Isotherm Modeling for Biosorption of Cu(II) and Ni(II) from Wastewater onto Brown Seaweed, *Cystoseira indica*

Shaik Basha
Marine Biotechnology and Ecology Div., Central Salt and Marine Chemicals Research Institute, Council of Scientific and Industrial Research, Bhavnagar 364002, Gujarat, India, and
Dept. of Chemical Engineering, S. V. National Institute of Technology Surat, Surat 395007, Gujarat, India

Z. V. P. Murthy
Dept. of Chemical Engineering, S. V. National Institute of Technology Surat, Surat 395007, Gujarat, India

B. Jha
Marine Biotechnology and Ecology Div., Central Salt and Marine Chemicals Research Institute, Council of Scientific and Industrial Research, Bhavnagar 364002, Gujarat, India

DOI 10.1002/aic.11606
Published online September 26, 2008 in Wiley InterScience (www.interscience.wiley.com).

The biosorption equilibrium isotherms of Cu(II) and Ni(II) from wastewater onto marine brown algae Cystoseira indica, which was chemically modified by various methods were studied and modeled. To predict the biosorption isotherms and to determine the characteristic parameters for process design, 21 one-, two-, three-, four-, and five-parameter isotherm models were applied to experimental data. The interaction among biosorbed molecules is repulsive and there is no association between them, and 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 *(0.9899–0.9976), low standard error (0.1202–0.0144), and sum of square error (0.0144–0.0495) 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) > Langmuir (two-parameter) > Radke-Prausnitz-II (three-parameter) > Fritz-Schluender (four-parameter) > Temkin (two-parameter).* © 2008 American Institute of Chemical Engineers *AIChE J,* 54: 3291–3302, 2008

Keywords: Cystoseira indica, biosorption, isotherm models, copper, nickel

Introduction

The presence of toxic heavy metals in water, resulting from rapid industrialization and technological advances, poses serious threat to human health and the environment, even at very low concentrations.[1,2] Environmental/chemical engineers and scientists are faced with the challenging task to develop appropriate low cost technologies for effluent

Additional Supporting Information may be found in the online version of this article.

Correspondence concerning this article should be addressed to Z. V. P. Murthy at zvpm2000@yahoo.com.

treatment. Recently, increasing interest in the application of biomass of diverse origin in heavy metals removal from various industrial effluents or water resources has been observed. Sorption with biomaterials has become an alternative to traditional methods of industrial wastewaters treatment, such as precipitation, adsorption, coagulation, etc and is relatively inexpensive, nonhazardous and may permit recovery of the metals from the sorbing biomass.[3–5] Several researchers investigated numerous biomass types and proposed excellent metal biosorbents including bacteria, fungi, algae, industrial wastes, etc.[5,6] However, the research and development of new biosorbent materials has focused especially on algae because of its high sorption capacity and its availability in almost unlimited amounts.[7]

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 the understanding of how many those components can be accommodated by a biosorbent. Therefore, the most appropriate way, in designing and assessing the performance of the sorption systems is to have an idea on sorption isotherms. Langmuir and Freundlich models (two-parameter models) are the most commonly used isotherms. Simplicity and easy interpretability are some of the important reasons for 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.[8,9] Thus, nonlinear methods would be a better way to obtain the equilibrium isotherm parameters. Most of the published literatures have used two or three isotherm models, mainly Freundlich, Langmuir, Dubinin-Radushkevich only. In this work, an attempt has been made to test most of the available isotherm models with the biosorption data obtained. Considering these, the efficacy of various forms of *Cystoseira indica* for the removal of Cu(II) and Ni(II) was assessed using the best fit of one-parameter model, Henry's law[10]; two-parameter models namely, Linear with intercept, Freundlich,[11] Langmuir,[12] modified Langmuir-1,[13] modified Langmuir-2,[14] Elovich,[15] Temkin,[16] Dubinin-Radushkevich (D-R),[17] Fowler and Guggenheim,[18] and Halsey[19]; three-parameter models namely, Redlich-Peterson,[20] Sips,[21] Khan,[22], Fritz-Schluender,[23] Radke-Prausnitz,[24] Toth,[25] and Koble-Carrigan[26]; four-parameter models, Fritz-Schluender[23] and Baudu[27]; and a five-parameter model, Fritz and Schluender[23] isotherms in their nonlinear form.

Materials and Methods

Reagents

All reagents used in this study were of analytical grade and Conc. HNO_3, Conc. HCl, and NaOH were obtained from Merck. All glassware and polypropylene flasks used were overnight immersed in 10% (v/v) HNO_3 and rinsed several times with distilled deionized water. For adjusting the pH of the medium 0.1 N solutions of NaOH and HCl were used.

Biomass and chemical modification

The brown alga *Cystoseira indica* was collected from the Saurashtra coast of Gujarat (Veraval), India and its dried biomass (designated as the raw biomass, RB) was subjected to various chemical treatments. The chemical modification of *C. indica* was carried out by the procedure reported elsewhere.[28] The biomasses CB1 and CB2 were obtained by cross-linking the RB with epichlorohydrin followed by washing with 70 and 20% aqueous 2-propanol, respectively. Another biomass, CB3 was obtained by oxidizing RB by potassium permanganate.[28,29] The surface area, pore volume, and pore size of various forms of *C.indica* were previously reported.[28]

Wastewater samples

The wastewater samples were collected from a metallurgical industry located in an industrial zone of Bharuch, Gujarat state, India. Triplicate samples were collected in polyethylene bottles and placed in a cooler for transportation to research laboratory. Metal species in the samples were identified and their initial concentrations determined using inductively coupled plasma atomic emission spectrometry (ICP-AES) before the biosorption cycles were initiated. They contained Cu, Ni, Cd, and Cr at 1305 ± 13.75, 1072 ± 6.58, 0.615 ± 0.02, and 0.917 ± 0.014 mg/L, respectively, with pH 0.9 ± 0.1. Because the wastewater had very high concentrations of copper and nickel, appropriate dilutions were made before use to the working range of these metals and also to ensure the other metals in below detectable range.

Sorption experiments and analytical method

All the experiments were conducted at a constant temperature of $25 \pm 1^{\circ}C$ to be representative of environmentally relevant conditions. Batch equilibrium sorption experiments were carried out in 250-mL Erlenmeyer flasks containing wastewater solutions (100 mL) of known concentrations. Known amounts of biomass (1.0 g/L) were added to each flask and the mixtures were agitated on the rotary shaker (200 rpm) at pH 6.0. The solution pH was adjusted to the required value by using HCl or NaOH. After the sorption equilibrium was reached (8 h), the solution was separated from the biomass by membrane filtration (Millipore 0.45-mm pore size) and the filtrates were analyzed by ICP-AES (ICP, Perkin–Elmer, Optima 2000) for Cu(II) and Ni(II) ions. All the instrumental conditions were optimized for maximum sensitivity as specified by the manufacturer.

All the biosorption experiments were repeated twice to confirm the results. The data were the mean values of two replicate determinations. Control experiments, processed without the addition of biosorbents, confirmed that the sorption of metals on the walls of glass flasks or in the filtration systems was negligible.

Metal uptake capacity

The amount of metal sorbed at equilibrium, q_e (mg/g) 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:

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

where, V is the volume of metal solution (L), C_i and C_e are the initial and equilibrium concentration of metal in solution (mg/L), 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 in order to be able to evaluate the fit of the equation to the experimental data.[30,31] 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:

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

SE can be defined as:

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

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 number of parameters in the regression model. The smaller SE and SSE values indicate the better curve fitting. F-ratio is the ratio of the mean square of the model to the mean square of the true error. A good model will have a high mean square for the model; therefore, the larger this ratio, the better the model "fits" the experimental data. In this study, the correlation coefficient, R^2, SE, SSE, F-ratio, and predicted q_m (wherever applicable) values are used to determine the best fit biosorption isotherm model.

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.[10,32] Applicability of models having the same number of parameters would provide theoretical insight rather than a mere comparison of model fitting. Therefore, in this study, models have been grouped on the basis of number of parameters. Twenty-one models have been analyzed (provided as Supporting Information). Out of 21 models, one model, Henry's Law has one parameter; 10 models have two; seven models have three; two models have four; and one model has five parameters. The batch experimental data (provided as Supporting Information) on equilibrium studies for the biosorption of Cu(II) and Ni(II) onto various forms of *C. indica* was tested to fit the above equilibrium models.

One- and two-parameter models

Among the isotherm models considered in this study, Henry's law is the simplest one having only one parameter and has been successfully applied in many cases.[8,28] The Henry's law model was applied to describe the experimental data obtained for the sorption of Cu(II) and Ni(II) onto *C. indica*. The values of R^2, SE, SSE, and F-ratio indicate that this model completely fails to predict the equilibrium isotherm (Tables 1 and 2). 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, this 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 provides 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, F-ratio 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 other two parameter models was studied.

The Freundlich isotherm is 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.[10–12,33] The value of n, of the Freundlich model, falling in the range of 1–10 indicates favorable sorption while K_L of Langmuir model is a coefficient attributed to the affinity between the sorbent and sorbate.[12,34] Model fits for both Langmuir and Freundlich isotherms along with experimental data for Cu(II) and Ni(II) are presented in Figures 1 and 2, respectively. The values of model constants along with the corresponding correlation coefficient, R^2, SE, SSE, and F-ratio values for all biosorbent-metal systems are presented in Tables 1 and 2. For the Freundlich equation, R^2 varied from 0.9584 to 0.9777; and for Langmuir, it varied from 0.9897 to 0.9985. Statistically, the Langmuir model provided a good fit to the experimental data with low SE, SSE, and high F-ratio values when compared with the Freundlich model. The Freundlich model accounts for the surface heterogeneity; however, the surface heterogeneity parameter in the Freundlich equation does not provide any significant improvement in model performance. The Freundlich model predicts

Table 1. Isotherm Constants for One and Two-Parameter Models for Cu^{2+} Biosorption onto *C. indica*

Models	Biomass			
	CB1	CB2	CB3	RB
	(± 95% confidence interval)			
Henry's Law				
K_{HE}	0.9075 (1.0342)	0.8374 (0.9648)	0.8733 (0.9704)	0.8812 (0.9911)
R^2	0.8702	0.8324	0.8611	0.8581
SE	7.2337	9.4553	7.9708	8.4726
SSE	261.63	447.02	317.67	338.92
F-ratio	29.919	21.122	26.129	24.806
Linear with intercept				
a	0.8842 (0.5142)	0.7564 (0.9561)	0.8480 (0.5342)	0.8665 (1.6427)
b	2.5231 (5.1421)	8.7683 (3.1467)	2.7961 (1.2647)	1.5933 (3.6742)
R^2	0.9711	0.9452	0.9622	0.9584
SE	6.9732	8.4645	7.7892	8.4339
SSE	254.29	358.30	309.01	355.96
F-ratio	134.51	69.874	101.82	92.287
Freundlich				
K_F(L/g)	1.2306 (2.0141)	1.9614 (1.4762)	1.1534 (2.0413)	1.0819 (3.1547)
n	1.0685 (2.1435)	1.2186 (1.8753)	1.0622 (2.3476)	1.0451 (1.2145)
R^2	0.9728	0.9584	0.9632	0.9592
SE	7.7269	8.2948	8.6692	9.3466
SSE	238.82	275.21	300.46	349.44
F-ratio	143.48	92.176	104.83	94.092
Langmuir				
q_m (mg/g)	143.31 (79.612)	137.17 (85.124)	132.71 (151.32)	154.54 (106.32)
K_L (L/mg)	0.0050 (1.3475)	0.0060 (0.1267)	0.0068 (0.0462)	0.0056 (1.3687)
R_L	0.03154	0.02849	0.02169	0.0426
R^2	0.9968	0.9922	0.9897	0.9955
SE	0.1089	0.1282	0.1564	0.1174
SSE	0.0320	0.0573	0.0726	0.0221
F-ratio	133.4	103.82	95.962	114.37
Modified Langmuir-1				
K_L (L/mg)	0.0036 (0.0231)	0.0056 (0.0012)	0.0017 (0.0492)	0.0016 (0.054)
n_L	−1.6121 (0.3451)	−1.4632 (3.5674)	−1.6453 (10.347)	−1.6327 (0.6791)
R^2	0.4043	0.4226	0.5467	0.5239
SE	4.2072	4.1899	3.1033	3.5242
SSE	0.3866	0.3246	0.0961	0.1389
F-ratio	2.9490	2.7568	6.2413	5.8465
Modified Langmuir-2				
η^2	128.67 (10.652)	118.97 (163.97)	123.09 (87.342)	124.62 (450.274)
K_L (L/mg)	0.0430 (1.1023)	0.0441 (2.4134)	0.0435 (1.4234)	0.0431 (0.0729)
R^2	0.7959	0.8622	0.7633	0.7658
SE	21.207	15.098	21.806	22.396
SSE	1799.06	911.83	1902.1	2006.4
F-ratio	15.578	25.029	13.191	13.084
Elovich				
K_E (L/mg)	1.3462 (0.0127)	1.3113 (0.0459)	1.3294 (3.4892)	1.3335 (5.6724)
q_m (mg/g)	1.1604 (0.0147)	1.1470 (0.1275)	1.1541 (0.6798)	1.1556 (5.3484)
R^2	0.9702	0.9324	0.9611	0.9581
SE	9.3387	12.206	10.290	10.938
SSE	261.63	447.02	317.61	358.92
F-ratio	48.984	20.705	37.101	34.312
Temkin				
K_T (L/mg)	0.0490 (0.0124)	0.0534 (0.0348)	0.0497 (0.1287)	0.0487 (0.2435)
$-\Delta H$ (kJ/mol)	−0.4032 (1.1468)	−0.4582 (5.1348)	−0.4233 (1.3472)	−0.4141 (0.9435)
R^2	0.9411	0.9693	0.9291	0.9264
SE	1.384	2.1265	2.8521	3.378
SSE	18.425	20.152	40.726	71.934
F-ratio	242.72	63.945	126.29	43.878
Dubinin-Radushkevich				
B (mol^2/kJ^2)	402.63 (10.267)	424.71 (51.087)	520.13 (100.679)	530.58 (395.13)
q_m (mg/g)	132.54 (1.3645)	122.22 (59.643)	133.81 (2.4679)	135.49 (512.367)
R^2	0.9401	0.9255	0.9681	0.9701
SE	12.280	11.096	15.119	14.280
SSE	726.36	492.55	914.44	815.75
F-ratio	33.246	48.741	31.762	36.274
Fowler–Guggenheim				
K_{FG} (L/mg)	0.2687 (5.6342)	0.3177 (0.0543)	0.2674 (2.1364)	0.2628 (2.3657)
W_{FG} (kJ/mol)	1.7524 (12.342)	1.7555 (20.314)	1.7560 (5.124)	1.7518 (0.6724)
R^2	0.6670	0.6770	0.6596	0.6518
SE	0.2500	0.2412	0.2512	0.2581
SSE	0.3569	0.1745	0.1894	0.1996
F-ratio	3.0042	3.1414	2.9070	2.8082

Table 2. Isotherm Constants for One- and Two-Parameter Models for Ni^{2+} Biosorption onto *C. indica*

Models	Biomass			
	CB1	CB2	CB3	RB
	(± 95% confidence interval)			
Henry's Law				
K_{HE}	0.9020 (0.1247)	0.8594 (0.4568)	0.8521 (2.3478)	0.8700 (1.9564)
R^2	0.8758	0.8740	0.8654	0.8630
SE	5.1999	5.1105	6.1218	6.3488
SSE	135.19	130.58	187.38	201.53
F-ratio	33.095	32.085	26.557	26.145
Linear with intercept				
a	0.8829 (0.0457)	0.8371 (2.3117)	0.8655 (1.1472)	0.8658 (5.6327)
b	1.6516 (0.0142)	1.9313 (0.3257)	1.1609 (5.6472)	0.3612 (4.5621)
R^2	0.9763	0.9749	0.9657	0.9630
SE	4.7456	4.6187	5.8159	6.0955
SSE	132.04	126.28	185.83	201.38
F-ratio	165.31	172.35	112.88	104.28
Freundlich				
K_F (L/g)	1.1593 (5.3478)	1.1491 (2.1346)	0.8063 (0.0467)	0.9373 (1.6845)
n	1.0587 (3.1645)	1.0685 (1.6759)	1.0037 (5.1672)	1.0167 (4.6732)
R^2	0.9777	0.9766	0.9665	0.9631
SE	5.5799	5.4197	6.8365	7.0853
SSE	124.54	117.49	186.95	200.70
F-ratio	175.52	167.37	124.63	104.60
Langmuir				
q_m (mg/g)	131.56 (105.624)	116.82 (167.68)	111.26 (85.624)	121.35 (201.34)
K_L (L/mg)	0.0065 (0.1435)	0.0070 (0.0723)	0.0073 (0.2671)	0.0075 (0.04629)
R_L	0.02986	0.02462	0.02213	0.0364
R^2	0.9968	0.9953	0.9908	0.9901
SE	0.1435	0.1562	0.2250	0.2721
SSE	0.0527	0.0481	0.0346	0.0422
F-ratio	125.9	118.22	105.07	98.015
Modified Langmuir-1				
K_L (L/mg)	0.0011 (1.3271)	0.0012 (0.0162)	0.0010 (1.246)	0.0016 (0.1294)
n_L	−1.2347 (0.2356)	−1.2946 (3.4134)	−1.1259 (1.5736)	−1.6294 (0.6472)
R^2	0.4453	0.4454	0.4331	0.4468
SE	0.5607	0.5598	0.5776	0.5506
SSE	1.2575	1.2539	1.3346	1.2130
F-ratio	2.9490	3.2116	3.2130	3.2095
Modified Langmuir-2				
η^2	102.33 (56.237)	97.515 (152.34)	96.492 (64.376)	98.085 (25.643)
K_L (L/mg)	0.0537 (0.2346)	0.0538 (0.6453)	0.0531 (0.6752)	0.0539 (0.1467)
R^2	0.7960	0.8002	0.7450	0.7442
SE	16.882	15.851	18.601	18.666
SSE	1140.1	1005.2	1384.6	1393.8
F-ratio	15.610	16.027	11.692	11.639
Elovich				
K_E (L/mg)	1.3436 (26.349)	1.3225 (52.643)	1.3188 (31.264)	1.3278 (10.247)
q_m (mg/g)	1.1594 (0.3642)	1.1514 (5.6715)	1.1500 (10.246)	1.1535 (0.2375)
R^2	0.9758	0.9740	0.9654	0.9630
SE	10.938	6.5976	7.9033	8.1962
SSE	135.19	130.58	187.38	201.53
F-ratio	60.514	56.304	41.966	39.062
Temkin				
K_T (L/mg)	0.0609 (1.2347)	0.0613 (0.1648)	0.0585 (2.6134)	0.0604 (1.2148)
$-\Delta H$ (kJ/mol)	−0.5055 (2.6271)	−0.5322 (0.1276)	−0.5225 (1.0249)	−0.5221 (3.6421)
R^2	0.9430	0.9450	0.9083	0.9065
SE	8.9230	8.3159	11.152	11.282
SSE	318.48	276.62	497.50	509.12
F-ratio	66.202	68.768	39.658	38.815
Dubinin-Radushkevich				
B (mol^2/kJ^2)	363.03 (54.327)	357.46 (100.34)	418.05 (237.62)	411.30 (69.963)
q_m (mg/g)	113.42 (1235.7)	107.59 (2137.5)	112.02 (697.64)	113.63 (892.34)
R^2	0.9054	0.9062	0.9820	0.9763
SE	11.4950	10.858	12.105	12.980
SSE	528.54	471.65	586.19	673.95
F-ratio	38.301	38.677	33.052	28.343
Fowler–Guggenheim				
K_{FG} (L/mg)	0.3568 (0.0246)	0.3581 (0.0846)	0.3417 (1.2835)	0.3490 (0.7961)
W_{FG} (kJ/mol)	1.7822 (10.267)	1.7812 (5.6792)	1.7920 (20.497)	1.7896 (9.6482)
R^2	0.6735	0.6755	0.6513	0.6535
SE	0.2456	0.2442	0.2598	0.2558
SSE	0.1811	0.1789	0.2025	0.1964
F-ratio	2.8082	3.1234	2.8019	2.8291

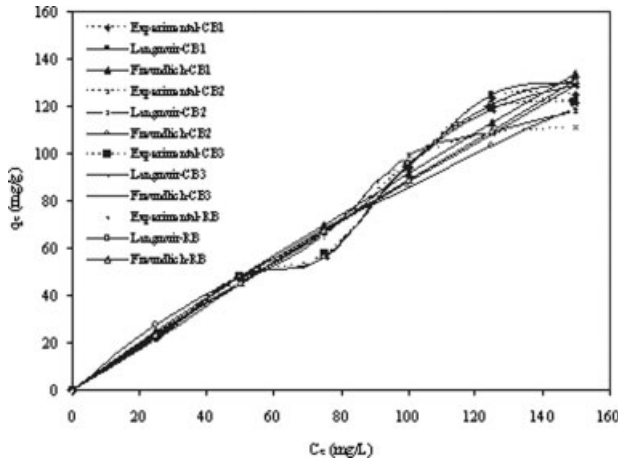

Figure 1. Langmuir and Freundlich isotherms obtained for the biosorption of Cu(II) onto *C. indica*.

that the metal concentration on the adsorbent will increase so 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 good fit when compared with the Freundlich model. Moreover, the separation factor (R_L) values (Tables 1 and 2) in the case of the Langmuir model indicated that metal sorption on to *C.indica* was favorable.

The modified Langmuir-1 equation describes temperature-dependent saturation coverage (T^{-n_L}), whereas modified Langmuir-2 equation accounts the surface heterogeneity of the sorbent in terms of first-order correction term (η) and both the equations have never been applied to liquid-phase sorption.[14,35,36] Both modified forms of the Langmuir equation, i.e., modified Langmuir-1 and Langmuir-2, do not improve the ability to fit the experimental data. However, the modified Langmuir-1 provided a satisfactory fit with R^2 values ranged 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 and involvement of several mechanisms in the sorption of Cu(II) and Ni(II) on to *C.indica*. However, both the modified forms of Langmuir equation did not provide any improvement when compared with the Langmuir equation.

The Elovich isotherm constants, K_E and q_m, as well as the coefficient of correlation, R^2, SE, SSE, and F-ratio and values are presented in Tables 1 and 2. In all cases, the Elovich isotherm exhibited satisfactory and higher coefficients of correlation (0.9324–0.9758), but lower than those obtained for Langmuir expression. In spite of the good correlation coefficients, the values of maximum biosorption capacity determined using the Elovich equation (Tables 1 and 2) are much lower than the experimental biosorbed amounts at equilibrium corresponding to the plateaus of the sorption isotherms. This means that the assumption of the exponential covering of sorption sites that implies multilayer sorption is not in agreement with the experiments in the studied concentration range. Therefore, the Elovich model is unable to describe the biosorption isotherms of Cu(II) and Ni(II) onto *C.indica*.

The parameters of the Temkin model as well as the nonlinear correlation coefficients (R^2) with SE, SSE, and F-ratio values are given in Tables 1 and 2. The satisfactory values of R^2 (0.9065–0.9693) and F-ratio (38.82–242.72) show an acceptable fit to the experimental data. The variation of biosorption 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 Cu(II) and Ni(II) onto *C.indica* have been analyzed by the Dubinin-Radushkevich equation. The isotherm constants along with the statistical parameters are presented in Tables 1 and 2. In all cases, the values of the correlation coefficients (0.9054–0.9820) are lower than Langmuir model but higher than other two-parameter models. Poor performance in terms of high SE and SSE values of the Dubinin-Radushkevich equation indicated the involvement of metal sorption mechanism other than van der Waals force.

The coefficients of correlation, SE, SSE, and F-ratio and the parameters of the Fowler-Guggenheim model are summarized in Tables 1 and 2. The values of R^2 indicate that this model completely fails to predict the equilibrium isotherm. However, the interaction energy, W, is positive, which indicates that there is repulsion between the biosorbed molecules.

The multilayer sorption is generally described by the Hasley model.[19] The present experimental data give poor fit as evidenced by zero correlation coefficients, high SSE, and SE values.

It can be observed from the above discussion that the predicted Langmuir isotherm curve fits better followed by the Freundlich and Temkin 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 as well as high F-ratio values.

Three-parameter models

The abilities of the three-parameter equations, Redlich-Peterson, Sips, Khan, Fritz-Schluender, Radke-Prausnitz (two

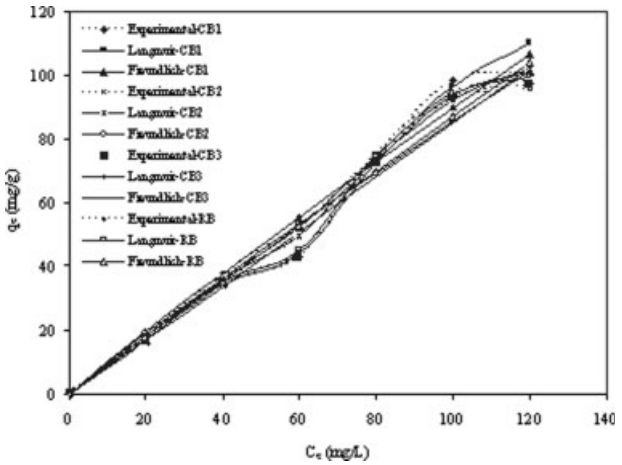

Figure 2. Langmuir and Freundlich isotherms obtained for the biosorption of Ni(II) onto *C. indica*.

Table 3. Isotherm Constants for Three-, Four- and Five-parameter Models for Cu^{2+} Biosorption onto *C. indica*

Models	Biomass			
	CB1	CB2	CB3	RB
		(± 95% confidence interval)		
Redlich-Peterson				
K_{RP} (L/g)	0.9670 (6.3495)	0.9692 (2.3674)	0.9260 (2.3972)	0.9310 (1.6739)
a_{RP} (L/mg)	1.074×10^{-15} (0.00024)	5.794×10^{-10} (2.67×10^{-15})	5.433×10^{-14} (6.85×10^{-9})	1.949×10^{-17} (0.0007)
β	0.6479 (0.0243)	0.6999 (0.0017)	0.6198 (0.0157)	0.7253 (0.0184)
R^2	0.9865	0.9896	0.9792	0.9712
SE	6.2737	4.7889	8.6211	9.0611
SSE	118.08	68.803	226.79	246.31
F-ratio	110.36	142.77	52.568	50.686
Sips				
K_S (L/g)	11520 (16248)	4737.5 (10247)	10934 (1247.3)	10050 (24301)
a_S (L/mg)	9.2675 (15.642)	16.299 (2.3641)	8.2192 (5.6784)	9.4683 (2.6742)
γ	0.8189 (0.0423)	0.7849 (1.2046)	0.7733 (1.9346)	0.8366 (0.0169)
R^2	0.9882	0.9922	0.9714	0.9710
SE	0.9380	0.7373	1.4212	1.4726
SSE	0.2639	0.1631	2.6049	2.6504
F-ratio	126.14	191.88	51.115	50.251
Khan				
q_m (mg/g)	0.6499 (3.4267)	1.3670 (0.6485)	0.5179 (2.3769)	0.4825 (10.247)
b_K (L/mg)	1.9852 (0.1347)	1.5725 (0.4372)	2.3467 (5.1367)	2.3303 (10.346)
a_K (L/g)	0.0647 (0.7531)	0.1812 (1.3241)	0.0589 (2.167)	0.0435 (0.9462)
R^2	0.8728	0.8585	0.8632	0.8592
SE	8.9199	9.5625	10.006	10.791
SSE	238.69	279.32	300.41	349.39
F-ratio	53.836	34.683	39.319	35.289
Fritz–Schluender				
q_{mFS} (mg/g)	6599.7 (167.53)	18955 (643.97)	10867 (1024.8)	13267 (2137.6)
K_{FS}	9.0353 (0.1547)	6.0515 (0.9736)	7.1559 (2.6492)	6.1454 (0.0649)
m_{FS}	0.8550 (0.0462)	0.7503 (0.0364)	0.7219 (0.9431)	0.7697 (2.3164)
R^2	0.9891	0.9895	0.9666	0.9630
SE	0.9048	0.8889	1.6191	1.6392
SSE	0.2456	0.2370	2.7864	2.8068
F-ratio	136.94	141.65	43.412	39.147
Radke-Prausnitz-I				
a_{RI} (mg/g)	0.9847 (6.3249)	1.0772 (3.4953)	0.9346 (4.6794)	0.9401 (3.6492)
r_{RI} (L/mg)	4943.6 (10.362)	2582.1 (203.46)	10988 (1037.2)	90868 (6928.5)
α_{RI}	−1.2193 (0.3458)	0.3660 (1.3164)	−1.3552 (2.0462)	−0.9494 (0.1362)
R^2	0.9781	0.9732	0.9669	0.9812
SE	1.0175	1.6836	2.4877	2.9122
SSE	2.8422	3.7711	8.5405	10.864
F-ratio	59.624	54.544	43.908	78.452
Radke-Prausnitz-II				
a_{RII} (mg/g)	130.19 (192.34)	116.11 (79.624)	125.91 (234.16)	128.04 (155.643)
r_{RII} (L/mg)	0.0034 (2.5267)	0.0057 (1.3472)	0.0072 (0.4672)	0.0039 (2.0144)
α_{RII}	0.2193 (0.0236)	0.3665 (0.0467)	0.3551 (0.9642)	0.8331 (1.0467)
R^2	0.9981	0.9953	0.9969	0.9961
SE	0.1928	0.2177	0.2070	0.2045
SSE	0.0801	0.0683	0.0387	0.0328
F-ratio	166.99	166.99	143.92	137.68
Toth				
q_m (mg/g)	15.585 (296.32)	15.164 (346.85)	15.249 (512.32)	15.309 (100.54)
b_T (L/g)	0.4569 (2.4672)	0.0311 (1.3695)	0.7424 (10.697)	0.3824 (5.6134)
n_T	−30.387 (0.2374)	−919.77 (20.3467)	−19.203 (10.637)	−2198.6 (16.349)
R^2	0.4267	0.4385	0.4334	0.4230
SE	0.6551	0.6273	0.6330	0.6569
SSE	1.2877	1.1806	1.2022	1.2947
F-ratio	1.1169	1.1717	1.1477	1.0999
Koble-Carrigan				
A_{KH} (mg/g)	7.7191 (100.36)	7.2887 (213.44)	7.4640 (56.987)	7.5085 (0.6792)
B_{KH} (L/g)	179.40 (0.6843)	171.49 (5.6247)	174.25 (21.367)	173.95 (84.691)
n_{KH}	63.365 (1.3691)	60.306 (5.3109)	61.301 (26.374)	61.385 (1.9634)
R^2	0.6321	0.6926	0.6435	0.6379
SE	115.55	106.60	111.26	112.38
SSE	40059	34094	37140	37893
F-ratio	2.3456	2.1354	2.2437	2.2784

Table 3. (Continued)

Models	Biomass			
	CB1	CB2	CB3	RB
Fritz–Schluender (Four-parameter)				
A	0.3328 (1.9536)	0.2448 (0.0679)	0.3946 (1.6572)	0.3261 (2.4852)
B_{FS}	7.4987 (5.1369)	6.9391 (1.3697)	2.9578 (0.4634)	2.1948 (1.2762)
α	0.8616 (0.0436)	0.8144 (0.0126)	1.2193 (0.9856)	1.2654 (2.1346)
β_{FS}	0.0648 (0.0564)	0.0538 (0.1364)	0.0903 (0.0162)	0.0982 (1.6438)
R^2	0.9948	0.9947	0.9888	0.9860
SE	0.5805	0.6853	0.7856	0.9641
SSE	0.0334	0.0496	0.0473	0.0865
F-ratio	43.359	43.025	20.725	18.957
Baudu				
q_{mo} (mg/g)	18.264 (100.36)	22.654 (69.327)	5.6789 (200.36)	10.263 (269.27)
b_o	0.0152 (1.1034)	0.0119 (0.9643)	0.9156 (5.6214)	0.1266 (3.6452)
x	0.3255 (2.1463)	0.9213 (0.0694)	0.8456 (2.6489)	1.0149 (0.0637)
y	−0.1469 (2.1647)	−1.3874 (0.6375)	−0.9598 (0.1643)	−0.6412 (1.3467)
R^2	0.7842	0.7816	0.7689	0.7812
SE	10.237	10.572	11.112	10.688
SSE	100.172	102.229	110.892	107.0332
F-ratio	10.2875	10.1572	9.9426	10.1357
Fritz–Schluender (Five-parameter)				
α_1 (mg/g)	142.96 (100.36)	131.16 (312.35)	137.13 (69.672)	139.84 (368.62)
α_1'	2.2465 (0.1342)	5.0606 (0.0896)	12.559 (1.8304)	8.3415 (2.6952)
α_2	0.0523 (0.2685)	0.0114 (1.0463)	0.0820 (0.9543)	0.0717 (3.3672)
β_1	0.5181 (0.0679)	0.6040 (3.6492)	0.9501 (1.6942)	0.9503 (0.0156)
β_2	0.9181 (0.0648)	0.9168 (0.0134)	0.9501 (1.0027)	0.9530 (0.0531)
R^2	0.9920	0.9929	0.9914	0.9901
SE	0.1336	0.1221	0.2089	0.2226
SSE	0.0178	0.0149	0.0436	0.0495
F-ratio	131.18	134.99	111.90	111.06

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), whereas 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. Tables 3 and 4 show the isotherm parameters obtained using nonlinear fitting analysis.

Among the isotherm models having three parameters, Redlich-Peterson has been most frequently employed in liquid phase sorption of heavy metals and organic compounds.[8,37,38] 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 the Henry's law form for $\beta = 0$. In this study, the Redlich- Peterson equation has established its capability to fit the experimental data satisfactorily (with R^2 between 0.9648 and 0.9896). However, SE and SSE values were higher than other three-parameter models except Khan and Koble-Carrigan. Also, it does not provide any improvement over the Radke-Prausnitz-II model (Tables 3 and 4). The β-values ranged from 0.60 to 0.74, 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, Sips isotherm[21] 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 fits adequately the experimental results. The exponent γ-value was in the range of 0.72–0.85, meaning that the sorption data obtained in this study is more of a Langmuir form rather than that of Freundlich, which was also confirmed by the results shown in Tables 1 and 2. Though the R^2 values of the Khan and Fritz-Schluender models were satisfactory (0.8585–0.8777 and 0.7983–0.9895, respectively), the predicted values of q_m by both the models do not match the experimental data (Tables 3 and 4). Therefore, these models are unable to fit the experimental data compared with other three-parameter models. Similarly, in spite of the good coefficients of correlation ($\geq$0.9631) and F-ratio ($\geq$39.252), the maximum sorption capacities for the studied metals determined using the three-parameter equations of Radke-Prausnitz-I (Tables 3 and 4) were lower than the biosorbed amounts at equilibrium corresponding to the plateaus of the isotherms. For all the cases except, the Ni(II)-CB2 system, the Radke-Prausnitz-I model exponent, α_{RI}, was negative and inadmissible. Consequently, the Radke-Prausnitz-I cannot describe the experimental equilibrium data.

The Radke-Prausnitz-II model correctly simulates the biosorption isotherms of the studied metals (Figures 3 and 4). The coefficients of correlation are good ($R^2 \geq 0.9899$) for all the tested systems. The SE, SSE, and F-ratio values lie between 0.1048–0.4325, 0.0164–0.0912, and 137.6–178.45, respectively. The biosorption maximum capacities determined using the Radke-Prausnitz-II model was comparable to experimental data and lower than the Langmuir model. The order of the equilibrium constant r_{RII} is similar to that of the parameter K_L of Langmuir. Hence, this model is precise for the experimental data among the three-parameter

Table 4. Isotherm Constants for Three-, Four- and Five-Parameter Models for Ni^{2+} Biosorption onto *C. indica*

Models	Biomass			
	CB1	CB2	CB3	RB
	(± 95% confidence interval)			
Redlich-Peterson				
K_{RP} (L/g)	0.9540 (2.3627)	0.9135 (5.6743)	0.8608 (3.1275)	0.9051 (0.0458)
a_{RP} (L/mg)	4.467×10^{-15} (1.25×10^{-10})	3.201×10^{-13} (5.42×10^{-7})	4.833×10^{-14} (2.43×10^{-4})	7.650×10^{-7} (0.0046)
β	0.6459 (5.3138)	0.6059 (2.4362)	0.7390 (0.0047)	0.6357 (2.4847)
R^2	0.9884	0.9881	0.9658	0.9648
SE	4.6465	4.4638	7.8677	7.9891
SSE	64.768	59.777	185.07	191.47
F-ratio	127.94	124.77	42.360	41.191
Sips				
K_S (L/g)	6599.7 (10.643)	18955 (196.34)	10867 (900.64)	13267 (26.374)
a_S (L/mg)	9.0353 (0.2137)	6.0515 (10.687)	7.1559 (100.36)	6.1454 (0.0024)
γ	0.8550 (0.0096)	0.7503 (0.0127)	0.7219 (0.0004)	0.7697 (0.0075)
R^2	0.9891	0.9895	0.9666	0.9630
SE	0.9048	0.8889	1.6191	1.6392
SSE	0.2456	0.2370	2.7864	2.8068
F-ratio	136.94	141.65	43.412	39.147
Khan				
q_m (mg/g)	0.7103 (10.652)	0.8753 (5.946)	0.2505 (0.0043)	0.6787 (7.621)
b_K (L/mg)	1.6868 (0.0062)	1.3454 (10.369)	3.1737 (0.0247)	1.3905 (0.0069)
a_K (L/g)	0.0562 (0.5134)	0.0652 (1.3682)	0.0122 (5.6432)	0.0167 (0.648)
R^2	0.8777	0.8766	0.8655	0.8631
SE	6.4407	6.2547	7.8942	8.1791
SSE	124.44	117.36	186.95	200.69
F-ratio	65.876	62.815	42.066	39.231
Fritz–Schluender				
q_{mFS} (mg/g)	0.1979 (0.0015)	0.0606 (2.1473)	1.1869 (1.6842)	1.3729 (0.0029)
K_{FS}	3.806×10^{18} (26736)	2.861×10^{17} (5.36×10^{9})	1.579×10^{19} (6.82×10^{6})	9.074×10^{12} (16958)
m_{FS}	−2.7779 (1.3642)	−6.5781 (0.0246)	−1.5556 (3.1462)	−1.5022 (1.3497)
R^2	0.7983	0.8830	0.9311	0.9328
SE	0.4775	0.1131	0.1624	0.2121
SSE	0.6840	0.0384	0.2324	0.1350
F-ratio	3.4718	8.6834	20.283	72.785
Radke-Prausnitz-I				
a_{RI} (mg/g)	0.9723 (0.0028)	0.9338 (2.3672)	0.9342 (25.682)	1.0742 (82.347)
r_{RI} (L/mg)	92878 (3.4681)	10479 (613.58)	4.4066 (0.0367)	7.1508 (0.1964)
α_{RI}	−0.9494 (0.0048)	−1.006 (0.0014)	−1.1743 (3.4293)	0.9014 (1.3679)
R^2	0.9812	0.9810	0.9656	0.9631
SE	1.9122	1.6408	2.8901	3.1769
SSE	4.8641	5.4582	10.764	12.582
F-ratio	78.452	77.575	42.111	39.252
Radke-Prausnitz-II				
a_{RII} (mg/g)	104.33 (59.637)	98.982 (162.34)	102.66 (49.628)	103.88 (72.651)
r_{RII} (L/mg)	0.0058 (0.1967)	0.0079 (0.0624)	0.0057 (0.3627)	0.0122 (0.0274)
α_{RII}	0.9494 (0.0256)	0.9624 (0.0112)	0.9743 (1.0034)	0.9014 (0.0039)
R^2	0.9982	0.9910	0.9965	0.9899
SE	0.1048	0.1403	0.1086	0.4325
SSE	0.0912	0.0164	0.0167	0.1699
F-ratio	178.45	167.47	142.11	139.25
Toth				
q_m (mg/g)	14.145 (151.36)	13.837 (1.3672)	13.626 (95.637)	13.669 (200.37)
b_T (L/g)	52947 (1.3694)	673154 (6234.5)	413494 (136.95)	300903 (2469.3)
n_T	−241.33 (1.3612)	−170.19 (6.7128)	−139.16 (20.379)	−210.47 (7.3694)
R^2	0.4469	0.4470	0.4347	0.4475
SE	0.6464	0.6455	0.6661	0.6345
SSE	1.2538	1.2501	1.3311	1.2075
F-ratio	1.0999	1.2129	1.1536	1.2152
Koble-Carrigan				
A_{KH} (mg/g)	27.520 (0.0238)	26.266 (1.3694)	25.928 (0.0672)	26.454 (5.6314)
B_{KH} (L/g)	142.34 (0.3671)	136.27 (3.6723)	127.69 (0.0579)	138.82 (0.9437)
n_{KH}	116.27 (1.0142)	111.04 (10.368)	107.11 (0.0247)	111.39 (5.9537)
R^2	0.7215	0.7518	0.7426	0.7348
SE	66.681	63.445	63.676	64.804
SSE	13338	12077	12162	12598
F-ratio	5.6420	6.3241	5.9426	5.8472

Table 4. (Continued)

Models	Biomass			
	CB1	CB2	CB3	RB
Fritz–Schluender (Four-parameter)				
A	0.3818 (200.34)	0.3576 (5.6237)	0.2704 (10.395)	0.3623 (0.0006)
B_{FS}	2.5504 (24.672)	1.7015 (50.361)	8.9546 (0.0679)	2.2664 (0.0062)
α	0.8359 (0.0008)	0.8442 (0.0062)	0.8144 (4.3279)	0.8531 (10.382)
β_{FS}	0.0595 (1.3486)	0.0589 (7.3259)	0.0782 (0.2861)	0.0577 (6.3495)
R^2	0.9967	0.9971	0.9903	0.9867
SE	0.8026	0.6775	0.9749	0.9806
SSE	0.0688	0.0469	0.0845	0.0985
F-ratio	149.730	151.374	121.803	119.38
Baudu				
q_{mo} (mg/g)	10.413 (167.38)	14.692 (0.3692)	10.163 (0.0069)	12.516 (78.632)
b_o	0.4205 (10.349)	0.5527 (8.6273)	0.5871 (0.0571)	0.6216 (0.0009)
X	0.7032 (3.7602)	0.9027 (10.628)	1.9549 (0.0038)	1.5483 (0.0462)
Y	−0.8546 (1.3615)	−1.4762 (10.372)	−0.3459 (0.0024)	−0.8463 (4.627)
R^2	0.7891	0.7834	0.7689	0.7825
SE	1.6235	1.5726	2.1591	1.6882
SSE	3.1272	2.9227	5.1492	4..1532
F-ratio	12.959	13.015	10.722	12.926
Fritz–Schluender (Five-parameter)				
α_1 (mg/g)	121.91 (92.367)	103.14 (69.482)	106.48 (200.64)	112.37 (88.602)
α_1'	2.0504 (10.652)	2.3286 (0.3642)	1.4874 (0.0611)	1.2918 (0.0063)
α_2	0.0110 (0.6486)	0.0408 (1.3672)	0.0109 (2.6738)	0.0436 (0.1037)
β_1	0.5737 (0.0062)	0.6582 (0.0024)	0.8013 (2.349)	0.8232 (0.0951)
β_2	0.8612 (0.0271)	0.9243 (0.0704)	0.8336 (2.6049)	0.8324 (0.0509)
R^2	0.9976	0.9918	0.9903	0.9899
SE	0.1202	0.1359	0.2152	0.2210
SSE	0.0144	0.0184	0.0463	0.0488
F-ratio	138.96	130.35	112.35	110.93

models. The values of R^2, q_m as well as F-ratio of Toth model indicate that this model completely fails to predict the equilibrium isotherm. Also, the Toth model exponent, n_T were negative and inadmissible.

The Koble-Carrigan[26] 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 F-ratio as well as 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: Radke-Prausnitz-II > Sips > Redlich-Peterson.

Four- and five-parameter models

The biosorption data were analyzed according to the nonlinear form of the four-parameter isotherm models. Very good fitting of the experimental results of sorption isotherms is obtained using the four-parameter model of Fritz-Schluender (Figures not shown). From Tables 3 and 4, the coefficients of correlation (≥0.9860) were very good and the SE and SSE values were in the range of 0.0309–0.9806 and 0.0334–0.0985, respectively. The values of α and β_{FS} for all

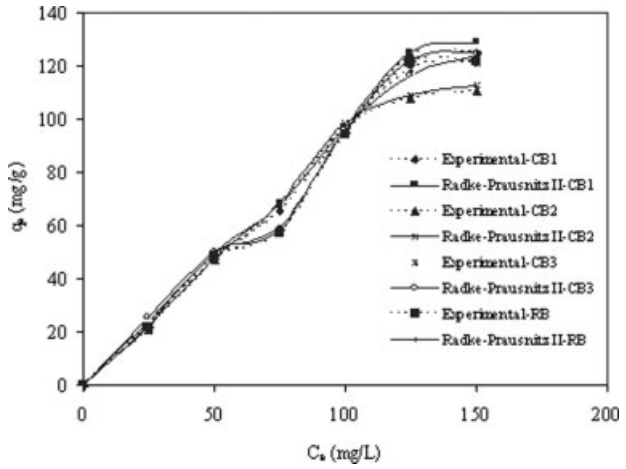

Figure 3. Radke-Prausnitz II isotherm obtained for the biosorption of Cu(II) *C. indica*.

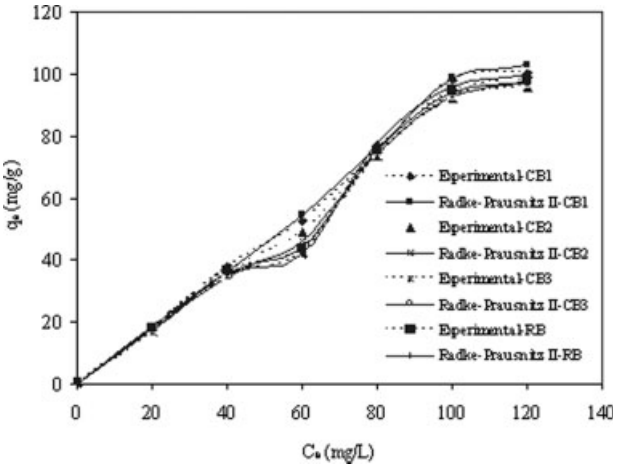

Figure 4. Radke-Prausnitz II isotherm obtained for the biosorption of Ni(II) *C. indica*.

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.

The calculated parameters of equilibrium biosorption isotherms of Cu(II) and Ni(II) onto various forms of *C.indica* by the Baudu model are given in Tables 3 and 4. An appropriate fit was not obtained using the model of Baudu. Also, the values of the maximum biosorption capacity obtained using the Baudu isotherms were very much lower than the experimental results. Therefore, this model cannot describe the experimental data.

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 isotherms is obtained using the five-parameter model of Fritz-Schluender (Figures 5 and 6). From Tables 3 and 4, high correlation coefficients ($\geq$0.9899) and low SE ($\leq$ 0.2226) and SSE ($\leq$ 0.0495) 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 Radke-Prausnitz-II model 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 were equal to unity. This model is empirical in nature with a larger numbers 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, which is observed in this study. 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 Cu(II) and Ni(II) on both raw and treated biomass of *C.indica* were studied and modeled using 21 well-known isotherm models. Out of the 21 isotherm models, some models are based on well-established theoretical concepts, and their application indicates that the types of sorption mechanisms in operation during biosorptive uptake of Cu(II) and Ni(II). Most of the models having two or more parameters, namely, Langmuir, Freundlich, Temkin, Freundlich, 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 Freundlich and Temkin. The classification of the three-parameter models according to the simulation of the biosorption isotherms was: Radke-Prausnitz-II > Sips > Redlich-Peterson. The four-parameter equation of Fritz-Schluender simulates well the experimental results, but the equation of Radke-Prausnitz-II (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. This 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, based on Ockham's razor approach, it could be concluded that the Langmuir model provides a suitable description of the experimental data.

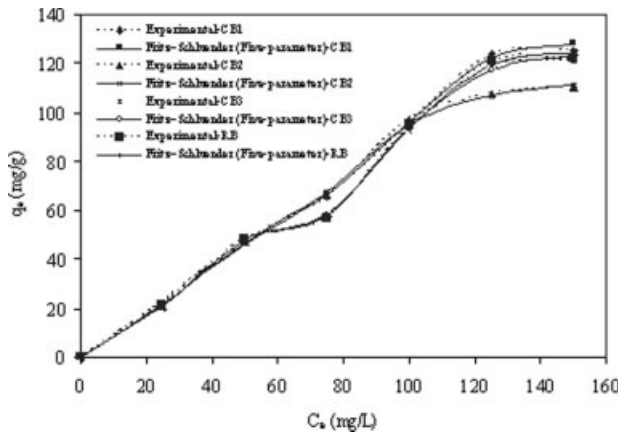

Figure 5. Fritz-Schluender (Five-parameter) isotherm obtained for the biosorption of Cu(II) *C. indica*.

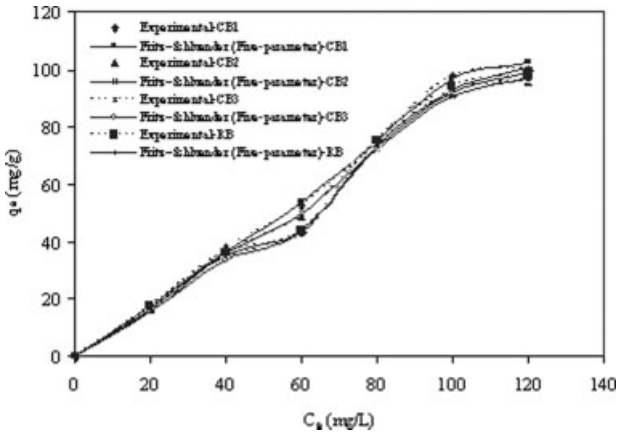

Figure 6. Fritz-Schluender (Five-parameter) isotherm obtained for the biosorption of Ni(II) *C. indica*.

Acknowledgments

Authors (SB, BJ) thanks Dr. P. K. Ghosh, Director, Central Salt and Marine Chemicals Research Institute (CSMCRI) and Dr. (Mrs.) K. H. Mody, Group Leader of Marine Environment, CSMCRI for their constant encouragement and support throughout the work.

Notation

a_K = Khan model exponent
a_R = Radke-Prausnitz isotherm constant
a_{RP} = Redlich-Peterson model constant, L/mg
A = Fritz-Schluender four-parameter model constant
A_{KC} = Koble-Carrigan isotherm constant
b_K = Khan isotherm constant
b_T = Toth isotherm constant
b_{Te} = constant in Temkin sorption isotherm, J/ mol
B = constant in Dubinin-Radushkevich sorption model, mol^2/ kJ^2
B_{FS} = constant in Fritz-Schluender four-parameter model

B_{KC} = Koble-Carrigan isotherm constant
C_e = equilibrium concentration of sorbate in solution, mg/L
e = Polanyi potential, kJ/mol
K_F = Freundlich isotherm constant, L/g
K_{FG} = Fowler-Guggenheim equilibrium constant, L/mg
K_{HE} = Henry's law constant, L/g
K_H = Halsey isotherm constant
K_L = Langmuir isotherm equilibrium binding constant, L/mg
K_{RP} = Redlich-Peterson isotherm constant, L/g
K_S = Sips isotherm constant, L/g
K_T = Temkin isotherm constant, L/mg
m = number of experimental data points
n = exponent in Freundlich isotherm
n_H = Halsey isotherm constant
n_{KC} = Koble-Carrigan model exponent
n_T = Toth isotherm constant
p = number of parameters in the sorption isotherm
q_e = amount of sorbate sorbed at equilibrium, mg/g
q_i = observed sorption capacity of batch experiment i
q_m = maximum sorption capacity, mg/g
q_t = amount of sorbate sorbed at time t, mg/g
Q_i = estimated sorption capacity of batch experiment i
r_R = Radke-Prausnitz isotherm constant
R = universal gas constant, 8.314 J/ mol/ K
R^2 = correlation coefficient
R_L = Langmuir separation factor
SE = standard error
SSE = sum of squares error
W_{FG} = the interaction energy between adsorbed molecules, kJ/mol
α = Radke-Prausnitz isotherm constant
α_1 = Fritz-Schluender five-parameter model sorption capacity, mg/g
α_1' = Fritz-Schluender five-parameter model constant
α_2 = Fritz-Schluender five-parameter model constant
α_{FS} = Fritz-Schluender four-parameter model exponent
β = Redlich-Peterson isotherm constant
β_1 = Fritz-Schluender five-parameter model exponent
β_2 = Fritz-Schluender five-parameter model exponent
β_{FS} = Fritz-Schluender four-parameter model exponent
γ = Sips model exponent
θ = surface coverage

Literature Cited

1. Xiao B, Thomas KM. Adsorption of aqueous metal ions on oxygen and nitrogen functionalized nanoporous activated carbons. *Langmuir*. 2005;21:3892–3902.
2. Deng S, Bai RB, Chen JP. Aminated polyacrylonitrile fibers for lead and copper removal. *Langmuir*. 2003;19:5058–5064.
3. Kaewsarn P. Biosorption of copper(II) from aqueous solutions by pre-treated biomass of marine algae *Padina sp*. *Chemosphere*. 2002; 47:1081–1085.
4. Basha S, Murthy ZVP. Seaweeds for engineering metal biosorption: a Review. In: Mason LG, editor. *Focus on Hazardous Materials Research*. Hauppauge, New York: Nova Science Publishers, 2007:165–209.
5. Bailey SE, Olin TJ, Bricka RM, Adrian DD. A review of potentially low-cost sorbents for heavy metals. *Water Res*. 1999;33:2469–2479.
6. Volesky B. *Sorption and Biosorption*. Montreal-St. Lambert, Quebec, Canada: BV Sorbex, Inc., 2003.
7. Klimmek S, Stan HJ, Wilke A, Bunke G, Buchholz R. Comparative analysis of the biosorption of cadmium, lead, nickel and zinc by algae. *Environ Sci Technol*. 2001;35:4283–4288.
8. Ho YS. Selection of optimum sorption isotherm. *Carbon*. 2004;42:2115–2116.
9. Kumar KV, Sivanesan S. Isotherm parameters for basic dyes onto activated carbon: comparison of linear and non-linear method. *J Hazard Mater*. 2006;129:147–150.
10. Faust SD, Aly OM. *Adsorption Processes for Water Treatment*. Stoneham, MA: Butterworth, 1987:1–23.
11. Freundlich HMF. Uber die adsorption in lasugen. *Z Phys Chem (Leipzig)*. 1906;57:385–470.
12. Langmuir I. The constitution and fundamental properties of solids and liquids. *J Am Chem Soc*. 1916;38:2221–2295.
13. Yang RT, Doong SJ. Gas separation by pressure swing adsorption: a pore diffusion model for bulk separation. *AIChE J*. 1985;31:1829–1842.
14. O'Brien JA, Myers AL. Physical adsorption of gases on heterogeneous surfaces series expansion of isotherms using central moments of the adsorption energy distribution. *J Chem Soc Faraday Trans 1*. 1984;80:1467–1477.
15. Elovich SY, Larinov OG. Theory of adsorption from solutions of non electrolytes on solid. I. Equation adsorption from solutions and the analysis of its simplest form. II. Verification of the equation of adsorption isotherm from solutions. *Izv Akad Nauk SSSR, Otd Khim Nauk*. 1962;2:209–216.
16. Temkin MJ, Pyzhev V. Recent modifications to Langmuir isotherms. *Acta Physicochim URSS*. 1940;12:217–225.
17. Dubinin MM. The potential theory of adsorption of gases and vapors for adsorbents with energetically non-uniform surface. *Chem Rev*. 1960;60:235–266.
18. Fowler RH, Guggenheim EA. *Statistical Thermodynamics*. London: Cambridge University Press, 1939:431–450.
19. Halsey G. Physical adsorption on non-uniform surfaces. *J Chem Phys*. 1948;16:931–937.
20. Redlich O, Peterson DL. A useful adsorption isotherm. *J Phys Chem*. 1959;63:1024–1026.
21. Sips R. Structure of a catalyst surface. *J Chem Phys*. 1948;16:490–495.
22. Khan AR, Ataullah R, Al-Haddad A. Equilibrium adsorption studies of some aromatic pollutants from dilute aqueous solutions on activated carbon at different temperatures. *J Colloid Interface Sci*. 1997;194:154–165.
23. Fritz W, Schluender EU. Simultaneous adsorption equilibria of organic solutes in dilute aqueous solution on activated carbon. *Ceram Eng Sci Proc*. 1974;29:1279–1282.
24. Radke CJ, Prausnitz JM. Adsorption of organic solutes from dilute aqueous solution of activated carbon. *Ind Eng Chem Fund*. 1972;11:445–451.
25. Toth J. Calculation of the BET-compatible surface area from any Type I isotherms measured above the critical temperature. *J Colloid Interface Sci*. 2000;225:378–383.
26. Koble RA, Carrigan TE. Adsorption isotherms for pure hydrocarbons. *Ind Eng Chem*. 1952;44:383–387.
27. Baudu M. *Etude des interactions solute-fibres de charbon actif. Application et regeneration, Ph.D. Thesis*. France: Universite de Rennes I, 1990.
28. Basha S, Murthy ZVP, Jha B. Biosorption of hexavalent chromium by chemically modified seaweed, *Cystoseira indica*. *Chem Eng J*. 2008;137:480–488.
29. Jeon C, Park JY, Yoo YJ. Characteristics of metal removal using carboxylated alginic acid. *Water Res*. 2002;36:1814–1824.
30. Ho YS, Porter JF, McKay G. Equilibrium isotherm studies for the biosorption of divalent metal ions onto peat: copper, nickel and lead single component systems. *Water Air Soil Pollut*. 2002;141:1–33.
31. Kundu S, Gupta AK. Arsenic adsorption onto iron oxide-coated cement (IOCC): regression analysis of equilibrium data with several isotherm models and their optimization. *Chem Eng J*. 2006;122:93–106.
32. Malek A, Farooq S. Comparison of isotherm models for hydrocarbon adsorption on activated carbon. *AIChE J*. 1996;42:3191–3201.
33. Aksu Z, Kutsal TA. Bioseparation process for removing lead(II) ions from waste water by using *C. vulgaris*. *J Chem Technol Biotechnol*. 1991;52:109–118.
34. Treybal RE. *Mass-Transfer Operations*, 3rd ed. Tokyo: McGraw-Hill, 1981.
35. Yang RT, Doong SJ. Gas separation by pressure swing adsorption: a pore diffusion model for bulk separation. *AIChE J*. 1985;31:1829–1842.
36. Maurya NS, Mittal AK. Applicability of equilibrium isotherm models for the biosorptive uptakes in comparison to activated carbon-based adsorption. *J Environ Eng-ASCE*. 2006;132:1589–1599.
37. Ho YS, McKay G. Sorption of dye from aqueous solution by peat. *Chem Eng J*. 1998;70:115–124.
38. Sag Y, Aktay YA. Comparative study for the sorption of Cu(II) ions by chitin and chitosan: application of equilibrium and mass transfer models. *Sep Sci Technol*. 2002;37:2801–2822.

Manuscript received May 6, 2008, and revision received July 13, 2008.