JOBIMB, 2022, Vol 10, No 1, 1-4
https://doi.org/10.54987/jobimb.v10i1.655

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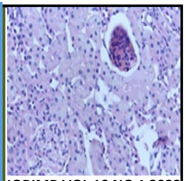

JOBIMB VOL 10 NO 1 2022
Cyclamate-exposed Kidney Cells

Kinetic Study of Malathion Biosorption Using Dry Cells of an Isolated *Bacillus* sp. S14

Ibrahim Alhaji Sabo[1]*, Salihu Yahuza[2], Abdussamad Abubakar[3] and Bilal Ibrahim Dan-Iya[4]

[1] Department of Microbiology, Faculty of Pure and Applied Sciences, Federal University Wukari, P.M.B. 1020 Wukari, Taraba State, Nigeria.
[2]Department of Microbiology and Biotechnology, Faculty of Science, Federal University Dutse, P.M.B., 7156, Dutse, Jigawa State, Nigeria.
[3]Department of Microbiology, Faculty of Science, Bauchi State University, Gadau, PMB 65, Nigeria.
[4]Pharmacy Technician Department, College of Health Sciences and Technology, Kano Nigeria.

*Corresponding author:
Ibrahim Alhaji Sabo
Department of Microbiology,
Federal University Wukari,
Taraba State,
PMB 1020
Email: ibrahimsabodzk@dzk.com

HISTORY

Received: 15th April 2022
Received in revised form: 18th June 2022
Accepted: 15th July 2022

KEYWORDS

Malathion
Kinetics
Adsorption
Bacillus sp
Pollutants

ABSTRACT

Pesticides Pollutants are a major ecological issue because they kill organisms that are not their intended targets. Even in trace amounts, their diversity, toxicity, and durability are harmful to natural systems. High levels of malathion in the air, water, or food can make breathing difficult, tighten the chest, cause nausea, cramps, diarrhoea, watery eyes, impaired vision, salivation, perspiration, headaches, and even cause death. Two kinetic models—pseudo-1st- and pseudo-2nd order were used to examine the sorption isotherm of malathion onto *Bacillus* sp. S14, and they were fitted using non-linear regression. The pseudo-1st order model was found to be the best model by 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). A kinetic study employing the pseudo-1st order model at 150 PPM yielded an equilibrium sorption capacity qe of 4.19 mg/g (95% confidence interval from 4.137448 to 4.257148) and a pseudo-1st-order rate constant, k1 of 0.53. (95 percent confidence interval from 0.510371 to 0.559508). Further analysis is required to give evidence for the chemisorption mechanism commonly associated with this kinetic.

INTRODUCTION

Pesticides are required for current agricultural operations. Pesticides not only kill undesired pests and insects, but also boost agricultural yield. Agriculture production in India rose by 100% while cropping land expanded by just 20% [1]. Because pesticides are being used more frequently to boost agricultural output, it is becoming more and more important to remove pesticide residue from the environment. The influents, effluents, and sludge of biological wastewater treatment plants in North America have been found to include a variety of harmful chemicals [2]. Malathion is an organophosphate insecticide that is used to kill insects on agricultural crops and stored products, as well as in gardens and other outdoor places where trees and shrubs are grown. It is also used to eliminate mosquitoes, medflies, fleas on pets, and head lice on people. If Malathion is discharged into the soil, it will mildly attach to the soil and be prone to considerable biodegradation and hydrolysis. The reported half-lives in soil range between 4 and 6 days [2–4]. Malathion disrupts the normal operation of the nervous system, affecting the function of other organs indirectly [5–11]. People are thus inadvertently exposed to pesticides in trace amounts through a variety of meals. According to reports, symptoms of acute organophosphorus poisoning include difficulty in breathing, vomiting, nausea, diarrhoea, excessive salivation, impaired vision, headaches, giddiness, loss of consciousness, and death [1,4].

Pesticides can be removed from water samples using a variety of adsorbents, including activated carbon, straw, lignocellulosic substrate from the agricultural industry, baggasse fly ash, coal fly ash, charcoal from agricultural waste, and bark. One of the efficient alternative techniques for removing pesticides from contaminated water samples is biosorption. As an alternate approach, biosorption has been utilised to eliminate hazardous contaminants from water samples [12–16]. According

https://doi.org/10.54987/jobimb.v10i1.655

to research conducted by the United States Geological Survey, more than 90% of the water and fish samples gathered from major rivers or streams were contaminated with pesticides. Agriculture and urban land use have an impact on the pesticide-contaminated rivers and streams. India is currently ranked tenth in the world in terms of pesticide consumption [1].The present study investigates the kinetic analysis of Malathion biosorption by dry cells of an isolated *Bacillus* sp. S14.

MATERIALS AND METHODS

Data acquisition and fitting

Data from Figure 5 of a previously published work [2] were digitised using the software Webplotdigitizer 2.5 [17]. The data was then nonlinearly regressed using the curve-fitting software CurveExpert Professional software (Version 2.6.5). Digitization using this software has been acknowledged by many researchers for its reliability and accuracy [18–20], [21]. The data was then nonlinearly regressed using two different kinetic models in the curve-fitting software CurveExpert Professional (Version 2.6.5) as previously used by Shukor et al. [22] **(Table 1).**

Table 1. Kinetics Models utilized in this study

Model	Equation	Reference
Pseudo-1st order	$q_t = q_e(1 - e^{-K_1 t})$	[23]
Pseudo-2nd order	$q_t = \frac{K_2 {q_e}^2 t}{(1 + K_2 q_e t)}$	[23]

Statistical analysis

Some of the most widely used statistical discriminatory methods are 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) were used in this research [24,25].

The RMSE was calculated using **(Eqn. 1)** [26], and a smaller number of factors is expected to result in a lower RMSE value. The number of experimental data is n, the number of experimental and predicted data is Obi, and the number of parameters is p.

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

Because R^2, or the coefficient of determination, does not account for the number of parameters in a model, the adjusted R^2 is used to overcome this constraint. In the equation **(Equations 2 and 3)**, the total variance of the y-variable is denoted by S_y^2, where RMS stands for Residual Mean Square.

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

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

The Akaike Information Criterion (AIC) is a criterion based on information theory. It finds a balance between the goodness of fit of a model and its complexity [27]. The corrected Akaike information criterion (AICc) is used to handle data with many parameters but few values [28]. The AICc is calculated as follows **(Eqn 4)**, where p denotes the number of parameters and n is the number of data points. A model with a lower AICc value is considered more accurate [28].

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

Aside from the AICc, another statistical tool based on information theory is the Bayesian Information Criterion (BIC) **(Eqn. 5)**. The number of parameters is penalised more precisely by this error function than by AICc[29].

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

The Hannan-Quinn information criterion (HQC) is an additional error function approach based on information theory **(Eqn. 6)**. Because of the ln ln n term in the equation, the HQC is extremely consistent in contrast to AIC [28];

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

The Accuracy Factor (AF) and Bias Factor (BF) are two further error function analyses that derive from Ross's work [30]. These error functions test the goodness-of-fit of models statistically but do not penalise for the number of parameters **(Eqns. 7 and 8)**

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

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

RESULTS AND DISCUSSION

Malathion has been classified as a toxicity class III pesticide and a general use pesticide by the Environmental Protection Agency (GUP) [1]. Because they are sprayed directly onto the land, they have the potential to contaminate natural water sources because they can leak into surface water or move into the earth. Biosorption using dead microbial biomass has many benefits, including the lack of toxicity issues and the need for nutrient supply. Storage and usage of the nonviable biomass are simple. When using strains that could be pathogenic, health risks are also removed. Additionally, when they are utilised in processes leading to simple process start-up and management, it does not necessitate the inclusion of nutrients for cell growth and starting up.

The biosorption isotherm data from a previously published work [2] on the Biosorption of malathion by dry cells of an isolated *Bacillus* sp. S14 were analysed using two models—pseudo-1st and pseudo-2nd order and fitted with non-linear regression (**Figs. 1-2**). The pseudo-first-order model was found

https://doi.org/10.54987/jobimb.v10i1.655

to be the best by 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) (**Table 2**). Using the pseudo-1st order model, kinetic analysis at 150 ppm produced an equilibrium sorption capacity (q_e) of 4.60973 mg/g (with a 95% confidence interval between 4.542239 and 4.677213) and a pseudo-1st-order rate constant (k_1) of 0.145988. (95 % confidence interval from 0.128159 to 0.163818). Therefore the result of the data acquired from previously published work Figure 5 [2] revealed that the dry cells of *Bacillus* sp. S14 was effective in eliminating malathion from the solution. Further investigation is needed to offer proof of the mechanism commonly associated with this kinetic

Table 2. Error functions for regressed models analysis

Model	p	RMSE	adR^2	AICc	BIC	HQC	AF	BF
Pseudo-1st order	2	0.029	1.000	-33.77	-47.88	-49.11	1.006	0.999
Pseudo-2nd order	2	0.093	0.995	-17.560	-31.67	-32.90	1.028	1.007

Note:
RMSE Root mean Square Error
P no of parameters
adR^2 Adjusted Coefficient of determination
BF Bias factor
A accuracy factor
AICc Adjusted Akaike Information Criterion
BIC Bayesian Information Criterion
HQC Hannan–Quinn information criterion

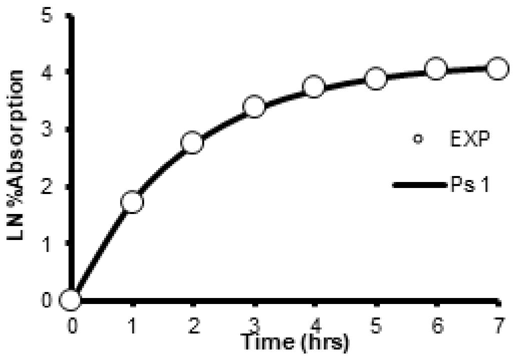

Fig. 1. Kinetics of the sorption of malathion onto *Bacillus* sp. S14 as modeled using the pseudo-1st-order model.

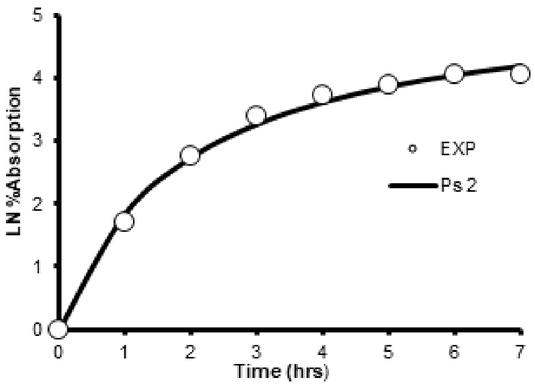

Fig. 2. Kinetics of the sorption of malathion onto *Bacillus* sp. S14 as modeled using the pseudo-2nd-order model.

CONCLUSION

Finally, the Malathion onto *Bacillus* sp S14 was successfully predicted using two models—pseudo-1st and pseudo-2nd order and fitted using non-linear regression. Statistical analysis using 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) revealed that the pseudo-1st order model was the best. Nonlinear regression analysis employing the pseudo-1st order model yielded an equilibrium sorption capacity q_e of 4.19 mg/g (95 percent confidence interval from 4.137448 to 4.257148) and a pseudo-1st-order rate constant, k_1 of 0.53. (95 percent confidence interval from 0.510371 to 0.559508).To support the mechanism typically associated with this kinetic, Further analysis is needed. The parameter values are represented using the nonlinear regression approach in the 95 percent confidence interval range, making it easier to compare the results to those from previous studies.

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