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

Ibrahim Alhaji Sabo1*, Salihu Yahuza2, Abdussamad Abubakar3 and Bilal Ibrahim Dan-Iya4

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

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 influxes, 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, 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 (adjR²), bias factor (BF), accuracy factor (AF), corrected AICc (Akaike Information Criterion), Bayesian information criterion (BIC), and Hannan-Quinn information criterion (HQIC). 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 0.559 508). Further analysis is required to give evidence for the chemisorption mechanism commonly associated with this kinetic.
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       | \( q_t = q_e(1 - e^{-Kt}) \) | [23] |
| Pseudo-2nd order       | \( q_t = \frac{Kq_e}{(1 + Kq_e t)} \) | [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 (HQC), 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 \( p \).

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

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.

\[
Adjusted \ (R^2) = 1 - \frac{RMSE}{S_y} \quad (\text{Eqn. 2})
\]

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

The Akaike Information Criterion (AICc) 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].

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

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).

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

\[
\text{Accuracy factor} = 10 \left( \frac{\sum_{i=1}^{n} \log \left( \frac{P_d_i}{Ob_i} \right)}{n} \right) \quad (\text{Eqn. 8})
\]

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
to be the best by statistical analysis based on root-mean square error (RMSE), adjusted coefficient of determination (adj$R^2$), 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](https://example.com/table2.png)

Table 2. Error functions for regressed models analysis

| Model         | P | no of parameters | adj$R^2$ | 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
adj$R^2$: Adjusted Coefficient of determination
AICc: Akaike Information Criterion
BIC: Bayesian Information Criterion
HQC: Hannan-Quinn information criterion

The result of the data acquired from the experiment was 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 (adj$R^2$), 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.

**REFERENCES**

1. Liani C, Katoch SS. Biosorption of Malathion pesticide using Spirogyra sp. Surjit Singh Katoch Int J Environ Agric Res DOI EJAR ISSN. 2017;3(3):15–20.
2. Adhikari S, Chattopadhyay P, Ray L. Biosorption of malathion by dry cells of an isolated bacillus sp. S14. Chem Speciat Bioavailab. 2010;22(3):207–13.
3. Adhikari S, Chattopadhyay P, Ray L. Continuous removal of malathion by immobilised biomass of Bacillus species S14 using a packed bed column reactor. Chem Speciat Bioavailab. 2012;24(3):167–75.
4. Yadamari T, Yakkala K, Battala G, Gurijala RN. Biosorption of Malathion from Aqueous Solutions Using Herbal Leaves Powder. Am J Anal Chem. 2011;02(08):37–45.
5. Sinha S, Yadav G, Kaushik BR, Dousse S, Janghel D. Histopathological Impact of Malathion on the testicular cells of freshwater crabs Bartytellus cunicularia. (WESTWOOD, 1836). World J Pharm Pharm Sci. 2018;7:997–1007.
6. Walker WW, Stojanovic BJ. Malathion degradation by an Arthropod species. J Environ Qual. 1974;3(1):4–10.
7. Mostafa IY, Fahkri IM, Bahig MRE, El-Zawahry YA. Metabolism of organophosphorous insecticides - XIII. Degradation of malathion by Rhizobium spp. Arch Für Mikrobiol. 1972;86(3):221–4.
8. Paris DF, Lewis DL, Wolfe NL. Rates of Degradation of Malathion by Bacteria Isolated from Aquatic Systems. Environ Sci Technol. 1975;9(2):135–8.
9. Konrad JG, Chesters G, Armstrong DE. Soil degradation of malathion, a phosphorodithioate insecticide. Soil Sci Soc Am J. 1969;33(2):259–62.
10. Gupta VK, Jain CK, Ali I, Chandra S, Agarwal S. Removal of lindane and malathion from wastewater using bagasse fly ash - A sugar industry waste. Water Res. 2002;36(10):2483–90.
11. Chatterjee S, Das SK, Chakravarty R, Chakrbari A, Ghosh S, Guha AK. Interaction of malathion, an organophosphorus pesticide with Rhizopus oryzae biomass. J Hazard Mater. 2010;174(1–3):47–53.
12. Sabo IA, Yahuza S, Dan-Iya BI, Abubakar A. Kinetic Analysis of the Adsorption of Malachite Green onto Graphene Oxide Sheets Integrated with Gold Nanoparticles. J Biochem Microbiol Biotechnol. 2021 Dec 31;9(2):48–52.
13. Yang C, Yu H, Jiang H, Qiao C, Liu R. An engineered microorganism can simultaneously detoxify cadmium, chlorpyrifos, and γ-hexachlorocyclohexane. J Basic Microbiol. 2016;56(7):820–6.
14. Nguyen LN, Hai FJ, Yang S, Kang J, Leusch FDL, Roddick F, et al. Removal of pharmaceuticals, steroid hormones, phytoestrogens, UV-filters, industrial chemicals and pesticides by Trametes versicolor: Role of biosorption and biodegradation. Int Biodeter Biodegr. 2014;88:169–75.
15. Nomikou N, Hughes P, McHale AP. Use of an electric field-assisted biosorption process in the removal of hazardous or precious toxic materials. JOBIMB, 2022, Vol 10, No 1, 1-4.

This work is licensed under the terms of the Creative Commons Attribution (CC BY) (http://creativecommons.org/licenses/by/4.0/).
species from wastewater streams. J Chem Technol Biotechnol. 2006;81(9):1514–9.

16. Aksu Z. Application of biosorption for the removal of organic pollutants: A review. Process Biochem. 2005;40(3–4):997–1026.

17. Rohatgi A. WebPlotDigitizer User Manual 4.3. HttparohatgiinfoWebPlotDigitizerapp Accessed June 2 2014, 2020;1–17.

18. Dan-Iya BI, Yahuza S, Sabo IA. Kinetic Analysis of the Adsorption of Chromium onto Calcium Alginate Nanoparticles. Bull Environ Sci Sustain Manag E-ISSN 2716-5353. 2021;5(2):8–13.

19. Sabo IA, Yahuza S, Dan-Iya BI, Abubakar A. Kinetic Analysis of the Adsorption of Malachite Green onto Graphene Oxide Sheets Integrated with Gold Nanoparticles. J Biochem Microbiol Biotechnol. 2021;9(2):48–52.

20. Halimi M, Wan Johari W, Mohd Ali M, Shahruddin N. Isolation of molybdenum-reducing bacterium; Serratia sp. Strain MIE2 from agriculture soil and its potential use in soil bioremediation. J Biochem Microbiol Biotechnol. 2017;5(2):12–8.

21. Sabo IA, Yahuza S, Shukor MY. Molybdenum Blue Production from Serratia sp. strain DRY5: Secondary Modeling. Bioremediation Sci Technol Res. 2021;9(2):21–4.

22. Abubakar M, Ahmad SA, Yasid NA, Rahman MFA, Alias SA, Hassan NAA, et al. Mathematical modelling of the growth of an Antarctic bacterium Rhodococcus sp. strain ADL36 on palm oil. In 10-3 Midori-cho, Tachikawa, Tokyo, Japan: National Institute of Polar Research (NIPR); 2018. Available from: http://id.nii.ac.jp/1291/00015259/

23. Ho YS, McKay G. Pseudo-second order model for sorption processes. Process Biochem. 1999;34(5):451–65.

24. Aisami A, Shukor MYA. Predictive Mathematical Modelling of the Total Number of COVID-19 Cases for the Kingdom of Saudi Arabia. J Environ Microbiol Toxicol. 2020 Jul 31;8(1):11–5.

25. Yahuza S, Dan-Iya BI, Sabo IA. Modelling the Growth of Enterobacter sp. on Polyethylene. J Biochem Microbiol Biotechnol. 2020 Jul 31;8(1):42–6.

26. Motulsky HJ, Ransnas LA. Fitting curves nonlinear regression : review a practical. FASEB J. 1987;1(5):365–74.

27. Aike HAI. A New Look at the Statistical Model Identification. 1974;

28. Burnham, and Anderson DR. Model Selection and Multimodel Inference: A Practical Information-Theoretic Approach. second edi. Anderson KPBDR, Model, editors. Springer Science & Business Media.; 2002.

29. Kass RE, Raftery AE. Bayes factors. J Am Stat Assoc. 1995;90(430):773–95.

30. Ross T, McMeekin TA. Predictive microbiology. Int J Food Microbiol. 1994;23(3–4):241–64.