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Kinetic Analysis for the Removal of Copper Using *Durvillaea antarctica*

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ABSTRACT

Existing techniques for the treatment of pollutants include membrane separation, ion exchange, precipitation, and transformation and biosorption. Of all 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 reduction of copper by *Durvillaea antarctica*, an alga that lives as south as the Antarctic region can be an efficient and low-cost tool for remediation of copper. In this study, the kinetics of copper biosorption is modelled according to the pseudo-first order, pseudo-second order and Elovich models. Statistical analysis based on root-mean-square error (RMSE), adjusted coefficient of determination (adjR^2), bias factor (BF), accuracy factor (AF) and corrected AICc (Akaike Information Criterion) showed that the pseudo-second order model is the best model. Kinetic analysis using the pseudo-second order model at 0.15 mM copper gave a value of equilibrium sorption capacity q_e of 0.150 mmol g^{-1} (95% confidence interval from 0.149 to 0.151) and a value of the pseudo-second-order rate constant, k_2 of 8.605 (95% confidence interval from 7.016 to 10.194).

INTRODUCTION

Copper (Cu) is abundant in the surroundings and required for the conventional growth and metabolic process of most living creatures. Irregular quantities of copper ingestion may range between quantities so little as to stimulate a dietary insufficiency to quantities excessive they can be extremely harmful. Copper is one of the first metals laboured by people some seventy to eighty centuries in the past [1]. The first recognized item of hammered copper was discovered approximately 6000 BCE. The copper alloy brass originated in Roman periods. Copper stems from the Latin cuprum, which is a corruption of cyprium, Cyprus is the source of Egyptian and Roman copper [1]. The metabolic significance of copper in animals and plants had not been thought prior to the 1920's when illnesses as a result of copper insufficiency turned to be acknowledged. Copper insufficiency in vertebrates, for instance, is associated to anemia, gastrointestinal disorder, aortic aneurisms, bone development irregularities, and death [2].

Toxicity to copper in terrestrial higher plants is uncommon but happens on mining areas and instances where copper-rich manures or fungicides are utilized exceedingly [3]. Copper is considered the most dangerous of the heavy metals in marine and freshwater ecology, and frequently builds up and results in irreparable damage to some species at levels merely over the quantities needed for growth and reproduction [4]. On the other hand, in comparison with lower forms, mammalians and birds are relatively not affected to copper [1].

Copper pollution in the recent years has only just began to take centre stage with several reports studying the effect of copper exposure to Antarctic organisms [5,6]. In anticipation of a copper pollution in the future in the Arctic and Antarctica,

several remediation approach has been suggested with biosorption being one of the least destructive [7,8].

In order to understand the mechanism of biosorption in these organisms, the correct assignment of the kinetics and isotherms of biosorption is urgently needed. In many instances, a linearized from of an obviously nonlinear curve of these data is popularly reported in the literature. Linearization of nonlinear data disrupts the error structure of the data preventing and it is more difficult to estimate uncertainty, which is commonly shown in the form of a 95% confidence interval range [9]. In this study the published data from a copper biosorption experiment on the seaweed *Durvillaea Antarctica* [7] 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

Table 1. Kinetic models utilized in this study.

Model	Equation	Reference
Pseudo-1st order	$q_t = q_e(1 - e^{-K_1 t})$	[10]
Pseudo-2nd order	$q_t = \frac{K_2 {q_e}^2 t}{(1 + K_2 q_e t)}$	[11]
Elovich	$q_t = \frac{1}{\beta ln\alpha\beta} + \frac{1}{\beta lnt}$	[12]

MATERIALS AND METHODS

Data acquisition and fitting

Data from Figure 2 from a published work [7] were downloaded and processed using the software Webplotdigitizer 2.5 [13] which digitizes the scanned figure into a comma separated data. This method has been utilized by many researchers and acknowledged for its reliability [14,15]. The generated comma separated data were then inputted into the curve-fitting software CurveExpert Professional software (Version 1.6) utilizing the Marquardt algorithm.

Statistical analysis

In several instances, the F-test has been used as a discriminatory method to choose the best model. However, F-test only works for nested models [9]. Due to this, other statistical discriminatory methods that take into account penalty to number of parameters used were utilized and include 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)**, [9], 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.

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

The coefficient of determination or R^2 does not take into account the number of parameters in models, hence, in order to solve this issue, the adjusted R^2 is utilized. the total variance of the y-variable is denoted by s_y^2 is and RMS is the Residual Mean Square.

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

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

The Akaike Information Criterion (AIC) handles the trade-off between the goodness of fit and the complexity of a model and is based on the information theory [16]. The Akaike information criterion (AIC) with correction or AICc is a corrected version of the AIC, and is utilized to handle data with a smaller number of values or a high number of parameters [17]. The AICc is calculated as follows (**Eqn. 4**);

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

Where *p* signifies the quantity of parameters and *n* signify the quantity of data points. The model having the smallest AICc value is more likely correct [17].

Accuracy Factor (AF) and Bias Factor (BF) are statistical evaluation of models originating from the work of Ross [18] to test for the goodness-of-fit of the models and were calculated (**Eqns. 5 and 6**) as follows;

$$\text{Bias factor} = 10^{\left(\sum_{i=1}^{n}\log\frac{(Pd_i/Ob_i)}{n}\right)} \quad (5)$$

$$\text{Accuracy factor} = 10^{\left(\sum_{i=1}^{n}\log\frac{|(Pd_i/Ob_i)|}{n}\right)} \quad (6)$$

RESULTS AND DISCUSSION

The absorption kinetics data of biosorption isotherm experiment from a published work [7] on the biosorption of copper by *D. antarctica* were analyzed using three models—pseudo-1st, pseudo-2nd and Elovich, and fitted using non-linear regression. The Elovich model failed to fit the data and was abandoned. The results of the fitting for the two other curves were visually acceptable (**Figs. 1-2**).

Statistical analysis based on root-mean-square error (RMSE), adjusted coefficient of determination (adjR^2), bias factor (BF), accuracy factor (AF) and corrected AICc (Akaike Information Criterion) showed that the pseudo-second order model is the best model. Kinetic analysis using the pseudo-second order model at 0.15 mM copper gave a value of equilibrium sorption capacity q_e of 0.150 mmol g^{-1} (95% confidence interval from 0.149 to 0.151) and a value of the pseudo-second-order rate constant, k_2 of 8.605 (95% confidence interval from 7.016 to 10.194).

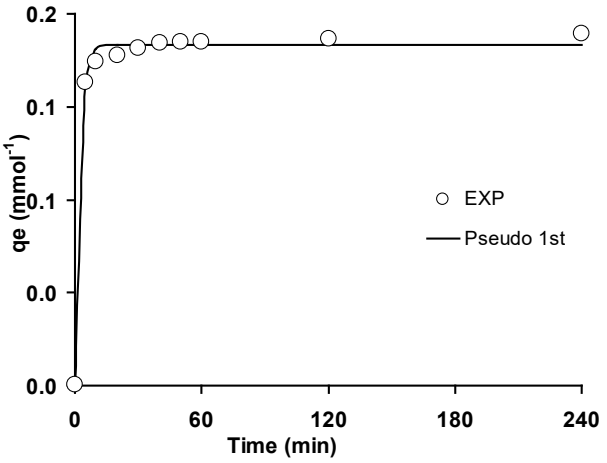

Fig. 1. Kinetics of Cu (II) adsorption on *D. antarctica* dead biomass at pH 5.0 as modelled using the pseudo-1st order model

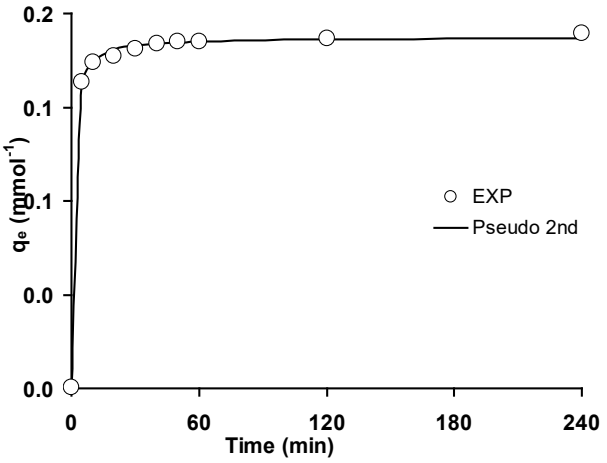

Fig. 2. Kinetics of Cu (II) adsorption on *D. antarctica* dead biomass at pH 5.0 as modelled using the pseudo-2nd order model.

Table 2. Error function analysis of regressed models

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Model	p	RMSE	adR^2	AF	BF	AICc
Pseudo-1st order	2	0.003	0.994	1.016	1.000	-102.17
Pseudo-2nd order	2	0.001	0.999	1.005	1.000	-121.76

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

Potential rate controlling steps such as chemical reaction processes and mass transport and the mechanism of sorption and can be gleamed from the kinetic models developed to fit the experimental data. Kinetic models that are popularly utilized include pseudo-1st order equation, the pseudo-2nd order equation and the Elovich equation. In the pseudo first order reaction, the concentration of one relative reactant is provided in great excessive level resulting its level to be constant and this results in the reactant to be absorbed at the expressed constant rate, simply because the rate is dependent upon a single concentration of the reactants. In the event the rate controlling step is film diffusion, the rate of the adsorption will be inversely related to the particle size, the film thickness and with the distribution coefficient. In this instance, the name physisorption is given since the rate-limiting step is diffusion and not determined by the concentrations of both reactant (physical exchange). In the pseudo second order reaction, the rate-controlling step is tied up to chemical reaction, and this is called chemisorption. In this instance, the adsorption's mechanism is chemically rate controlling. The sorption kinetics normally adhere to a reversible 2nd-order reaction at a ratio of low sorbate/sorbent (first order at very low ratios), and 2 reversible second order reactions which are competitive at a higher ratio of sorbate/sorbent [19].

The mechanism of chemisorption should be demonstrated furthermore, for instance, through the evaluation of activation energies from the experiments performed at a specific temperatures) or by checking out the dependences of process rates on the sizes of sorbent particles [20]. The pseudo-2nd order kinetics model has been reported to be the best model in several studies [21–24] including copper biosorption [22,25–27]

CONCLUSION

In conclusion, extensive modelling of a nonlinearized data shows a different best model compared to the original linearized data regression. The pseudo-2nd order model was found to be the best model based on extensive error function analysis. This difference can lead to a different interpretation of the kinetics of adsorption.

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REFERENCES

1. Schroeder HA, Nason AP, Tipton IH, Balassa JJ. Essential trace metals in man: copper. J Chronic Dis. 1966 Sep;19(9):1007–34.
2. Rajput V, Minkina T, Sushkova S, Behal A, Maksimov A, Blicharska E, et al. ZnO and CuO nanoparticles: a threat to soil organisms, plants, and human health. Environ Geochem Health. 2019 May 20;
3. Sabullah MK, Sulaiman MR, Abd Shukor MY, Shamaan NA, Khalid A, Ahmad SA. In vitro and in vivo effects of *Puntius javanicus* cholinesterase by copper. Fresenius Environ Bull. 2015;24(12 B):4615–4621.
4. Padrilah SN, Ahmad SA, Yasid NA, Sabullah MK, Daud HM, Khalid A, et al. Toxic effects of copper on liver and cholinesterase of *Clarias gariepinus*. Environ Sci Pollut Res. 2017;24(28):22510–22523.
5. Ahmad SA, Halmi MIE, Shukor MY, Shamaan NA, Syed MA. Effect of metal ions on the molybdenum-reducing activity of *S. marcescens* strain DrY6. J Environ Microbiol Toxicol. 2013;1(1):5–8.
6. Holan JR, King CK, Sfiligoj BJ, Davis AR. Toxicity of copper to three common subantarctic marine gastropods. Ecotoxicol Environ Saf. 2017 Feb;136:70–7.
7. Cid H, Ortiz C, Pizarro J, Barros D, Castillo X, Giraldo L, et al. Characterization of copper (II) biosorption by brown algae *Durvillaea antarctica* dead biomass. Adsorption. 2015 Nov 1;21(8):645–58.
8. Mechirackal Balan B, Shini S, Krishnan KP, Mohan M. Mercury tolerance and biosorption in bacteria isolated from Ny-Ålesund, Svalbard, Arctic. J Basic Microbiol. 2018 Apr;58(4):286–95.
9. Motulsky HJ, Ransnas LA. Fitting curves to data using nonlinear regression: a practical and nonmathematical review. FASEB J Off Publ Fed Am Soc Exp Biol. 1987;1(5):365–74.
10. Lagergren S. Zurtheorie der sogenannten adsorption gelösterstoffe. K Sven Vetenskapsakademiens. 1898 Jan 1;24(4):1–39.
11. Ho YS, McKay G. Pseudo-second order model for sorption processes. Process Biochem. 1999 Jul 1;34(5):451–65.

12. Zeldovich J. Über den mechanismus der katalytischen oxydation von CO an MnO_2. Acta Physicochim URSS. 1934;1:364–499.
13. Rohatgi A WebPlotDigitizer. http://arohatgi.info/WebPlotDigitizer/app/ Accessed June 2 2014.; 2015.
14. Halmi MIE, Shukor MS, Johari WLW, Shukor MY. Mathematical modelling of the degradation kinetics of *Bacillus cereus* grown on phenol. J Environ Bioremediation Toxicol. 2014;2(1):1–5.
15. Khare KS, Phelan Jr FR. Quantitative comparison of atomistic simulations with experiment for a cross-linked epoxy: A specific volume–cooling rate analysis. Macromolecules. 2018;51(2):564–575.
16. Akaike H. New look at the statistical model identification. IEEE Trans Autom Control. 1974;AC-19(6):716–23.
17. Burnham KP, Anderson DR. Model Selection and Multimodel Inference: A Practical Information-Theoretic Approach. Springer Science & Business Media; 2002. 528 p.
18. Ross T, McMeekin TA. Predictive microbiology. Int J Food Microbiol. 1994;23(3–4):241–64.
19. Qurie M, Khamis M, Manassra A, Ayyad I, Nir S, Scrano L, et al. Removal of Cr(VI) from aqueous environments using micelle-clay adsorption. Sci World J. 2013;Article ID 942703:7.
20. Khamizov RKh, Sveshnikova DA, Kucherova AE, Sinyaeva LA. Kinetic model of batch sorption processes: Comparing calculated and experimental data. Russ J Phys Chem A. 2018 Oct 1;92:2032–8.
21. Xie S, Yang J, Chen C, Zhang X, Wang Q, Zhang C. Study on biosorption kinetics and thermodynamics of uranium by *Citrobacter freudii*. J Environ Radioact. 2008 Jan 1;99(1):126–33.
22. Kazmi M, Feroze N, Naveed S, Javed SH. Biosorption of copper(II) on *Prunus amygdalus* shell: Characterization, biosorbent size analysis, kinetic, equilibrium and mechanistic studies. Korean J Chem Eng. 2011 Jul 11;28(10):2033.
23. Copello GJ, Pesenti MP, Raineri M, Mebert AM, Piehl LL, de Celis ER, et al. Polyphenol–SiO2 hybrid biosorbent for heavy metal removal. Yerba mate waste (*Ilex paraguariensis*) as polyphenol source: Kinetics and isotherm studies. Colloids Surf B Biointerfaces. 2013 Feb 1;102:218–26.
24. Dahri MK, Lim LBL, Mei CC. Cempedak durian as a potential biosorbent for the removal of Brilliant Green dye from aqueous solution: equilibrium, thermodynamics and kinetics studies. Environ Monit Assess. 2015 Aug 1;187(8):546.
25. Nadeem R, Hanif MA, Mahmood A, Jamil MS, Ashraf M. Biosorption of Cu(II) ions from aqueous effluents by blackgram bran (BGB). J Hazard Mater. 2009 Sep 15;168(2):1622–5.
26. Feroze N, Kazmi M, Ramzan N. Dead immobilized *Rhizopus arrhizus* as a potential biosorbent for copper removal. Korean J Chem Eng. 2013 Jan 1;30(1):95–100.
27. Khalid A, Kazmi MA, Habib M, Jabeen S, Shahzad K. Kinetic & equilibrium modelling of copper biosorption. J Fac Eng Technol. 2015 Nov 24;22(1):131-145–145.