Short communication

Biosorption of nickel(II) ions onto *Sargassum wightii*: Application of two-parameter and three-parameter isotherm models

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Abstract

Biosorption of nickel(II) ions from aqueous solution onto *Sargassum wightii* has been studied and the equilibrium isotherms were determined. The experimental data obtained at different pH conditions (pH 3.0–4.5) have been analyzed using five two-parameter models (Langmuir, Freundlich, Temkin, Dubinin–Radushkevich and Flory–Huggins) and five three-parameter models (Redlich–Peterson, Sips, Khan, Radke–Prausnitz and Toth). In order to determine the best fit isotherm, three error analysis methods were used to evaluate the data: correlation coefficient, residual root mean square error and chi-square test. The error analysis demonstrated that the three-parameter models better described the nickel biosorption data compared to two-parameter models. In particular, Toth equation provided the best model for nickel biosorption data at all pH conditions examined.
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1. Introduction

Biosorption is a proven technology for the removal of heavy metal ions from synthetic and real industrial effluents. Several researchers investigated numerous biomass types and proposed excellent metal biosorbents including bacteria, fungi, algae and industrial wastes [1,2]. They often described the potential of biosorbents by sorption isotherms. Sorption isotherm is the plot of sorption uptake (Q) and the final equilibrium solute concentration (C_f). Modeling of biosorption isotherm data is important for predicting and comparing biosorption performance. Two, three and even four-parameter isotherm models are available for modeling adsorption data [3]. It is very common in the published literature that Langmuir and Freundlich models (two-parameter models) were used to describe the biosorption isotherm. Simplicity, physical meaning/easily interpretable and well-established models are some of the important reasons frequently used for extensive usage of these models. Two-parameter models are usually preferred because, in spite of their simplicity, they can be easily linearized. Also, there is no critical reason to use more complex models if two-parameter models can fit the data well. In spite of this, few three-parameter models such as Redlich–Peterson and Sips model were also used by few investigators to describe the biosorption isotherm [4].

Linear regression has been frequently used to evaluate the model parameters. However, transformations of non-linear isotherm equations to linear forms usually result in parameter estimation error and distort the fit [5].

Considering this, the present work aimed at using 10 isotherm models in non-linear form to describe the sorption data generated from nickel(II) biosorption using *Sargassum wightii*.

2. Materials and methods

2.1. Biosorbent and experimental procedure

S. wightii, a brown marine alga, was collected in Mandapam (Tamilnadu, India). The samples were washed with distilled water, then sun-dried and finally grounded to an average particle size of 0.767 mm, which was subsequently used in biosorption experiments.

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Experiments were conducted by adding 0.2 g of algal biomass to a series of Erlenmeyer flasks containing 100 mL solutions of desired nickel concentrations (prepared using NiSO$_4$·6H$_2$O). The flasks were agitated at 150 rpm in a rotary shaker. The initial solution pH was adjusted using 0.1 M HCl or 0.1 M NaOH. After 12 h of contact time, the algal biomass was separated from nickel solution by centrifugation at 3000 rpm for 10 min. The nickel content in the supernatant was determined using flame atomic absorption spectrophotometer (AAS 6VARIO; Analytik Jena, Germany). The nickel uptake was calculated as follows:

$$Q = \frac{V(C_0 - C_f)}{M} \tag{1}$$

where Q is the nickel uptake (mg/g); C_0 and C_f the initial and equilibrium nickel concentrations in the solution (mg/L), respectively; V the solution volume (L); and M the mass of biosorbent (g). All the experiments were carried out in duplicates, and the deviations were within 5%.

2.2. Equilibrium studies

In order to optimize the design of a sorption system for the removal of metals from effluents, it is important to establish the most appropriate correlation for equilibrium curves. Experimental isotherm data acquired at different pH conditions were fitted to 10 different models of sorption isotherms: Langmuir, Freundlich, Temkin, Dubinin–Radushkevich, Flory–Huggins, Redlich–Peterson, Sips, Khan, Radke–Prausnitz and Toth isotherm models.

2.3. Non-linear regression analysis

All the model parameters were evaluated by non-linear regression using MATLAB® software. The optimization procedure requires an error function to be defined in order to be able to evaluate the fit of the equation to the experimental data [6]. Apart from the correlation coefficient (R^2), the residual root mean square error (RMSE) and the chi-square test were also used to measure the goodness-of-fit. RMSE can be defined as:

$$\text{RMSE} = \sqrt{\frac{1}{m-2}\sum_{i=1}^{m}(Q_i - q_i)^2} \tag{2}$$

where Q_i is the observation from the batch experiment, q_i is the estimate from the isotherm for corresponding Q_i and m is the number of observations in the experimental isotherm. The smaller RMSE value indicates the better curve fitting [5].

The chi-square test can be defined as:

$$\chi^2 = \sum_{i=1}^{m} \frac{(Q_i - q_i)^2}{q_i} \tag{3}$$

If data from model are similar to the experimental data, χ^2 will be a small number [6].

3. Results and discussion

3.1. Effect of pH

The pH of the metal solution usually plays an important role in the biosorption of metals. Preliminary examination of *S. wightii* on the basis of nickel biosorption potential revealed that highest nickel uptake was observed in the pH range of 3.0–4.5 [7]. Therefore, biosorption isotherm experiments were carried out in these pH ranges by varying initial nickel concentration from 100 to 1000 mg/L (Fig. 1). Nickel uptake was found to increase as the pH increases from 3.0 and reached maximum at pH 4.0. Further increase in pH resulted in decreased nickel uptake. This may be due to nature of binding sites in *Sargassum* biomass and their pK_a values [8]. Also, hydrogen ion competition at low pH and solution chemistry of metals are other important factors responsible for variation of metal uptake at different pH values [9].

3.2. Two-parameter models

3.2.1. Langmuir isotherm

The Langmuir adsorption isotherm has traditionally been used to quantify and contrast the performance of different biosorbents. It was originally developed to describe the gas–solid phase adsorption of activated carbon. In its formulation, binding to the surface was primarily by physical forces and implicit in its derivation was the assumption that all sites possess equal affinity for the sorbate. Its use was extended to empirically describe equilibrium relationships between a bulk liquid phase and a solid phase [10]. It has produced good agreement with wide variety of experimental data and may be represented as follows:

$$Q = \frac{Q_{max}b_L C_f}{1 + b_L C_f} \tag{4}$$

where Q_{max} is the maximum metal uptake (mg/g) and b_L the Langmuir equilibrium constant (L/mg). The Langmuir model served to estimate the maximum metal uptake values where they
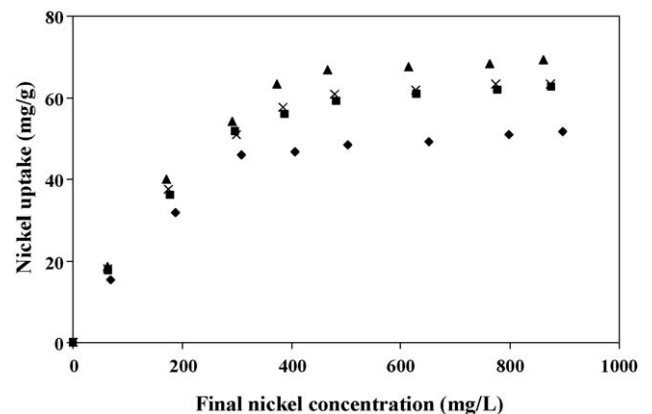

Fig. 1. Effect of pH on nickel biosorption onto *Sargassum wightii* (biomass dosage = 2 g/L; agitation rate = 150 rpm, temperature = 30 °C). Initial solution pH: (♦) pH 3.0; (■) pH 3.5; (▲) pH 4.0; (×) pH 4.5.

Table 1
Isotherm constants of two-parameter models for nickel biosorption onto *S. wightii*

Two-parameter models		pH			
		3.0	3.5	4.0	4.5
Langmuir	Q_{max}	63.2	76.1	81.2	79.1
	b_L	0.0054	0.0055	0.0065	0.0057
	R^2	0.982	0.989	0.986	0.991
	RMSE	2.949	3.041	3.904	2.375
	χ^2	1.613	1.433	2.474	0.951
Freundlich	K_F	2.85	3.52	3.97	3.74
	n_F	2.24	2.23	2.22	2.24
	R^2	0.921	0.940	0.936	0.942
	RMSE	6.643	6.365	7.845	7.222
	χ^2	6.276	5.256	6.957	5.966
Temkin	b_{Te}	0.517	0.431	0.401	0.433
	a_{Te}	40.1	49.9	70.2	62.4
	R^2	0.828	0.782	0.812	0.801
	RMSE	9.868	13.024	15.077	13.142
	χ^2	17.239	24.370	29.259	24.342
Dubinin–Radushkevich	Q_D	51.9	62.9	69.5	64.1
	B_D	0.0023	0.0021	0.0020	0.0021
	E (kJ/mol)	14.81	15.25	15.62	15.39
	R^2	0.960	0.939	0.940	0.942
	RMSE	4.106	6.873	7.435	6.919
	χ^2	2.767	6.447	6.591	6.370
Flory–Huggins	K_{FH}	161.6	223.8	289.7	247.6
	n_{FH}	3.45	3.46	3.67	3.64
	ΔG° (kJ/mol)	−12.81	−13.63	−14.28	−13.88
	R^2	0.825	0.816	0.785	0.841
	RMSE	8.726	8.974	9.125	8.315
	χ^2	14.236	16.236	16.987	13.479

could not be reached in the experiments. The constant b_L represents affinity between the sorbent and sorbate. Both Q_{max} and b_L increases with increasing pH from 3.0 to 4.0, while further increase in pH decreases both constants (Table 1). High values of b are reflected in the steep initial slope of a sorption isotherm, indicating desirable high affinity. Thus, for good biosorbents in general, high Q_{max} and a steep initial isotherm slope (i.e., high b) are desirable [10]. Therefore, *S. wightii* performed well in nickel biosorption at pH 4.0 compared to other pH values examined. Among two-parameter models, high correlation coefficients and low RMSE and chi-square values were observed in the case of Langmuir model (Table 1).

3.2.2. Freundlich isotherm

The Freundlich isotherm is originally empirical in nature, but was later interpreted as sorption to heterogeneous surfaces or surfaces supporting sites of varied affinities. It is assumed that the stronger binding sites are occupied first and that the binding strength decreases with the increasing degree of site occupation. It may be represented as follows:

$$Q = K_F C_f^{1/n_F} \tag{5}$$

where K_F is the Freundlich constant (L/g) and n_F the Freundlich exponent. At pH 4.0, both K_F and $1/n_F$ reached their corresponding maximum values this implies that the binding capacity reaches the highest value and the affinity between the biomass and nickel ions was also higher than other pH values investigated (Table 1).

3.2.3. Temkin isotherm

The derivation of the Temkin isotherm assumes that the fall in the heat of sorption is linear rather than logarithmic, as implied in the Freundlich equation [11]. The heat of sorption of all the molecules in the layer would decrease linearly with coverage due to sorbate/sorbent interactions [12]. The Temkin isotherm has generally been applied in the following form:

$$Q = \frac{RT}{b_{Te}} \ln(a_{Te} C_f) \tag{6}$$

where b_{Te} is the Temkin constant related to heat of sorption (J/mol); a_{Te} the Temkin isotherm constant (L/g), R the gas constant (8.314 J/mol K) and T the absolute temperature (K).

The Temkin sorption potential, a_{Te}, increases with increase in pH and reached maximum value of 70.2 L/g at pH 4.0. The Temkin constant, b_{Te}, related to heat of sorption decreased as the pH increases and reached the lowest value at pH 4.0 (Table 1). However, the model unable to describe the data, compared to other two-parameter models, as low correlation coefficients and high RMSE and chi-square values were observed (Table 1).

3.2.4. Dubinin–Radushkevich isotherm

Another popular equation for the analysis of isotherms of a high degree of regularity is that proposed by Dubinin [13]. They have reported that the characteristic sorption curve is related to the porous structure of the sorbent. The isotherm is as follows:

$$Q_e = Q_D \exp(-B_D \varepsilon_D^2) \tag{7}$$

$$\varepsilon_D = RT \ln\left(1 + \frac{1}{C_f}\right) \tag{8}$$

where Q_D is the Dubinin–Radushkevich model constant (mg/g); B_D the Dubinin–Radushkevich model constant (mol²/kJ²) and ε_D the Polanyi potential. The mean energy of sorption, E, is calculated by the following equation:

$$E = \frac{1}{\sqrt{2B_D}} \tag{9}$$

The Dubinin–Radushkevich constants and mean free energy are given in Table 1. The constant Q_D agrees well with experimental data and the maximum value of 69.49 mg/g was observed at pH 4.0. The magnitude of E is useful for estimating the type of sorption reaction. The E values obtained were around 15 kJ/mol, which are in the energy range of an ion-exchange reaction, i.e., 8–16 kJ/mol [14]. This supports the fact that biosorption of nickel by *S. wightii* may be an ion exchange reaction.

3.2.5. Flory–Huggins isotherm

The Flory–Huggins model [15] was chosen in order to account for the degree of surface coverage characteristics of the sorbate on the sorbent. The isotherm is as follows:

$$\log \frac{\theta}{C_0} = \log K_{FH} + n_{FH} \log(1 - \theta) \tag{10}$$

where $\theta = (1 - C_f/C_0)$ is the degree of surface coverage, K_{FH} is the Flory–Huggins model equilibrium constant and n_{FH} the Flory–Huggins model exponent.

Both Flory–Huggins constants (K_{FH} and n_{FH}) increases with increase in pH and reached their corresponding maximum values at pH 4.0 (Table 1). Furthermore, the equilibrium constant, K_{FH} was used to compute the Gibbs free energy of spontaneity (ΔG°). The ΔG° is related to K_{FH} as follows:

$$\Delta G^\circ = -RT \ln K_{FH} \tag{11}$$

The negative values of ΔG° (Table 1) confirmed the feasibility of the process and the spontaneous nature of nickel(II) biosorption onto *S. wightii*.

3.3. Three-parameter models

3.3.1. Redlich–Peterson isotherm

Redlich and Peterson [16] incorporated the features of the Langmuir and Freundlich isotherms into a single equation and presented a general isotherm equation as follows:

$$Q = \frac{K_{RP} C_f}{1 + a_{RP} C_f^{\beta_{RP}}} \tag{12}$$

where K_{RP} is the Redlich–Peterson model isotherm constant (L/g), a_{RP} the Redlich–Peterson model constant (L/mg); β_{RP} the Redlich–Peterson model exponent. The exponent, β_{RP}, lies between 0 and 1. There are two limiting behaviors: Langmuir form for $\beta = 1$ and Henry's law form for $\beta = 0$.

The Redlich–Peterson isotherm constants for biosorption of nickel ions onto *S. wightii* are furnished in Table 2. The isotherm constant K_{RP} and exponent β_{RP} increases with pH and reached maximum at pH 4.0. In contrary, a reverse trend was observed with a_{RP}, which was lowest at pH 4.0. It is worth noting that β_{RP} values were close to unity, i.e., the data can preferably be fitted with Langmuir model.

3.3.2. Sips isotherm

Sips or Langmuir–Freundlich isotherm has the following form:

$$Q = \frac{K_S C_f^{\beta_S}}{1 + a_S C_f^{\beta_S}} \tag{13}$$

where K_S is the Sips model isotherm constant (L/g); a_S the Sips model constant (L/mg) and β_S the Sips model exponent. At low sorbate concentrations it effectively reduces to the Freundlich isotherm and thus does not obey Henry's law. At high sorbate concentrations, it predicts a monolayer sorption capacity characteristic of the Langmuir isotherm [4].

Similar to Redlich–Peterson model constants, the same trend was observed for Sips model constants (Table 2). The exponent

Table 2
Isotherm constants of three-parameter models for nickel biosorption onto *S. wightii*

Three-parameter models		pH			
		3.0	3.5	4.0	4.5
Redlich–Peterson	K_{RP}	0.402	0.401	0.407	0.406
	a_{RP}	0.0153	0.0099	0.0063	0.0111
	β_{RP}	0.861	0.903	0.925	0.857
	R^2	0.965	0.979	0.968	0.968
	RMSE	3.784	4.521	6.984	6.259
	χ^2	2.330	2.966	4.350	3.789
Sips	K_S	0.415	0.429	0.448	0.439
	a_S	0.0061	0.0049	0.0048	0.0053
	β_S	0.950	0.957	0.987	0.977
	R^2	0.978	0.982	0.984	0.988
	RMSE	2.959	3.293	3.434	2.705
	χ^2	1.580	1.442	1.479	0.958
Khan	Q_{max}	55.2	65.2	73.1	65.2
	b_K	0.0065	0.0072	0.0073	0.0068
	a_K	0.949	0.912	0.895	0.909
	R^2	0.979	0.985	0.982	0.986
	RMSE	3.106	3.223	5.222	2.926
	χ^2	1.817	1.699	3.506	1.209
Radke–Prausnitz	a_R	59.2	66.3	73.2	69.1
	r_R	5.13	5.04	5.03	5.10
	β_R	0.349	0.380	0.405	0.387
	R^2	0.940	0.950	0.943	0.952
	RMSE	4.876	5.733	6.431	5.365
	χ^2	5.079	5.623	6.015	4.629
Toth	Q_{max}	52.6	65.0	71.2	65.2
	b_T	0.0043	0.0046	0.0051	0.0049
	n_T	0.462	0.511	0.559	0.532
	R^2	0.994	0.995	0.991	0.995
	RMSE	1.388	1.951	2.722	1.879
	χ^2	0.339	0.657	1.209	0.565

β_S values were close to unity. It means that nickel sorption data obtained in this study is more of Langmuir form rather than that of Freundlich, which was also confirmed in Table 1.

3.3.3. Khan isotherm

The simplified form of Khan model [3] can be expressed as:

$$Q = \frac{Q_{max} b_K C_f}{(1 + b_K C_f)^{a_K}} \tag{14}$$

where b_K is the Khan model constant and a_K the Khan model exponent. The maximum uptake values (Q_{max}) were well predicted by the model with relatively high correlation coefficients and minimum RMSE and chi-square values (Table 2).

3.3.4. Radke–Prausnitz isotherm

Radke–Prausnitz isotherm can be represented as:

$$Q = \frac{a_R r_R C_f^{\beta_R}}{a_R + r_R C_f^{\beta_R-1}} \tag{15}$$

where a_R and r_R are Radke–Prausnitz model constants and β_R the Radke–Prausnitz model exponent. The nickel biosorption

data do not correlate well with Radke–Prausnitz model and this confirmed by high RMSE and chi-square values (Table 2).

3.3.5. Toth isotherm

Toth isotherm [17], derived from potential theory, has proven useful in describing sorption in heterogeneous systems such as phenolic compounds on carbon. It assumes an asymmetrical quasi-Guassian energy distribution with a widened left-hand side, i.e., most sites have sorption energy less than the mean value [4]. It can be represented as:

$$Q = \frac{Q_{max} b_T C_f}{[1 + (b_T C_f)^{1/n_T}]^{n_T}} \tag{16}$$

where b_T is the Toth model constant and n_T the Toth model exponent. It is obvious that for $n_T = 1$ this isotherm reduces to the Langmuir sorption isotherm equation.

The maximum biosorption capacity agrees very well with the experimental data (Table 2). The other two constants b_T and n_T were maximum at pH 4.0. On the basis of correlation coefficient, RMSE and chi-square test, the Toth model better described the sorption isotherm data compared to other three-parameter models (Table 2).

4. Conclusions

In this paper, equilibrium isotherm data obtained during biosorption of nickel onto *S. wightii* at different pH conditions were fitted using different two-parameter and three-parameter models. From the results obtained, the following comments can be made:

- Among two-parameter models, the Langmuir model better described the isotherm data with high R^2 and low values of RMSE and χ^2.
- In the case of three-parameter models, the Toth model was found to provide closest fit to the equilibrium experimental data even better than Langmuir model.
- From Dubinin–Radushkevich and Flory–Huggins models, it was inferred that biosorption of nickel by *S. wightii* may be an ion exchange and spontaneous process.

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