Estimation of Isotherm Parameters for Biosorption of Cd(II) and Pb(II) onto Brown Seaweed, *Lobophora variegata*

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The biosorption equilibrium isotherms of Cd(II) and Pb(II) from aqueous solution onto both raw and treated biomass of *Lobophora variegata* were studied and modeled. To predict the biosorption isotherms and to determine the characteristic parameters for process design, 19 one-, two-, three-, four-, and five-parameter isotherm models were applied to experimental data. Results show that in general the accuracy of models to fit experimental data improves with the number of parameters. Biosorption isotherm modeling shows that the interaction of Cd(II) and Pb(II) with the *L. variegata* surface is localized to monolayer sorption. The interaction among biosorbed molecules is repulsive, and there is no association between them. Biosorption is carried out on energetically different sites and is an endothermic process. The five-parameter Fritz−Schluender model gives the most accurate fit with high R^2 (0.9960 to 0.9978), low standard error (SE) (0.0334 to 0.0129), and residual or sum of square error (SSE) (0.0066 to 0.0137) values to all experimental data in comparison to other models. The biosorption isotherm models fitted the experimental data in the order: Fritz−Schluender (five-parameter) > Toth (three-parameter) > Fritz−Schluender (four-parameter) > Langmuir (two-parameter) > Temkin (two-parameter).

Introduction

The presence of toxic heavy metals in water resulting from rapid industrialization and technological advances is a worldwide environmental problem. Recently, increasing interest in the application of biomass of diverse origin in heavy metals removal from diluted, large-volume solutions has been observed. Sorption with biomaterials has become an alternative to traditional methods of industrial wastewater treatment, such as precipitation, adsorption, coagulation, etc. and is relatively inexpensive and nonhazardous and may permit recovery of the metals from the sorbing biomass.[1–3] Several researchers investigated numerous biomass types and proposed excellent metal biosorbents including bacteria, fungi, algae, industrial wastes, etc.[4,5]

In general, sorption processes were found to proceed through varied mechanisms such as external mass transfer of solute, intraparticle diffusion, and adsorption at sites. Unless extensive data are available, it is impossible to predict the rate-determining step involved in the process. However, sorption isotherm equations, which explain the process at equilibrium conditions, provide an easier solution to this complex problem. No matter how many components are present in the system, the biosorption equilibria of pure components are the essential ingredient for understanding how many of those components can be accommodated by a biosorbent. Therefore, the most appropriate way to design and assess the performance of the sorption systems is to have an idea on sorption isotherms. The Langmuir and Freundlich models (two-parameter models) are the most commonly used isotherms. Simplicity and easy interpretability are some of the important reasons for the extensive use of these models. Moreover, linear regression has been frequently used to evaluate the model parameters. However, transformations of nonlinear isotherm equations to linear forms usually result in parameter estimation error and distort the fit.[6,7] Thus, nonlinear methods would be a better way to obtain the equilibrium isotherm parameters. Most of the published literature has used two or three isotherm models, mainly Freundlich, Langmuir, and Dubinin–Radushkevich. In the present work, an attempt has been made to test most of the available isotherm models with the sorption data obtained. Considering these, the efficacy of *Lobophora variegata* for the removal of Cd(II) and Pb(II) was assessed using the best fit of the one-parameter model, Henry's law;[8] the two-parameter models, namely, linear with intercept, Freundlich,[9] Langmuir,[10] modified Langmuir,[11] Elovich,[12] Temkin,[13] Dubinin–Radushkevich (D−R),[14] and Halsey;[15] the three-parameter models, namely, Redlich−Peterson,[16] Sips,[17] Khan,[18] Fritz−Schluender,[19] Radke−Prausnitz,[20] Toth,[21] and Koble−Carrigan;[22] the four-parameter models, Fritz−Schluender[19] and Baudu;[23] and a five-parameter model, Fritz and Schluender[19] isotherms in their nonlinear form.

Experimental Section

Materials. The chemicals used in this study were of analytical reagent grade. The stock solution of Cd(II) and Pb(II) (10 $\text{mmol}\cdot\text{L}^{-1}$ for each ion) was prepared by dissolving a weighed quantity of the respective nitrate salts in double distilled water. The concentrations of metal solutions ranged from (0.5 to 5.5) $\text{mmol}\cdot\text{L}^{-1}$. Before mixing with the biosorbent, the pH of each solution was adjusted to the appropriate value for the sorption of Cd(II) and Pb(II) ions by adding 0.1 M NaOH or 0.1 M HNO_3.

Preparation of the Biosorbent. The brown alga *Lobophora variegata* was collected from Okha port (Latitude 22°28.580'N, Longitude 69°04.254'E), Arabian Sea, India. The alga was washed twice with running tap water and five times with deionized water. The washed biomass was oven-dried at 60 °C

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10.1021/je700547j CCC: $40.75

for 24 h, crushed with an analytical mill, sieved (size fraction of (300 to 600) μm), and stored in polyethylene bottles for use. The raw biomass was chemically modified by a pretreatment with $CaCl_2$. A sample of 20 g of dried biomass was treated with 0.2 M $CaCl_2$ solution (400 mL) for 24 h under slow stirring (150 rpm). The solution pH was kept constant at pH 5.0. The calcium-treated biomass was repeatedly washed with deionized water to remove excess calcium from the biomass. The biomass was then heated in an oven at 60 °C for 24 h and sieved for particle size of (300 to 600) μm.[24]

Biosorption Experiments and Analytical Method. All the experiments were conducted at a constant temperature of (25 ± 2) °C to cater to environmentally relevant conditions. Batch equilibrium biosorption experiments were carried out in 250 mL Erlenmeyer flasks containing cadmium and lead nitrate solutions (100 mL) of known concentrations which varied from (0.5 to 5.5) $\text{mmol}\cdot\text{L}^{-1}$. Weighed amounts of biomass (200 mg) were added to each flask, and the mixtures were agitated on a rotary shaker. The pH solution was adjusted to the required value (5.0) by using HNO_3 or NaOH. After 6 h of agitation, the solution was separated from the biomass by membrane filtration (Millipore 0.45 mm pore size), and the filtrates were analyzed by atomic absorption spectroscopy (AA-680, atomic absorption/flame emission spectrophotometer, Shimadzu) for Cd(II) and Pb(II) ions. All the instrumental conditions were optimized for maximum sensitivity as specified by the manufacturer.

All the biosorption experiments were repeated twice to substantiate the results. The data shown are the mean values of two replicate determinations.

Metal Uptake Capacity. The amount of metal sorbed at equilibrium, q_e ($\text{mmol}\cdot\text{g}^{-1}$), which represents the metal uptake, was calculated from the difference in metal concentration in the aqueous phase before and after biosorption, as per the following equation

$$q_e = \frac{V(C_i - C_e)}{W} \tag{1}$$

where V is the volume of metal solution (L); C_i and C_e are the initial and equilibrium concentration of metal in solution ($\text{mmol}\cdot\text{L}^{-1}$), respectively; and W is the mass of dry seaweed (g).

Nonlinear Regression Analysis. All the model parameters were evaluated by nonlinear regression using the DATAFIT software (Oakdale Engineering, USA). The optimization procedure required an error function to be defined to be able to evaluate the fit of the equation to the experimental data.[25,26] Apart from the regression coefficient (R^2), the residual or sum of square error (SSE) and the standard error (SE) of the estimate were also used to gauge the goodness-of-fit. SSE can be defined as

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

SE can be defined as

$$\text{SE} = \sqrt{\frac{1}{m-p}\sum_{i=1}^{m}(Q_i - q_i)^2} \tag{3}$$

where q_i is the observation from the batch experiment i; Q_i is the estimate from the isotherm for corresponding q_i; m is the number of observations in the experimental isotherm; and p is the number of parameters in the regression model. The smaller SE and SSE values indicate the better curve fitting.

Results and Discussion

Biosorption equilibrium data are generally represented in the form of isotherm models. The existing sorption isotherm models are based on different theoretical assumptions and consist of a different number of constants. To compare the applicability of these models to describe the biosorption equilibrium, the common basis could be the number of parameters in a model because some isotherm models, for example, Langmuir, can be derived using more than one theoretical approach.[8,27] Applicability of models having the same number of parameters would provide theoretical insight rather than a mere comparison of model fitting. Therefore, in the present study, models have been grouped on the basis of number of parameters. Nineteen models have been analyzed. Out of 19, one model, Henry's Law, has one parameter; eight models have two; five models have three; two models have four; and one model has five parameters (provided as Supporting Information). The batch experimental data (provided as Supporting Information) on equilibrium studies for the biosorption of Cd(II) and Pb(II) onto both raw and treated biomass of *L. variegata* were tested to fit the above equilibrium models.

One- and Two-Parameter Models. Among the isotherm models considered in the present study, Henry's law is the simplest one having only one parameter and has been successfully applied in many cases.[8,28] The Henry law model was applied to describe the experimental data obtained for the sorption of Cd(II) and Pb(II) onto *L. variegata*. The values of R^2, SE, and SSE indicate that this model completely fails to predict the equilibrium isotherm (Table 1). This may be due to the unavailability of sorption data in the lower range of metal concentration. In liquid-phase sorption, the equilibrium sorption data are generally obtained at higher equilibrium concentrations, where the sorbent surface is almost at the verge of saturation. Therefore, the present study supports the fact of the failure of Henry's law at the high residual solute concentration range. However, high concentrations may suggest the applicability of a model having a linear relationship between q_e and C_e at the latter part of the equilibrium isotherm curve. This requirement may be partly fulfilled using the "linear with intercept" model, i.e., Henry's law equation with a constant term. The addition of a constant term in Henry's law allows the model to incorporate the basic characteristics of the equilibrium isotherm curve at the high concentration range. A comparison of regression parameters revealed the improvement in R^2 and lower SE and SSE values by linear with intercept over Henry's law. An increase in the parameter in the isotherm model definitely improved the capability of modeling the experimental data. However, this capability may also be improved by providing a new placement of the model constant and dependent variables in the equation, keeping the degree of freedom the same. In this regard, the applicability of the other two parameter models was studied.

The Freundlich isotherm was originally empirical in nature but was later interpreted as sorption to heterogeneous surfaces or surfaces supporting sites of varied affinities and has been used widely to fit experimental data of liquid-phase sorption, whereas the Langmuir isotherm model is an analytical equation basically developed for gas-phase adsorption on homogeneous surfaces of glass and metals and predicts a single maximum binding capacity.[8–10,29] The value of n, of the Freundlich model, falling in the range of 1 to 10, indicates favorable sorption, while K_L of the Langmuir model is a coefficient attributed to the affinity between the sorbent and sorbate.[10,30] Model fits for both Langmuir and Freundlich isotherms along with experimental

Table 1. Isotherm Constants for One- and Two-Parameter Models for Cd^{2+} and Pb^{2+} Biosorption on Biomass of *Lobophora variegata*

	raw biomass		treated biomass	
models	Cd^{2+}	Pb^{2+}	Cd^{2+}	Pb^{2+}
Henry's Law				
K_{HE}	0.2921	0.3466	0.3190	0.3676
R^2	0.8479	0.8104	0.8670	0.8643
SE	1.1961	1.1794	1.1975	1.1171
SSE	1.3846	1.3225	1.4951	1.3706
Linear with Intercept				
a	0.3680	0.3728	0.3330	0.3706
b	0.2907	0.1004	0.3190	0.3676
R^2	0.9278	0.9171	0.9694	0.9644
SE	0.1424	0.1820	0.0990	0.1233
SSE	0.1825	0.2983	0.0882	0.1368
Freundlich				
K_F ($L \cdot g^{-1}$)	0.2938	0.4547	0.4251	0.4683
n	1.2738	1.0309	1.1002	1.1022
R^2	0.9061	0.9288	0.9489	0.9722
SE	0.1906	0.1059	0.0711	0.0485
SSE	0.1455	0.0561	0.0303	0.0141
Langmuir				
q_m ($mmol \cdot g^{-1}$)	2.8652	2.8050	2.3140	2.6040
K_L ($L \cdot mmol^{-1}$)	0.1572	0.1061	0.0978	0.0669
R_L	0.7608	0.8249	0.8364	0.9863
R^2	0.9819	0.9747	0.9903	0.9907
SE	0.0362	0.0586	0.0306	0.0352
SSE	0.0118	0.0310	0.0085	0.0111
Modified Langmuir				
K_L ($L \cdot mmol^{-1}$)	0.00036	0.00056	0.00175	0.00159
n_L	−1.2149	−1.1389	−0.9190	−1.0114
R^2	0.8471	0.9098	0.9667	0.9639
SE	0.2072	0.1899	0.1033	0.1242
SSE	0.3866	0.3246	0.0961	0.1389
Elovich				
K_E ($L \cdot mmol^{-1}$)	1.0001	1.0044	0.9673	1.0025
q_m ($mmol \cdot g^{-1}$)	1.0006	1.0022	0.9836	1.0012
R^2	0.8479	0.8104	0.8670	0.8643
SE	0.2192	0.2007	0.1090	0.1309
SSE	0.3846	0.3225	0.0951	0.1372
Temkin				
K_T ($L \cdot mmol^{-1}$)	2.3795	1.7663	1.8246	1.6509
$-\Delta H$ ($kJ \cdot mol^{-1}$)	−3.7462	−3.1876	−3.6749	−3.1107
R^2	0.9798	0.9611	0.9737	0.9639
SE	0.1062	0.1659	0.2012	0.1919
SSE	0.1016	0.2478	0.3645	0.3315
Dubinin–Radushkevich				
B ($mol^2 \cdot kJ^{-2}$)	0.4862	0.6436	0.7393	0.7592
q_m ($mmol \cdot g^{-1}$)	2.5933	3.1616	3.1256	3.5745
R^2	0.9815	0.9715	0.9409	0.9824
SE	0.0720	0.1066	0.1377	0.0865
SSE	0.0467	0.1023	0.1706	0.0674
Halsey				
K_H ($L \cdot g^{-1}$)	$1.54 \cdot 10^{46}$	$1.32 \cdot 10^{49}$	$1.75 \cdot 10^{62}$	$1.51 \cdot 10^{70}$
n_H	693.60	756.26	867.62	1516.22
R^2	0.00	0.00	0.00	0.00
SE	0.5315	0.6529	0.7265	0.6549
SSE	2.5426	3.1649	4.6972	3.8602

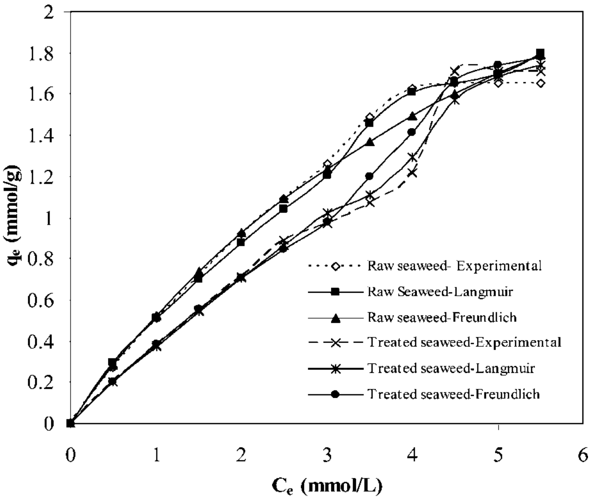

Figure 1. Langmuir and Freundlich isotherms obtained for the biosorption of Cd(II) onto both raw and treated biomass of *L. variegata*.

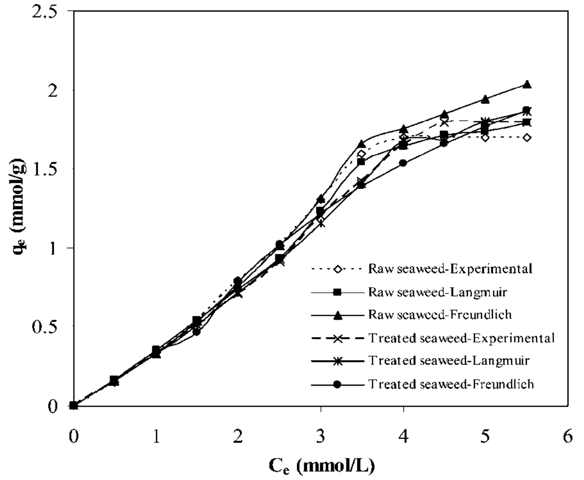

Figure 2. Langmuir and Freundlich isotherms obtained for the biosorption of Pb(II) onto both raw and treated biomass of *L. variegata*.

data for Cd(II) and Pb(II) are presented in Figures 1 and 2, respectively. The values of model constants along with the corresponding correlation coefficient, R^2, SE, and SSE values for all biosorbent−metal systems are presented in Table 1. For the Freundlich equation, R^2 varied from 0.9061 to 0.9722, and for Langmuir, it varied from 0.9747 to 0.9907. Statistically, the Langmuir model provided a good fit to the experimental data with low SE and SSE values as compared to the Freundlich model. The Freundlich model accounts for the surface heterogenity; however, the surface heterogeneity parameter in the Freundlich equation does not provide any significant improvement in model performance. The Freundlich model predicts that the metal concentration on the adsorbent will increase as long as there is an increase in the metal concentration in the liquid phase. However, the experimental evidence indicates that an isotherm plateau is reached at a limiting value of the solid-phase concentration. This plateau is not predicted by the Freundlich equation. Thus, in all of the cases, the Langmuir model provided a good fit as compared to the Freundlich model. Moreover, the separation factor (R_L) values in the case of the Langmuir model indicated (Table 1) that metal sorption onto *L. variegata* was favorable.

The modified Langmuir equation describes temperature-dependent saturation coverage (T^{-n_L}) and has never been applied to liquid-phase sorption.[31] However, the modified Langmuir equation provided a satisfactory fit with R^2 values ranging from 0.8471 to 0.9667. The value of the exponent term, n_L, is negative for all systems. This indicated that metal sorption could be favored at high temperature. Therefore, the mechanism of the sorption process could be endothermic in nature. The increase in the sorption of metals with temperature indicated that sorption was due to the combination of physical, chemical, and ion-exchange processes.[32] The negative value of n_L is indicative of the involvement of several mechanisms in the sorption of Cd(II) and Pb(II). Therefore, for liquid-phase sorption, the modified Langmuir equation provided a satisfactory fit. However, the modified Langmuir equation did not provide any significant improvement as compared to the Langmuir equation.

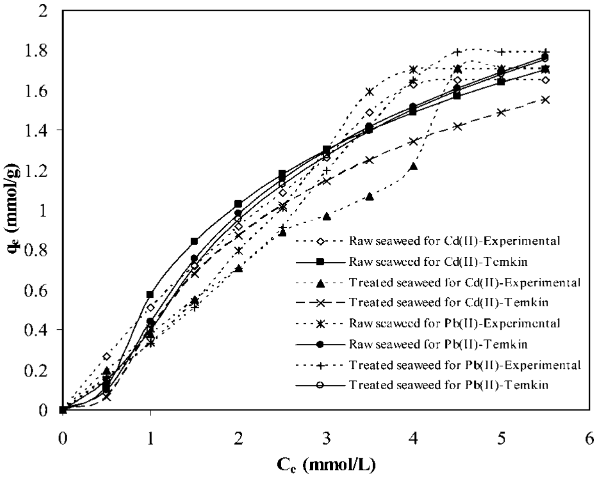

Figure 3. Temkin isotherm obtained for the biosorption of Cd(II) and Pb(II) onto both raw and treated biomass of *L. variegata*.

The Elovich isotherm constants, K_E and q_m, as well as the coefficient of correlation, R^2, SE, and SSE values are presented in Table 1. In all cases, the Elovich isotherm exhibited lower coefficients of correlation, but higher than those obtained with the Halsey model. Also, the values of maximum biosorption capacity determined (Table 1) are lower than the experimental biosorbed amounts at equilibrium corresponding to the plateaus of the sorption isotherms. Therefore, the Elovich model is unable to describe the biosorption isotherms of Cd(II) and Pb(II) onto *L. variegata*.

The parameters of the Temkin model as well as the nonlinear correlation coefficients (R^2) with SE and SSE values are given in Table 1. Figure 3 shows the theoretical plots of this isotherm compared with the experimental data. The higher values of R^2 (0.9611 to 0.9798) show a satisfactory fit to the experimental data. The variation of adsorption energy, $\Delta Q = (-\Delta H)$, is negative for all the studied systems, which indicated that the biosorption reaction is endothermic.

The liquid-phase biosorption of Cd(II) and Pb(II) onto *L. variegata* has been analyzed by the Dubinin–Radushkevich equation. The isotherm constants along with the statistical parameters are presented in Table 1. In all cases, the values of the correlation coefficients (0.9409 to 0.9824) are lower than the Langmuir model but higher than all other two-parameter models.

The multilayer sorption is generally described by the Hasley model.[13] The present experimental data give poor fit as evidenced by zero correlation coefficients and high SSE and SE values.

It can be observed from the above discussion that the predicted Langmuir isotherm curve fits best, followed by the Temkin and Freundlich models. Upon comparing all the isotherm models, the isotherm curve predicted by the Langmuir model coincides with the experimental curve with a high correlation coefficient and low SSE and SE values.

Three-Parameter Models. The abilities of the three-parameter equations, Redlich−Peterson, Sips, Khan, Fritz−Schluender, Radke−Prausnitz (two models), Toth, and Koble−Carrigan isotherms, to model the equilibrium biosorption data were examined. These models can be classified into two categories. The first category includes models that express the sorption capacity, q_m as an implicit function of the equilibrium concentration (Khan, Fritz−Schluender, Toth, Koble−Carrigan), while the second category consists of models that express the sorption capacity as an explicit function of the equilibrium concentration (Sips, Radke−Prausnitz). It is also important to note that the models considered in the first group are empirical in nature, while the second group is based on thermodynamic considerations. Table 2 shows the isotherm parameters obtained using nonlinear fitting analysis.

Among the isotherm models having three parameters, the Redlich−Peterson model has been the most frequently employed in liquid-phase sorption of heavy metals and organic compounds.[6,32,33] It incorporates the features of the Langmuir and Freundlich isotherms into a single equation. There are two limiting behaviors: the Langmuir form for $\beta = 1$ and Henry's law form for $\beta = 0$. In the present study, the Redlich−Peterson equation has established its capability to fit the experimental data satisfactorily ($R^2 = 0.9708$ to 0.9787). However, it does not provide any improvement over the Toth model (Table 2). The β values ranged from 0.57 to 0.72; i.e., the data can preferably be fitted with the Langmuir model. This is confirmed by the satisfactory fit of the data to the Langmuir model.

At low sorbate concentrations, the Sips isotherm[17] 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. The Sips equation adequately fits the experimental results. The exponent γ value was in the range of 0.8476 to 0.9817, meaning that the sorption data obtained in this study are more of a Langmuir form rather than that of Freundlich, which was also confirmed by the results shown in Table 1.

Though the R^2 values of the Khan and Fritz−Schluender models were satisfactory (0.9508 to 0.9707 and 0.9690 to 0.9870, respectively), the predicted values of q_m by both the models do not match the experimental data (Table 2). Therefore, these models are unable to fit the experimental data compared to other three-parameter models. Similarly, in spite of the good coefficients of correlation (≥ 0.9508) and low SE (≤ 0.1771) and SSE (≤ 0.1487) values, the maximum sorption capacities for the studied metals determined using the three-parameter equations of Radke−Prausnitz (Table 2) were either lower or higher than the biosorbed amounts at equilibrium corresponding to the plateaus of the isotherms. For the Pb(II)-raw biomass system, the maximum biosorption capacity obtained by the model of Radke−Prausnitz-II is abnormally high and inadmissible. Consequently, the two equations of Radke−Prausnitz cannot describe the experimental equilibrium data.

The Toth model correctly simulates the biosorption isotherms of the studied metals (Figure 4). The coefficients of correlation are good ($R^2 \geq 0.9902$) for all the tested systems. The SE and SSE values lie between 0.0454 and 0.1074 and 0.0154 and 0.0924, respectively. The biosorption maximum capacities determined using the Toth model were comparable to experimental data and lower than those for the Langmuir model. The order of the equilibrium constant b_T is similar to that of the parameter K_L of Langmuir. The same order as that of the equilibrium constant b_T is obtained for the parameter n_T. Hence, this model is precise for the experimental data among the three-parameter models.

The Koble−Carrigan[22] model is essentially a Freundlich isotherm that approaches a sorption maximum at high concentrations of sorbate, and this model is valid when $n > 1$. This isotherm showed a poorer fit than the other three-parameter models as evidenced by the low correlation coefficient and high SSE and SE values.

The results obtained using the three-parameter equations show that the best-fitted biosorption isotherm models were determined to be in the order: Toth > Sips > Redlich−Peterson.

Table 2. Isotherm Constants for Three-, Four-, and Five-Parameter Models for Cd^{2+} and Pb^{2+} Biosorption on Biomass of *Lobophora variegata*

	raw biomass		treated biomass	
models	Cd^{2+}	Pb^{2+}	Cd^{2+}	Pb^{2+}
Redlich−Peterson				
K_{RP} (L·g^{-1})	6.4418	1.8894	1.6463	1.7504
a_{RP} (L·mmol^{-1})	0.4673	0.1276	0.1206	0.1174
β	0.7214	0.6282	0.6389	0.5781
R^2	0.9711	0.9708	0.9787	0.9722
SE	0.0259	0.0356	0.0617	0.0382
SSE	0.0040	0.0076	0.0228	0.0879
Sips				
K_S (L·g^{-1})	0.6220	0.3043	0.3616	0.2987
a_S (L·mmol^{-1})	0.2636	0.1484	0.1471	0.0323
γ	0.9881	0.9654	0.8476	0.8570
R^2	0.9747	0.9817	0.9693	0.9865
SE	0.0694	0.0905	0.1051	0.0080
SSE	0.0386	0.0656	0.0884	0.0516
Khan				
q_m (mmol·g^{-1})	12.806	198.274	0.4164	39.1245
b_K (L·mmol^{-1})	0.0486	0.0026	0.8154	0.0108
a_K (L·g^{-1})	2.8282	29.2941	0.0827	03.0498
R^2	0.9525	0.9508	0.9688	0.9707
SE	0.0742	0.1487	0.1059	0.1187
SSE	0.0441	0.1771	0.0898	0.1129
Fritz−Schluender				
q_{mFS} (mmol·g^{-1})	0.0126	0.0020	0.5556	0.8526
K_{FS}	39.7582	224.729	0.5953	82116.03
m_{FS}	2.2977	3.1261	0.0955	6.2686
R^2	0.9823	0.9729	0.9690	0.9870
SE	0.0493	0.1103	0.1056	0.0790
SSE	0.0194	0.0974	0.0893	0.0499
Raadke−Prausnitz-I				
a_{RI} (mmol·g^{-1})	0.4027	0.4268	5.4210	0.4027
r_{RI} (L·mmol^{-1})	22123	129655	0.3889	22123
α_{RI}	−4.4798	−5.8806	0.9349	−4.4752
R^2	0.9857	0.9847	0.9690	0.9857
SE	0.0828	0.0827	0.1056	0.0828
SSE	0.0549	0.0547	0.0892	0.0549
Raadke−Prausnitz-II				
a_{RII} (mmol·g^{-1})	12.806	198.272	0.4616	39.121
r_{RII} (L·mmol^{-1})	0.0486	2.5947	0.8154	0.0108
α_{RII}	2.8285	29.2941	0.0827	3.0498
R^2	0.9725	0.9508	0.9688	0.9707
SE	0.0742	0.1771	0.1059	0.1187
SSE	0.0441	0.1487	0.0898	0.1129
Toth				
q_m (mmol·g^{-1})	1.674	1.7061	1.7959	1.8157
b_T (L·g^{-1})	0.1497	0.1059	0.1003	0.0724
n_T	0.4805	0.4759	0.5276	0.6813
R^2	0.9938	0.9993	0.9985	0.9902
SE	0.04539	0.0693	0.1074	0.0686
SSE	0.0154	0.0384	0.0924	0.0377
Koble−Carrigan				
A_{KH} (mmol·g^{-1})	2.3594	2.0501	3.9621	2.6044
B_{KH} (L·g^{-1})	0.2636	0.1484	0.0090	0.1147
n_{KH}	1.3881	2.2654	0.9646	1.8476
R^2	0.8847	0.8817	0.8689	0.8865
SE	0.1694	0.1905	0.2059	0.2803
SSE	0.3862	0.5328	0.7898	0.8516
Fritz−Schluender (Four-Parameter)				
A	0.4979	0.3157	1.1269	1.9786
B_{FS}	0.1526	0.1088	0.1002	0.0673
α	0.8860	0.8682	0.9389	0.7244
β_{FS}	0.9431	0.9412	0.8031	0.8425
R^2	0.9976	0.9945	0.9939	0.9967
SE	0.0309	0.0443	0.1129	0.0425
SSE	0.0066	0.0137	0.0892	0.0126
Baudu				
q_{mo} (mmol·g^{-1})	8.4159	24.6869	0.7663	13.206
b_o	0.0605	0.0117	0.9001	0.0206
x	0.7593	1.9123	−0.9999	1.4013
y	−0.5827	−1.2914	0.9389	−0.8034
R^2	0.9892	0.9836	0.9690	0.9813
SE	0.0623	0.0572	0.1129	0.0688
SSE	0.0272	0.0229	0.0892	0.0332
Fritz−Schluender (Five-Parameter)				
α_1	1.7878	1.5708	1.8565	2.5018
α'_1	3.5908	4.9754	1.0384	7.9462
α_2	0.00018	0.00441	0.00324	0.00842
β_1	0.8860	0.8686	0.9398	0.7445
β_2	0.9432	0.9413	0.9392	0.9476
R^2	0.9973	0.9971	0.9960	0.9978
SE	0.0334	0.0479	0.0129	0.0374
SSE	0.0066	0.0137	0.0492	0.0084

Four- and Five-Parameter Models. The biosorption data were analyzed according to the nonlinear form of the four-parameter isotherm models. An excellent fitting of the experimental results of adsorption isotherms is obtained using the four-parameter model of Fritz−Schluender (Figure 5). From Table 2, the coefficients of correlation (≥ 0.9939) were very good, and the SE and SSE values were in the range of 0.0309 to 0.1129 and 0.0066 to 0.0892, respectively. The values of α and β_{FS} for all the tested systems approach unity; i.e., the data can preferably be fitted with the Langmuir model. An agreement has also been noticed between the B_{FS} and the Langmuir constant K_L.

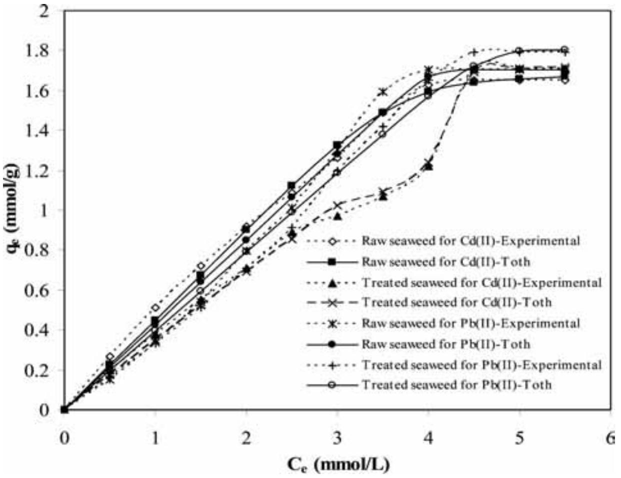

Figure 4. Toth isotherm obtained for the biosorption of Cd(II) and Pb(II) onto both raw and treated biomass of *L. variegata.*

The calculated parameters of equilibrium biosorption isotherms of Cd(II) and Pb(II) on both raw and treated biomass by the Baudu model are given in Table 2. An appropriate fit was obtained using the model of Baudu. However, the values of the maximum biosorption capacity obtained using the Baudu isotherm were very much higher or lower than the experimental results. Therefore, this model cannot describe the experimental data in spite of satisfactory R^2 and low SE and SSE values.

The biosorption data were analyzed according to the nonlinear form of the five-parameter isotherm model of Fritz−Schluender. An accurate fitting of the experimental results of the biosorption

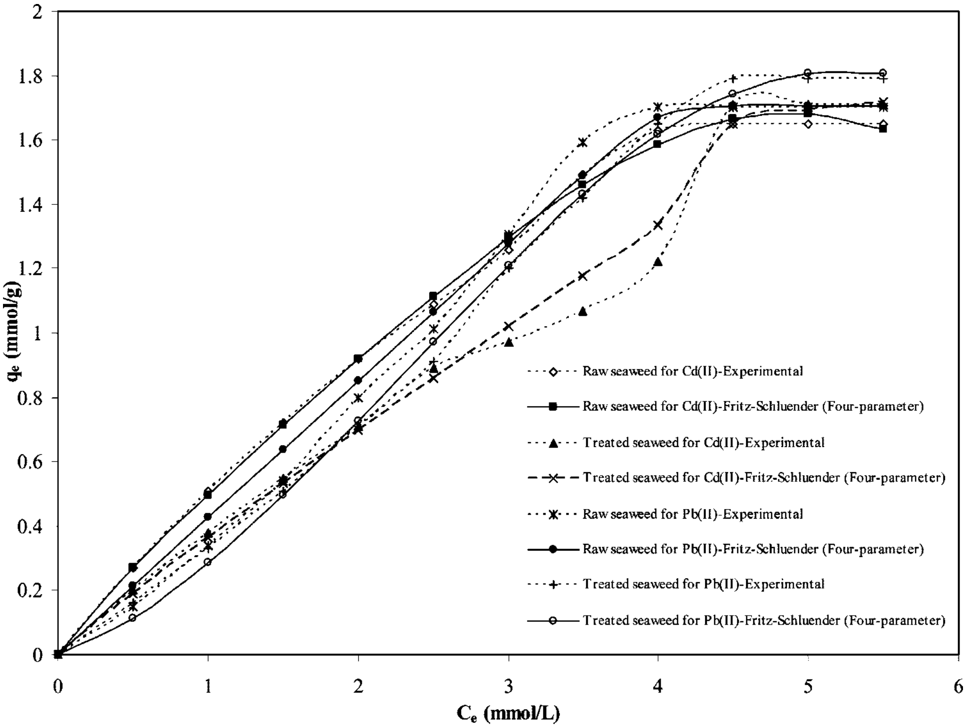

Figure 5. Fritz−Schluender (three-parameter) isotherm obtained for the biosorption of Cd(II) and Pb(II) onto both raw and treated biomass of *L. variegata*.

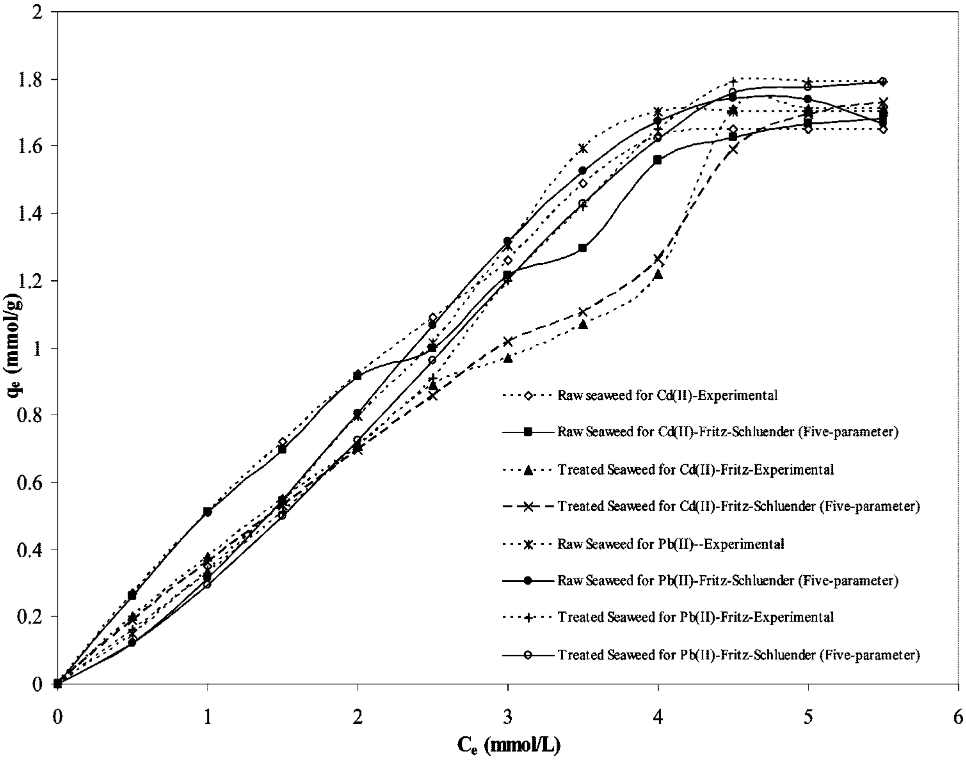

Figure 6. Fritz−Schluender (five-parameter) isotherm obtained for the biosorption of Cd(II) and Pb(II) onto both raw and treated biomass of *L. variegata*.

isotherms is obtained using the five-parameter model of Fritz−Schluender (Figure 6). From Table 2, high correlation coefficients (≥ 0.9960) and low SE (≤ 0.1219) and SSE (≤ 0.0137) values were obtained for the studied systems. The values of the maximum biosorption capacity obtained using the Fritz−Schluender equation are higher than those calculated by the Toth model and lower than the Langmuir model. The five-parameter model of Fritz−Schluender is reduced to the Langmuir model when the exponents β_1 and β_2 are equal to unity. This model is empirical in nature with a larger number of constants. The increased number of constants would be able to simulate the model variations more accurately. In the case of biosorptive processes, the factors affecting sorption are large. So, in the absence of a theoretical model that could account for the chemical heterogeneity of the surface and simultaneous prevalence of different sorption mechanisms, probably an isotherm model having a greater number of model constants should be able to predict better. In the present study, this is observed. However, the Fritz−Schluender model is mathematically more complex, and its solution requires the application of nonlinear regression techniques. Thus, limiting the routine application of the model may not be widely practiced.

Conclusions

Biosorption isotherms of Cd(II) and Pb(II) on both raw and treated biomass of *L. variegata* were studied and modeled using 19 well-known isotherm models. Out of the 19 isotherm models, some models are based on well-established theoretical concepts, and their application indicates the types of sorption mechanisms in operation during biosorptive uptake of Cd(II) and Pb(II). Most of the models having two or more parameters, namely, Langmuir, Freundlich, modified Langmuir, Temkin, Freundlich, Toth, Sips, Redlich−Peterson, and Fritz−Schluender, could predict the sorption equilibrium well, with a varying degree of correlation. Among the two-parameter models, the predicted Langmuir isotherm curve fits better followed by Temkin and Freundlich. The classification of the three-parameter models according to the simulation of the biosorption isotherms was: Toth > Sips > Redlich−Peterson. The four-parameter equation of Fritz−Schluender simulates well the experimental results, but the equation of Toth (three-parameter) was better. Among all the tested equations, an excellent and perfect representation of the experimental results was obtained using the five-parameter equation of Fritz−Schluender. The present study shows that the adjustment of more parameters makes possible a better fitting of the equilibrium isotherms. However, the mode of covering of the sorption sites on the biosorbent surface is not possible by the models with more than two parameters owing to the fact that they do not adapt a thermodynamic model such as those of Langmuir or Elovich. Therefore, on the basis of Ockham's razor approach, it could be concluded that the Langmuir model provides a suitable description of the experimental data.

Acknowledgment

The authors acknowledge the kind support of Dr. P. K. Ghosh, Director, CSMCRI during the course of the study.

Supporting Information Available:

Tables related to various isotherm models and a figure related to an experimental sorption isotherm for Cd(II) and Pb(II). This material is available free of charge via the Internet at http://pubs.acs.org.

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Received for review September 21, 2007. Accepted November 16, 2007. The financial support received from GSBTM, Department of Science and Technology, Govt of Gujarat, and Ministry of Earth Sciences, Govt of India, for carrying out this project is thankfully acknowledged.

JE700547J