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Kinetic Analysis of the Adsorption of Glyphosate onto Palm Oil Fronds Activated Carbon

Hartinie Marbawi[1,2], Muhammad Arif Mukhriz Ros Saidon Khudri[3], Ahmad Razi Othman[3], Mohd Izuan Effendi Halmi[4], Jualang Azlan Gansau[2] and Nur Adeela Yasid[1]*

[1]Department of Biochemistry, Faculty of Biotechnology and Biomolecular Sciences, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, D.E, Malaysia.
[2]Biotechnology Programme, Faculty of Science and Natural Resources, Universiti Malaysia Sabah, 88400 Kota Kinabalu, Sabah
[3]Department of Chemical Engineering, Faculty of Engineering and Built Environment, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, D.E, Malaysia.
[4]Department of Soil Management, Faculty of Agriculture, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, D.E, Malaysia.

*Corresponding author:
Dr. Nur Adeela Yasid,
Department of Biochemistry,
Faculty of Biotechnology and Biomolecular Sciences,
Universiti Putra Malaysia
43400 Serdang
Selangor, Malaysia
Email: adeela@upm.edu.my

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ABSTRACT

Existing techniques for the treatment of pollutants include membrane separation, ion exchange, precipitation, transformation and biosorption. Of all of this technology, biosorption has several positive aspects which include low operating expenses, very efficient detoxification of toxicants at low concentrations, low amount of disposal materials and does not need nutrient requirements as in bacterial-based remediation, the latter of which is limited by the presence of heavy metals and other toxicants. The biosorption of glyphosate on palm oil fronds activated carbon can be an efficient and low-cost tool for remediation of glyphosate. The absorption kinetics data of biosorption isotherm on the biosorption of glyphosate on palm oil fronds activated carbon 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-second order model is the best model. Kinetic analysis using the pseudo-second order model at 250 mg/L glyphosate gave a value of equilibrium sorption capacity q_e of 94.12 mg g^{-1} (95% confidence interval from 89.913 to 98.332) and a value of the pseudo-second-order rate constant, k_2 of 0.02 (95% confidence interval from 0.012 to 0.023). Further analysis is needed to provide proof for the chemisorption mechanism usually tied to this kinetic.

INTRODUCTION

Glyphosate is a type of non-selective, broad-spectrum active ingredient in many herbicide formulations used effectively in controlling weeds. Glyphosate dominates world herbicide consumption with an increase of 15–fold since 1996 and nearly 8.6 billion kg have applied over the world in the last decade [1]. Extensive and constant application of GP-based herbicide resulted in its accumulation in soils and runoff to water environment. Glyphosate may contaminate water system through agricultural runoff, water irrigation, spillage, spray drift or leaching and much related with the herbicide properties which is polar and highly soluble in water (11.6 g/L, 25 ◦C) [2–4].

Occurrence of glyphosate in various quantities in water environment including stream, surface water, ground water and sea water reported worldwide [5–8]. In Malaysia, glyphosate residue and its metabolite aminomethylphosphonic acid (AMPA) (1.0-2.0 mg/L) has been detected in surface water (1.0-2.0 mg/L) and soil and sediments (5.0-6.0mg/kg) at the river close to oil palm plantation in Tasik Chini, Pahang [9]. Glyphosate contamination becomes a major toxicity concern for both the environment and human health represented by increasing numbers of recent toxicological studies [11-13].

The potential environmental and health hazard caused by glyphosate provokes interest for remediation of glyphosate from the environment. Various strategies for the removal of glyphosate from water has been applied which include biological and physicochemical treatment, advanced oxidation and combined treatment [10,13]. Among the available treatments, biosorption offers an economical and eco-friendly approach for removal of pollutant from aqueous environment.

Biosorption defined as a physicochemical metabolism-independent process resulting in the removal of substances from solution by biological material. The technique has been initially used for removal of metal and related elements but the application is currently expanding for removal of various organic target substances such as dyes, steroids, pharmaceuticals, drugs and pesticides [14–16].

A number of research has been conducted on glyphosate adsorption using various materials such as resin, biopolymer membrane, magnetic nanocomposite and commercially available activated carbon and biochar [17–20], however, not much work has been done on biosorption of glyphosate using agricultural by-products [22-23]. In addition, data on glyphosate biosorption need to explore further by well-designed and proper kinetic and isotherm experiment.

The correct assignment of the kinetics and isotherms of biosorption is urgently needed in order to understand the mechanism of biosorption of glyphosate. The linearization from of an obviously nonlinear curve can provide issues on the error structure of the data making it extra difficult to estimate uncertainty of the parameters of the kinetics which are commonly shown in the form of a 95% confidence interval range [24]. In addition, the transformation of data for linearization can result in the introduction of error into the independent variable. 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 Langmuir model [25].

In this study the published data from a glyphosate biosorption experiment on palm oil fronds activated carbon [23] is remodeled with several more kinetic models (**Table 1**) 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

Table 1. Kinetic models utilized in this study.

Model	Equation	Reference
Pseudo-1st order	$q_t = q_e(1 - e^{-K_1 t})$	[26]
Pseudo-2nd order	$q_t = \dfrac{K_2 q_e{}^2 t}{(1 + K_2 q_e t)}$	[27]
Elovich	$q_t = \dfrac{1}{\beta ln\alpha\beta} + \dfrac{1}{\beta lnt}$	[28]

MATERIALS AND METHODS

Data acquisition and fitting

Data from Figure 1 from a published work [23] were digitized using the sotware Webplotdigitizer 2.5 [29]. Digitization using this software has been acknowledged for its reliability [30,31]. The data were then nonlinearly regressed using the curve-fitting software CurveExpert Professional software (Version 1.6).

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)**, [24], and smaller number of parameters is expected to give a smaller RMSE values. 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.

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

As R^2 or the coefficient of determination ignores the number of 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.

$$Adjusted\,(R^2) = 1 - \frac{RMS}{s_Y^2} \qquad \text{(Eqn. 2)}$$

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

The Akaike Information Criterion (AIC) is based on the information theory. It balances between the goodness of fit of a particular model and the complexity of a model [32]. To handle data having a high number of parameters or a smaller number of values corrected Akaike information criterion (AICc) is utilized [33]. 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 [33].

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

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 [34].

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

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 [33];

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

Further error function analysis that originates from the work of Ross [35] are 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 number of parameter (**Eqns. 7 and 8**).

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

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

RESULTS AND DISCUSSION

The absorption kinetics data of biosorption isotherm experiment from a published work [23] on the biosorption of glyphosate on palm oil fronds activated carbon 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-1st 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-second order model is the best model. Kinetic analysis using the pseudo-second order model at 250 mg/L glyphosate gave a value of equilibrium sorption capacity q_e of 94.12 mg g^{-1} (95% confidence interval from 89.913 to 98.332) and a value of the pseudo-second-order rate constant, k_2 of 0.02 (95% confidence interval from 0.012 to 0.023). In the works originally published, there was no modelling works carried out.

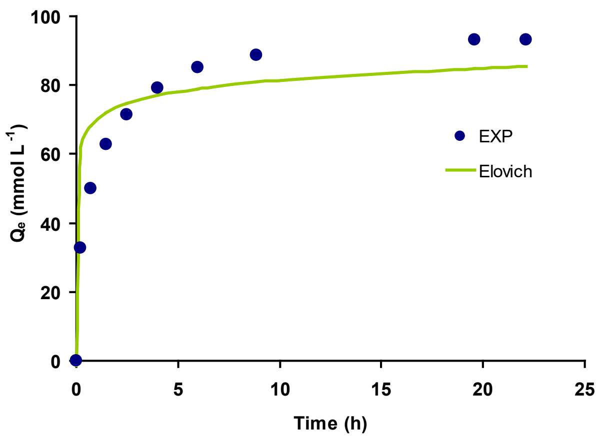

Fig. 1. Kinetics of on the biosorption of glyphosate on palm oil fronds activated carbon modelled using the Elovich model.

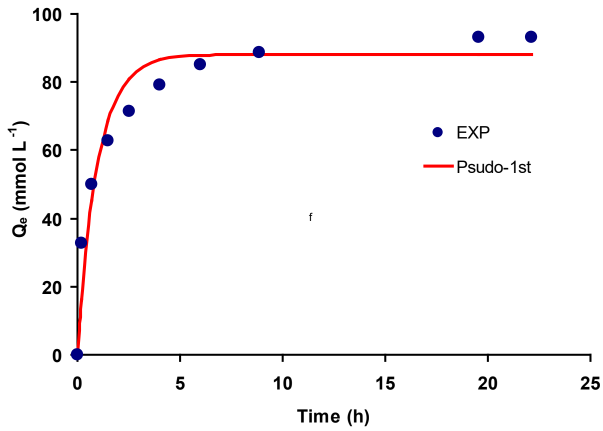

Fig. 2. Kinetics of on the biosorption of glyphosate on palm oil fronds activated carbon modelled using the pseudo-1st order model.

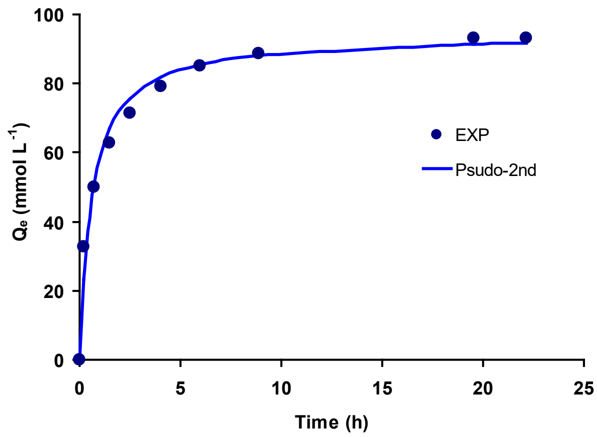

Fig. 3. Kinetics of on the biosorption of glyphosate on palm oil fronds activated carbon modelled using the pseudo-2nd order model.

Table 2. Error function analysis of regressed models.

Model	p	RMSE	adR^2	AICc	BIC	HQC	AF	BF
Pseudo-1st order	2	7.587	0.935	59.45	51.42	50.09	1.120	0.945
Pseudo-2nd order	2	3.858	0.982	43.22	35.19	33.86	1.052	0.979
Elovich	2	13.335	0.715	72.98	64.95	63.62	1.153	1.048

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 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 circumstance, 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 [36]. However, to confirm the mechanism is a 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 [37]. The pseudo-2nd order kinetics model has been reported to be the best model in several studies [38–41] including pesticides biosorption such as 2,4-dichlorophenoxyacetic [42], bromopropylate [43], butachlor [44], paraquat [45] and chlorpyrifos and monocrotophos [46].

CONCLUSION

In conclusion, the biosorption of glyphosate on palm oil fronds activated carbon 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-second 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

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