

Kinetic Studies on the Biosorption of the Brominated Flame Retardant 4-Dibromodiphenyl ether (BDE-3) using Coconut Palm Leaf Powders

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ABSTRACT

Methods such as membrane isolation, ion replacements, precipitation, transformation and biosorption are proven approaches to contaminant control. Biosorption has all of these technological features including low operating costs, very efficient detoxifying of toxicities at low volumes, minimal amounts of removal components and nutrient requirement, as well as bacterial remediation, which are limited to the presence of heavy metals and other toxicants. The biosorption of BDE-3 on coconut leaves powder on the biosorption of BDE-3 from coconut leaves powder were analyzed 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-2nd order model is the best model. Kinetic analysis using the Pseudo-2nd order model gave a value of equilibrium sorption capacity q_e for 0.01 g per L adsorbent of 488.16 mg g⁻¹ (95% confidence interval from 463.68 to 512.64) and a value of the Pseudo-2nd-order rate constant, k_2 of 0.00019 (95% confidence interval from 0.00010 to 0.00027) while the equilibrium sorption capacity q_e for 0.002 g per L adsorbent of 2403.61 mg g⁻¹ (95% confidence interval from 2313.99 to 2493.22) and a value of the Pseudo-2nd-order rate constant, k_2 of 0.000043 (95% confidence interval from 0.000027 to 0.000059). These calculated values will be very useful in designing effective sorption experiment and understanding the limitations of the system developed.

INTRODUCTION

Flame retardants from polybrominated diphenyl ethers (PBDEs) are commonly integrated into many consumer goods, such as plastics, mobile devices, textiles, construction supplies, wiring insulation materials and foam upholstery [1,2] Since the 1970s, BDEs have been used to comply with fire safety legislation by extending flame dispersion and intervening with polymeric material ignition [3]. In the PBDE family, there are 209 potential congeners, and one of the most widely used compounds is 4-bromodiphenyl ether (BDE-3). In comparison to reactive brominated flame retardants (BFRs) chemically bound to the polymer, mechanically blended additive BFRs such as PBDEs do not form chemical bonds with the polymeric matrix and appear

to elute out into the atmosphere [4,5]. As BDE-3 and BDE-15 are the most abundant photodegradation products of higher brominated PBDEs, considerable levels of both congeners have been found in the environment [6–8].

PBDE was formally established by the United Nations Environment Programmes (UNEP) in 2009 as a new form of persistent organic contaminants (POPs) [9]. Many other characteristics have led to their environmental persistence, namely chemical inertness, long half-life, low vapor pressure, good lipid solubility and degradation resistance [10]. This lipophilic PBDEs have chemical properties that are somewhat close to those of thyroid hormones and are also thought to be endocrine disruptors that may induce cancer and trigger

neurodevelopmental defects [11,12]. The toxicity consequences of PBDEs have become a global issue and thus the search for the right remediation approaches for the PBDE-contaminated ecosystem is of the greatest reputation. Currently, three remediation pathways frequently used for PBDEs are anaerobic biodegradation, photochemical degradation and adsorption. For example, PBDE-47 was reported to be photodegraded in the presence of non-ionic surfactant solutions Brij 35, Brij 58, Tween 80, with the greatest result shown by Brij 35, and the most prevalent photoproducts were BDE-28, BDE-15 and BDE-3 [13].

The vast amount of money needed to operate carbon-based adsorption is limited, despite it being widely used as an efficient adsorbent for the elimination of many organic pollutants. There is therefore urgent need for inexpensive, robust and non-hazardous adsorbents. These substitute adsorbents may be bioadsorbents and waste from agriculture or manufacturing. Agricultural wastes such as spent leaves of tea [14], pineapple leaf [15] and inexpensive materials like chitosan and zeolites [16] have been successfully utilized for adsorbing compounds such as dyes [17–24] and heavy metals [25–35].

In particular, there are four enticing factors that have brought out agricultural waste applications, such as alternative adsorbents; a) highly abundant; b) not/simple pretreatment or activation before use; c) regeneration free, compared to carbon activation requiring regeneration; resulting in the adsorbents needing less control and maintenance. The use of these possible adsorbents in waste water management is sadly adversely impacted by poor post-application disposal and lack of documentation for actual wastewater systems [3]. Coconut palm trees are widely cultivated in various tropical countries, such as Malaysia, Taiwan, China, India, Thailand, and Indonesia. The leaves are often used as compost or they are burnt on the field after harvest.

The major components of these leaves are cellulose, lignin, and hemicelluloses; thus studies have measured how low-cost adsorbents for waste water management are used in subtropical plants and leaves [36–38]. The use of these leaves is doubly valuable, since they are an adsorbent naturally and eliminate agricultural waste. The usage is particularly advantageous because this waste not only turns it into an essential material but also stops it from being burnt on site and minimizes the cost of disposal [39–44].

In a previous study, the evaluation of coconut palm leaf powders as potential low-cost adsorbents for removing BDE-3 and BDE-15 from aqueous solutions was attempted [3]. To understand the process of biosorption of compounds, the proper assignment of kinetics and bio-sorption isotherms is desperately essential. Linearization of an otherwise nonlinear curve will trigger problems with the datas' error structure, making estimates of uncertainties of kinetic parameters, typically depicted as 95 percent confidence interval, tremendously hard [45]. In this study the biosorption of BDE-3 from coconut palm leaf powders [3] was remodeled 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.

METHODS

Data acquisition, handling and fitting

Data from figure 4 from a published work [3] were first digitized using the software Webplotdigitizer 2.5 [46]. The data need to be converted into the sorption capacity at time *t* or *q_t* of which this study did to be able to calculate the sorption capacity at equilibrium or *q_e*. will convert which is the amount of PBDE absorbed per g of adsorbent. The data were then nonlinearly regressed using the curve-fitting software CurveExpert Professional software (Version 1.6) using several popular kinetic models (Table 1).

Table 1. Kinetic models utilized in this study.

Model	Equation	Reference
Pseudo-1 st order	$q_t = q_e(1 - e^{-K_1t})$	[47]
Pseudo-2 nd order	$q_t = \frac{K_2q_e^2t}{(1 + K_2q_e t)}$	[48]
Elovich	$q_t = \frac{1}{\beta \ln \alpha \beta} + \frac{1}{\beta \ln t}$	[49]

Statistical analysis

The RMSE was calculated according to Eq. (1) [45], adjusted *R*² (Eqns. 2 and 3), corrected Akaike information criterion (AICc) is utilized [50] and calculated as in Eqn. 4), Bayesian Information Criterion (BIC) (Eqn. 5) [51], Hannan–Quinn information criterion (HQC) (Eqn. 6) [50] and Ross [52] Accuracy Factor (AF) and Bias Factor (BF) (Eqns. 7 and 8) were utilized as discriminatory method to select for the best model.

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

$$Adjusted (R^2) = 1 - \frac{RMS}{s_y^2} \tag{Eqn. 2}$$

$$Adjusted (R^2) = 1 - \frac{(1 - R^2)(n - 1)}{(n - p - 1)} \tag{Eqn. 3}$$

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

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

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

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

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

RESULTS AND DISCUSSION

The absorption kinetics data that were fitted using non-linear regression and 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) shows that the Elovich model was the poorest in fitting and that the Pseudo-2nd order model is the best model. Kinetic analysis using the Pseudo-2nd order model gave a value of equilibrium sorption capacity q_e for 0.01 g per L adsorbent of 488.16 mg g⁻¹ (95% confidence interval from 463.68 to 512.64) and a value of the Pseudo-2nd-order rate constant, k_2 of 0.00019 (95% confidence interval from 0.00010 to 0.00027) while the equilibrium sorption capacity q_e for 0.002 g per L adsorbent of 2403.61 mg g⁻¹ (95% confidence interval from 2313.99 to 2493.22) and a value of the Pseudo-2nd-order rate constant, k_2 of 0.000043 (95% confidence interval from 0.000027 to 0.000059).

The discrepancy from the originally published works is as a result of the values of the data was not converted into the sorption capacity at time t or q_t of which will not give the calculated the sorption capacity at equilibrium or q_e . The values obtained in this work is not much different from the values obtained using similar modelling exercise of BDE-3 to spent black tea waste [53].

Table 2. Error function analysis of regressed models of the biosorption of 3-BDE on 0.01 g per L of coconut leaves powder.

Model	p	RMSE	$adjR^2$	AICc	BIC	HQC	AF	BF
Pseudo-1st order	2	23.410	0.976	59.79	45.68	44.45	1.037	1.000
Pseudo-2nd order	2	13.133	0.993	51.70	37.59	36.36	1.019	1.000
Elovich	2	43.014	0.919	68.31	54.20	52.97	1.073	0.933

Note:
 RMSE Root mean Square Error
 p no of parameters
 $adjR^2$ Adjusted Coefficient of determination
 BF Bias factor
 AF Accuracy factor
 AICc Adjusted Akaike Information Criterion
 BIC Bayesian Information Criterion
 HQC Hannan-Quinn Criterion

Table 3. Error function analysis of regressed models of the biosorption of 3-BDE on 0.002 g per L of coconut leaves powder.

Model	p	RMSE	$adjR^2$	AICc	BIC	HQC	AF	BF
Pseudo-1st order	2	95.479	0.984	79.47	65.36	64.13	1.029	1.000
Pseudo-2nd order	2	49.034	0.996	70.14	56.03	54.80	1.013	1.000
Elovich	2	354.361	0.513	97.83	83.72	82.49	1.009	1.000

Note:
 RMSE Root mean Square Error
 p no of parameters
 $adjR^2$ Adjusted Coefficient of determination
 BF Bias factor
 AF Accuracy factor
 AICc Adjusted Akaike Information Criterion
 BIC Bayesian Information Criterion
 HQC Hannan-Quinn Criterion

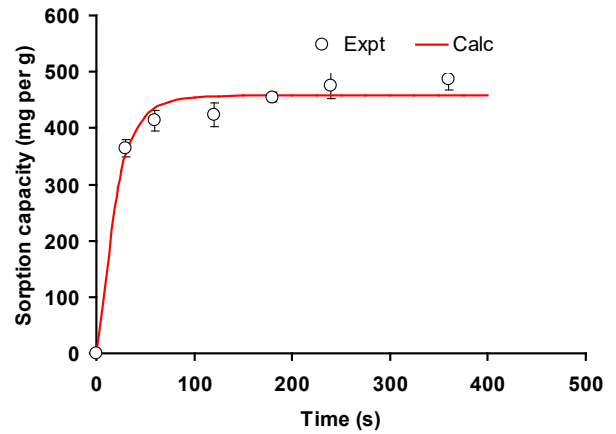


Fig. 1. Kinetics of on the biosorption of BDE-3 on 0.01 g per L coconut leaves powder modelled using the Pseudo-1st model.

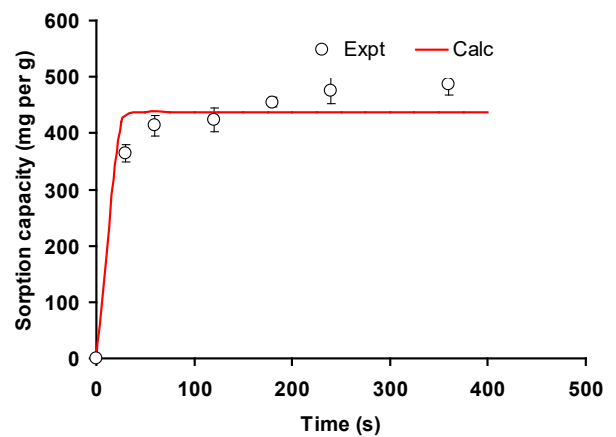


Fig. 2. Kinetics of on the biosorption of BDE-3 on 0.01 g per L coconut leaves powder modelled using the pseudo-2nd order model.

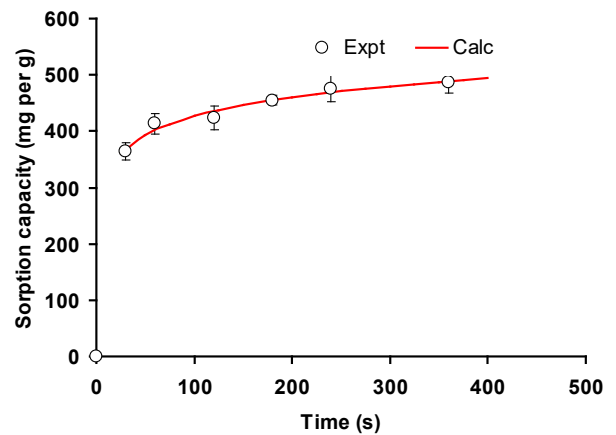


Fig. 3. Kinetics of on the biosorption of BDE-3 on 0.01 g per L coconut leaves powder modelled using the Elovich model.

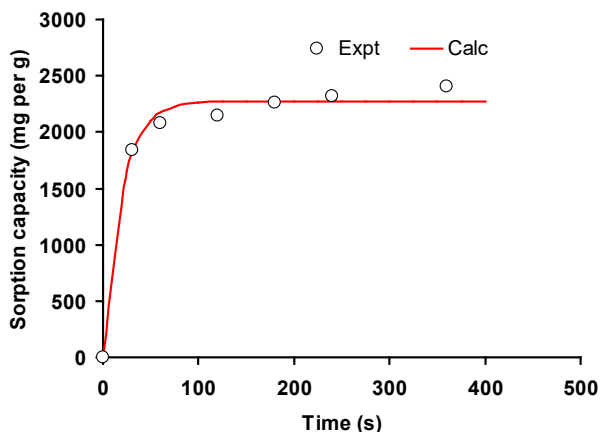


Fig. 4. Kinetics of on the biosorption of BDE-3 on 0.002 g per L coconut leaves powder modelled using the Pseudo-1st model.

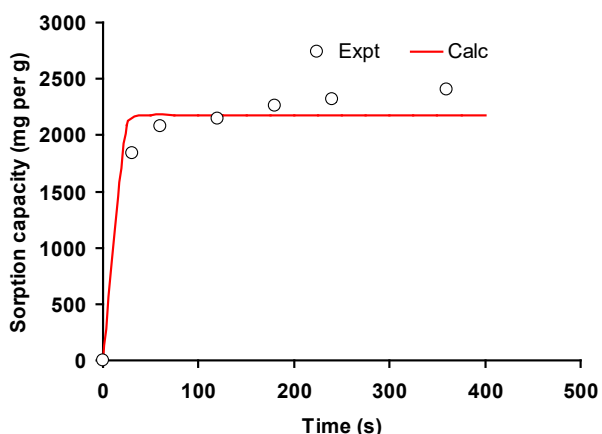


Fig. 5. Kinetics of on the biosorption of BDE-3 on 0.002 g per L coconut leaves powder modelled using the pseudo-2nd order model.

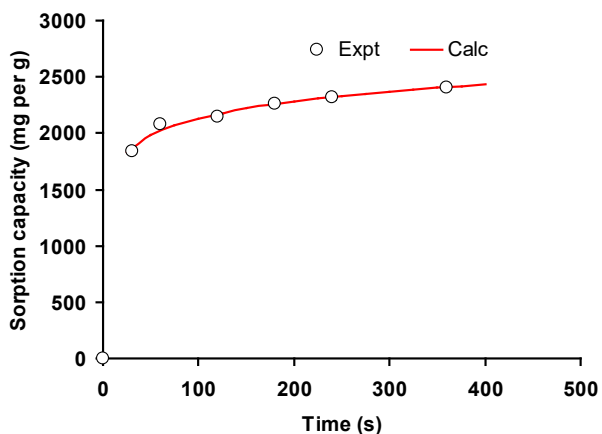


Fig. 6. Kinetics of on the biosorption of BDE-3 on 0.002 g per L coconut leaves powder modelled using the Elovich model.

Table 2. Constants obtained from the modelling exercise for BDE-3 using 0.01 g per L adsorbent (coconut leaves powder).

Kinetic model	Parameter	Values	(95% confidence interval)	Values from [3]
Pseudo-1st order	q_e (mg per g)	458.07	(428.65 to 487.49)	-n.a.
	k_1 (s^{-1})	0.05	(0.029 to 0.069)	-n.a.
Pseudo-2nd order	q_e (mg per g)	488.16	(463.68 to 512.64)	-n.a.
	K_2 (s^{-1})	0.00019	0.00010	to -n.a.
Elovich	α (mg per g per s)	0.02	(0.015 to 0.026)	-n.a.
	β (g per mg)	3269.14	(-3638.67 to 10176.96)	to -n.a.

Note: -n.a. not available

Table 3. Constants obtained from the modelling exercise for BDE-3 using 0.002 g per L adsorbent (coconut leaves powder).

Kinetic model	Parameter	Values	(95% confidence interval)	Values from [3]
Pseudo-1st order	q_e (mg per g)	2270.75	(2151.68 to 2389.81)	to -n.a.
	k_1 (s^{-1})	0.052	(0.034 to 0.070)	-n.a.
Pseudo-2nd order	q_e (mg per g)	2403.61	(2313.99 to 2493.22)	4.43
	K_2 (s^{-1})	0.000043	(0.000027 to 0.000059)	to 0.0284
Elovich	α (mg per g per s)	0.005	(0.004 to 0.006)	-n.a.
	β (g per mg)	40381.01	(-45785.40 to 126547.42)	to -n.a.

Note: -n.a. not available

Two types of adsorption kinetics are commonly used; pseudo-1st order and pseudo-2nd order. In the late 19th century Lagergren introduced the pseudo-1st order kinetics while the pseudo-2nd order kinetics was introduced in the middle of the 80's and gain prominence in 1999 when Ho and McKay suggest the pseudo-2nd order kinetics to be the dominant mechanism and the thousands of literature citations have proven this point [54]. These kinetical models can reveal the potential rate regulation measures and sorption mechanism such as mass transfer processes and whether reactions are physical or chemical.

There is a constant concentration of the adsorbate in the pseudo first order reaction when it is set at the level of saturation, resulting in a constant adsorption of the adsorbate. In the event that film diffusion regulates the rate, by stirring the device and using smaller particle size adsorbents, the reciprocal relationship between rate and particle size, the distribution coefficient and the film thickness can be resolved. The name physisorption is given in this situation as the rate-limiting process is diffusion and is independent of the degree of both reactants (physical exchange).

It is expected that chemical reactions regulate the rate-control phase, a mechanism known as chemisorption, in a reaction controlled by a pseudo-2nd order reaction. Under these conditions, a reversible second-order reaction at low adsorbate/adsorbent ratios fits the sorption kinetics, whereas two competitive second-order reversible reactions occur at higher sorbate/sorbent ratios [55]. Critics have, however, cautioned against rushing to the conclusion that the process is a chemisorption based solely on evidence from kinetics. Further proof, including the measurement effects of the activation energies by repeating the experiment at different temperatures and also by testing the process speeds based on the sizes of the adsorbent particle, should be supplemented. [56]. Furthermore, the data points need to be increased to more than twenty, especially at earlier times, and this will help distinguish statistically whether a reaction is in the first or second order. Moreover, instead of the common correlation coefficient value,

advanced error functions should be used as discriminant error functions as carried out in this work [57–59].

In the original work, the pseudo-2nd order kinetics model was used without resorting to existing comparison of the mathematical model, but the fact that the PSO model is the better model demonstrates its broad use and suitability in biosorption work. In many instances, the PSO model has been identified as the best model [22,60–62] including the adsorption of tris-(2,3-dibromopropyl) isocyanurate are best modelled using a Pseudo-1st order [63], adsorption of flame retardants such as tetrabromobisphenol A [64,65], BDE-47 [66], 4-BDE [59], hexabromocyclododecane [67], and the sorption of the OPFRs; tri(n-butyl) phosphate (TnBP), tris(2-butoxyethyl) phosphate (TBEP), and tris(2-chloroethyl) phosphate (TCEP) on Pahokee peat soil [68], the adsorption of tetrakis (hydroxymethyl) phosphonium chloride (THPC) on biochar [69] and the adsorption of tricresyl phosphate onto graphene nanomaterials [70].

CONCLUSION

Three kinetics models were successfully used to fit BDE-3 sorption data on coconut leaves powder, which pseudo-1st, pseudo-2nd and Elovich. Statistical analysis based on root-mean-square error (RMSE), adjusted coefficient of determination ($\text{adj}R^2$), accuracy factor (AF), bias factor (BF), corrected AICc Bayesian Information Criterion (BIC), (Akaike Information Criterion) and Hannan–Quinn information criterion (HQC) showed that the Pseudo-2nd order model is the best model giving valuable parameters such as the equilibrium sorption capacity q_e and the Pseudo-2nd-order rate constant, k_2 , which can be further utilized in isothermal modelling analysis.

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