylene blue dye using novel phosphonate cellulose acetate membrane from synthetic aqueous solutions [24].

CONCLUSION

In conclusion, the biosorption of 4-BDE onto Biochar-immobilized *Sphingomonas* sp. was successfully modelled using three models—pseudo-1st, pseudo-2nd and Elovich, and fitted using non-linear regression. Statistical analysis based on root-mean-square error (RMSE), adjusted coefficient of determination (adjR^2), bias factor (BF), accuracy factor (AF), corrected AICc (Akaike Information Criterion), Bayesian Information Criterion (BIC) and Hannan–Quinn information criterion (HQC) showed that the pseudo-1st order model is the best model giving valuable parameters such as the equilibrium sorption capacity q_e and the pseudo-second-order rate constant, k_2, which can be further utilized in isothermal modelling analysis. Kinetic analysis using the pseudo-1st order model at 400 mg/L 4-BDE gave a value of equilibrium sorption capacity q_e of 31.89 mg g^{-1} (95% confidence interval from 30.37 to 33.42) and a value of the pseudo-1st-order rate constant, k_1 of 0.22 (95% confidence interval from 0.019 to 0.025). Further analysis is needed to provide proof for the mechanism usually tied to this kinetic.

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