Kinetic Analysis of the Adsorption of Lead(II) onto an Antarctic Sea-Ice Bacterial Exopolysaccharide

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INTRODUCTION

Mining, electroplating, alloy preparation, pulp-paper, fertiliser, and other industrial operations are releasing heavy metals into the environment at an increasing rate. The accumulation of heavy metals in the food chain and the severe health concerns they cause to living beings have made the issue of pollution involving these substances of paramount importance [1] Throughout the Earth's crust, lead can be found; it is a naturally occurring hazardous element. Due to its widespread use, it has polluted vast areas, exposed countless people, and seriously affected public health in a number of countries. The mining, smelting, manufacturing, and recycling industries, as well as the continuous use of lead-based paint and aviation fuel in some nations, are all major contributors to environmental pollution. The production of lead-acid car batteries accounts for more than 85 percent of the world's lead usage. However, lead is also used in a wide variety of other items, including pigments, paints, solder, stained glass, lead crystal glassware, ammunition, ceramic glazes, jewellery, toys, cosmetics, and traditional remedies [2,3]

Lead can be found in drinking water if the pipes carrying the water are made of lead or if the pipes are attached using lead-based solder. Most of the lead used in international trade now comes from recycled sources. Young children are more

ABSTRACT

Hypertension and kidney impairment are two of the many adult health problems that have been related to lead exposure. Women who are expecting a child are especially susceptible to the dangers of lead since it can have devastating consequences on the developing embryo. Existing techniques for the remediation of lead pollutant include membrane separation, ion exchange, precipitation 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 and low amount of disposal materials. The biosorption of the biosorption of lead(II) onto an Antarctic sea-ice bacterial exopolysaccharide is remodeled using nonlinear regression and the optimal mode was determined by a series of error function assessments. Statistical analysis showed that the best kinetic model for adsorption in salt-free water was pseudo-1st order while the best kinetic model for adsorption in seawater was pseudo-2nd order model. All error function analyses also supported these two best models. The kinetic constants values for salt-free water and seawater shows large difference in terms of adsorption in salt-free water and seawater. A higher equilibrium biosorption capacity for lead (II) or \( q_e \) values were exhibited for both \( k_1 \) and \( k_2 \) rate constants in seawater indicating a more efficient adsorption in seawater. Adsorption in seawater increased the \( q_e \) values from 51.11 (mg/g) (95% confidence interval from 49.75 to 52.44) to 92.98 (mg/g) (95% C.I. from 91.01 to 94.95) In addition, the \( h \) value, (mg/g.min) indicates a stronger driving force to accelerate the diffusion of adsorbate from seawater onto the adsorbent. The results suggest fundamental difference of sorption mechanism and functional groups are involved in salt-free and seawater.

KEYWORDS
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susceptible to lead's harmful effects, and it can have long-lasting, devastating effects on their health, especially on their brain and nervous system development. Lead has been linked to an increased risk of hypertension and renal damage in adults. [4–6]. Pregnant women are particularly vulnerable to the effects of lead exposure, which can result in a variety of adverse outcomes for the baby. Lead levels in drinking water that above the legal limit of 0.05 mg/L have been linked to anemia, hepatitis, encephalopathy, and nephritic syndrome [2,7,8].

Biosorption is a promising approach for the removal of heavy metals from wastewater because of its high biosorption capacity and selectivity, low cost, and low environmental risk. Several studies have found that microorganism biomass has a capacity and selectivity, low cost, and low environmental risk. Several studies have found that microorganism biomass has a higher affinity for Pb(II) biosorption than other heavy metals such as Cd(II) and Hg(II) [9]. To defend themselves from the extreme cold and high salt of the Antarctic, several microorganisms secrete exopolysaccharides (EPS). When ice melts, the salinity of the water below it can change from sea level to three times that of the ocean above it, exposing the ice-trapped bacteria to hyposaline conditions. It is reasonable to assume that Antarctic EPSs played a significant role in protecting organisms within ice floes from ice-crystal damage, buffering against pH and salinity fluctuations, and alleviating other chemical stresses such heavy metals though the mechanism was not so evident. It has been found that the molecular weight of EPSs produced by sea-ice isolates is 5–10 times higher than the average of other isolated marine EPSs [10–12]. Due to their appealing structure and physicochemical properties, EPSs generated by sea-ice isolates may be useful biosorbents for the removal of heavy metals from saltwater [13].

In order to fully understand the biosorption process of toxicants, it is crucial to assign the kinetics and isotherms of biosorption appropriately. Estimating uncertainty of the parameters 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.

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

(Eqn. 2)

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

(Eqn. 3)

The Akaike Information Criterion (AICc) is based on the information theory. It balances between the goodness of fit of a particular model and the complexity of a model [22]. To handle data having a high number of parameters or a smaller number of values corrected Akaike information criterion (AICc) is utilized [23]. 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 [23].

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

(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 [24].

$$BIC = n \ln \left( \frac{RSS}{n} \right) + k \ln(n)$$

(Eqn. 5)

A further error function method based on the information theory is the Hannan–Quinn information criterion (HQIC) (Eqn. 6). The HQC is strongly consistent unlike AIC due to the ln ln $n$ term in the equation [23];

$$HQC = n \times \ln \left( \frac{RSS}{n} \right) + 2 \times k \times \ln(\ln n)$$

(Eqn. 6)
Further error function analysis that originates from the work of Ross [25] 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).

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

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

RESULTS AND DISCUSSION

The adsorption kinetics data of biosorption isotherm experiment from a published work [13] on the biosorption of lead (II) on an Antarctic sea-ice bacterial exopolysaccharide 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 (Figs. 1-6). Statistical analysis based on root-mean-square error (RMSE), adjusted coefficient of determination (adjR²), accuracy factor (AF), bias factor (BF), Bayesian Information Criterion (BIC), corrected AICc (Akaike Information Criterion), and Hannan–Quinn information criterion (HQC) were carried out to find the best model.

Fig. 1. Kinetics of on the biosorption of lead(II) onto an Antarctic sea-ice bacterial exopolysaccharide in salt-free water modelled using the Elovich model.

Fig. 2. Kinetics of on the biosorption of lead(II) onto an Antarctic sea-ice bacterial exopolysaccharide in seawater modelled using the Elovich model.

Fig. 3. Kinetics of on the biosorption of lead(II) onto an Antarctic sea-ice bacterial exopolysaccharide in salt-free water modelled using the pseudo-1st order model.

Fig. 4. Kinetics of on the biosorption of lead(II) onto an Antarctic sea-ice bacterial exopolysaccharide in seawater modelled using the pseudo-1st order model.

Fig. 5. Kinetics of on the biosorption of lead(II) onto an Antarctic sea-ice bacterial exopolysaccharide in salt-free water modelled using the pseudo-2nd order model.

Fig. 6. Kinetics of on the biosorption of lead(II) onto an Antarctic sea-ice bacterial exopolysaccharide in seawater modelled using the pseudo-2nd order model.
The best kinetic model for adsorption in salt-free water was Pseudo-1\(^{st}\) with a reasonably large difference in terms of corrected Akaike Information Criterion (>5 absolute unit) to the next best model, which was pseudo-2\(^{nd}\) order and the worst model was Ellovich (Table 2). On the other hand, the best kinetic model for adsorption in seawater was Pseudo-2\(^{nd}\) with also a reasonably large difference in terms of corrected Akaike Information Criterion (>5 absolute unit) to the next best model, which was pseudo-1\(^{st}\) order and the worst model was Ellovich (Table 3). All error function analyses also supported these two best models.

The kinetic constants values for salt-free water and seawater shows large difference in terms of adsorption in salt-free water and seawater (Table 4). A higher equilibrium biosorption capacity for lead (II) or \(q_e\) values were exhibited for both \(k_1\) and \(k_2\) rate constants in sea water indicating a more efficient adsorption in seawater. Adsorption in seawater increased the \(q_e\) values from 51.11 (mg/g) (95% confidence interval from 49.75 to 52.44) to 92.98 (mg/g) (95% C.I. from 91.01 to 94.95) In addition, the \(h\) value, (mg/min) utilized to calculate the initial adsorption rate constant, was also higher in seawater, where a higher \(h\) value indicates a stronger driving force to accelerate the diffusion of adsorbate from solution onto the adsorbent [26].

In the event the reaction is governed by a pseudo-2\(^{nd}\) order reaction, chemical reaction controls the rate-controlling step, and when this happen the process is called chemisorption. Under this circumstances, 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 [32]. 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 [33].

The pseudo-2\(^{nd}\) order kinetics model has been reported to be the best model in several lead sorption studies such as lead(II) sorption by *Cephalosporium aphidicola* [34], on sesame leaf [35], on *Spirodea polyrhiza* [36] and on the lead-resistant bacteria *Delftia lacustris* Strain-MS3 [37] to name a few. In general, the pseudo-2\(^{nd}\) was the best model for metal sorption such as the biosorption of Cr(VI) to magnetic iron oxide nanoparticle-multi-walled carbon nanotube [38], Cu(II) adsorption onto functionalized cellulose beads from Tunisian almond (*Prunus dulcis*) shell [39] and the sorption of Zn(II) by *Streptomyces ciscaucasicus* [40].

On the other hand, the pseudo-1\(^{st}\) order model has also been reported to be the best model for lead(II) sorption onto biobeads immobilised biomass of *P. laurentii* strain RY1 [41], coco-peat biomass [42] and in several other metal sorption works [43-50]. In the majority of reported cases involving biosorption, pseudo-first-order kinetics are typically applicable to the first stage of the adsorption process, rather than the complete contact time range [51].

In addition to influencing the surface charge and double-layer capacitance of the hydrated particles, salinity can also affect the activities of the adsorbate in solution, which in turn can affect adsorption. Increases in ionic strength typically result in a greater aggregation of suspended particles. The necessity of solute diffusion into interaggregate pores, as a result of increased aggregation, is likely to increase the time dependent partition of sorption. Concurrently, the exterior surface and the rapidly reversible component of sorption both decreases. In this way, sorption might appear to decrease, depending on the reaction time employed [52]. The results obtained shows a contrasting results similar to a previous study [52] and may require more research to understand this contrasting results.

**CONCLUSION**

In conclusion, the biosorption of the biosorption of lead(II) onto an Antarctic sea-ice bacterial exopolysaccharide was successfully modelled using three models—pseudo-1\(^{st}\), pseudo-2\(^{nd}\) and Ellovich, and fitted using non-linear regression. Statistical analysis showed that the best kinetic model for adsorption in salt-free water was pseudo-1\(^{st}\) order while the best kinetic model for adsorption in seawater was pseudo-2\(^{nd}\) order model. All error function analyses also supported these two best models. The kinetic constants values for salt-free water and seawater shows large difference in terms of adsorption in salt-free water and seawater. A higher equilibrium biosorption capacity for lead(II) or \(q_e\) values were exhibited for both \(k_1\) and \(k_2\) rate constants in sea water indicating a more efficient adsorption in seawater. In addition, a higher \(h\) value indicates a stronger driving force to accelerate the diffusion of adsorbate from solution onto the adsorbent. From these findings, it appears that the sorption mechanism and functional groups involved in saltwater and freshwater environments are fundamentally different.

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**Table 2. Error function analysis for salt-free water kinetic models.**

| Model       | \(p\) | RMSE \(P \) | \(\text{adR}^2\) | AICc | BIC | HQC | AF | BF |
|-------------|-------|-------------|-----------------|-----|-----|-----|----|----|
| Pseudo-1\(^{st}\) order | 2     | 1.212       | 0.997           | 0.966 | 16.00 | 5.60 | 4.35 | 1.033 | 0.984 |
| Pseudo-2\(^{nd}\) order | 2     | 1.857       | 0.992           | 0.989 | 23.68 | 13.27 | 12.03 | 1.035 | 1.010 |
| Ellovich    | 2     | 4.567       | 0.949           | 0.932 | 39.88 | 29.47 | 28.23 | 1.100 | 1.021 |

**Table 3. Error function analysis for seawater kinetic models.**

| Model       | \(p\) | RMSE \(P \) | \(\text{adR}^2\) | AICc | BIC | HQC | AF | BF |
|-------------|-------|-------------|-----------------|-----|-----|-----|----|----|
| Pseudo-1\(^{st}\) order | 2     | 4.152       | 0.983           | 0.978 | 38.16 | 27.76 | 26.51 | 1.037 | 1.000 |
| Pseudo-2\(^{nd}\) order | 2     | 1.832       | 0.997           | 0.986 | 23.34 | 13.43 | 11.78 | 1.015 | 1.000 |
| Ellovich    | 2     | 3.525       | 0.988           | 0.984 | 35.22 | 24.81 | 23.57 | 1.028 | 1.001 |

**Table 4. Calculated constants for salt-free- and seawater kinetic models.**

| Model       | \(k_1\) (per min) | \(q_e\) (mg/g) | \(h\) (mg/g/min) | \(\text{Beta} (g/mg)\) |
|-------------|-------------------|----------------|------------------|-------------------|
| Pseudo-1\(^{st}\) | 0.139 (0.123 to 0.155) | 0.714 (0.491 to 0.938) | 51.11 (49.753 to 52.441) | 89.864 (86.038 to 93.691) |
| Pseudo-2\(^{nd}\) | 0.004 (0.003 to 0.005) | 0.014 (0.011 to 0.017) | 54.834 (52.213 to 57.456) | 92.98 (91.006 to 94.954) |
| Ellovich    | 10.87             | 188.62         | 120.55           | 3289490.3 to 4801164.7 |

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