Effects of biosorption parameter: kinetics, isotherm and thermodynamics for Ni(II) biosorption from aqueous solution by Circinella sp.

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Abstract Circinella sp. was employed as a biosorbent for removal of Ni(II) from aqueous solution. The biosorption kinetics and isotherms were investigated. The effect of several parameters, such as biosorbent dosage, contact time, initial concentration, pH and temperature, on biosorption process was evaluated. The kinetic studies indicated that the biosorption followed pseudo-second order kinetic model. Biosorption behaviour of Ni(II) on Circinella sp. was expressed by both Langmuir and Freundlich isotherms. The equilibrium data fit better to the Langmuir model compared to the Freundlich model in concentration range studied (1.0-3.0 mM). The thermodynamic parameters (ΔG⁰, ΔH⁰ and ΔS⁰) were also determined, and it was found that the Ni(II) biosorption by Circinella sp. was spontaneous and endothermic in nature.

Keywords: biosorption, Circinella sp., equilibrium, kinetic, nickel

INTRODUCTION

So far, a number of studies of metal removal from solution have been launched because of the ecological effects of toxic metals released into the environment (Volesky, 1990; Volesky, 2007). Environmental pollution from man-made sources can easily create local conditions of elevated metal presence and this case could lead to some hazardous effects on animals and humans (Volesky, 1990; Bhatnagar and Minocha, 2010). Mercury, lead, cadmium, arsenic, antimony, copper, zinc, nickel, cobalt etc. are toxic heavy metals coming from the various sources, and are accumulated into the environment. Nickel containing effluents are common due to their large number of industrial uses ranging from electroplating to long-life batteries. Elevated levels of nickel are harmful for the environment, and it has also carcinogenic effect (Volesky, 1990). The investigation of nickel removal from aqueous solution has
major importance due to its toxicity (Vijayaraghavan et al. 2006; Hanif et al. 2007; Liu and Xu, 2007; Öztürk, 2007; Padmavathy, 2008).

A number of methods based on ion exchange, electrochemical treatment, membrane technologies, evaporation recovery, chemical oxidation or reduction, and chemical precipitation for the removal of toxic metals from aqueous solutions are usually ineffective or extremely expensive (Volesky, 1990). Therefore, new technologies that can accumulate toxic metals at affordable costs are required. Biosorption based on sorption of heavy metals by live or inactivated biomass is a relatively novel technology and represents a potentially cost-effective way for removal of heavy metals from aqueous solutions (Kalyani et al. 2004; Amini et al. 2009; Cayllahua et al. 2009; Fereidouni et al. 2009; Gialamoudis et al. 2009; Gupta et al. 2010; Pahlavanzadeh et al. 2010).

Living or dead forms of microbial cells, bacteria, fungi and algae have been used as biosorbents in (Volesky, 1990). Biosorption of metal ions by biosorbent occurs thanks to one or a combination of metal-binding mechanisms such as complexation, coordination, chelation, ion exchange, adsorption and inorganic microprecipitation.

The use of fungal biomasses as biosorption materials is very convenient because of their inexpensive production methods based on simple fermentation techniques (Maurya et al. 2006). Since fungal cell walls and their components play a major role in the biosorption (Alpat et al. 2008), fungal biomasses are used in the biosorption of various metal ions (Gadd and White, 1989; Magyarosy et al. 2002; Pal et al. 2006; Čerňanský et al. 2007; Meigl et al. 2007; Mashitah et al. 2008). The main group of the fungal cell walls is different polysaccharides, and they are complexed with proteins, lipids, and other substances in many cases. While the outer layer of the fungal cell wall is formed of glucans, mannans, or galactans, the inner layer is formed of the arrangement of chitin chains - a polymer of N-acetyl-D-glucosamine-, cellulose chains-a polymer of D-glucopyranose-, noncellulosic glucan-polymers of hexose and pentose and sometimes of uronic acids-. Continuous transition exists between these outer and inner layers. There are also pigments, polyphosphates and inorganic ions in the fungal cell wall. The variations among the fungal cell walls depend on the stages of the life cycle of the organism and on culture conditions (Volesky, 1990).

Some fungi, such as Absidia, Cunninghamamella, Mucor and Rhizopus, show excellent biosorption for metal ions (Brady et al. 1999) because of the high chitin and chitosan content of the cell walls (Carlile et al. 2001). Circinella sp. firstly used for biosorption of Ni(II) in this study is a mucor-like species in the order Mucorales (Absidiaceae family). Circinella sp. takes place in the fungus class Zygomycetes, and the main components of cell wall of Zygomycetes class are chitin, chitosan and polyglucronic acid. While chitin and chitosan are the sponge members of cell wall in Zygomycetes, glucronic acid and mannoproteins are gel-like polymers (Carlile et al. 2001). Circinella sp. can be prepared easily, and its components of the cell wall are very effective on biosorption of metal ions (Brady et al. 1999; Alpat et al. 2008). Therefore, Circinella sp. was chosen as a biosorbent for the removal of Ni(II) from aqueous solutions.

The first objective of the present study is to determine sorption capacity of Circinella sp. for removal of Ni(II) from aqueous solution. The second objective is to investigate kinetics and mechanism of biosorption of nickel on Circinella sp. The effects of biomass dosage, contact time, solution pH, metal ion concentration and temperature on biosorption process were evaluated.
MATERIALS AND METHODS

Microorganism and culture conditions

The micro-organisms used in this study were *Circinella* sp. TEM was obtained from Culture Collection of Industrial and Molecular Microbiology Research Laboratories, Biology Department, Ege University, Turkey. Potato Dextrose Agar medium (PDA; Merck, Darmstadt, Germany) was used for cultivation. Following incubation for 5 days at 25°C, spores were extracted by Na-lauryl sulphate (1%) and then counted with Thoma Lam. *Circinella* sp. was cultured in 125 mL of liquid medium comprising (g L⁻¹): bacteriological peptone, 10; sucrose, 20; KH₂PO₄, 1; NaNO₃, 1; MgSO₄.7H₂O, 0.5 in 500 mL of Erlenmeyer flasks. 1.0 x 10⁷ spores were inoculated to the medium. Cultures were grown at 25°C on an orbital shaker at 150 rpm for 5 days. The biomass was readily separated from the broth by decanting, washed three times with 250 mL aliquots of distilled, deionised water, and then lyophilized (Edwards Freeze Dryer, UK). The resultant biosorbent was homogenized using a Sorvall Omni-mixer (Brady et al. 1999; Alpat et al. 2008). The average particle size > 500 µm of the biosorbent was used in the experiments.

Metal solution

Stock solution of metal used in this study was prepared (50 mM) by dissolving the desired quantity of Ni(NO₃)₂.6H₂O (Merck, Darmstadt, Germany) in deionized water. Other concentrations were obtained daily by dilution of stock solution before each biosorption study. All pH adjustments were made by using reagent grade HNO₃ (Riedel-de Haën, Germany) and NaOH (Merck, Darmstadt, Germany).

Biosorption studies

The biosorption of Ni(II) on *Circinella* sp. was studied by batch technique. 50.0 mg of inactivated cells were mixed with 10 mL of the Ni(II) solutions in an Erlenmeyer flask, and flasks were agitated on a shaker at 40°C. The effects of biomass dosage, contact time, metal ion concentration, temperature and pH on the biosorption of Ni(II) were studied. The period of contact time was varied from 1 to 60 min. Following the equilibration time, the mixtures were filtered from the 0.2 µm micro-pore, and liquid phase was used to estimate metal ion concentrations. All the biosorption experiments were repeated three times in order to confirm the results. The results were the mean values of three replicate determinations.

Desorption studies

Ni(II) loaded biosorbent was filtered and washed three times with deionized water to remove any residual Ni(II) solution. Then, the biomass was placed in the Erlenmeyer flask containing 10 mL of desorbing agent for batch desorption experiments. Five desorbing agents, HCl, HNO₃, NaNO₃, EDTA and distilled water were used to recover the biosorbed Ni(II). The mixtures were agitated on a shaker for 60 min at room temperature (25 ± 2°C). At the end of the contact time, biomass was separated by micro-pore filtration, and so the concentration of Ni(II) released into the filtrate was determined. Each experiment was repeated three times and the results are the average values.
Analysis of metal ions

The concentration of unbiosorbed Ni(II) in the biosorption medium was determined by atomic absorption spectrophotometer (Analytikjena Nova 300) with an air-acetylene flame. Each experiment was repeated three times and the results are the average values.

The amount of Ni(II) biosorbed on *Circinella* sp. was calculated by using the following expression:

\[
q_t = \frac{(C_0 - C_t) V}{m}
\]

[Equation 1]

where \( q_t \) is the amount of Ni(II) biosorbed on unit mass of the biomass \( \text{mol g}^{-1} \) at time \( t \); \( C_0 \) and \( C_t \) are the initial Ni(II) concentration \( \text{mM} \) and Ni(II) concentration \( \text{mM} \) at time \( t \), respectively; \( V \) is the volume of the aqueous phase \( \text{L} \); and \( m \) is the weight of the *Circinella* sp. \( \text{g} \).

SEM measurements

The surface morphologies of *Circinella* sp. were investigated by scanning electron microscopy (SEM) instrument (JEOL JSM-6060 SEM) combined with energy dispersive X-ray spectroscopy (EDS). The samples mounted on the plate were kept under vacuum, and then coated with gold particles before the SEM measurements. SEM micrographs of biosorbent were analyzed before and after biosorption of Ni(II).

RESULTS AND DISCUSSION

SEM characterization of the biomass

The SEM micrographs of *Circinella* sp. before and after biosorption of 1.0 mM of Ni(II) were given in Figure 1. The results of elemental analysis were also given in Table 1. The results obviously show the difference between before and after loading of Ni(II) on the biomass surface. According to the elemental analysis results, a significant amount of Ni(II) was loading on to the biomass via the sorption ability of microorganism. The reason why some elements such as Ca, Mg and P were obtained in addition to Ni in the analysis may be the cultivation medium of microorganism and its cell wall components.

Effect of biomass dosage

To determine the optimum biomass dosage for biosorption of Ni(II), different biomass dosages ranging from 2.0 to 15 g L\(^{-1}\) were chosen. It was observed that the biosorption of Ni(II) was higher at biomass dosage of 5.0 g L\(^{-1}\) than 2.0 g L\(^{-1}\), 2.5 g L\(^{-1}\) and 4.0 g L\(^{-1}\), and it was almost constant at higher than 5.0 g L\(^{-1}\). Therefore, the
optimum biomass dosage was chosen as 5.0 (g L⁻¹), and it was used in the subsequent experiments.

**Effect of contact time**

The equilibrium time required for biosorption of Ni(II) on *Circinella* sp. was obtained by studying biosorption of Ni(II) at various contact times for 2.0 mM Ni(II). Figure 2 shows the effect of contact time of Ni(II) on *Circinella* sp. It can be seen that the biosorption process occurred very rapid in 15 min, and Ni(II) uptake capacity value reached equilibrium at 60 min. No further increase in the level of bounded Ni(II) after 60 min. Therefore, 60 min was selected as equilibrium time for biosorption process.

**Effect of temperature**

Figure 3 shows the biosorption of Ni(II) for varied temperatures at 60 min of contact time. As shown in Figure 3, biosorption capacities were found for 2 mM Ni(II) at 20ºC, 30ºC, 40ºC and 60ºC as 2.51 x 10⁻⁴ mol/g, 2.57 x 10⁻⁴ mol/g, 2.67 x 10⁻⁴ mol/g and 2.37 x 10⁻⁴ mol/g, respectively. It was observed that the biosorption capacity of *Circinella* sp. decreased over 40ºC. The increase in biosorption of Ni(II) with temperature may be attributed to two factors. One is an increase in the number of active surface sites available for biosorption on the biosorbent. The other is the decrease in the thickness of the boundary layer surrounding the biosorbent with temperature and its positive effect on the mass transfer resistance of Ni(II) in the boundary layer. The decrease in biosorption capacity of *Circinella* sp. above 40ºC may be attributed to the deactivation of the biosorbent surface or the destruction of some active sites on the biosorbent surface. As a result, the optimum temperature for Ni(II) biosorption was chosen as 40ºC for subsequent experiments.

**Effect of solution pH**

It is well known that solution pH is an important parameter affecting biosorption of heavy metal ions. Biosorption process occurs by means of adsorption, ion exchange, and covalent binding with the biosorptive sites of the fungal cell wall. Fungal cell wall has hydroxyl, carboxyl, amino, sulfhydryl and amino functional groups. The solution pH can change the solubility of metal ions and the ionization state of the functional groups on the fungal cell wall (Bayramoğlu et al. 2003). The main cell wall constituents of *Circinella* sp. used in this study are chitin, chitosan and polygluchronic acid, and it has carboxylate, hydroxyl and amino functional groups. The negative charges of functional groups, carboxylate and phosphate provide the biosorption of metal ions (Say et al. 2001).

The effect of Ni(II) biosorption on *Circinella* sp. was investigated at optimized contact time by varying the pH of nickel solution from 2.0 to 10.0. The initial pH values of Ni(II) solutions were adjusted before mixing with the biosorbent. Figure 4 depicts the plot of metal biosorption capacity (mol g⁻¹) versus different pHs. At a pH of 2.0, the amount of Ni(II) uptake is small. As pH increases, the amount of Ni(II) uptake increases. The maximum uptake was observed at pH of 6.0 for 2.0 mM Ni(II) at 60 min of contact time. While the amount of Ni(II) uptake decreases at higher pH value, the hydrogen ions compete with metal ions for the exchange sites in the system at low pH value. Therefore, the low biosorption capacities lower than 6.0 are attributed to hydrogen ions. On the other hand, at low pH values, fungal cell wall ligands are saturated with
the hydronium ions, and repulsive forces prevent the effective biosorption of metal ions on the cell wall (Kalyani et al. 2004). The lower uptake of Ni(II) at above the pH of maximum biosorption may be attributed to the reduced solubility and precipitation of nickel (Harris and Ramelow, 1990).

**Biosorption kinetics of Ni(II)**

A kinetic study with different time intervals using optimum biomass dosage, solution pH and temperature was carried out (Figure 5). For different initial concentrations of metal ion solutions ranging from 1.0 mM to 3.0 mM Ni(II), the plot of amount biosorbed, $q_t$ (mol $g^{-1}$) versus time, $t$ (s) is shown on the Figure 5. It was observed that the amount of Ni(II) biosorption increased thanks to increasing both initial concentration of Ni(II) and reaction times. The maximum amount of biosorbed Ni(II) was found $3.19 \times 10^{-4}$ mol $g^{-1}$ for concentration of 3.0 mM Ni(II) under optimum experimental conditions.

The kinetics of the biosorption data were evaluated through the use of three different kinetic models- pseudo-first order, pseudo-second order, and intra-particle diffusion kinetic models. These kinetic models were given below:

**Pseudo-first order kinetic model**

The pseudo-first order rate expression given by Lagergren can be represented as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}$$

[Equation 2]

where $k_1$ (s$^{-1}$) is the rate constant of biosorption, $q_e$ and $q_t$ are amounts of metal ion biosorbed (mol $g^{-1}$) on biosorbent, at equilibrium, and at time $t$ (s), respectively. The rate constants, $k_1$, were calculated from the plots of log $(q_e - q_t)$ versus $t$ for different concentrations of Ni(II). Because the correlation coefficients were lower than 0.99, and disagreement between experimental and calculated values of equilibrium biosorption capacity ($q_e$) was in question, the biosorption of Ni(II) on *Circinella* sp. was not well fitted a pseudo-first order kinetic model (Table 2).

**Pseudo-second order kinetic model**

The pseudo-second order kinetic model based on adsorption equilibrium capacity can be expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

[Equation 3]
where \( k_2 \) is the pseudo-second order rate constant (g mol\(^{-1}\) s\(^{-1}\)). The experimental and calculated values of \( q_e \) showed a good agreement (Table 2). The correlation coefficients for the pseudo-second order kinetic model were higher than 0.99, and there was good agreement between experimental and calculated values of equilibrium biosorption capacity (\( q_e \)) indicating the applicability of this kinetic model for the biosorption process of Ni(II) on Circinella sp.

Intra-particle diffusion kinetic model

The intra-particle diffusion kinetic model was also examined by using the intra-particle diffusion from the following equation:

\[
q_t = k_{id} \sqrt{t} + C
\]

[Equation 4]

where \( k_{id} \) is the intra-particle diffusion rate constant (mol s\(^{-1/2}\) g\(^{-1}\)) and \( C \) is the intercept of the plot of \( q_t \) versus \( \sqrt{t} \). Figure 6 presents the intra-particle diffusion model of Ni(II) biosorption on Circinella sp. at different concentrations of Ni(II). Figure 6 shows two separate portions: the first linear portion of the plot is attributed to the boundary layer diffusion, and the second linear portion to intra-particle diffusion. Therefore, the intra-particle diffusion is not the rate limiting step for the whole reaction. The results using various kinetic models of Ni(II) biosorption on Circinella sp. were given in Table 2.

Activation energy of Ni(II) biosorption on Circinella sp.

The activation energy of Ni(II) biosorption on Circinella sp. was calculated from the Arrhenius plot using Arrhenius equation:

\[
\ln k_2 = \ln k_0 - \frac{E_a}{RT}
\]

[Equation 5]

where \( k_2 \) is the rate constant of pseudo-second order (g mol\(^{-1}\) s\(^{-1}\)), \( k_0 \) is the temperature independent factor (g mol\(^{-1}\) s\(^{-1}\)), \( E_a \) is the activation energy of biosorption (kJ mol\(^{-1}\)), \( R \) is the gas constant (8.314 J K\(^{-1}\) mol\(^{-1}\)), and \( T \) is the solution temperature (K).

According to the linear plot of \( \ln k_2 \) against 1/T, the correlation coefficient (R\(^2\)) was found to be 0.9925. The activation energy for the biosorption system of Ni(II) on Circinella sp. was calculated from the slope of the plot. The activation energy in the range of 5-40 kJ mol\(^{-1}\) suggests a physisorption process, while the activation energy in the range of 40-800 kJ mol\(^{-1}\) indicates a chemisorption process (Nollet et al. 2003;
Mashitah et al. 2008). The $E_a$ value for 2.0 mM initial concentration of Ni(II) was 15.2 kJ mol$^{-1}$. This result indicated that the biosorption of Ni(II) on Circinella sp. was endothermic and the process followed physisorption mechanism.

Biosorption isotherm modelling

The modelling of the biosorption process on Circinella sp. was obtained by using different adsorption isotherms. In order to clarify the adsorption isotherms, Langmuir and Freundlich equations were chosen. The Langmuir equation can be expressed as:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m}$$

[Equation 6]

where $q_e$ is the amount of metal ion biosorbed on a biosorbent (mol g$^{-1}$) at equilibrium time, $q_m$ is monolayer capacity of the biosorbent (mol g$^{-1}$), $K_L$ is the biosorption constant (L mol$^{-1}$), and $C_e$ is equilibrium concentration of metal ion in solution (mol L$^{-1}$).

The Freundlich equation in logarithmic form can be given as:

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

[Equation 7]

where $K_F$ and $n$ are empirical Freundlich constants, and indicative of adsorption capacity and adsorption intensity, respectively, $q_e$ and $C_e$ are like in the Langmuir equation described above. The value of $n$ is generally between 2 to 10.

The shape and favourability of the biosorption process can be identified by means of a dimensionless separation factor ($R_L$). $R_L$ is calculated as follows:

$$R_L = \frac{1}{1 + K_L C_e}$$

[Equation 8]

where $K_L$ indicates the Langmuir constant, and $C_e$ is the equilibrium concentration. According to the value of $R_L$, the isotherm shape can be explained as unfavourable ($R_L > 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$). The $R_L$ values for the biosorption of Ni(II) on Circinella sp. were in the ranges 0.16-0.54, 0.14-0.56 and
Biosorption of Ni(II) by Circinella sp.

0.15-0.58 for 20°C, 30°C and 40°C at solution pH of 6.0 depict that the biosorption process was favourable.

The parameters for two isotherms obtained from experimental data are given in Table 3.

The maximum experimental biosorption capacity of Circinella sp. used in this study was found to be 18.66 mg g⁻¹ (3.19 x 10⁻⁴ mol g⁻¹) for Ni(II) at 40°C. This value is better than many of fungal biomasses ( Dönmez and Aksu, 2001; Zouboulis et al. 2003; Saiano et al. 2005; Moore et al. 2008; Padmavathy, 2008).

Biosorption thermodynamics

The thermodynamic parameters for the biosorption process such as change in free energy (ΔG⁰), enthalpy (ΔH⁰) and entropy (ΔS⁰) were evaluated using the following equations:

\[ \ln K_L = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \]

[Equation 9]

\[ \Delta G^0 = -RT \ln K_L \]

[Equation 10]

where \( K_L \) is the Langmuir constant related to the energy of biosorption, \( R \) is the gas constant (8.314 J mol⁻¹ K⁻¹), and \( T \) is the absolute temperature (K). The values of \( \Delta H^0 \) and \( \Delta S^0 \) can be calculated, respectively, from the slope and intercept of the van't Hoff plot of \( \ln K_L \) versus \( 1/T \) (Figure 7).

The calculated values of \( \Delta H^0 \), \( \Delta S^0 \) and \( \Delta G^0 \) or biosorption of Ni(II) on Circinella sp. were given in Table 4. The positive value of \( \Delta H^0 \) confirms that the biosorption process of Ni(II) is endothermic. The negative value of \( \Delta G^0 \) at various temperatures indicates the feasibility and spontaneity of the biosorption process. The increase in \( \Delta G^0 \) with the increase temperature indicates that the biosorption is more favourable at high temperatures. The positive value of \( \Delta S^0 \) shows the affinity of biosorbent for Ni(II) and it also confirms an increase in the randomness at the solid-solution interface during the biosorption process.

Desorption studies

Because of the economic success and reuse of the biomass, desorption studies have an importance for the biosorption process. The efficiency of desorption and preservation of biosorption capacity of biosorbent are important factors to choice the desorbing agents. To evaluate the efficiency of desorbing agents, 0.1 M of HCl,
HNO₃, NaNO₃, EDTA solutions and deionized water were used. Figure 8 shows the desorption efficiencies of desorbing agents under batch experimental conditions. The recovery percentage of Ni(II) with deionized water was found to be 1.550%. This value was very insignificant for desorption of Ni(II). The maximum recovery efficiency of 100.0% was found with HCl and EDTA. In addition, HNO₃ resulted in high recovery efficiency of 93.00%. NaNO₃ solution showed a desorption efficiency of 16.00%. The low desorption efficiency of NaNO₃ solution can be attributed to the greater affinities of divalent cations for the negative charged sites on the biosorbent than monovalent cations. HCl and EDTA showed the maximum efficiency for the desorption process. This result obtained with EDTA can be attributed to the strong complexing ability to Ni(II). HCl was selected as an effective desorbing agent due to the similar result with EDTA, and low cost of HCl. The concentration effect of HCl solutions on desorption process was also studied. The desorption efficiencies based on the concentration of HCl was given in Table 5. The results show that a concentration of 0.1 M HCl can effectively remove the biosorbed Ni(II).

In order to evaluate the reusability of the biosorbent, biosorption-desorption cycle of Ni(II) was repeated for six times using the desorbing agent as 0.1 M HCl. It was found that the Ni(II) successively uptake for six cycles. Following the six cycles, biosorption biosorbent efficiency of the decreases about 9.2%. As a result, it can be claimed that Circinella sp. has good potential to biosorption and desorption of Ni(II).

CONCLUDING REMARKS

Circinella sp., a mucor-like species in the order Mucorales, was firstly used for biosorption of Ni(II). The present study shows that the biomass of Circinella sp. can be effectively used for removal of Ni(II) from aqueous solutions because of its reasonable biosorption capacity, easy production, and low cost.

The results of the biosorption of Ni(II) on Circinella sp. at a pH of 6.0 showed that temperature and initial concentration of metal ion greatly influenced the uptake capacity of the biosorbent. The biosorption capacity increased with an increase both in temperature up to 40°C and in the concentration of the metal ions up to 3.0 mM. The Langmuir model fitted better than the Freundlich model for the biosorption process in the concentration range (1.0-3.0 mM) at all the temperatures studied. The maximum Ni(II) biosorption capacity, qmax, on Circinella sp. was found to have an intermediate value of 18.66 mg g⁻¹ compared to other biosorbents reported in the literature. The biosorption kinetics followed the pseudo-second order kinetic model. The biosorption rate constants increase with an increase in temperature. Negative value of ΔG° and positive value of ΔH° were observed indicating, respectively, the spontaneous and endothermic nature of nickel(II) ion biosorption on Circinella sp. Desorption studies conducted showed that the Ni(II) biosorbed on Circinella sp. could be desorbed effectively using 0.1 N HCl. It was found that the Ni(II) successively uptake for six cycles. Following the six cycles biosorption efficiency of the biosorbent decreases about 9.2%.

As a result, Circinella sp. was successfully used in native form for biosorption and desorption of Ni(II). Our results are very promising to further large scale biosorption studies. Biosorption capacity of Circinella sp. can also be improved with various immobilization techniques.
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APPENDIX
FIGURES

Fig. 1 SEM micrographs and spectrums on *Circinella* sp.
(a) before biosorption of Ni(II).
(b) after biosorption of Ni(II).

Fig. 2 Effect of contact time on biosorption of Ni(II) (biomass dosage: 5 g L⁻¹; concentration of Ni(II): 2.0 mM; temperature: 40°C; pH: 6).
Fig. 3 Effect of temperature on biosorption of Ni(II) (biomass dosage: 5 g L$^{-1}$; concentration of Ni(II): 2.0 mM; contact time: 60 min; pH: 6).

Fig. 4 Effect of solution pH on biosorption of Ni(II) (biomass dosage: 5 g L$^{-1}$; concentration of Ni(II): 2.0 mM; temperature: 40°C; contact time: 60 min).
Fig. 5 Biosorption kinetics for Ni(II) on *Circinella* sp. (biomass dosage: 5 g L⁻¹; temperature: 40°C; pH: 6.0).

Fig. 6 Plot of the intra-particle diffusion kinetic model for biosorption of Ni(II) on *Circinella* sp. at different concentrations (biomass dosage: 5 g L⁻¹; temperature: 40°C; pH: 6.0).
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Fig. 7 The van’t Hoff plot for the biosorption of Ni(II) on *Circinella* sp. (biomass dosage: 5 g L$^{-1}$; pH: 6.0; contact time: 60 min).

\[ y = -928.1x + 11304 \]
\[ R^2 = 0.9943 \]

Fig. 8 Efficiency of desorbing agents (biomass dosage: 5 g L$^{-1}$; contact time: 60 min; temperature: 25 ± 2°C; pH: 6.0).
### TABLES

#### Table 1. Elemental analysis results of Circinella sp.

<table>
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<th>Conc. (wt. %)</th>
<th>Component</th>
<th>Conc. (wt. %)</th>
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</table>

(kV: 20.0; take off angle: 35.0º; elapsed live time: 100.0)

#### Table 2. Kinetic values calculated according to the pseudo-first order, pseudo-second order and intra-particle diffusion kinetic models.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Experimental value</th>
<th>Pseudo-first order</th>
<th>Pseudo-second order</th>
<th>Intra-particle diffusion</th>
</tr>
</thead>
<tbody>
<tr>
<td>T (ºC)</td>
<td>Concentration (mM)</td>
<td>q_e (mol g^-1)</td>
<td>k_1 (g mol^-1 s^-1)</td>
<td>R^2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>1.0 6.0 x 10^-4</td>
<td>1.04x10^-4</td>
<td>1.15x10^-2</td>
<td>0.9515</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>1.5 6.0 2.24 x 10^-4</td>
<td>1.97 x 10^{-4}</td>
<td>1.15 x 10^{-2}</td>
<td>0.9581</td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>2.0 6.0 2.67 x 10^-4</td>
<td>1.39 x 10^{-4}</td>
<td>9.21 x 10^{-2}</td>
<td>0.9341</td>
</tr>
<tr>
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</tr>
<tr>
<td>40</td>
<td>2.5 6.0 3.06 x 10^-4</td>
<td>2.34 x 10^{-4}</td>
<td>1.61 x 10^{-2}</td>
<td>0.9324</td>
</tr>
<tr>
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<td></td>
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</tr>
<tr>
<td>40</td>
<td>3.0 6.0 3.19 x 10^-4</td>
<td>1.89 x 10^{-4}</td>
<td>1.15 x 10^{-2}</td>
<td>0.9012</td>
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<tr>
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</tr>
<tr>
<td>30</td>
<td>2.0 6.0 2.57 x 10^-4</td>
<td>1.52 x 10^{-4}</td>
<td>9.21 x 10^{-2}</td>
<td>0.9512</td>
</tr>
<tr>
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<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>2.0 6.0 2.51 x 10^-4</td>
<td>1.74 x 10^{-4}</td>
<td>1.15 x 10^{-2}</td>
<td>0.9796</td>
</tr>
</tbody>
</table>
Biosorption of Ni(II) by *Circinella* sp.

### Table 3. Parameters of Langmuir and Freundlich isotherms.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>pH</th>
<th>Langmuir isotherm</th>
<th>Freundlich isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$K_L$ (L mol$^{-1}$)</td>
<td>$q_m$ (mol g$^{-1}$)</td>
</tr>
<tr>
<td>20</td>
<td>6.0</td>
<td>3402</td>
<td>3.51x10$^{-3}$</td>
</tr>
<tr>
<td>30</td>
<td>6.0</td>
<td>3815</td>
<td>3.42x10$^{-3}$</td>
</tr>
<tr>
<td>40</td>
<td>6.0</td>
<td>4165</td>
<td>3.74x10$^{-3}$</td>
</tr>
</tbody>
</table>

### Table 4. Thermodynamic parameters for biosorption of Ni(II) on *Circinella* sp.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>$\Delta G^0$ (kJ mol$^{-1}$)</th>
<th>$\Delta H^0$ (kJ mol$^{-1}$)</th>
<th>$\Delta S^0$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>-19.81</td>
<td>7.72</td>
<td>0.094</td>
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<tr>
<td>30</td>
<td>-20.77</td>
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<tr>
<td>40</td>
<td>-21.69</td>
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<td></td>
</tr>
</tbody>
</table>

### Table 5. Effect of HCl concentration on desorption.

<table>
<thead>
<tr>
<th>Concentration of HCl</th>
<th>Desorption efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 M</td>
<td>100</td>
</tr>
<tr>
<td>0.5 M</td>
<td>90</td>
</tr>
<tr>
<td>1.0 M</td>
<td>89</td>
</tr>
</tbody>
</table>