Biosorption of nickel from protonated rice bran

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Abstract

In the present study biosorption technique, the accumulation of metals by biomass was used for the removal of nickel from aqueous medium. The rice bran in its acid treated (H_3PO_4) form was used as a low cost sorbent. The adsorption characteristics of nickel on protonated rice bran were evaluated as a function of pH, biosorbent size, biosorbent dosage, initial concentration of nickel and time. Within the tested pH range (pH 1–7), the protonated rice bran displayed more resistance to pH variation, retaining up to 102 mg/g of the nickel binding capacity at pH 6. Meanwhile, at lower pH values the uptake capacity decreased. The % age removal of nickel was maximum at 0.25 g of biosorbent dose and 0.25 mm biosorbent size. At the optimal conditions, metal ion uptake was increased as the initial metal ion concentration increased up to 100 mg/L. Kinetic and isotherm experiments were carried out at the optimal pH 6.0 for nickel. The metal removal rate was rapid, with 57% of the total adsorption taking place within 15–30 min. The Freundlich and Langmuir models were used to describe the uptake of nickel on protonated rice bran. The Langmuir and Freundlich model parameters were evaluated. The equilibrium adsorption data was better fitted to Langmuir adsorption isotherm model. The adsorption followed pseudo second-order kinetic model. The thermodynamic assessment of the metal ion-rice bran biomass system indicated the feasibility and spontaneous nature of the process and $\Delta G°$ values were evaluated as ranging from -22.82 to -24.04 kJ/mol for nickel sorption. The order of magnitude of the $\Delta G°$ values indicated an ion-exchange physiochemical sorption process.
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1. Introduction

As today's technology progresses, the natural environment suffers from the detrimental effects of pollution. The natural process of transportation of metal ions between soil and water consolidates metal contamination in high concentrations that affect the areas of natural ecosystems [1]. The majority of toxic metal pollutants are waste products of industrial and metallurgical processes. Their concentrations have to be reduced to meet ever increasing legislative standards. According to the World Health Organization [2], the metals of most immediate concern are cadmium, chromium, cobalt, copper, lead, nickel, mercury and zinc. The effluents from metal finishing processes may contain up to 10 mg/L of copper, chromium, nickel and zinc.

Heavy metal releases to the environment have been increasing continuously as a result of industrial activities and technologi-

cal development, posing a significant threat to the environment and public health because of their toxicity, accumulation in the food chain and persistence in nature. It is therefore important to develop new methods for metal removal and recovery from dilute solutions (1–100 mg/L) and for the reduction of heavy metal ions to very low concentrations. The use of conventional technologies, such as ion exchange, chemical precipitation, reverse osmosis and evaporative recovery for this purpose is often inefficient and/or very expensive [3–6].

Biosorption, which is a property of certain types of inactive, dead microbial biomass to bind and concentrate heavy metals from even very dilute aqueous solutions, is one of the most promising technologies involved in the removal of toxic metals from industrial waste streams and natural waters [7,8]. Biosorption can be considered a collective term for a number of passive, metabolism independent, accumulation processes and may include physical and/or chemical adsorption, ion exchange, coordination, complexation, chelation and microprecipitation. Biomass cell walls, consisting mainly of polysaccharides, proteins and lipids, offer many functional groups that can bind metal

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ions such as carboxylate, hydroxyl, sulphate, phosphate and amino groups. In addition to these functional binding groups, polysaccharides often have ion-exchange properties [9,7,10]. Non-living biomass appears to present specific advantages in comparison to the use of living microorganisms. Dead cells are not subjected to metal toxicity and nutrient supply is not necessary. Moreover, the pretreatment and killing of biomass either by physical or chemical treatments [11,10] or cross-linking [4] are known to improve the biosorption capacity of biomass.

Bran is a by-product from the milling of rice, consisting of the large kernel with a part the germ. It is used in some applications mainly as a fertilizer or fuel [12]. Rice bran contains different vitamins, carbohydrates, potassium, nitrogen and phosphorus compounds, which induce to water to contact with it. These compounds not only have no pollution effects but they are nutritious to the plants. Therefore, the use of bran to eliminate pollution from water reveals the significance of the bran or natural products. Unfortunately up to now only a few studies have been carried out in this field. Rice bran was used in *in vitro* study for determination of capacity for Hg, Cd and Pb [13], bioscavenging of Cu(II) ion from aqueous solution [14] and removal of mercury from waste water [15]. In this study, efficiency of rice bran in removal of heavy metal nickel was investigated in detail in its acid treated form. The influence of initial concentration of heavy metal, pH, biosorbent size, biosorbent dose and contact time on biosorption of metal ions were studied.

2. Methodology

2.1. Chemicals and instruments

All chemicals were pro-analysis grade and were purchased from E. Merck Company (Darmstadt, Germany). Metal concentrations were measured with a Perkin-Elmer (AAnalyst 300) atomic absorption spectrophotometer. A TOA.V. pH meter (HM 30P) was used to check the pH of the metal solutions. Other instruments such as shaker (PA 250/25. H), Octagon siever (OCT-DIGITAL 4527-01) and Shimadzu (AW 220) electric balance were used.

2.2. Rice bran collection

The biosorbent ice bran was collected from different shellers of Sialkot and Hafizabad, Pakistan. The samples were than dried at 70 °C for 1 week.

2.3. Protonation of rice bran with acids

Rice bran was protonated with three acids HCl, H_2SO_4 and H_3PO_4 according to Ref. [4]. The biomass after each treatment was washed with deionized water until the pH of the wash solution was in near neutral range (pH 6.8–7.2). After this the biomass was dried at 60 °C for 24 h in a drying oven.

2.4. Batch laboratory binding capacity experiments

Binding capacity experiments were performed with the protonated biomass as well as controls for metal studied. The experiments were conducted using solutions of nickel in the form of $NiSO_4 \cdot 6H_2O$. The solutions prepared using distilled water had an initial metal concentration of 100 mg/L. Known amounts of biomass were contacted with each metal solution. The reaction mixture was agitated at 120 rpm on orbital shaker (PA 250/25. H) for 4 h, filtrate was obtained by filtering the reaction mixture through a filter and analysed for metal concentration. Nickel adsorption losses to the flask walls and to the filter paper were negligible. All experiments were carried out at 30 °C. The effects of following parameters such as pH, biomass size, biomass dose, initial metal ion concentration and contact time were studied. Bioadsorption experiments were carried out in duplicate.

2.5. Metal analysis

Metal concentrations were measured using a Perkin-Elmer (AAnalyst 300) atomic absorption spectrophotometer. The wavelength used for the analysis of the metal in this study was 232 nm. The instrument was calibrated within the linear range of analysis and a correlation coefficient of 0.98 or greater was obtained for the calibration curve. The instrument was periodically checked throughout the analysis with known standards. Three readings were obtained for each sample, and a mean value was computed along with standard deviations for each sample. The amount bound on the biomass was assumed to be the difference between the initial metal concentration and that found in the supernatant. The nickel uptake was calculated by the simple concentration difference method [16].

3. Results and discussion

In order to protonate the biomass rice bran, it was treated by HCl, H_2SO_4 and H_3PO_4. Time given to the biosorbent for acidic treatment was 2, 4 and 12 h. The adsorption capacity of acid treated rice bran and untreated rice bran was compared and it was noted that among the three acids, H_3PO_4 was greatly enhanced the adsorption capacity. The adsorption capacity for untreated rice bran was 39.76 mg/g. The adsorption capacity for HCl treated biosorbent for 2, 4 and 12 h was 53.50, 66.80 and 68.70 mg/g, respectively. Similarly the adsorption capacity for H_2SO_4 treated biosorbent for 2, 4 and 12 h was 62.80, 72.80 and 79.30 mg/g, respectively, and for H_3PO_4 treated biosorbent for 2, 4 and 12 h was 68.50, 77.60 and 101.90 mg/g, respectively. So the highest metal uptake (101.9 mg/g) was obtained by H_3PO_4 treated rice bran which was than used for further study.

3.1. pH profile studies for nickel binding

Sorption of heavy metals from aqueous solutions depends on properties of adsorbent and molecules of adsorbate transfer from the solution to the solid phase. It has been also reported that biosorption capacities for heavy metals are strongly pH sensitive and that adsorption increases as solution pH increases [17,18].
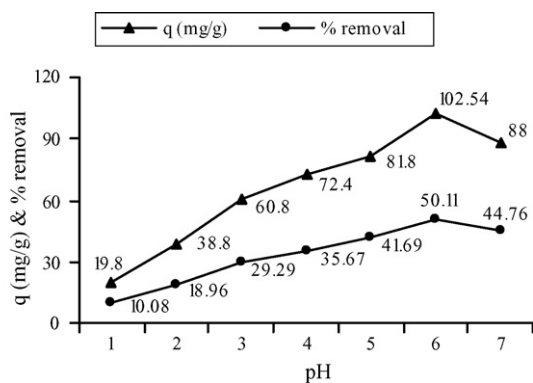
Fig. 1. Effect of pH on biosorption of nickel.

Initial investigation of biosorption capability of rice bran for nickel at different values of pH (1–7) (Fig. 1) showed that the rice bran possessed maximum sorption capacity for the cationic metal ion at pH value 6. At pH values above the isoelectric point, there was a net negative charge on the cell wall components and the ionic state of ligands such as carboxyl, phosphate and amino groups will be such as to promote a reaction with metal cations. At lower pH the overall surface charge on the cells became positive and the presence of H^+ ions hinder the access of metal ions by repulsive forces to the surface functional groups, consequently decreasing the percentage of metal removal [19]. So at pH bellow 3, an uptake of nickel was less, probably due to the cation competition effects with oxonium (hydronium) ion H_3O^+. Furthermore at higher pH poorly soluble hydroxyl species was formed and precipitation of nickel would occur [20]. So at pH 7 biosorption of cationic metal decreased probably because of chemical precipitation. Sorption studies were meaningless above pH 7 due to the formation of insoluble products in investigated solution, what is in accordance with the solubility products of metal hydroxide as follows: $K_{sp}(Ni(OH)_2) = 10–14$ [21]. According to the results of this initial experiment, the further biosorption investigations were performed at pH 6 as an optimal value.

3.2. Effect of biosorbent size and doze

The effect of altering the sorbent particle size showed that there was a more removal of nickel by smaller particles (Fig. 2). The adsorption capacities (q) for different granular sizes of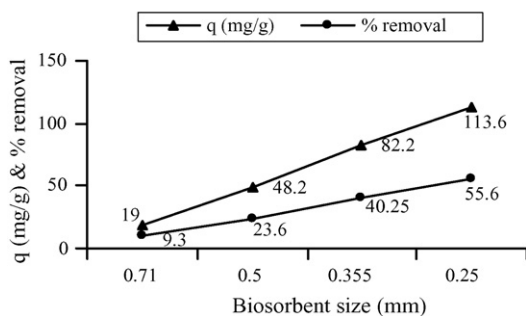 acid pretreated *Oryza sativa* bran 0.250, 0.335, 0.500 and 0.710 mm were 113.60, 82.20, 48.20 and 19.00 mg/g and percentage removals of nickel were 55.60, 40.25, 23.60 and 9.30%, respectively. This was most probably due to increase in the total surface area which provided more sorption sites for metal ions. The enhanced removal of sorbate by smaller particles has been noted previously during a study into the removal of colour by silica [22]. The maximum adsorption was occurred with 0.250 mm biosorbent size.

Biosorbent dose seemed to have a great influence in biosorption process. Dose of biomass added into the solution determine the number of binding sites available for adsorption. The results of the effect of protonated rice bran dose (Fig. 3) showed that nickel uptake values increased with a decrease in biomass dose, though this cannot be attributed to a greater biosorption capacity. In this case the relevant parameter is the percentage of removed nickel. An increase in biomass quantities strongly affects the quantities of nickel removed from aqueous solutions to a certain limit and than decreases. Adsorption capacities (q) for different doses of biosorbent 0.05, 0.01, 0.15, 0.20, 0.25 and 0.30 g, at pH 6.0 were 106.80, 57.00, 41.20, 31.90, 26.10 and 21.00 mg/g and percentage removals of nickel were 52.20, 55.70, 60.40, 62.40, 63.70 and 61.50%, respectively. The critical value of dose of protonated rice bran was 0.25 g for nickel.

3.3. Kinetic study

Kinetic study revealed that maximum biosorption capacities and metal removal efficiencies for nickel were achieved generally in the first 30 min of contact. Metal removal and sorption were also rapid during this period. Fig. 4 shows the time course of
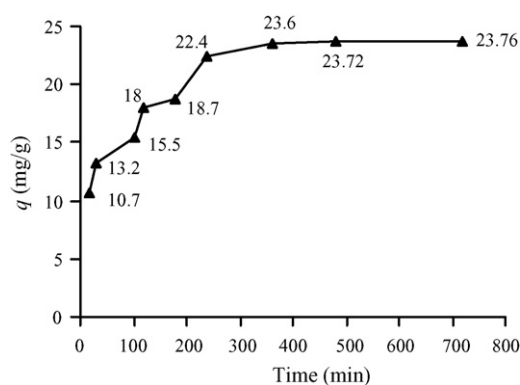

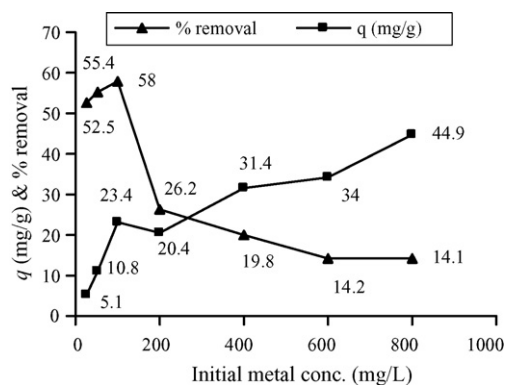Fig. 3. Effect of biosorbent doze on biosorption of nickel.

Fig. 2. Effect of biosorbent size on biosorption of nickel.

Fig. 4. Effect of sorption time on biosorption of nickel.

Fig. 5. Effect of initial metal concentration on biosorption of nickel.

Fig. 6. The pseudo first-order (Lagergren) plot.

biosorption, when the initial pH was 6 and the initial metal concentrations (C_0) were 100 mg/L. In the first 5 min, sorption took place very rapidly and then it continued at a relatively slower rate up to maximum sorption. Equilibrium was reached in a contact time of 4 h. This figure also verifies that sorption took place in two stages: a very rapid surface adsorption and a slow intracellular diffusion. Similar results were reported by [23,22,17], while in some other studies single-step uptake was suggested for different biosorbents [11].

3.4. Effect of initial concentrations of nickel ions

The apparent capacity of protonated rice bran for nickel metal was determined at the different concentrations. Fig. 5 clarifies the relation between capacities and the metal ion concentrations, which shows that as the metal ion concentration increased the capacity increased until 44.90 mg/g. At lower 25, 50, 100 ppm concentrations, the percentage removal of nickel was 52.50, 55.40, 58.00%, respectively. The maximum removal of nickel was occurred at 100 ppm. In general, the data indicated that sorption capacity increased with increase in initial metal ion concentration for nickel on the biomass. This sorption characteristic indicated that surface saturation was dependent on the initial metal ion concentrations. At low concentrations, adsorption sites took up the available metal more quickly. However, at higher concentrations, metal needed to diffuse to the biomass surface by intraparticle diffusion and greatly hydrolyzed ions will diffuse at a slower rate. The maximum metal ion sorption of an adsorbent may be determined from column experiments, by the use of a large excess of the adsorbate.

3.5. Kinetic modeling

In order to investigate the mechanism of biosorption of nickel by protonated rice bran and the potential rate-controlling steps, such as mass transport and chemical reactions, kinetic models were used to test experimental data. Mathematical models that can describe the behaviour of batch biosorption process operated under different experimental conditions are very useful for scale up process optimization. A number of models with varying degrees of complexity have been developed to describe the kinetics of metal biosorption in batch systems. According
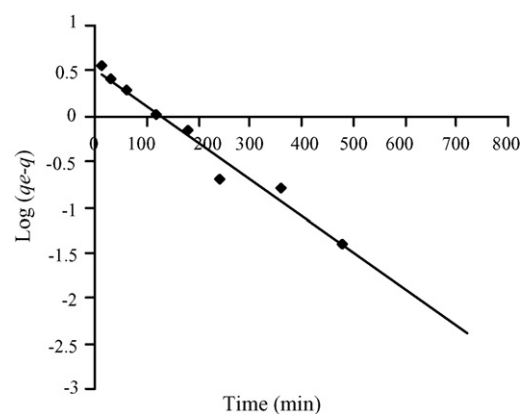
to the kinetic model selection criteria, proposed by [24], several reaction-based and diffusion-based models were tested for the stimulation of the obtained experimental data. The finally selected kinetic models will be those, which not only fit closely the data, but also represent reasonable sorption mechanism. In this study two different kinetic models were used to adjust the experimental data of nickel biosorption on protonated rice bran. These kinetic models included pseudo first-order Lagergren and pseudo second-order [25,26]. The pseudo first-order Lagergren model is expressed as

$$\log(q_e - q) = \log q_e - \frac{k_{1,ads}}{2.303} \tag{1}$$

where q_e (mg/g) and q are the amounts of adsorbed metal ions on the biosorbent at the equilibrium and at any time t, respectively; $k_{1,ads}$ (min^{-1}) is the Lagergren rate constant of the first-order biosorption. q_e and $k_{1,ads}$ can be calculated from the slopes and the intercept of the plot $\log(q_e - q)$ versus t (Fig. 6).

The Lagergren first-order rate constant k_1 and q_e determined from the model indicates that this model had failed to estimate q_e since the experimental value of q_e differs from estimated one.

The best fit for the experimental data of this study was achieved by the application of pseudo second-order kinetic equation. The pseudo second-order model is based on the assumption that biosorption follows a second-order mechanism. So, the rate of occupation of adsorption sites is proportional to the square of the number of unoccupied sites:

$$\frac{t}{q} = \frac{1}{k_{2,ads}q_e^2} + \frac{1}{q_e t} \tag{2}$$

where $k_{2,ads}$ is the rate constant of second-order biosorption (g/mg min). q_e and $k_{2,ads}$ can be calculated from the slope and the intercept of the plot t/q versus t (Fig. 7).

It is important to notice that it is not necessary to estimate the experimental value of q_e for the application of such a model. The coefficient of correlation for second-order kinetic model was equal to 1 and the estimated value of q_e also agreed with the experimental one. Both factors suggest that the sorption of nickel ions followed the second-order kinetic model, indicating that the rate-limiting step was a chemical biosorption process between nickel and protonated rice bran. Similar conclusions
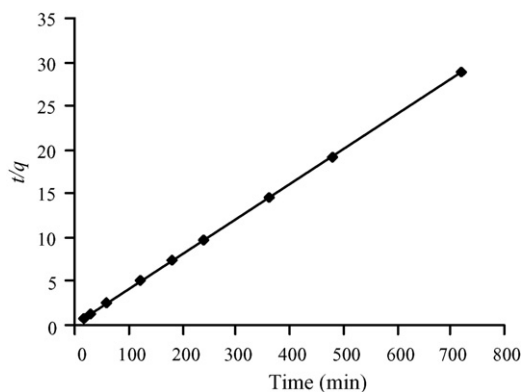
Fig. 7. The pseudo second-order plot.

Fig. 8. The Langmuir plot.

Table 1
The pseudo first-order (Lagergren) parameters

q_{exp} (mg/g)	25.04
k_1 (min^{-1})	0.00921
q_e (mg/g)	3.38
R^2	0.9712

Table 2
The pseudo second-order parameters

q_{exp} (mg/g)	25.04
k_2 (g/mg min)	0.00882
q_e (mg/g)	25.20
R^2	1.000

were found by Ho and McKay as a result of an analysis of data from literature. They reported that most of the sorption systems follow a pseudo second-order kinetic model [27]. The pseudo first-order Lagergren model and pseudo second-order parameters are given in Tables 1 and 2, respectively.

3.6. Equilibrium modeling

The biomass exhibited adsorption isotherms of Langmuir and Freundlich, which is a characteristic of the biomass substrate containing both micropores and mesopores [28]. Modeling the equilibrium data is fundamental for the industrial application of biosorption since it gives information for comparison among different biomaterials under different operational conditions, designing and optimizing operating procedures [29]. To examine the relationship between sorbed (q_e) and aqueous concentrations (C_e) at equilibrium, sorption isotherm models are widely employed for fitting the data, of which the Langmuir and Freundlich equations are the most widely used. To get the equilibrium data, initial nickel concentrations were varied while the biomass weight in each sample was kept constant. Four hours of equilibrium periods for sorption experiments were used to ensure equilibrium conditions. This time was chosen considering the results of kinetics of nickel removal by protonated rice bran which was presented prior to this one.

If the metal ions are taken up independently on a single type of binding site in such a way that the uptake of the first metal ion
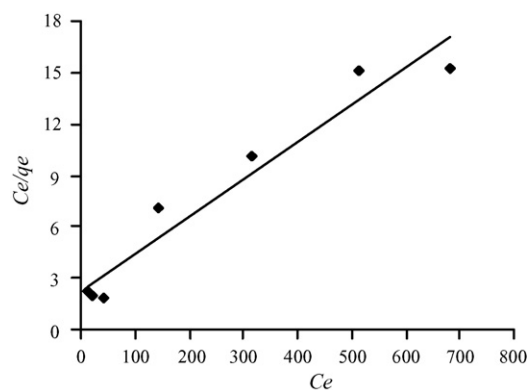
does not affect the sorption of the next ion, then the sorption process would follow the Langmuir adsorption isotherm equation, which was linearised to the form:

$$\frac{C_e}{q_e} = \frac{1}{q_0 K_L} + \frac{1}{q_0 C_e}$$ (3)

where q_0 and K_L are the Langmuir constants.

The capacity of protonated rice bran biomass in binding with nickel was determined by plotting C_e/q_e against C_e using the above equation. Fig. 8 shows the data linearised to fit the Langmuir equation. The plots of specific sorption (C_e/q_e) against equilibrium concentration (C_e) gave the linear isotherm parameters of q_0, K_L and the coefficient of determination and these are presented in Table 3. The R^2 values suggested that the Langmuir isotherm provided a good model of the sorption system. The sorption capacity, q_0 which is a measure of the maximum adsorption capacity corresponding to complete monolayer coverage, showed that the protonated rice bran had a mass capacity for nickel (46.51 mg/g). The adsorption coefficient, K_L which is related to the apparent energy of adsorption for nickel was 0.00943 dm^3/g. This indicates that not all binding sites may be available for nickel binding due to its relatively larger hydration energy.

The Freundlich equation is another model which has been commonly used to describe adsorption isotherms. Its linearised form is represented by Eq. (4) [30]:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$ (4)

where q_e is the amount adsorbed per unit mass of adsorbent and C_e is the equilibrium concentration (mg/L).

The plot of $\log q_e$ versus $\log C_e$ was linear (Fig. 9) and constants K_F and n can be evaluated from the slopes and intercepts. The Freundlich constants are shown in Table 4. It was found that the adsorption equilibrium data was better fitted by the

Table 3
The Langmuir isotherm parameters

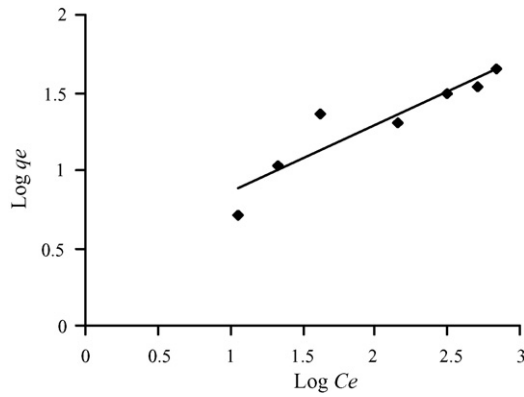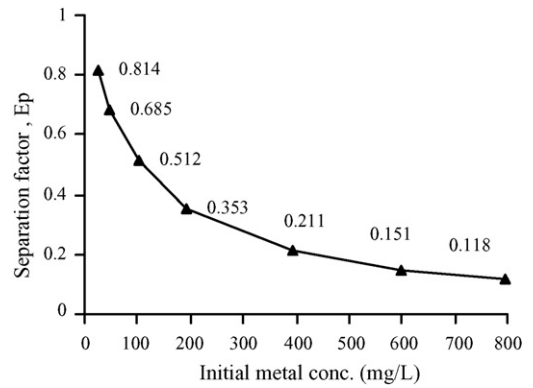|	
q_{exp} (mg/g)	44.90
q_0 (mg/g)	46.51
K_L (dm^3/g)	0.00943
R^2	0.9414

Fig. 9. The Freundlich plot.

Fig. 10. The calculated separation factor profile for nickel as a function of metal ion concentration (mg/L).

Table 4
The Freundlich isotherm parameters

q_{exp} (mg/g)	44.90
q_e (mg/g)	44.31
K	2.64
n	2.313
R^2	0.8506

Langmuir isotherm, although it can also be modeled by the Freundlich isotherm, in the concentration range studied, since it presented the greater coefficient of correlation. The maximum value for limiting capacity of protonated rice bran for nickel ($q_e = 46.51$ mg/g) at pH 6. The values of correlation coefficients generated by linear regressions performed on isotherm data were in accordance with literature [31].

The shape of the Langmuir isotherm can be used to predict whether a sorption system is favourable or unfavourable in a batch adsorption process [32]. Accordingly, the essential features of the Langmuir isotherm were expressed in terms of a dimensionless constant called the equilibrium parameter, E_p which is defined by the following relationship:

$$E_p = \frac{1}{1 + K_L C_e} \quad (5)$$

where E_p is a dimensionless equilibrium parameter or separation factor, K_L constant from Langmuir equation and C_e is initial metal ion concentration.

The parameter, E_p, indicates the shape of the isotherm and nature of the sorption process as given below:

Values of E_p	Type of isotherm
$E_p > 1$	Unfavourable isotherm
$E_p = 1$	Linear isotherm
$E_p = 0$	Irreversible isotherm
$0 < E_p < 1$	Favourable isotherm

The values of E_p for nickel were calculated and plotted against initial metal ion concentration. The data (Fig. 10) showed that, the sorption of nickel on the protonated rice bran increased as the initial metal ion concentration increased from 25 to

800 ppm, indicating that adsorption is even favourable for the higher initial metal ion concentrations. The sorption process was favourable for nickel removal at all concentrations investigated.

To account for the adsorption behaviour of the metal ions on the protonated rice bran, the Langmuir type equation related to surface coverage was used. The equation is expressed as follows:

$$\frac{\theta}{1 - \theta} = KC \quad (6)$$

where K is the adsorption coefficient and θ is surface coverage.

The fraction of biomass surface covered by metal ions was studied by plotting the surface coverage values (θ) against metal ions concentration. The data is presented in Fig. 11. The figure shows that increase in initial metal ion concentration for nickel increased the surface coverage on the biomass until the surface was nearly fully covered with a monomolecular layer. Further examination of Fig. 11 reveals that the surface coverage ceased to vary significantly with concentration of metal ion at high concentrations and the reaction rate became independent of the metal ion concentration. The overall adsorption process indicates that the biomass will be highly effective in removing trace amounts of nickel ions in aqueous effluent.

The apparent Gibbs free energy of the adsorption processes (ΔG°_{ads}) corresponding to nickel ion on the biomass was evaluated using the Bockris–Swinkel's adsorption isotherm equation
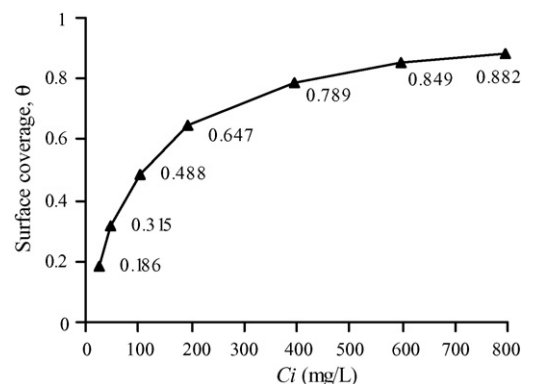

Fig. 11. A plot of surface coverage (θ) against concentration (mg/L).

Table 5
Apparent Gibbs free energy $\Delta G^{\circ}_{\text{ads}}$ (kJ/mol) of the metal ions between the biomass and aqueous phase

C_i (Mg/L)	$\Delta G^{\circ}_{\text{ads}}$
24.2	−24.04
48.7	−23.85
101.1	−23.85
194.5	−23.30
395.7	−23.02
597.4	−22.89
95.4	−22.82

as reported by [33]. The equation is expressed as

$$G^{\circ}_{\text{ads}} = -2.303RT \log \left[\frac{55.4\theta}{C_0(1-\theta)\theta} + \frac{n(1-\theta)^{n-1}}{n^n} \right] \quad (7)$$

where C_0 is the initial concentration of nickel ion in the solution.

The values of $\Delta G^{\circ}_{\text{ads}}$ were then evaluated at various initial metal ion concentrations. The data is presented in Table 5. The negative values of ΔG° indicated the spontaneous adsorption nature of nickel ion by the protonated rice bran adsorbent and suggested strong adsorption of nickel ions on the biomass surface. In general, it is of note that up to −20 kJ/mol are consistent with electrostatic interaction between charged molecules and surface indicative of physisorption while more negative than −40 kJ/mol involve chemisorption. The order of magnitude of the values indicates a physicochemical mechanism for the adsorption of metal ions on to the protonated rice bran.

4. Conclusion

1. Rice bran biomass was selected for studying biosorption due to its originality as well as to access the possibility of utilizing a waste biomass to eradicate the metal pollution.
2. Rice bran can be obtained without excessive cost. Thus, non-living biomass of rice bran presents sufficient biosorption capacity for nickel ions, in comparison with other types (sources) of biosorbent materials found in literature.
3. The obtained results show that pH, biomass size, biomass dose, initial metal concentration and contact time highly affect the overall metal uptake capacity of biosorbent.
4. The present results demonstrate that the Langmuir model fits better than the Freundlich model for the adsorption equilibrium data in the examined concentration range.
5. The suitability of a pseudo second-order chemical reaction for the sorption of nickel ions onto this biomass is apparent, as this kinetic model describes adequately the largest part of the process.

Acknowledgement

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