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ORIGINAL PAPER

# On the biosorption, by brown seaweed, *Lobophora variegata*, of Ni(II) from aqueous solutions: equilibrium and thermodynamic studies

**Shaik Basha · Santlal Jaiswar · Bhavanath Jha**

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**Abstract** The biosorption equilibrium isotherms of Ni(II) onto marine brown algae *Lobophora variegata*, which was chemically-modified by $CaCl_2$ were studied and modeled. To predict the biosorption isotherms and to determine the characteristic parameters for process design, twenty-three one-, two-, three-, four- and five-parameter isotherm models were applied to experimental data. The interaction among biosorbed molecules is attractive 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 regression coefficient, $R^2$ (0.9911–0.9975) and *F*-ratio (118.03–179.96), and low standard error, SE (0.0902–0.0.1556) and the residual or sum of square error, SSE (0.0012–0.1789) 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) > Freundlich (two-parameter) > Langmuir (two-parameter) > Khan (three-parameter) > Fritz–Schluender (four-parameter). The thermodynamic parameters such as $\Delta G^0$, $\Delta H^0$ and $\Delta S^0$ have been determined, which indicates the sorption of Ni(II) onto *L. variegata* was spontaneous and endothermic in nature.

**Keywords** *Lobophora variegata* · Biosorption · Isotherm models · Nickel · Thermodynamics

**List of symbols**

| | |
|---|---|
| $A$ | Constant in linear with intercept isotherm model |
| $a_K$ | Khan model exponent |
| $a_R$ | Radke-Prausnitz isotherm constant |
| $a_{RP}$ | Redlich-Peterson model constant (l $mg^{-1}$) |
| $a_S$ | Sips isotherm constant |
| $A$ | Fritz-Schluender four-parameter model constant |
| $A_{HJ}$ | Harkins–Jura model constant |
| $A_{KC}$ | Koble-Carrigan isotherm constant |
| $B$ | Constant in linear with intercept isotherm model |
| $b_K$ | Khan isotherm constant |
| $b_T$ | Toth isotherm constant |
| $b_{Te}$ | Constant in Temkin sorption isotherm (J $mol^{-1}$) |
| $B$ | 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 |

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S. Basha · S. Jaiswar · B. Jha (✉)
Discipline of Marine Biotechnology & Ecology,
Central Salt and Marine Chemicals Research Institute
(Council of Scientific and Industrial Research),
Bhavnagar 364 002, Gujarat, India
e-mail: bjha@csmcri.org

$C_e$ Equilibrium concentration of sorbate in solution (mg $l^{-1}$)
$E$ Polanyi potential (kJ $mol^{-1}$)
$F$ Frukin model constant
$K_F$ Freundlich isotherm constant (l $g^{-1}$)
$K_{FG}$ Fowler–Guggenheim equilibrium constant (l $mg^{-1}$)
$K_{HE}$ Henry's law constant (l $g^{-1}$)
$K_L$ Langmuir isotherm equilibrium binding constant (l $mg^{-1}$)
$K_{RP}$ Redlich-Peterson isotherm constant (l $g^{-1}$)
$K_S$ Sips isotherm constant (l $g^{-1}$)
$K_T$ Temkin isotherm constant (l $mg^{-1}$)
$M$ 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 $g^{-1}$)
$q_i$ Observed sorption capacity of batch experiment i
$q_m$ Maximum sorption capacity (mg $g^{-1}$)
$q_t$ Amount of sorbate sorbed at time t (mg $g^{-1}$)
$Q_i$ Estimated sorption capacity of batch experiment i
$r_R$ Radke-Prausnitz isotherm constant
$R$ Universal gas constant, 8.314 J $mol^{-1}$ $K^{-1}$
$R^2$ Correlation coefficient
$R_L$ Langmuir separation factor
SE Standard error
SSE Sum of squares error
$W_{FG}$ The interaction energy between adsorbed molecules (kJ $mol^{-1}$)
$A$ Radke-Prausnitz isotherm constant
$\alpha_1$ Fritz-Schluender five-parameter model sorption capacity (mg $g^{-1}$)
$\alpha'_1$ Fritz-Schluender five-parameter model constant
$\alpha_2$ Fritz-Schluender five-parameter model constant
$\alpha_{FS}$ Fritz-Schluender four-parameter model exponent
$\beta$ Redlich-Peterson isotherm constant
$\beta_1$ Fritz-Schluender five-parameter model exponent
$\beta_2$ Fritz-Schluender five-parameter model exponent
$\beta_{FS}$ Fritz-Schluender four-parameter model exponent
$\gamma$ Sips model exponent
$\theta$ Surface coverage
$\Delta G^0$ Gibbs free energy change (kJ $mol^{-1}$)
$\Delta H^0$ Enthalpy change (kJ $mol^{-1}$)
$\Delta S^0$ Entropy change (kJ $mol^{-1}$ $K^{-1}$)

## Introduction

The contamination of water bodies by toxic heavy metallic cations is a global environmental problem. In recent years, increasing awareness of the environmental impact of heavy metals has prompted a demand for the purification of industrial waters prior to discharge into natural waters. Wastewaters containing nickel originate from the metal-processing industries, steel foundries, electroplating, battery, printing, aircraft and motor vehicle industries, and mining and refining processes (Eckenfelder 1989; Denkhaus and Salniknow 2002). Although nickel is not considered to be toxic at low levels, like other pollutant metals, it accumulates in the food chain and once adsorbed into the body cannot be easily excreted. The adverse effect of nickel on humans is its allergic reaction; nickel can also cause lung and nasal sinus cancers (Volesky 1990). These harmful effects of Ni(II) necessitate its removal from wastewaters before release into streams (Rengaraj et al. 2007). For this reason, the Water, Sanitation and Hygiene (WSH) under the World Health Organization (WHO) established the toxic limits of permissible concentrations of nickel at a level of Ni and insoluble compounds of Ni 1 mg $m^{-3}$, soluble compounds of Ni 0.1 mg $m^{-3}$, nickel carbonyl of 0.05–0.12 mg $m^{-3}$ and nickel sulfide of 1 mg $m^{-3}$ (Zafar et al. 2007).

A number of techniques for removal of Ni(II) from wastewaters like ion exchange (EPA 1981), chemical precipitation (Dean et al. 1972; McAnally et al. 1984) coagulation/flocculation (Nilsson 1971), complexation/sequestration (Peryasamy and Namasivayam 1995), adsorption on activated carbon (Bhattacharyya and Cheng 1987), electrochemical operations

(Peryasamy and Namasivayam 1995), ultrafiltration, or electrochemical deposition, do not seem to be economically feasible for water and wastewater treatment because of their relatively high costs or incomplete metal removal or generation of toxic sludge/other waste product that require disposal (Volesky and Holan 1995). This has led to the development of alternative low cost technologies for the removal of Ni(II) from wastewaters. In the past few decades, biosorption using various biomaterials like marine algae, fungal biomass, waste activated sludge, and digested sludge as the adsorbents have emerged as a potential alternative technique to the existing methods for Ni(II) removal (Ajmal et al. 2000; Aksu 2002; Vijayaraghavan et al. 2006a; Zafar et al. 2007; Chen et al. 2008).

Of the many types of biosorbents used by several investigators, seaweeds have proved to be the most efficient and practical biomass for the removal of heavy metal ions from aqueous solutions (Davis et al. 2003). Apart from its compatibility with almost all heavy metal ions, its macroscopic appearance, rigidity and easy availability are the important factors which make seaweeds an ideal candidate for removal of heavy metals. Of the three common seaweeds, brown seaweeds are extensively used for biosorption. Recent investigations by various groups have shown that selected species of brown seaweeds possess impressive sorption capacities for the removal of Ni(II) (Kalyani et al. 2004; Sheng et al. 2004; Tsui et al. 2006; Vijayaraghavan et al. 2005, 2006a; Ozer et al. 2008; Chen et al. 2008). However, the equilibrium and thermodynamic studies on the use of chemically modified seaweed for Ni(II) removal from aqueous solutions are very limited (Tsui et al. 2006; Vijayaraghavan et al. 2006b; Chen et al. 2008). *Lobophora variegata,* abundantly available seaweed along Suarashtra-Kutchch coast of India, may be economically used as a potential biosorbent for heavy metal removal from aqueous solutions. It was pretreated in order to enhance the sorption performance and also to strengthen it for sorption process applications.

## Materials and methods

### Materials

The chemicals used in this study were of analytic reagent grade and supplied by Merck India. Ni(II) solutions were obtained by diluting 1.0 g $l^{-1}$ of stock Ni(II) solution which was prepared by dissolving nickel chloride ($NiCl_2$) into double distilled water. The concentrations of metal solutions ranged from 10 to 250 mg $l^{-1}$. Before mixing with the biosorbent, the pH of each solution was adjusted to the appropriate value for the sorption of Ni(II) ions by adding 0.1 M NaOH or 0.1 M $HNO_3$.

### Preparation of the biosorbents

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 for 24 h, crushed with an analytical mill, sieved (size fraction of 300–600 μm) and stored in polyethylene bottles for use. The raw biomass was chemically modified by a pre-treatment 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 300–600 μm (Matheickal et al. 1999).

### Biosorption experiments

The influence of pH on biosorption of Ni(II) was studied in the pH range 2.0 to 5.0 by batch method. Here, 100 ml aliquots of the adsorbates solution (initial concentration: 150 mg $l^{-1}$) were taken with 0.2 g adsorbent into 250 ml Erlenmeyer flasks and agitated on the rotary shaker (200 rpm) for well mixing.

Batch equilibrium biosorption experiments were carried out in 250 ml Erlenmeyer flasks containing nickel chloride solutions (100 ml) of known concentrations which varied from 10 to 250 mg $l^{-1}$. Weighed amounts of biomass (0.2 g) were added to each flask and the mixtures were agitated on the rotary shaker. The pH solution (4.5) was adjusted to the required value by using $HNO_3$ or NaOH. The equilibrium experiments were conducted at different temperatures viz. 20, 30, 40, and 50°C using constant temperature (±2°C) water bath. After 6 h of

agitation, the final pH (4.4) was measured, the solution was separated from the biomass by membrane filtration (Millipore 0.45 mm pore size) and the filtrates were stored for analysis.

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 biosorbent, confirmed that the sorption of metals on the walls of glass flasks or in the filtration systems was negligible.

### Analytical procedure

Metal concentration was determined by inductively coupled plasma atomic emission spectrometry (ICP, Perkin–Elmer, Optima 2000). The amount of metal biosorbed at equilibrium, $q$ (mg $g^{-1}$), which represents the metal uptake, was calculated from the difference in metal concentration in the aqueous phase before and after biosorption using the following equation:

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

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 $l^{-1}$), respectively, and $W$ is the mass of dry seaweed (g).

### Non-linear regression analysis

All the model parameters were evaluated by non-linear regression using the DATAFIT® software (Oakdale Engineering, USA). The optimization procedure requires an error function to be defined in order to be able to evaluate the fitness of the equation to the experimental data (Kundu and Gupta 2006). 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 suits the experimental data. In the present study, the correlation coefficient, $R^2$, SE, SSE, $F$-ratio and predicted $q_e/q_m$ (wherever applicable) values were used to determine the best fit biosorption kinetic as well as isotherm model.

## Results and discussion

### Effect of pH

Many studies on heavy metal biosorption have indicated that pH is an important parameter affecting the biosorption process (Matheickal et al. 1999; Sanchez et al. 1999). The effect of pH on biosorption was studied and the results showed that the biosorption of Ni(II) increased with pH up to 4.5, and then declined with further increase in pH for both raw and treated biomass of *L. variegata* (Figure provided as supporting information). The maximum equilibrium uptake of Ni(II) was found as 35.86 and 39.63 mg $g^{-1}$ at pH 4.5 for raw and treated biomass, respectively. The equilibrium Ni(II) binding capacity of the biosorbents decreased by increasing pH value to 5.0. Solution pH influences both cell surface metal binding sites and metal chemistry in water. The low metal biosorption at pH below 3 may be explained on the basis of active sites being protonated, resulting in a competition between $H^+$ and $M^{2+}$ for occupancy of the binding sites (Ajmal et al. 2000). The increase in metal removal as the pH increases can be explained on the basis of decrease in competition between protons and metal cations for the same functional groups by decrease in the positive surface charge resulting in a lower electrostatic repulsion between the surface and metal ions (Aksu 2001). The decrease in the Ni(II) at pH 5 may be attributed to the complexation of Ni(II) by OH groups which would prevent the metal adsorption.

## Equilibrium modeling

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. In order to compare the applicability of these models to describe the biosorption equilibrium, the common basis could be the number of parameters in a model as some isotherm models, for example, Langmuir can be derived using more than one theoretical approach (Faust and Aly 1987; Malek and Farooq 1996). 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 categorized based on a number of parameters. Twenty-three models have been analyzed (provided as supporting information). Out of which, one model, Henry's Law has single parameter; eleven models have two; eight 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 Ni(II) onto various forms of *L. variegata* was 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 a single parameter and has been successfully applied in many cases (Faust and Aly 1987; Xue et al. 2001). The Henry's law model was applied to describe the experimental data obtained for the sorption of Ni(II) onto *L. variegata.* The values of $R^2$, SE, SSE and $F$-ratio indicate that this model completely fails to predict the equilibrium isotherm (Table 1). This may be due to the non-availability of sorption data in the lower range of Ni(II) concentration. In liquid-phase sorption, the equilibrium sorption data are generally obtained at higher equilibrium concentrations, where the sorbent surface is almost on 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 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, SSE values by Linear with intercept over Henry's law. An increase in the parameter in the isotherm model definitely improves 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, maintaining the degree of freedom the same. In this regard, the applicability of other two parameter models was studied.

The Freundlich isotherm (Freundlich 1906) is empirical in nature, but was later interpreted as sorption to heterogeneous surface or surfaces supporting sites of varied affinities, and has been used widely to fit experimental data of liquid phase sorption whereas Langmuir isotherm (Langmuir 1916) 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 (Radke and Prausnitz 1972; Fritz and Schluender 1974; Aksu and Kutsal 1991; Khan et al. 1997). The value of $n$, of Freundlich model, falling in the range of 1–10 indicates conducive sorption while $K_L$ of Langmuir model is a coefficient attributed to the affinity between the sorbent and sorbate (Radke and Prausnitz 1972; Vadivelan and Kumar 2005). Figure 1a, b shows the theoretical plots of Freundlich isotherm compared with experimental data for raw and treated seaweed, respectively. The values of model constants along with the corresponding correlation coefficient, $R^2$, SE and SSE values for biosorbent–metal systems at different temperatures are presented in Table 1. For the Freundlich equation, $R^2$ varied from 0.9896 to 0.9998; and for Langmuir, it varied from 0.8862 to 0.9785 at various temparatures. Statistically, the Freundlich model commensurate to the experimental data with low SE, SSE and high $F$-ratio values as compared to Langmuir model. However, the separation factor ($R_L$) values incase of Langmuir model indicated (Table 1) that Ni(II) sorption onto *L. variegata* was favorable.

**Table 1** Isotherm constants for one- and two-parameter models for Ni(II) biosorption onto various biomass of *Lobophora variegata*

| Models | Temperature (°C) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 20 | | 30 | | 40 | | 50 | |
| | Raw | Treated | Raw | Treated | Raw | Treated | Raw | Treated |
| *Henry's law* | | | | | | | | |
| $K_{HE}$ | 0.1146 (0.1050) | 0.1442 (0.1357) | 0.1459 (0.1527) | 0.1781 (0.2107) | 0.2097 (0.1790) | 0.2968 (0.3494) | 0.1423 (0.1324) | 0.1731 (0.1876) |
| $R^2$ | 0.9425 | 0.9066 | 0.8530 | 0.8530 | 0.8527 | 0.8527 | 0.8722 | 0.8722 |
| SE | 1.8140 | 3.5979 | 4.3014 | 4.3014 | 6.9275 | 6.9275 | 3.9488 | 3.9488 |
| SSE | 32.907 | 125.535 | 185.024 | 185.024 | 479.90 | 479.90 | 141.63 | 141.63 |
| *F*-ratio | 167.2 | 63.042 | 58.042 | 58.042 | 57.914 | 57.914 | 60.348 | 60.348 |
| *Linear with intercept* | | | | | | | | |
| A | 0.6574 (0.0184) | 0.7537 (1.0131) | 0.4237 (3.4213) | 0.7425 (2.4123) | 0.4237 (0.1143) | 0.5748 (1.1142) | 0.6473 (4.1780) | 0.5217 (2.3471) |
| B | 1.6516 (0.0142) | 1.9313 (0.3257) | 1.1609 (5.6472) | 0.3612 (4.5621) | 1.6516 (0.0142) | 1.9313 (0.3257) | 1.1609 (5.6472) | 0.3612 (4.5621) |
| $R^2$ | 0.9562 | 0.9234 | 0.8932 | 0.9025 | 0.8963 | 0.9027 | 0.9261 | 0.9468 |
| SE | 0.5649 | 3.1462 | 4.3675 | 3.6827 | 4.9561 | 3.7124 | 3.0214 | 2.9452 |
| SSE | 74.654 | 139.64 | 221.34 | 186.34 | 267.94 | 201.34 | 125.61 | 114.62 |
| *F*-ratio | 146.35 | 120.36 | 84.632 | 90.462 | 75.681 | 94.682 | 132.46 | 134.63 |
| *Freundlich* | | | | | | | | |
| $K_F$ (l $g^{-1}$) | 0.1146 (2.112) | 0.1102 (3.2243) | 0.8524 (1.2455) | 0.2485 (2.1124) | 1.0892 (4.1146) | 0.6171 (2.012) | 0.1625 (1.4522) | 0.2751 (4.1327) |
| *n* | 1.0494 (0.1274) | 1.0005 (0.7234) | 1.0261 (2.346) | 1.4481 (3.6754) | 1.5048 (2.6541) | 1.4836 (0.7647) | 1.1005 (4.2172) | 1.0286 (1.4232) |
| $R^2$ | 0.9897 | 0.9998 | 0.9966 | 0.9921 | 0.9896 | 0.9979 | 0.9964 | 0.9971 |
| SE | 0.2644 | 0.1017 | 0.1644 | 0.1862 | 0.2358 | 0.1153 | 0.1148 | 0.1148 |
| SSE | 0.4432 | 0.0267 | 0.2165 | 0.3121 | 0.4159 | 0.0849 | 0.0984 | 0.0795 |
| *F*-ratio | 459.62 | 857.36 | 654.27 | 584.63 | 448.62 | 756.34 | 685.31 | 714.27 |
| *Langmuir* | | | | | | | | |
| $q_m$ (mg $g^{-1}$) | 44.835 (74.126) | 48.623 (22.394) | 52.138 (69.358) | 57.301 (67.234) | 65.438 (104.21) | 84.853 (10.638) | 47.561 (55.674) | 49.483 (29.642) |
| $K_L$ (l $mg^{-1}$) | 0.1181 (0.0145) | 0.1870 (0.0746) | 0.2270 (1.0023) | 0.4041 (4.4621) | 0.5371 (4.3214) | 0.7205 (0.0412) | 0.9241 (4.146) | 0.9918 (0.0629) |
| $R_L$ | 0.02986 | 0.02462 | 0.02213 | 0.0364 | 0.02986 | 0.02462 | 0.02213 | 0.0364 |
| $R^2$ | 0.9497 | 0.9785 | 0.8862 | 0.9497 | 0.9513 | 0.9004 | 0.9641 | 0.9759 |
| SE | 0.1876 | 0.1722 | 0.5310 | 0.3480 | 0.3013 | 0.4548 | 0.2081 | 0.1962 |
| SSE | 0.2820 | 0.2354 | 3.4321 | 0.9215 | 0.7245 | 2.3106 | 0.3416 | 0.3180 |
| *F*-ratio | 575.569 | 582.45 | 331.161 | 475.57 | 478.265 | 436.354 | 507.67 | 489.656 |
| *Modified Langmuir-1* | | | | | | | | |
| $K_L$(l $mg^{-1}$) | 0.0112 (0.0215) | 0.0952 (0.1142) | 0.0498 (1.0423) | 0.1120 (1.4124) | 0.0546 (1.2213) | 0.1124 (1.1241) | 0.1124 (0.0145) | 0.9124 (0.1203) |
| $n_L$ | −0.1143 (0.5698) | −0.3156 (1.1126) | −1.5647 (2.4569) | −1.4236 (0.1123) | −0.1169 (0.7956) | −1.1123 (2.4635) | −1.1014 (0.1123) | −0.7469 (0.1347) |
| $R^2$ | 0.8142 | 0.7963 | 0.6269 | 0.7569 | 0.8214 | 0.7563 | 0.6012 | 0.6587 |
| SE | 1.2241 | 1.7458 | 2.1176 | 1.9452 | 1.0107 | 1.9598 | 2.5726 | 2.3501 |
| SSE | 5.6249 | 9.2461 | 19.625 | 15.624 | 3.1249 | 16.684 | 27.634 | 24.692 |
| *F*-ratio | 4.2874 | 3.2116 | 3.2145 | 3.7958 | 5.1241 | 3.4126 | 2.7825 | 2.2095 |

**Table 1** continued

| Models | Temperature (°C) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 20 | | 30 | | 40 | | 50 | |
| | Raw | Treated | Raw | Treated | Raw | Treated | Raw | Treated |
| *Modified Langmuir-2* | | | | | | | | |
| $\eta^2$ | 74.344 (41.455) | 102.34 (247.34) | 124.53 (17.245) | 123.44 (14.536) | 157.22 (94.341) | 211.22 (74.245) | 175.2 (54.371) | 153.77 (22.347) |
| $K_L$ (l mg$^{-1}$) | 0.0127 (1.4276) | 0.0874 (1.2574) | 0.0547 (0.9748) | 0.0947 (2.4138) | 0.0497 (1.5873) | 0.0856 (2.4321) | 0.0953 (0.4275) | 0.0867 (0.7523) |
| $R^2$ | 0.8112 | 0.8245 | 0.7324 | 0.7174 | 0.8011 | 0.8222 | 0.7540 | 0.7425 |
| SE | 1.1442 | 1.1451 | 1.7401 | 1.9166 | 1.5482 | 1.5851 | 1.6601 | 1.6966 |
| SSE | 11.040 | 10.052 | 18.446 | 23.448 | 11.412 | 15.052 | 17.014 | 17.938 |
| *F*-ratio | 15.312 | 16.421 | 10.423 | 9.6342 | 14.440 | 16.017 | 11.611 | 10.699 |
| *Elovich* | | | | | | | | |
| $K_E$(l mg$^{-1}$) | 0.6748 (26.349) | 0.7295 (52.643) | 0.7836 (31.264) | 0.7709 (10.247) | 0.8281 (26.349) | 0.9308 (52.643) | 0.7264 (31.264) | 0.7762 (10.247) |
| $q_m$ (mg g$^{-1}$) | 0.8392 (2.4122) | 0.8660 (5.1124) | 0.7836 (4.1142) | 0.8863 (2.3241) | 0.8281 (2.8742) | 0.9651 (7.1017) | 0.7264 (2.3411) | 0.7762 (3.1745) |
| $R^2$ | 0.6425 | 0.6766 | 0.5530 | 0.6324 | 0.5900 | 0.5527 | 0.6637 | 0.6722 |
| SE | 12.281 | 11.866 | 14.891 | 13.912 | 14.573 | 17.741 | 12.952 | 12.420 |
| SSE | 132.907 | 125.535 | 185.021 | 124.823 | 163.97 | 479.90 | 135.12 | 136.06 |
| *F*-ratio | 38.963 | 15.328 | 10.216 | 15.214 | 12.395 | 8.167 | 36.38 | 40.37 |
| *Temkin* | | | | | | | | |
| $K_T$ (l mg$^{-1}$) | 0.0691 (1.1425) | 0.0585 (0.3142) | 0.0751 (3.1142) | 0.0531 (0.7854) | 0.0886 (2.2012) | 0.0792 (1.1124) | 0.0671 (3.2114) | 0.0707 (4.2148) |
| $-\Delta H$ (kJ mol$^{-1}$) | −0.3278 (1.1247) | −0.2451 (1.1341) | −0.2230 (2.1425) | −0.2087 (1.2241) | −0.2112 (0.9475) | −0.1 413 (2.1347) | −0.2918 (2.4349) | −0.2445 (1.4421) |
| $R^2$ | 0.8971 | 0.8397 | 0.9435 | 0.7337 | 0.9473 | 0.9689 | 0.8133 | 0.8475 |
| SE | 2.5606 | 4.4163 | 2.8087 | 7.3940 | 2.9531 | 3.3518 | 4.4827 | 4.7371 |
| SSE | 59.011 | 175.538 | 71.003 | 492.01 | 78.488 | 101.11 | 180.85 | 201.96 |
| *F*-ratio | 64.254 | 47.172 | 150.57 | 24.802 | 162.03 | 81.625 | 36.251 | 50.041 |
| *Dubinin-Radushkevich* | | | | | | | | |
| $B$ (mol$^2$ kJ$^{-2}$) | 757.39 (401.23) | 1260.14 (963.02) | 486.83 (211.36) | 2279.8 (1634.2) | 390.39 (156.39) | 387.15 (220.37) | 1216.2 (756.38) | 1018.22 (801.36) |
| $q_m$ (mg g$^{-1}$) | 22.946 (1.0654) | 33.265 (2.1455) | 32.711 (0.9865) | 50.526 (11.236) | 63.576 (44.368) | 52.347 (6.3724) | 32.479 (2.3615) | 37.191 (7.6427) |
| $R^2$ | 0.7630 | 0.7456 | 0.7695 | 0.7329 | 0.6934 | 0.7749 | 0.7369 | 0.7144 |
| SE | 11.540 | 12.575 | 12.023 | 13.715 | 14.236 | 13.093 | 12.653 | 13.495 |
| SSE | 121.178 | 159.514 | 138.208 | 243.97 | 259.038 | 181.506 | 161.088 | 213.95 |
| *F*-ratio | 53.862 | 36.67 | 45.197 | 15.18 | 7.1436 | 21.367 | 33.781 | 19.154 |
| *Fowler–Guggenheim* | | | | | | | | |
| $K_{FG}$ (l mg$^{-1}$) | 0.0356 (0.0246) | 0.0548 (0.0846) | 0.0412 (1.2835) | 0.0612 (0.7961) | 0.0564 (0.0246) | 0.0847 (0.0846) | 0.0775 (1.2835) | 0.0924 (0.7961) |
| $W_{FG}$ (kJ mol$^{-1}$) | 3.1245 (10.267) | 4.3244 (5.6792) | 3.6871 (20.497) | 4.9652 (9.6482) | 4.1256 (10.267) | 5.1267 (5.6792) | 4.6521 (20.497) | 5.8419 (9.6482) |
| $R^2$ | 0.6542 | 0.6577 | 0.6425 | 0.6357 | 0.6982 | 0.6456 | 0.6213 | 0.6115 |
| SE | 1.2324 | 1.2547 | 1.2997 | 1.3127 | 1.2001 | 1.2914 | 1.4148 | 1.5744 |
| SSE | 3.2245 | 3.5575 | 4.1025 | 4.9724 | 2.9144 | 4.0119 | 5.4452 | 5.9974 |

**Table 1** continued

| Models | Temperature (°C) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 20 | | 30 | | 40 | | 50 | |
| | Raw | Treated | Raw | Treated | Raw | Treated | Raw | Treated |
| *F*-ratio | 21.316 | 23.615 | 18.957 | 16.369 | 29.641 | 19.237 | 14.621 | 11.378 |
| *Frumkin* | | | | | | | | |
| $f$ | 0.0112 (0.0427) | 0.0314 (0.0643) | 0.0156 (0.8571) | 0.0334 (1.1445) | 0.0175 (1.1104) | 0.0357 (1.1846) | 0.0192 (1.0078) | 0.0392 (1.4531) |
| $-\Delta G^0$ (kJ mol$^{-1}$) | 2.1455 (0.9447) | 3.2475 (1.2435) | 2.5437 (5.0417) | 4.2147 (1.2432) | 2.9643 (4.001) | 3.4785 (1.2441) | 3.4257 (5.1477) | 3.4967 (4.1142) |
| $R^2$ | 0.8443 | 0.8541 | 0.8712 | 0.8427 | 0.8447 | 0.8941 | 0.8432 | 0.8887 |
| SE | 1.9120 | 1.8211 | 1.5441 | 1.9209 | 1.9011 | 1.1158 | 0.9104 | 1.2608 |
| SSE | 3.5442 | 2.9546 | 2.2212 | 3.7773 | 3.6573 | 2.0118 | 1.9145 | 2.3459 |
| *F*-ratio | 24.135 | 27.652 | 29.265 | 22.246 | 21.118 | 39.957 | 23.627 | 34.621 |
| *Harkins–Jura* | | | | | | | | |
| $A_{HJ}$ | 121.04 (66.347) | 144.36 (75.367) | 101.69 (44.276) | 135.62 (69.342) | 112.64 (85.642) | 114.63 (44.369) | 95.648 (11.654) | 103.68 (44.367) |
| $B_{HJ}$ | 0.2266 (1.4177) | 0.6153 (2.1247) | 0.3267 (3.1417) | 0.8435 (2.4212) | 0.4165 (3.1101) | 0.9126 (4.1233) | 0.5471 (4.1278) | 1.2375 (3.4557) |
| $R^2$ | 0.8011 | 0.7894 | 0.7758 | 0.7912 | 0.8144 | 0.8188 | 0.7945 | 0.8342 |
| SE | 4.1453 | 4.8741 | 5.1246 | 4.4477 | 3.9422 | 3.8411 | 4.3611 | 3.1203 |
| SSE | 40.562 | 55.124 | 74.124 | 49.347 | 34.107 | 30.245 | 43.268 | 24.723 |
| *F*-ratio | 51.234 | 29.625 | 21.365 | 32.159 | 62.127 | 67.384 | 47.523 | 71.115 |

The modified forms of Langmuir equation, i.e., modified Langmuir-1 and Langmuir-2, describe temperature-dependent saturation coverage ($T^{-nL}$) and surface heterogeneity of sorbent, respectively (O'Brien and Myers 1984; Yang and Doong 1985). The results showed that both modified Langmuir-1 and Langmuir-2, do not improve the ability to fit the experimental data, however, both the forms provided satisfactory fit to the experimental data with $R^2$ values ranging from 0.6012 to 0.8214 and 0.7174 to 0.8245, respectively, at various temperatures and the value of exponent term, $n_L$ of modified Langmuir-1 was negative in all systems. This denoted that Ni(II) 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 dye with temperature indicated that sorption was due to the combination of physical, chemical, and ion-exchange processes (Ho and McKay 1998). The negative value of $n_L$ is suggestive of the involvement of several mechanisms in the sorption of Ni(II). Therefore, for liquid-phase sorption, both the modified forms of Langmuir model provided an acceptable fit.

The Elovich (Elovich and Larinov 1962) isotherm constants, $K_E$ and $q_m$, as well as the coefficient of correlation, $R^2$, SE, SSE and *F*-ratio values are presented in Table 1. In all cases, the Elovich isotherm exhibited lower coefficients of correlation as well as high SE and SSE values. Also, the values of maximum biosorption capacity determined (Table 1) were much lower than the experimentally biosorbed amounts at equilibrium corresponding to the plateaus of the sorption isotherm. Therefore, the Elovich model is unable to describe the biosorption isotherms of Ni(II) onto *L. variegata* at various temperatures.

The parameters of Temkin (Temkin and Pyzhev 1940) model as well as the regression coefficients ($R^2$) with SE, SSE and *F*-ratio values are given in Table 1. The moderate values of $R^2$ (0.7337 to 0.9744) and *F*-ratio (24.802 to 162.03) show a satisfactory fit to the experimental data. The variation of adsorption energy, $\Delta Q = (-\Delta H)$, is negative for

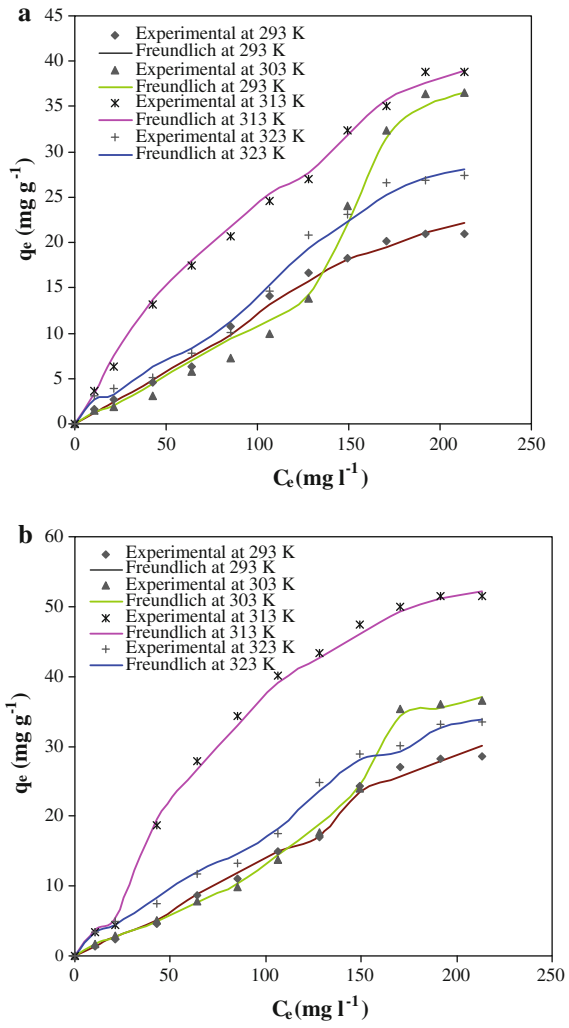


**Fig. 1** **a** Freundlich isotherm obtained for the biosorption of Ni(II) onto raw biomass of *L. variegata*. **b** Freundlich isotherm obtained for the biosorption of Ni(II) onto treated biomass of *L. variegata*

all the studied systems, which indicated that the biosorption reaction is endothermic.

The Dubinin–Radushkevich isotherm has been successfully applied to model gas-phase adsorption on activated carbon where the adsorption mechanism is constricted to van der Waals forces (Dubinin 1960; Chen and Yang 1994; Malek and Farooq 1996). Its application has been reported for liquid-phase adsorption on biological materials such as fungal biomass (Maurya and Mittal 2006). The liquid-phase biosorption of Ni(II) onto *L. variegata* have been analyzed by the Dubinin–Radushkevich equation at various temperatures. The isotherm constants along with the statistical parameters are presented in Table 1. In all cases, the values of the correlation coefficients are lower than the most commonly used isotherm models, i.e., Freundlich, Langmuir and Temkin isotherm models. Poor performance of the Dubinin–Radushkevich equation (SE and SSE values) indicated the involvement of Ni(II) sorption mechanisms other than van der Waals force. The Modified Langmuir-1 model also supported that the sorption of Ni(II) onto *L. variegata* may not be a case of physisorption as the value of $n_L$ was negative at various temperatures.

The statistical parameters of the Fowler–Guggenheim (Fowler and Guggenheim 1939) model indicate that both the models fail to predict the equilibrium isotherm. However, the interaction energy, $W_{FG}$, is positive, which indicates that there is attraction between the adsorbed molecules. Frumkin and Harkins–Jura (Basar 2006) isotherm constants along with statistical parameters are summarized in Table 1. Both the isotherms showed satisfactory fit to the experimental data with $R^2$ values ranged from 0.8432 to 0.8941 and 0.7758 to 0.8342 for Frumkin and Harkins–Jura models, respectively, at various temperatures, however, both SE and SSE values were >1. The positive $f$ values in case of Frumkin isotherm indicate that there is attractive interaction between the adsorbed species (Basar 2006). In general trend, attractive interaction decreases with increasing temperature.

It is axiomatic that the predicted Freundlich isotherm curve fits better followed by Langmuir and Temkin. Upon comparing all the isotherm models, the isotherm curve predicted by the Freundlich 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 (Redlich and Peterson 1959), Sips (Sips 1948), Khan (Khan et al. 1997), Fritz–Schluender (Fritz and Schluender 1974) Radke–Prausnitz (two models) (Radke and Prausnitz 1972), Toth (Toth 2000) and Koble–Carrigan (Koble and Carrigan 1952) 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 show the isotherm and statistical parameters obtained using non-linear 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 (Ho and McKay 1998; Sag and Aktay 2002; Ho 2004). 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 the present study, the Redlich–Peterson equation has established its capability to fit the experimental data satisfactorily (with $R^2$ between 0.9670 and 0.9909 at various temperatures). However, SE and SSE values were higher than Khan, Fritz–Schluender and Radke–Prausnitz-II models. Also, it does not provide any improvement over the Radke–Prausnitz-II model (Table 2). The $\beta$ values ranged from 0.16 to 0.0.49 i.e., the data can preferably be fitted with the Freundlich. This is confirmed by the satisfactory fit of the data to the Freundlich model.

At low sorbate concentrations, Sips isotherm (Sips 1948) 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 $\gamma$ value was in the range of 0.17–0.46, meaning that the sorption data obtained in this study is more of a Freundlich form rather than that of Langmuir, which was also confirmed by the results shown in Table 1. Though the $R^2$ values of the Fritz–Schluender and Radke–Prausnitz-I models were satisfactory (0.9658–0.9897 and 0.8125–0.9827, respectively), however, 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 very good regression coefficients ($\geq$0.9860) and $F$-ratio ($\geq$163.59), the maximum sorption capacities for the studied systems determined using the three-parameter equations of Radke–Prausnitz-II (Table 2) were lower than the biosorbed amounts at equilibrium corresponding to the plateaus of the isotherms. For all the cases except at temperature 50°C, the Radke–Prausnitz-II model exponent, $\alpha_{RI,}$ was negative and inadmissible. Consequently, the Radke–Prausnitz-II cannot describe the experimental equilibrium data.

The Khan model correctly simulates the biosorption isotherms of Ni(II)- *L. variegata* system at various temperatures (Fig. 2a, b). The regression coefficients were very good ($R^2 \geq 0.9847$) for the tested systems. The SE, SSE and $F$-ratio values varied from 0.0167–0.2449, 0.0047–0.2817 and 377.5–$1.04 \times 10^{20}$, respectively. The biosorption maximum capacities determined using the Khan model was comparable to experimental data. Hence, this model is precise for the experimental data among the three-parameter 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 model isotherm showed a poorer fit 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: Khan > Redlich–Peterson > Sips.

## 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 (Fritz and Schluender 1974) (Figures not shown). From Table 2, the coefficients of correlation ($\geq$0.9711) were very good and the SE and SSE values were in the range of 0.0826–0.3394 and 0.0688–0.5012, respectively. The values of $\alpha$ and $\beta_{FS}$ for all the tested systems were below 0.48 i.e. the data can preferably be fitted with the Freundlich model. The calculated parameters of equilibrium biosorption isotherms of Ni(II) onto *L. variegata* at various temperatures by the Baudu

**Table 2** Isotherm constants for three-, four- and five-parameter models for Ni(II) biosorption onto various biomass of *Lobophora variegata*

| Models | Temperature (°C) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 20 | | 30 | | 40 | | 50 | |
| | Raw | Treated | Raw | Treated | Raw | Treated | Raw | Treated |
| *Redlich-Peterson* | | | | | | | | |
| $K_{RP}$ (l g$^{-1}$) | 0.1407 (1.1134) | 0.1496 (2.2643) | 0.2422 (1.9148) | 0.4554 (1.0128) | 0.4354 (1.9647) | 0.4483 (3.2697) | 0.1514 (2.2279) | 0.1924 (0.9116) |
| $a_{RP}$ (l mg$^{-1}$) | $2.265 \times 10^{-6}$ ($1.49 \times 10^{-12}$) | $2.254 \times 10^{-8}$ ($1.22 \times 10^{-9}$) | $3.131 \times 10^{-8}$ ($3.57 \times 10^{-6}$) | $3.286 \times 10^{-8}$ ($5.11 \times 10^{-9}$) | $1.147 \times 10^{-8}$ ($3.76 \times 10^{-10}$) | $1.832 \times 10^{-5}$ (0.0019) | $1.874 \times 10^{-12}$ ($3.24 \times 10^{-8}$) | $1.919 \times 10^{-5}$ (0.0126) |
| $\beta$ | 0.2383 (1.2153) | 0.2821 (3.1142) | 0.1592 (0.1147) | 0.4855 (1.2247) | 0.4029 (3.1723) | 0.2685 (3.4126) | 0.1871 (0.0017) | 0.4863 (0.0547) |
| $R^2$ | 0.9796 | 0.9788 | 0.9909 | 0.9670 | 0.9827 | 0.9904 | 0.9727 | 0.9789 |
| SE | 1.2083 | 1.6999 | 1.1955 | 2.7604 | 1.7913 | 1.9743 | 1.8185 | 1.8678 |
| SSE | 11.680 | 23.117 | 11.441 | 60.961 | 25.671 | 31.185 | 26.456 | 27.911 |
| *F*-ratio | 192.55 | 185.56 | 436.14 | 117.27 | 228.57 | 414.06 | 142.52 | 185.869 |
| *Sips* | | | | | | | | |
| $K_S$ (l g$^{-1}$) | 0.0050 (1.4150) | 0.0403 (1.1134) | 0.0105 (0.1754) | 0.0047 (0.8725) | 0.0195 (1.2413) | 0.0015 (0.7244) | 0.0526 (1.4725) | 0.0144 (0.8246) |
| $a_S$ (l mg$^{-1}$) | 0.00014 (0.0141) | 0.0045 (0.0181) | 0.00019 (0.0134) | 0.00041 (0.0024) | 0.00075 (0.0017) | 0.00055 (0.0047) | 0.00062 (0.1422) | 0.00065 (0.0427) |
| $\gamma$ | 0.1734 (0.0011) | 0.3153 (0.0041) | 0.4529 (0.0011) | 0.4572 (0.0014) | 0.1990 (0.0114) | 0.3075 (0.0079) | 0.4568 (0.0045) | 0.4357 (0.0014) |
| $R^2$ | 0.9881 | 0.9826 | 0.9845 | 0.9684 | 0.9683 | 0.9725 | 0.9568 | 0.9805 |
| SE | 1.3673 | 1.5405 | 1.0534 | 2.6984 | 1.9569 | 2.1485 | 2.4568 | 2.3474 |
| SSE | 14.956 | 18.986 | 8.8774 | 58.254 | 30.638 | 44.215 | 44.265 | 44.267 |
| *F*-ratio | 332.69 | 226.81 | 254.22 | 122.91 | 122.52 | 199.26 | 95.624 | 204.56 |
| *Khan* | | | | | | | | |
| $q_m$ (mg g$^{-1}$) | 25.758 (14.634) | 30.344 (15.681) | 39.621 (5.6479) | 40.581 (22.364) | 38.653 (12.675) | 51.078 (2.3679) | 30.404 (15.647) | 32.473 (11.316) |
| $b_K$ (l mg$^{-1}$) | 0.0122 (0.0068) | 0.3469 (1.0124) | 0.0142 (1.1127) | 0.0544 (0.0041) | 0.0327 (0.0032) | 0.0891 (1.7932) | 0.3932 (3.1789) | 0.3665 (4.4459) |
| $a_K$ | 0.3864 (2.4231) | 0.3535 (0.0164) | 0.4319 (1.2191) | 0.5014 (0.0451) | 0.3914 (1.2874) | 0.1696 (1.1562) | 0.5663 (2.3592) | 0.4627 (1.2743) |
| $R^2$ | 0.9968 | 0.9847 | 0.9930 | 0.9870 | 0.9927 | 0.9876 | 0.9940 | 1.000 |
| SE | 0.0590 | 0.2449 | 0.0928 | 0.1572 | 0.0953 | 0.1523 | 0.0865 | 0.0167 |
| SSE | 0.0093 | 0.3059 | 0.0402 | 0.2817 | 0.0412 | 0.2378 | 0.0380 | 0.0047 |

**Table 2** continued

| Models | Temperature (°C) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 20 | | 30 | | 40 | | 50 | |
| | Raw | Treated | Raw | Treated | Raw | Treated | Raw | Treated |
| *F*-ratio | 616.69 | 345.90 | 532.91 | 377.56 | 501.83 | 390.47 | 587.30 | $1.04 \times 10^{20}$ |
| *Fritz–Schluender* | | | | | | | | |
| $q_{mFS}$ (mg $g^{-1}$) | 1.0516 (0.0115) | 32.457 (1.2675) | 1.1768 (3.4222) | 0.0505 (0.0102) | 1.4055 (0.0826) | 1.1834 (0.0416) | 0.5213 (5.1472) | 1.3659 (4.2469) |
| $K_{FS}$ | 0.3042 (12.365) | 2.5416 (0.3616) | 1.6452 (6.8212) | 2.9837 (0.7458) | 6.7236 (0.2575) | 3.6578 (0.0536) | 9.2331 (1.3647) | 0.4053 (6.3648) |
| $m_{FS}$ | 0.1027 (2.4452) | 0.2305 (1.9562) | 0.1649 (4.1643) | 0.2056 (0.0451) | 0.5643 (3.1542) | 0.3152 (2.5346) | 0.3241 (5.6241) | 0.1748 (3.3111) |
| $R^2$ | 0.9770 | 0.9866 | 0.9897 | 0.9658 | 0.9895 | 0.9769 | 0.9684 | 0.9772 |
| SE | 0.1537 | 0.1339 | 0.1624 | 0.2161 | 0.0886 | 0.1369 | 0.2416 | 0.2120 |
| SSE | 0.1890 | 0.1434 | 0.2324 | 0.3737 | 0.0629 | 0.1494 | 0.6212 | 0.3351 |
| *F*-ratio | 171.71 | 271.35 | 395.62 | 82.785 | 377.26 | 167.34 | 102.54 | 172.14 |
| *Radke-Prausnitz-I* | | | | | | | | |
| $a_{RI}$ (mg $g^{-1}$) | 0.1380 (0.0031) | 0.4044 (3.2164) | 0.2486 (5.1552) | 0.2168 (2.0362) | 0.4430 (0.0011) | 0.7234 (3.3162) | 0.1595 (5.1682) | 4.0996 (82.347) |
| $r_{RI}$ (l $mg^{-1}$) | 714,151 (5,604.3) | 0.3932 (613.58) | 0.3895 (1.3642) | 0.4281 (10.364) | 21.329 (6.2487) | 0.7234 (6.5674) | 8.0397 (0.0212) | 409.96 (10.964) |
| $\alpha_{RI}$ | 0.6627 (0.0075) | 0.6950 (0.0011) | 0.4281 (3.4374) | 0.3895 (1.0749) | 0.7234 (0.0014) | 0.2155 (0.0011) | 0.1134 (5.1243) | 0.6450 (2.4231) |
| $R^2$ | 0.9815 | 0.9640 | 0.8125 | 0.9125 | 0.9827 | 0.8926 | 0.9642 | 0.9778 |
| SE | 1.1490 | 2.0865 | 5.2653 | 4.0267 | 1.7916 | 6.2124 | 2.0809 | 1.9146 |
| SSE | 10.562 | 34.831 | 130.21 | 106.21 | 25.678 | 162.31 | 34.643 | 29.327 |
| *F*-ratio | 213.02 | 107.32 | 75.421 | 102.71 | 228.40 | 98.45 | 107.90 | 176.70 |
| *Radke-Prausnitz-II* | | | | | | | | |
| $a_{RII}$ (mg $g^{-1}$) | 15.373 (9.6234) | 22.115 (6.2034) | 28.289 (4.9628) | 29.040 (12.645) | 32.011 (5.1643) | 20.652 (159.62) | 15.1546 (64.314) | 16.4755 (1.2652) |
| $r_{RII}$ (l $mg^{-1}$) | 1.1790 (0.3564) | 0.0096 (0.6246) | 0.0043 (0.4562) | 0.0024 (0.2074) | 0.0058 (1.1327) | 0.0169 (1.1624) | 2.3448 (0.0227) | 1.3125 (0.0153) |
| $\alpha_{RII}$ | 0.4412 (0.0156) | 0.2264 (0.0221) | −0.3674 (0.0034) | −0.1572 (0.0016) | −0.7405 (0.0149) | −0.0169 (0.0316) | −0.3448 (0.0031) | −0.1730 (0.0014) |
| $R^2$ | 0.9872 | 0.9918 | 0.9908 | 0.9926 | 0.9984 | 0.9936 | 0.9860 | 0.9868 |
| SE | 0.1537 | 0.1047 | 0.0405 | 0.1012 | 0.0889 | 0.1004 | 0.2246 | 0.1367 |

**Table 2** continued

| Models | Temperature (°C) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 20 | | 30 | | 40 | | 50 | |
| | Raw | Treated | Raw | Treated | Raw | Treated | Raw | Treated |
| SSE | 0.1891 | 0.0877 | 0.0013 | 0.0724 | 0.0036 | 0.0581 | 0.4036 | 0.1496 |
| *F*-ratio | 171.70 | 484.52 | 338.94 | 502.26 | 475.29 | 562.31 | 163.59 | 169.14 |
| *Toth* | | | | | | | | |
| $q_m$ (mg $g^{-1}$) | 15.712 (2.164) | 13.837 (4.2381) | 17.145 (44.316) | 13.669 (25.364) | 18.215 (23.648) | 13.837 (1.3874) | 13.415 (3.6482) | 18.324 (44.327) |
| $b_T$ (l $g^{-1}$) | 13.215 (66.243) | 16.546 (1.3678) | 15.612 (100.24) | 15.628 (66.328) | 18.142 (5.621) | 16.295 (72.374) | 19.812 (112.36) | 18.264 (25.642) |
| $n_T$ | −185.21 (12.341) | −212.07 (7.1285) | −195.86 (44.657) | −242.14 (12.453) | −212.45 (16.375) | −231.49 (5.3647) | −198.21 (15.634) | −221.24 (11.395) |
| $R^2$ | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| SE | 1.5684 | 1.2433 | 2.2468 | 2.4326 | 3.4259 | 2.1429 | 2.8649 | 3.2480 |
| SSE | 9.2438 | 12.368 | 16.484 | 19.267 | 30.426 | 13.167 | 23.612 | 32.352 |
| *Koble–Carrigan* | | | | | | | | |
| $A_{KH}$ (mg $g^{-1}$) | 3.4561 (10.138) | 2.6497 (15.154) | 6.4897 (0.0512) | 1.2346 (10.304) | 9.4662 (0.0149) | 10.264 (0.3466) | 32.465 (5.1450) | 12.654 (0.1045) |
| $B_{KH}$ (l $g^{-1}$) | 42.364 (2.1422) | 124.54 (14.013) | 1423.4 (1.1479) | 1453.7 (723.17) | 132.45 (5.4501) | 1753.1 (3.6723) | 142.37 (71.279) | 452.3 (10.437) |
| $n_{KH}$ | 2.456 (0.2114) | 3.2453 (15.141) | 10.242 (0.0127) | 14.523 (0.9537) | 16.455 (7.1145) | 44.244 (10.145) | 107.42 (10.474) | 11.244 (2.4234) |
| $R^2$ | 0.7712 | 0.7522 | 0.7420 | 0.7748 | 0.7362 | 0.7518 | 0.7481 | 0.7598 |
| SE | 50.741 | 62.312 | 63.419 | 50.004 | 56.612 | 63.411 | 61.676 | 52.804 |
| SSE | 12,431 | 14,213 | 13,161 | 12,542 | 13,347 | 13,014 | 14,256 | 11,584 |
| *F*-ratio | 7.6420 | 6.4578 | 5.8642 | 4.1544 | 5.6420 | 5.3241 | 6.5246 | 6.8472 |
| *Fritz–Schluender (Four-parameter)* | | | | | | | | |
| *A* | 2.6911 (19.654) | 3.2125 (15.364) | 3.4192 (0.1646) | 1.7935 (10.236) | 0.2727 (5.2647) | 0.1392 (5.1248) | 2.1625 (0.0116) | 3.5100 (0.0126) |
| $B_{FS}$ | 15.184 (3.1245) | 31.482 (10.145) | 60.746 (5.1459) | 165.11 (15.162) | 53.336 (4.0172) | 3.3692 (15.237) | 89.347 (6.3874) | 87.187 (3.6541) |
| $\Im$ | 0.3367 (0.0101) | 0.1175 (0.0041) | 0.1015 (4.3016) | 0.2685 (10.002) | 0.1022 (0.0142) | 0.3947 (0.0968) | 0.1751 (3.1475) | 0.3367 (11.143) |
| $\beta_{FS}$ | 0.1199 (1.5842) | 0.4102 (3.4136) | 0.4457 (1.2261) | 0.4248 (3.1127) | 0.4865 (0.0637) | 0.1199 (2.9729) | 0.3420 (3.1417) | 0.5035 (2.1485) |

**Table 2** continued

| Models | Temperature (°C) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 20 | | 30 | | 40 | | 50 | |
| | Raw | Treated | Raw | Treated | Raw | Treated | Raw | Treated |
| $R^2$ | 0.9967 | 0.9792 | 0.9903 | 0.9762 | 0.9954 | 0.9907 | 0.9905 | 0.9711 |
| SE | 0.0826 | 0.3041 | 0.1049 | 0.3191 | 0.0915 | 0.0993 | 0.1021 | 0.3394 |
| SSE | 0.0688 | 0.4886 | 0.0842 | 0.4443 | 0.0754 | 0.0055 | 0.0801 | 0.5012 |
| *F*-ratio | 342.15 | 130.367 | 211.47 | 116.529 | 319.73 | 248.61 | 221.83 | 99.375 |
| *Baudu* | | | | | | | | |
| $q_{mo}$ (mg $g^{-1}$) | 5.6478 (16.318) | 10.248 (0.3114) | 6.1579 (0.4239) | 11.567 (2.4632) | 7.6282 (17.138) | 15.647 (1.2412) | 9.4781 (0.1142) | 12.347 (7.6032) |
| $b_o$ | 0.3241 (7.1349) | 0.4427 (1.4423) | 0.5014 (1.2241) | 0.4124 (0.0442) | 0.4245 (9.1414) | 0.3541 (2.4532) | 0.4274 (7.4234) | 0.4315 (0.0011) |
| *X* | 0.4125 (4.1402) | 0.3546 (4.1428) | 0.4237 (0.0014) | 0.3425 (0.0345) | 0.4275 (3.4203) | 0.3027 (7.1418) | 0.1145 (0.0011) | 0.1273 (0.2162) |
| *Y* | −0.4277 (1.2241) | −1.1142 (2.7244) | −0.3457 (0.1142) | −0.2475 (2.0144) | −0.2788 (2.1142) | −0.3472 (4.1142) | −0.3244 (0.4517) | −0.1142 (1.1427) |
| $R^2$ | 0.8894 | 0.8837 | 0.8691 | 0.8844 | 0.8886 | 0.8842 | 0.8612 | 0.8819 |
| SE | 2.6241 | 2.5734 | 3.1594 | 2.4294 | 2.6272 | 2.6831 | 3.2671 | 2.6885 |
| SSE | 16.135 | 14.922 | 37.109 | 36.184 | 19.562 | 17.922 | 49.149 | 21.353 |
| *F*-ratio | 42.957 | 33.114 | 19.841 | 36.217 | 40.824 | 43.012 | 17.716 | 29.926 |
| *Fritz–Schluender (Five-parameter)* | | | | | | | | |
| $\alpha_1$ (mg $g^{-1}$) | 27.647 (1.3649) | 32.642 (15.362) | 40.359 (90.624) | 44.364 (16.327) | 41.352 (10.637) | 54.357 (11.364) | 33.125 (70.64) | 36.263 (81.167) |
| $\alpha_1'$ | 0.2048 (14.611) | 0.6502 (2.1122) | 0.2677 (5.2041) | 0.1664 (0.0012) | 0.2435 (1.1652) | 0.5893 (4.1426) | 0.5360 (0.0367) | 0.2246 (0.0168) |
| $\alpha_2$ | 3.0157 (0.6486) | 1.6451 (1.3672) | 8.0855 (2.6738) | 0.2133 (0.1037) | 1.1102 (0.6486) | 5.1591 (1.3672) | 0.2533 (2.6738) | 4.2164 (0.1037) |
| $\beta_1$ | 0.4597 (0.0043) | 0.3516 (0.0011) | 0.3133 (2.2437) | 0.1275 (0.042) | 0.1254 (0.0045) | 0.3582 (0.0011) | 0.3113 (1.0349) | 0.2322 (0.0901) |
| $\beta_2$ | 0.3162 (0.0243) | 0.3149 (0.0104) | 0.3246 (1.2211) | 0.3321 (0.0715) | 0.4925 (0.0345) | 0.42115 (0.0514) | 0.4237 (1.6022) | 0.2469 (0.0509) |
| $R^2$ | 0.9935 | 0.9924 | 0.9962 | 0.9922 | 0.9975 | 0.9911 | 0.9943 | 0.9960 |
| SE | 0.1015 | 0.1304 | 0.0964 | 0.1451 | 0.0902 | 0.1556 | 0.0972 | 0.1022 |
| SSE | 0.0131 | 0.1020 | 0.0055 | 0.1263 | 0.0012 | 0.1789 | 0.0063 | 0.0627 |
| *F*-ratio | 145.24 | 156.13 | 159.82 | 128.58 | 179.96 | 118.03 | 166.35 | 153.38 |

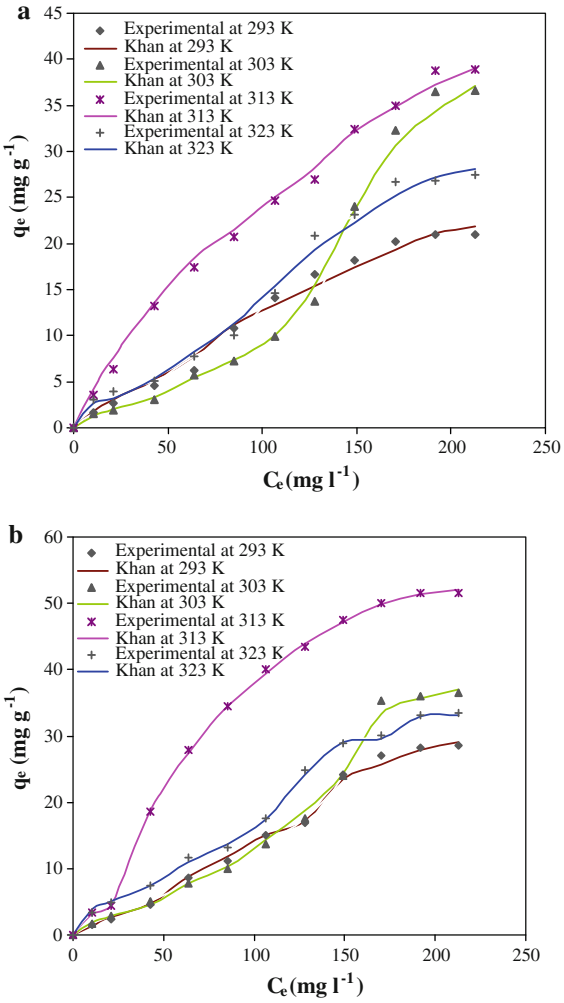


**Fig. 2** **a** Khan isotherm obtained for the biosorption of Ni(II) onto raw biomass of *L. variegata.* **b**. Khan isotherm obtained for the biosorption of Ni(II) onto treated biomass of *L. variegata*

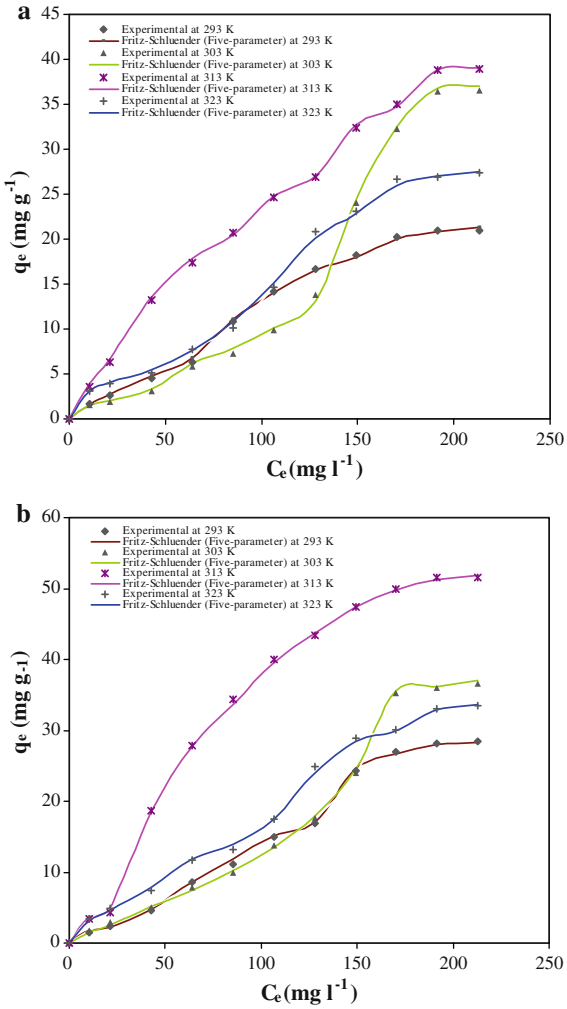


**Fig. 3** **a** Fritz–Schluender (Five-parameter) isotherm obtained for the biosorption of Ni(II) onto raw biomass of *L. variegata.* **b**. Fritz–Schluender (Five-parameter) isotherm obtained for the biosorption of Ni(II) onto treated biomass of *L. variegata*

(1990) model are presented in Table 2. An appropriate fit was not obtained using the model of Baudu as compared to Fritz–Schluender four-parameter model. Also, the values of the maximum biosorption capacity obtained using the Baudu isotherms were lower than the experimental results. Therefore, this model cannot describe the experimental data.

The biosorption data were analyzed according to the non-linear form of the five-parameter isotherm model of Fritz–Schluender (Fritz and Schluender 1974). An accurate fitting of the experimental results of the biosorption isotherms is obtained using the five-parameter model of Fritz–Schluender (Fig. 3a, b). From Table 2, high correlation coefficients (≥0.9 880) and low SE (≤0.1556) and SSE (≤0.1789) 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 Khan model and lower than the Langmuir model. The five-parameter model of Fritz–Schluender is reduced to the Langmuir model when the exponents $\beta_1$ and $\beta_2$ 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. 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.

Table 3 shows the experimental sorption capacity of Ni(II) by other low cost sorbents reported in the literature from aqueous solutions along with the present study result. It can be observed that Ni(II) sorption capacity of *L. variegata* was found to be higher and comparable to other low cost sorbents

**Table 3** Sorption capacities for Ni(II) using various biosorbents

| Biosorbent | Nickel | | Reference |
|---|---|---|---|
| | Sorption capacity (mg $g^{-1}$) | pH | |
| *Lobophora variegata* | 51.56 | 4.5 | Present study |
| *Ascophyllum nodosum* | 135.94 | 6.0 | Holan and Volesky (1994) |
| *Enteromorpha prolifera* | 36.8 | 4.3 | Ozer et al. (2008) |
| *Undaria pinnatifida* | 24.71 | 4.7 | Chen et al. (2008) |
| *Ascophyllum nodosum* | 114.99 | 5.0 | Leusch and Volesky (1995) |
| *Sargassum fluitans* | 43.02 | 5.0 | Leusch and Volesky (1995) |
| *Chlorella miniata* | 20.36 | 6.0 | Lau et al. (1999) |
| *Chlorella vulgaris* | 12.03 | 6.0 | Lau et al. (1999) |
| *Scenedesmus obliquus* | 30.17 | 4.0 | Donmez et al. (1999) |
| *Durvillaea potatorum* | 66.33 | 6.0 | Yu and Kaewsarn (2000) |
| *Sargassum hemiphyllum* | 35.39 | 5.0 | Tsui et al. (2006) |
| *Sargassum* sp. | 35.80 | 5.5 | Sheng et al. (2004) |
| *Padina* sp. | 36.98 | 5.5 | |
| *Ulva* sp. | 17.02 | 5.5 | |
| *Gracillaria* sp. | 16.43 | 5.5 | |
| *C. vulgaris* | 10.09 | – | Sandau et al. (1996) |
| *C. vulgaris* | 23.48 | 5.5 | Mehta and Gaur (2001) |
| *Pilayella littoralis* | 22.81 | 5.5 | Carrilho and Gilbert (2000) |
| *Ulva reticulate* | 46.51 | 4.5 | Vijayaraghavan et al. (2005) |
| *Chlorella miniata* | 2.99 | 7.4 | Wong et al. (2000) |
| *Lyngbya taylorii* | 38.16 | 4.7 | Klimmek et al. (2001) |
| *Padina pavonia* | 58.71 | 5.0 | Ofer et al. (2003) |
| *Tobacco dust* | 24.5 | 6.34 | Qi and Aldrich (2008) |
| *Biomatrix from rice husk* | 5.4 | 6.0 | Krishnani et al. (2008) |
| *Myriophyllum spicatum* | 5.8 | 5.0 | Wang et al. (1996) |
| *Myriophyllum spicatum* L. | 3.0 | 8.0 | Lesage et al. (2007) |
| *Lemna minor* L. | 59.0 | 5.0 | Saygideger et al. (2005) |
| *Penicillium chrysogenum* | 55.0 | 5.0 | Deng and Ting (2005) |
| *Cork biomass* | 10.5 | 5.2 | Chubar et al. (2003) |
| *Irish peat moss* | 14.5 | 4.5 | Sen Gupta et al. (2009) |
| *Lignin* | 5.98 | 6.0 | Guo et al. (2008) |
| Chitosan immobilized with reactive Blue 2 dye | 11.2 | 8.5 | Vasconcelos et al. (2007) |

except *Ascophyllum nodosum*, *Durvillaea potatorum*, *Padina pavonia* and *Lemna minor* L. Thus, the low cost material *L. variegata* may be used as an sorbent for the removal of Ni(II) bearing wastewaters.

### Thermodynamic parameters

The values of thermodynamic parameters are important for the practical application of biosorption process (Ozcan et al. 2006). The thermodynamic parameters viz. the standard free energy ($\Delta G^0$), enthalpy change ($\Delta H^0$), and entropy change ($\Delta S^0$) have been estimated to evaluate the feasibility and nature of the adsorption process. The Gibbs free energy change of the process is related to the equilibrium constant ($K_L$) by the following equation:

$$\Delta G^0 = -\mathrm{RT} \ln K_L \quad (4)$$

where $R$ is universal gas constant (8.314 J $K^{-1}$ $mol^{-1}$). According to thermodynamics, the Gibbs free energy change is also related to enthalpy change and entropy change at constant temperature by the following Eq. (5):

$$\ln K_a = \left(\frac{\Delta S^0}{R} - \frac{\Delta H^0}{\mathrm{RT}}\right) \quad (5)$$

The values of $\Delta H^0$ and $\Delta S^0$ are calculated from the slope and intercept of the plots of ln $K_a$ versus $1/T$ (Figure provided in supporting information).

Negative values of $\Delta G^0$ indicated that the biosorption process was favorable and spontaneous in nature for Ni(II) onto both raw and treated biomass of *L. variegata*. (Table 4). It may be noted that with the increase in temperature from 20 to 40°C for Ni(II) biosorption, the value of $\Delta G^0$ decreased from −4.71 to −10.72 and −5.83 to −10.91 kJ $mol^{-1}$ for raw and treated biomasses of *L. variegata*, respectively. Thus biosorption enhanced at higher temperature, though slightly. The positive value of enthalpy change ($\Delta H^0$) confirmed the endothermic nature of the biosorption process. In the sorption studies of heavy metals, the observed enthalpy is comprised of contributions from the energetic effects associated with intrinsic biosorption step, dehydration effects of the metal ions inside the aqueous solution, in addition to any plausible contribution from the physical/chemical changes that the sorption sites might undergo as a result of sorption. Due to the complex nature of the biosorption process in liquid–solid systems, it is usually not easy to depict correlations between different sorption systems, especially if the experimental conditions do not match (Sekar et al. 2004). The endothermic nature of biosorption was reported in earlier studies. Tsezos and Volesky (1984) reported a slight increase in cation sorption by seaweed biomass with increase in temperature from 4 to 55°C. Similarly, Aksu (2002) recorded increase in Ni(II) biosorption by dried biomass of *Chlorella vulgaris* with enhancement of temperature from 15 to 45°C.

The calculated values of $\Delta S^0$ refer to the entropy change of the biosorption system which can have positive or negative values. The positive entropy change ($\Delta S^0$) for the present reaction indicated good affinity of the metal towards the biosorbents and that the change, either physical or chemical occurred spontaneously (Gupta et al. 2005).

## Conclusion

Biosorption isotherms of Ni(II) on both raw and treated biomass of *L. variegata* were studied and

**Table 4** Thermodynamic parameters for Ni(II) biosorption onto *Lobophora variegata*

| System | Temperature (°C) | $\Delta G^0$ (kJ $mol^{-1}$) | $\Delta H^0$ (kJ $mol^{-1}$) | $\Delta S^0$ (kJ $mol^{-1}$ $K^{-1}$) |
|---|---|---|---|---|
| Ni(II)-raw biomass | 20 | −4.714 | 6.662 | 24.645 |
| | 30 | −6.523 | | |
| | 40 | −8.979 | | |
| | 50 | −10.724 | | |
| Ni(II)-treated biomass | 20 | −5.836 | 5.308 | 20.601 |
| | 30 | −7.976 | | |
| | 40 | −9.745 | | |
| | 50 | −10.914 | | |

modeled using 23 well-known isotherm models. Out of the 23 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 Ni(II). Among the two-parameter models, the predicted Freundlich isotherm curve fits better followed by Langmuir. The classification of the three-parameter models according to the simulation of the biosorption isotherms was: Khan > Redlich–Peterson > Sips. The four-parameter equation of Fritz–Schluender simulates well the experimental results, but the equation of Khan (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. The thermodynamic parameters evaluated reveal the spontaneous and endothermic nature of Ni(II) biosorption process on *Lobophora variegata*, and the adsorption takes place with the increase of entropy.

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