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Mechanistic Modelling of the Adsorption of Aqueous Pb(II) by Metabolically Inhibited Bacterial Cultures from Industry

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This study delves into the mechanistic modelling of literature results for the adsorption of aqueous Pb(II) by metabolically inhibited bacterial cultures from the industrial sector. Employing a multi-compartmented mathematical model based on Langmuir's mechanistic multi-surface adsorption, the study explores the adsorption process onto multiple heterogeneous surfaces operating simultaneously. The mathematical model is elucidated, and its parameters are optimized using experimental data obtained from various biosorbents.
The results highlight the efficacy of the proposed multi-surface Langmuir kinetic models in predicting the adsorption kinetics of Pb(II) for diverse adsorbents. The study underscores the potential of multi-surface Langmuir modelling in capturing surface heterogeneity. The sensitivity analysis reveals the models' responsiveness to variations in adsorption rate constants (k_{ad}), emphasizing the necessity of precise parameterization for robust predictions. These sensitivities have significant implications for the accurate modelling of Pb(II) adsorption kinetics, guiding advancements in effective wastewater treatment strategies.

1. Introduction

Lead (Pb) stands out as one of the most perilous heavy metals, constituting a significant menace as a primary contaminant in soil, plants, and water. Therefore, the removal and recovery of heavy metals are critical (Chatterjee et al., 2012). Pb, alongside cadmium, mercury, and arsenic, is recognized among the four heavy metals with severe implications for human health, affecting the peripheral and central nervous systems, kidneys, and blood pressure (Tiwari et al., 2013). The propensity of lead to accumulate in human bones, resulting in a gradual release over time, adds to its adverse effects even after exposure ceases (Needleman, 2004). Lead poisoning has further been associated with mental retardation, behavioral disorders, and reduced sperm count in men when blood concentrations exceed 0.4 ppm (Hörstmann & Brink, 2019).
A study by Naik and Dubey (2013) emphasizes the substantial increase in lead accumulation due to human activities, surpassing levels observed 300 years ago by over 1000 times. Human exposure to Pb(II) happens through ingesting contaminated food and water, as well as inhaling aerosols and dust particles (Chimhundi et al., 2021). The World Health Organization (WHO) sets the threshold limits for Pb(II) in drinking water at 0.05 ppm, while the Environmental Protection Agency (EPA) establishes the limit for industrial wastewater at 0.05 mg/L (Arbabi et al., 2015). Therefore, finding effective treatments for contaminated wastewater before discharge is crucial. Elevated concentrations of Pb in the environment are often attributed to human activities like metalworking and the use of Pb-additives in products such as paints and gasoline (Brink et al., 2019). Additionally, human-induced Pb recirculation appears more extensive than the natural Pb cycle, resulting in a global pollution issue (Brink et al., 2019).While current wastewater treatment methods, including membrane filtration, chemical precipitation, ion exchange, and electrodialysis, aim to address lead pollution by transforming Pb(II) ions into a less harmful state, an extra treatment step is required for the recovery of Pb(0) (Veenhuyzen et al., 2021). However, these techniques face limitations, such as low efficiency and high operating costs (Yang et al., 2019). In contrast, adsorption offers advantages like heightened efficiency, minimized production of chemical and biological sludge, regenerable adsorbents, cost-effectiveness, and potential metal recovery (Gupta et al., 2013).

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Despite these benefits, the industrial application of adsorption is hindered by the need for improved kinetic modeling (Muedi et al., 2021). Common adsorption kinetic models, such as the pseudo first-order, pseudo second-order, and interparticle diffusion models, are empirical and lack scalability in their parameters (Lohrentz et al., 2023). Similarly, widely used isotherm models suffer from limited scalability, except for the mechanistic Langmuir isotherm (1917) isotherm (Lohrentz et al., 2023).Recognizing this gap, the present study focused on kinetically modeling previously published adsorption data on a variety of biosorbents for Pb(II) adsorption (Kpai et al., 2023). The proposed model was based on work previously published by Lohrentz et al (2023). The model involves a multi-compartmented mathematical description based on Langmuir's mechanistic multi-surface adsorption (Langmuir, 1917), which accounts for non-idealities in the adsorbent surface by simulating multiple dissimilar homogeneous surfaces undergoing parallel adsorption.

2. Mathematical model description and solution method

The mathematical model employed a multi-compartment system with adsorption taking place onto multiple heterogeneous surfaces operating in parallel. The adsorption process was modeled using the well-known derivation of the Langmuir isotherm (Langmuir, 1917), with the modification that the adsorption included multiple different adsorption sites. The model and initial conditions are described in equations 1:

$$\frac{dQ_i}{dt} = k_{ad,i} C \theta_i - k_{de,i}(1-\theta_i), Q_i|_o = 0$$
$$\theta_i = 1 - \frac{Q_i}{Q_{max,i}}, k_{de,i} = \frac{k_{ad,i}}{K_{L,i}} \text{ and } C = C_o - \sum Q_i \frac{W}{V} \quad (1)$$

Here, Q_i represents the adsorption capacity at time *t* onto surface site *i* (mg/g), $k_{ad,i}$ (L/g) and $k_{de,i}$ (mg/g) denote the adsorption and desorption rate constants of surface *i*, respectively. *C* denotes the concentration of adsorbate in the medium (mg/L), θ_i indicates the available surface fraction of surface *i* (dimensionless), $Q_{max,i}$ indicate the maximum adsorption capacities of surface *i*, and $K_{L,i}$ represents the Langmuir equilibrium constant for surface *i*. $\frac{W}{V}$ represents the adsorbent concentration loaded in the reactor (g/L). Both $Q_{max,i}$ and $K_{L,i}$ were obtained from the isotherm fits of the experimental data.The differential equations were solved using a simple Euler integration method implemented in Microsoft Excel 365 utilising the following descritised method (equation 2 and 3):

$$\frac{dQ_i}{dt} \approx \frac{\Delta Q_i}{\Delta t} \approx k_{ad,i}\left(C_o - \sum Q_i \frac{W}{V}\right)\left(1 - \frac{Q_i}{Q_{max,i}}\right) - \frac{k_{ad,i}}{K_{L,i}} \frac{Q_i}{Q_{max,i}} \quad (2)$$

$$Q_i(t) = Q_i(t-\Delta t) - \left[k_{ad,i}\left(C_o - \sum Q_i(t-\Delta t)\frac{W}{V}\right)\left(1 - \frac{Q_i(t-\Delta t)}{Q_{max,i}}\right) - \frac{k_{ad,i}}{K_{L,i}} \frac{Q_i(t-\Delta t)}{Q_{max,i}}\right]\Delta t \quad (3)$$

With Δt the incremental time step (min).

The fitted parameters ($k_{ad,i}$) were optimised using the built in “Solver” function in Excel utilising the GRG Nonlinear solving method which minimised the calculated sum of square errors (SSE) between the predicted and measured Q values.

3. Results and discussion

The kinetic data employed in the model fitting and the isotherm data ($Q_{max,i}$ and $K_{L,i}$) were extracted from the study conducted by Kpai et al. (2023), with the isotherm data detailed in Table 1.

Table 1: Isotherm data from Kpai et al. (2023) used for kinetic model fits

Adsorbents	SS	C1	C2	Cons	PB	KP
			Single surface Langmuir			
Q_{max}(mg/g)	141.20	208.50	193.80	220.40	153.20	217.70
K_L(L/mg)	3.68	0.258	0.058	0.025	0.022	0.043
R^2	0.648	0.644	0.681	0.788	0.350	0.568
			Dual surface Langmuir			
Q_{max1}(mg/g)	72.46	86.07	52.61	0	45.82	46.13
Q_{max2}(mg/g)	83.83	144.20	156.70	221.40	430.80	223.60
K_{L1}(L/mg)	∞	∞	∞	∞	∞	∞
K_{L2}(L/mg)	0.024	0.035	0.022	0.025	0.0013	0.015
R^2	0.827	0.833	0.737	0.788	0.648	0.664

The adsorbents used were metabolically inactive sewage sludge (SS), commercial culture 1 (C1), commercial culture 2 (C2), a consortium used for Pb reduction experiment (Cons), *Paraclostridium bifermentans* isolated from Cons (PB) and *Klebsiella pneumoniae* isolated from Cons (KP) (Kpai et al., 2023). The decision to fit the model for one and two surfaces was informed by the reported fits for the single and dual-surface Langmuir isotherm models presented by Kpai et al. (2023). The designated surfaces for the dual surface Langmuir model were labelled as surface 1 and surface 2, with corresponding variables indicated through subscripts.

Figure 1 presents the results derived from the kinetic fits and Table 2 summarizes the optimized parameters for the models. The successful prediction of kinetic data is evident for both Langmuir models (Figure 1 and 2), reflecting their effectiveness in capturing the underlying mechanisms.

The coefficients of determination (R^2) for single surface Langmuir model fits were exceptionally high (>0.98) for all adsorbents, except for PB, which displayed an R^2 of 0.793. This suggests that PB has a highly heterogeneous surface compared to the others and cannot be accurately modelled using a single surface Langmuir kinetic model. This observation aligns with significant differences in R^2 values between the single surface Langmuir isotherm (0.350) and the dual surface Langmuir isotherm (0.648) for PB, as presented in Table 1. Notably, two adsorbents (Cons and KP) exhibited convergence to a single surface model, irrespective of the $k_{ad,1}$ value. This suggests a homogeneous surface for these adsorbents. However, upon analyzing the isotherm fit results for KP (refer to Table 1), it becomes apparent that KP possesses a heterogeneous surface. However, surface 1, associated with $k_{ad,1}$, exhibits an extremely slow adsorption rate compared to surface 2, indicating its negligible contribution to the adsorption kinetics within the 180-minute experimental timeframe.

Furthermore, the R^2 values for the dual surface Langmuir model were either equal to or greater than those for the single surface model across all adsorbents. In instances where R^2 values were equal, the dual surface model reduced to the single surface model since $k_{ad,1}$ values of 0 provided the best data prediction. These results underscores the dual surface Langmuir model's ability to more accurately capture surface heterogeneity, which the single surface Langmuir model fails to predict (Largitte & Pasquier, 2016).

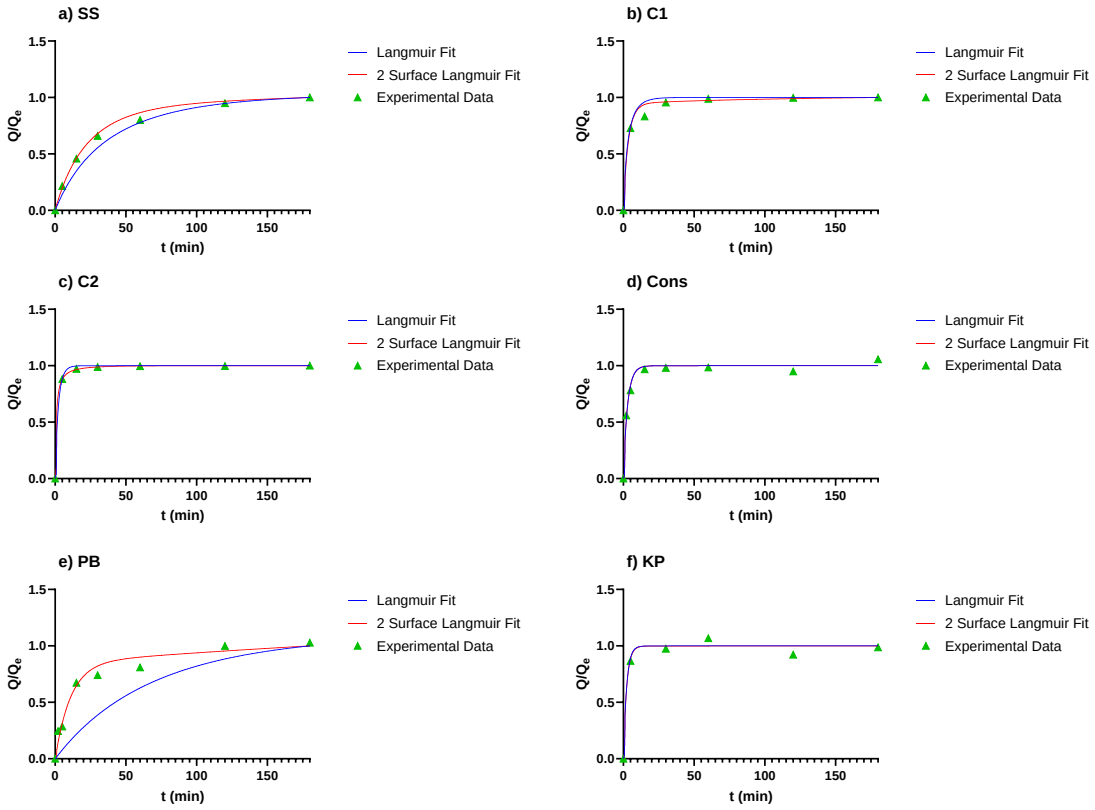

Figure 1: Optimised fits for the single and dual surface Langmuir kinetic models.

To evaluate the models' sensitivity to the fitted parameters (k_{ad}), the relative Sum of Squared Errors (SSE) concerning the baseline SSE, represented as SSE/SSEbaseline, was plotted against the relative k_{ad} to the baseline kad ($k_{ad}/k_{ad,baseline}$ and $k_{ad,i/kad,i\ baseline}$) following the approach by Brink et al. (2011). Figures 2 and 3

illustrate these relationships. Notably, Figures 2 and 3 reveal that the minimum SSE values align with the baseline k_{ad} and $k_{ad,i\ baseline}$, indicating the identification of optimal solutions.

Table 2: Parameters from kinetic model fits

Adsorbents	SS	C1	C2	Cons	PB	KP
			Single surface Langmuir Kinetics			
k_{ad}(mg/g)	0.0212	0.217	0.289	0.225	0.0081	0.160
R^2	0.969	0.980	0.999	0.988	0.793	0.986
			Dual surface Langmuir			
$k_{ad,1}$(mg/g)	0.00887	0.0493	0.744	0	0.00115	0
$k_{ad,2}$(mg/g)	0.0189	0.138	0.000149	0.225	0.0275	0.160
R^2	0.996	0.987	1.000	0.988	0.973	0.986

Figure 2 depicts varying sensitivities of the single surface Langmuir model fits for different adsorbents. C2 exhibits the most significant sensitivity, with a more than twofold increase in SSE/SSEbaseline observed for a 10% change in $k_{ad}/k_{ad,baseline}$. Conversely, PB demonstrates the least sensitivity to changes in k_{ad}. However, it is crucial to note that PB exhibits the poorest fit for the single-phase Langmuir model, suggesting potential limitations in the model's predictability for PB adsorption.

The remaining models show considerable sensitivity to changes in k_{ad}, with KP and C1 being the least sensitive (after PB). Despite this, a 30% increase in $SSE/SSE_{baseline}$ is still observed with a 20% change in k_{ad}. This underscores the models' sensitivity to variations in k_{ad} and emphasizes the importance of accurate parameterization for robust predictions.

The sensitivity analysis for the dual-phase Langmuir model is presented in the heat-map shown in Figure 3. Black squares in the heat-map represent SSE/SSEbaseline values exceeding 2, indicating exceptionally high sensitivity. Once again, C2 emerges as the most responsive to variations in k_{ad}, exhibiting an $SSE/SSE_{baseline}$ increase greater than 2 for any change (either direction) in $k_{ad,1}$ and any decrease in $k_{ad,2}$. The model demonstrates reduced sensitivity to an increase in $k_{ad,2}$, a trend likely influenced by the relative magnitudes of $k_{ad,2}$ (0.000149 L/g) compared to $k_{ad,1}$ (0.744 L/g), as evident in Table 2. This implies that, given the three-orders-of-magnitude slower adsorption onto surface 2 compared to surface 1, the overall impact of an increased $k_{ad,2}$ is minimal. Interestingly, the same cannot be said for a decrease in $k_{ad,2}$.

The sensitivity analysis for the SS model reveals it to be the second most sensitive, exhibiting a substantial increase in all directions of $k_{ad,i}$. Both Cons and KP demonstrate sensitivity to changes in $k_{ad,2}$ while remaining entirely insensitive to changes in $k_{ad,1}$. This behavior is attributed to the previously mentioned convergence of the dual surface Langmuir model to the single surface model for these particular adsorbents.

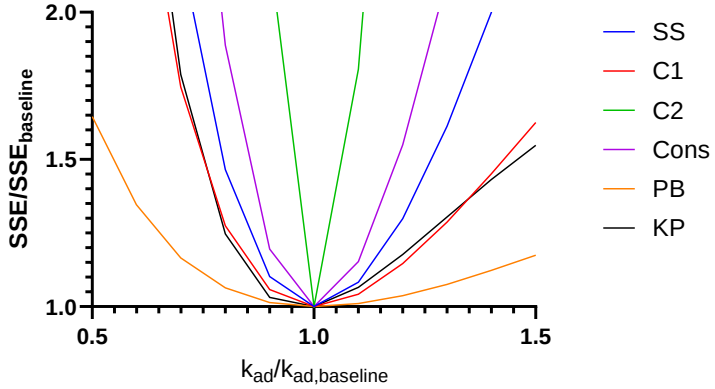

Figure 2: The sensitivity of the relative SSE to the baseline SSE (the optimized results in Figure 1) against the relative k_{ad} to the baseline k_{ad}. The slopes of the curves indicate the rate of increase of error with change in the k_{ad} and therefore provides a guage of the sensitivity of the model to the fitted parameter.

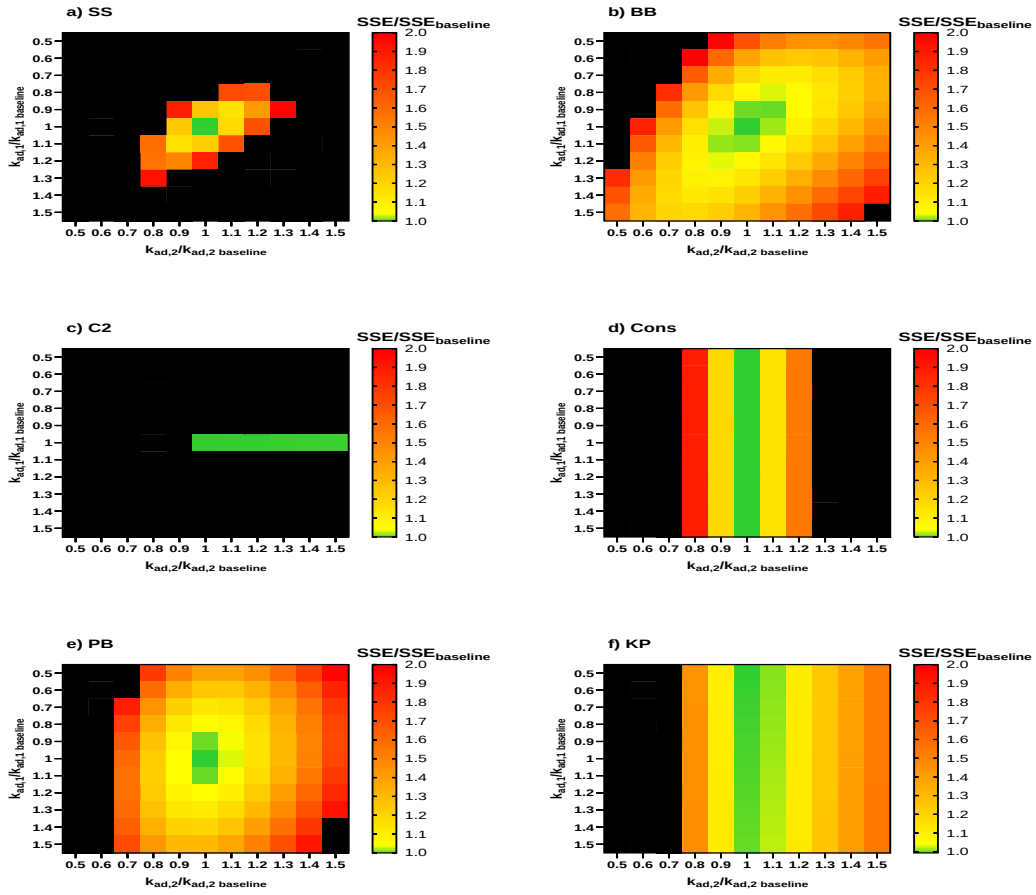

Figure 3: Heat maps of the sensitivity of the relative SSE against the relative $k_{ad,1}$ and $k_{ad,2}$. The rate of change of the colours indicates the sensitivity of the model to the fitted parameters ($k_{ad,1}$ and $k_{ad,2}$).

4. Conclusions

The results reveal the effectiveness of the proposed Langmuir kinetic models in predicting the adsorption kinetics of Pb(II) for different adsorbents, including metabolically inactive sewage sludge (SS), commercial cultures (C1 and C2), a consortium (Cons), *P. bifermentans* (PB), and *K. pneumoniae* (KP). The study emphasizes the potential of multi-surface Langmuir modeling in capturing surface heterogeneity. The sensitivity analysis underscores the models' responsiveness to variations in adsorption rate constants (k_{ad}) and emphasizes the importance of accurate parameterization for robust predictions. Overall, the study contributes valuable insights into the mechanistic understanding of Pb(II) adsorption kinetics, facilitating advancements in effective wastewater treatment strategies.

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