Int. J. Environ. Res., 9(4):1147-1156, Autumn 2015
ISSN: 1735-6865

Removal and Recovery of Nickel Ions from Aqueous Solutions using *Bacillus sphaericus* Biomass

Aryal, M.

Faculty of Chemical Engineering, Department of Chemistry, Aristotle University of Thessaloniki, Thessaloniki, 54124, Greece

Received 14 Oct. 2014; Revised 6 Jan. 2015; Accepted 15 Jan. 2015

ABSTRACT: This paper discusses the biosorption of Ni(II) ions from aqueous solutions by *Bacillus sphaericus* biomass. The biosorption process was affected by the solution pH, biomass concentration, contact time, temperature and initial Ni(II) concentration respectively. The sorption kinetics and equilibrium data were described well with the pseudo-second order kinetic model and the Freundlich isotherm model. The maximum monolayer biosorption capacity value of *Bacillus sphaericus* biomass for Ni(II) ions was calculated at 55.55 mg/g using the Langmuir isotherm model. The thermodynamic study shows the Ni(II) biosorption was spontaneous and exothermic in nature. The change in heat of sorption (ΔH^o) and the isosteric heat of sorption (ΔH_r) values indicate the physical sorption as the predominant mechanism for Ni(II) biosorption. The Ni(II) ions were recovered effectively from *Bacillus sphaericus* biomass using 0.1 M HNO_3 and can be recycled. FTIR results showed that carboxylic and amine groups of *Bacillus sphaericus* cells were responsible for Ni(II) binding.

Key words: *Bacillus sphaericus*, Ni(II), Biosorption, Desorption, Biomass characterization

INTRODUCTION

The heavy metals are not biodegradable and can be accumulated in living tissues. The presence of these metals in water even in low concentration can affect living organisms due to their toxic and carcinogenic nature. The nickel is found in industrial wastewater, since it is associated with a number of industrial sources, including mining and metallurgy, electroplating, Nickel-Cadmium batteries, printing, chemical industries, pigments, electronic or computer equipment, preparation of alloys and fertilizers (Bhattacharyya *et al.*, 2009; Kasprzak *et al.*, 2003). Long term exposure to nickel has been found to cause health problems such as allergy, respiratory system, lung and kidney diseases, cardiovascular and gastrointestinal irritation (Kasprzak *et al.*, 2003). Therefore, the tolerance limit of nickel ions in drinking water has been suggested not exceed than 0.5 mg/L (WHO, 2006).

Different conventional methods such as adsorption, membrane separation, filtration, chemical oxidation or reduction, evaporative recovery, ion exchange, and reverse osmosis have been applied to remove heavy metals from wastewater (Aryal and Liakopoulou-Kyriakides, 2015). These technologies are inconvenient for treatment of industrial effluents having less than 100 mg/L of dissolved metal ions. In recent years, biosorption has become one of the alternative treatment technologies to remove heavy metals from aqueous solutions (Aryal *et al.*, 2010). The advantages of biosorption technique over conventional methods are the use of cheap biosorbents, high metal binding capacity, selectivity, rapidity, recovery of metals in concentrated form, reusability of biomass and no generation of toxic wastes.

The use of dead biomass and its derivatives for removal of heavy metals has been extensively studied. Some biosorbents such as *Acacia leucocephala* (Subbaiah *et al.*, 2009), *Azadirachta indica* (Bhattacharyya *et al.*, 2009), *Bacillus pumilus* (Wierzba and Latala, 2010), *Exiguobacterium* sp. (Amer *et al.*, 2014), *Elaeagnus Angustifolia (*Amiri *et al.*, 2014*), Mucor hiemalis* (Shroff and Vaidya, 2011), *Pseudomonas fluorescens* (Wierzba and Latala, 2010), *Pseudomonas* sp. (Gialamouidis *et al.*, 2009), *Rhodococcus opacus* (Cayllahua *et al.*, 2009), *Salvadora persica* L. branches (Ileri *et al.*, 2014), *Staphylococcus xylosus* (Gialamouidis *et al.*, 2009), *Streptomyces rimosus* (Selatnia *et al.*, 2004), and

*Corresponding author E-mail: mahendraaryalnp@yahoo.com

grapefruit peel (Torab-Mostaedi *et al.*, 2013) have been used to remove Ni(II) ions from the aqueous solutions. However, only a few bacterial sorbents have been reported with high biosorption capacity for Ni(II) ions (Gialamouidis *et al.*, 2009; Wierzba and Latala, 2010).

Nickel is an important transition metal and its natural resources are going to be depleted in the near future due to industrial, agricultural and household uses. The recovery of Ni(II) ions from wastewater may be an alternative source to compensate such natural resources. Therefore, recovery of Ni(II) ions plays an important role not only in economizing the ore sources but also in reducing environmental pollution. *Bacillus sphaericus* biomass was examined for the purpose, pursuing study on nickel bioremediation. The effect of initial pH, biomass concentration, sorption time, temperature, and initial Ni(II) ions concentration were investigated. Kinetic, equilibrium and thermodynamic studies were also carried out. In addition, FT-IR analysis was used to confirm the interaction between Ni(II) ions and biomass surface groups.

MATERIALS & METHODS

Bacillus sphaericus was isolated from a contaminated soil in a mining industry near Stratoni, Chalkidiki, Greece. It was cultivated in Luria-Bertani broth containing 1.0 % tryptone, 0.5 % yeast extract and 0.5 % NaCl (Scharlau Chemie S.A., Barcelona, Spain) at 30 °C, using a rotary shaker of an incubator at 180 rpm (Sanyo, MIR-153, Osaka, Japan). Cells were harvested by centrifugation (Kubota 5922, Tokyo, Japan) at 2000 g for 20 min at the static phase of growth, 24 h incubation and autoclaved (Systec, Greiz, Germany) at the 121 °C for 20 min before their use. Moisture content was determined by drying a pre-weighted amount of the cells in an oven (Heraeus KT 5050, West Midlands, U. K.) at the 100 °C for 10 h.

Ni(II) stock solution at 1000 mg/L was prepared from $NiSO_4.6H_2O$ (Merck, Darmstadt, Germany). The biosorption of Ni(II) on *Bacillus sphaericus* biomass at varying initial pH values from 1.0 to 7.0, biomass concentration from 1.0 to 7.0, sorption time from 0 to 60 min and temperature from 20 to 50 °C at 50 mg/L of Ni(II) concentration were carried out. The effect of initial Ni(II) concentration on the retaining capacity of *Bacillus sphaericus* biomass was studied from 10 to 400 mg/L at pH 5.0, biomass concentration 1.0 g/L and equilibrium time 30 min respectively. After sorption, Ni(II) concentration in the supernatant solutions was determined by photometric method with dimethylglyoxime as complexion agent at 366 nm (Shimadzu UV-160A, Kyoto, Japan) (APHA, 1975). All experiments were performed in duplicate and the mean values were used in the data analysis.

Biosorption experiments were first conducted with initial concentration of Ni(II) ions at 50 mg/L. For desorption experiments, Ni(II)-loaded biomass was suspended using 0.1 M HNO_3 for 60 min, where solid to liquid ratio was kept at 1.0 g/L. In order to investigate the possible reusability of the biomass, the same biomass was used upto five consecutive sorption-desorption cycles.

Bacillus sphaericus biomass before and after sorption of Ni(II) ions was studied using Fourier Transform Infrared Spectrophotometer (Equinox 55, AXS Bruker, USA). Potassium bromide disks were prepared by mixing 1 mg of lyophilized samples with 200 mg KBr, and the spectra were recorded from 400 to 4000 /cm with a resolution number 2 /cm.

Mathematical description

The amount of Ni(II) ions sorbed by the biomass is given by the following equation;

$$Q_e = \frac{V.(C_o - C_e)}{W} \quad (1)$$

Where Q_e is the amount of Ni(II) sorbed by the bacterial cells (mg/g) at equilibrium, C_o is the initial concentration of Ni(II) (mg/L), C_e is the concentration of Ni(II) at equilibrium (mg/L), V is the initial volume of Ni(II) solution (L), and W is the mass of the sorbent (g). Pseudo first-order kinetic model considers that the rate of occupation of sorption sites is proportional to the number of unoccupied sites (Lagergren, 1898).

$$\frac{dQ_t}{dt} = k_1(Q_e - Q_t) \quad (2)$$

The linear form of equation (2) can be written as follows;

$$\ln(Q_e - Q_t) = \ln Q_e - k_1.t \quad (3)$$

Where Q_e and Q_t are the amount of metal ions sorbed (mg/g) at equilibrium and given time, t (min), and k_1 is the first-order rate constant (per min) respectively. Pseudo second-order kinetic model assumes that the rate of occupation of sorption sites is proportional to the square of the number of unoccupied sites (Ho and McKay, 1999).

$$\frac{dQ_t}{dt} = k_2(Q_e - Q_t)^2 \quad (4)$$

The linear form of this model is given by following equation;

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^{\,2}} + (\frac{1}{Q_e}).t \quad (5)$$

Where k_2 is the rate constant of pseudo second-order sorption (g/mg.min).

Intra-particle diffusion model explains the diffusion mechanism of the sorption process and the linear form

of this model can be expressed as (Webi and Chakravort, 2004);

$$Q_t = k_{id}.t^{0.5} + C \quad (6)$$

Where k_{id} is the initial intra-particle diffusion rate (mg/g $min^{0.5}$) and C is the intercept of the plot.

Langmuir equation relies on the assumption that there are a finite number of binding sites, which are homogeneously distributed over the adsorbent surface, having the same affinity for adsorption of a single molecular layer and there is no interaction between adsorbed molecules (Langmuir, 1918).

$$Q_e = \frac{Q_{max} \cdot b \cdot C_e}{1 + b \cdot C_e} \quad (9)$$

The linear form of Langmuir model is given by following equation;

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_{max}} + \frac{1}{Q_{max}.b} \quad (10)$$

Where C_e is the residual metal concentration (mg/L), Q_e is the amount of metal sorbed (mg/g) at equilibrium, Q_{max} is the maximum uptake capacity corresponding to site saturation (mg/g) and b is the biomass metal binding affinity (L/mg).

Freundlich equation assumes that the sorption energy of a metal binding to a site on an adsorbent depends on whether the adjacent sites are already occupied or not (Freundlich, 1906).

$$Q_e = K_f \cdot (C_e)^{\frac{1}{n}} \quad (11)$$

The linear form of Freundlich equation can be expressed as;

$$\ln Q_e = \ln K_f + (\frac{1}{n}) \ln C_e \quad (12)$$

Where, K_f and n are the constants describing sorption capacity and intensity respectively.

Standard Gibbs free energy change (ΔG^o) indicates the degree of spontaneity of the sorption process.

$$\Delta G^o = -RT \ln K_c \quad (13)$$

Where K_c is the distribution coefficient ($\frac{Q_e}{C_e}$).

The change in heat of sorption (ΔH^o) and entropy (ΔS^o) are related to standard Gibbs free energy change (ΔG^o).

$$\Delta G^o = \Delta H^o - T\Delta S^o \quad (14)$$

Equations (13) and (14) can be combined as;

$$\ln K_c = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R} \quad (15)$$

The magnitude of isosteric heat of biosorption (ΔH_r) at constant coverage can be calculated by means of the Clausius-Clapeyron equation;

$$\frac{d(\ln C_e)}{dT} = -\frac{\Delta H_r}{RT^2} \quad (16)$$

The linear form of equation (16) can be written as;

$$\ln C_e = \frac{\Delta H_r}{RT} + K \quad (17)$$

The isosteric heat of biosorption can be calculated from the slope of a plot between $\ln C_e$ and $1/T$.

The percentage of Ni(II) ions desorption from Ni(II)-loaded biomass can be obtained from the following relations;

$$Desorption(\%) = \left(\frac{C_{desorption,i}}{C_{in} - C_{sorption,i} + \frac{M_i}{V}} \right) \times 100 \quad (18)$$

Where,

$$M_i = V\left(i.C_{in} - \sum_{i=1}^{n} C_{sorption,i} - \sum_{i=1}^{n} C_{desorption,i} \right)$$

Where i is the number of sorption-desorption cycles, C_{in} is the initial Ni(II) concentration (mg/L), $C_{sorption,i}$ is the Ni(II) concentration in solution after biosorption in cycle i (mg/L), $C_{desorption,i}$ is the Ni(II) concentration after desorption in cycle i (mg/L), M_i is the amount of Ni(II) remaining on biomass after i number of cycles (mg) and V is the solution volume (L) (Gialamouidis *et al.*, 2009).

The Chi-square test can be used to determine the accuracy of mathematical models. The error function can be evaluated by the following non-linear Chi-square test;

$$\chi^2 = \sum \frac{(Q_e - Q_{e,m})^2}{Q_{e,m}} \quad (19)$$

Where Q_e and $Q_{e,m}$ are the experimental and calculated values of the equilibrium uptake capacity from the model (mg/g). The lower value of the error function (χ^2) suggests the best fit of mathematical models to experimental data.

RESULTS & DISCUSSION

The initial pH of the aqueous solution influences not only the dissociation of functional groups on the active sites of the biomass but also the solution-Ni(II) ions chemistry. The effect of pH on the equilibrium uptake capacity of *Bacillus sphaericus* biomass for Ni(II) ions from aqueous solutions at initial Ni(II) concentration 50 mg/L, biomass concentration 1.0 g/L and contact time 60 min is illustrated in Fig. 1. The maximum equilibrium uptake capacity of Ni(II) ions was observed at pH 5.0. This Figure shows that the equilibrium sorption capacity increases from 2.59 to 26.65 mg/g with increasing pH from 1.0 to 5.0 and

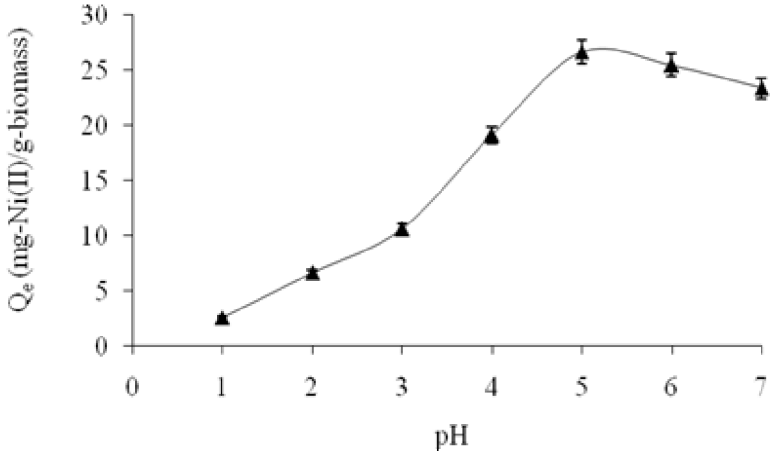

Fig. 1 Effect of pH on Ni(II) biosorption using *Bacillus sphaericus* biomass

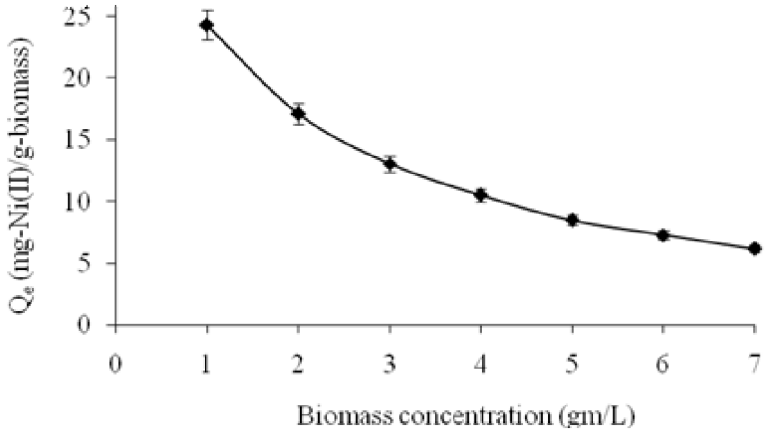

Fig. 2. Effect of biomass concentration on Ni(II) biosorption using *Bacillus sphaericus* biomass

decreasing from 26.65 to 23.34 mg/g with an increase in pH from 5.0 to 7.0. The same trend has also been reported elsewhere (Torab-Mostaedi *et al.*, 2013; Subbaiah *et al.*, 2009; Cayllahua *et al.*, 2009). The lower sorption capacity at low pH values may be due to the presence of excess H_3O^+ ions competing with the Ni(II) ions for the same binding sites. The decrease in equilibrium uptake capacity at higher pH than 5.0 may be due to the precipitation of Ni(II) ions as hydroxides, which interfere the biosorption process (Aryal and Liakopoulou-Kyriakides, 2014).

Fig. 2 shows the effect of biomass concentration on Ni(II) sorption at initial Ni(II) concentration 50 mg/L, pH 5.0 and contact time 60 min respectively. The maximum equilibrium capacity of Ni(II) ions was observed at 1.0 g/L. The results indicate that uptake capacity of *Bacillus sphaericus* biomass for Ni(II) ions was decreased from 24.29 to 6.16 mg/g with increase in biomass concentration from 1.0 to 7.0 g/L. This decrease in sorption capacity of Ni(II) with an increase in biomass concentration in a fixed volume is probably due to the strong limitations of Ni(II) species mobility in the biosorption medium, leaving some binding sites unsaturated during Ni(II) sorption (Divyasree *et al.*, 2014; Aryal and Liakopoulou-Kyriakides, 2011; Aryal *et al.*, 2011).

The effect of contact time for Ni(II) removal of *Bacillus sphaericus* biomass at initial Ni(II) concentration 50 mg/L, pH 5.0 and biomass concentration 1.0 g/L is given in Fig. 3. The results show that the sorption capacity for Ni(II) ions on *Bacillus sphaericus* biomass was increased with increase in contact time and equilibrium was reached at 25 min. The sorption equilibrium time at 25 min might be a result of sorption-desorption processes occurring after saturation of Ni(II) ions on biomass surface (Divyasree *et al.*, 2014). After 25 min of equilibrium time, equilibrium uptake capacities were almost constant, suggesting that an equilibrium balance for sorption process. The results further show that sorption was fast in the early stages

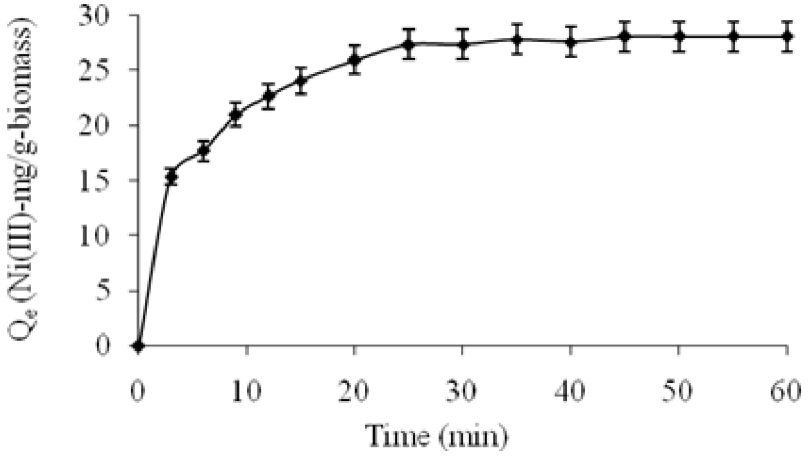

Fig. 3. Effect of contact time on Ni(III) biosorption using *Bacillus sphaericus* biomass

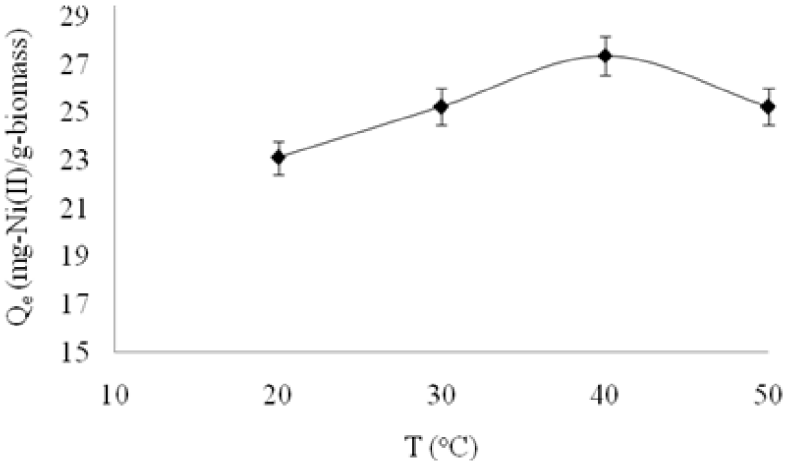

Fig. 4. Effect of temperature on Ni(III) biosorption using *Bacillus sphaericus* biomass

and was relatively slow to increase in contact time up to 25 min, signifying that Ni(II) biosorption seems to be followed by two-phase sorption mechanism (Torab-Mostaedi *et al.*, 2013).

Fig. 4 shows the equilibrium uptake capacity of *Bacillus sphaericus* biomass for Ni(II) at initial Ni(II) concentration 50 mg/L, pH 5.0 and biomass concentration 1.0 g/L as a function of temperatures. The maximum removal capacity of Ni(II) ions by *Bacillus sphaericus* biomass was determined at 40 °C. The results indicate that uptake capacity of Ni(II) increases with increasing temperature from 20 to 40 °C and then decreases at higher temperature than 40 °C.

The increase in sorption capacity of Ni(II) with increasing temperature from 20 to 40 °C may be attributed to the increase in kinetic energy of Ni(II) and biomass species, whereas the decrease in sorption capacity higher than 40 °C may be due to the decrease in surface activity indicating that Ni(II) sorption on biomass surface is an exothermic process (Aryal and Liakopoulou-Kyriakides, 2011).

The initial metal ions concentration provides the necessary driving force to overcome the resistance to the mass transfer of metal ions between aqueous and solid phases (Aryal *et al.*, 2010). The effect of initial Ni(II) ions concentration on equilibrium uptake capacity by *Bacillus sphaericus* biomass at pH 5.0, biomass concentration 1.0 g/L, contact time 30 min and temperature 40 °C is shown in Fig. 5. When the initial Ni(II) concentration was 10 mg/L, the equilibrium uptake capacity and sorption efficiency were 9 mg/g and 90.09 % respectively. In addition, when the initial Ni(II) concentration was 400 mg/L, the equilibrium uptake capacity and sorption efficiency were 83.01 mg/g and 20.75 % respectively.

Fig. 5 also shows that the amount of equilibrium sorption capacity increases upon increasing initial Ni(II) ions concentration. This can be explained by the

Table 1. Kinetic parameters, correlation coefficients and error functions of Ni(II) sorption onto *Bacillus sphaericus* biomass at initial Ni(II) concentration 50 mg/L, pH 5.0, temperature 40 °C and biomass concentration 1.0 g/L respectively

$Q_{e,exp}$ (mg/g)	Pseudo-first order kinetic model				Pseudo-second order kinetic model			
	k_1 (min^{-1})	$Q_{e,cal}$ (mg/g)	R^2	χ^2	k_2 (mg/g min)	$Q_{e,cal}$ (mg/g)	R^2	χ^2
27.35	0.125	19.53	0.985	2.239	0.007	32.25	0.994	0.744

Table 2. Langmuir and Freundlich parameters of Ni(II) sorption onto *Bacillus sphaericus* biomass at pH 5.0, temperature 40 °C and biomass concentration 1.0 g/L.

Langmuir constants				Freundlich constants			
Q_{max} (mg/g)	b (L/mg)	R^2	χ^2	K_f [(mg/g)/(L/mg)$^{1/n}$]	n (g/L)	R^2	χ^2
55.55	0.19	0.971	14.69	7.31	2.35	0.999	0.012

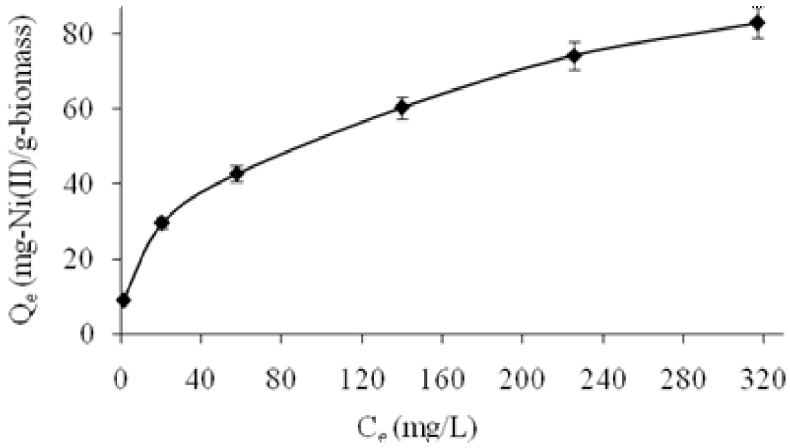

Fig. 5. Effect of initial Ni(II) concentration on equilibrium uptake capacity using *Bacillus sphaericus* biomass

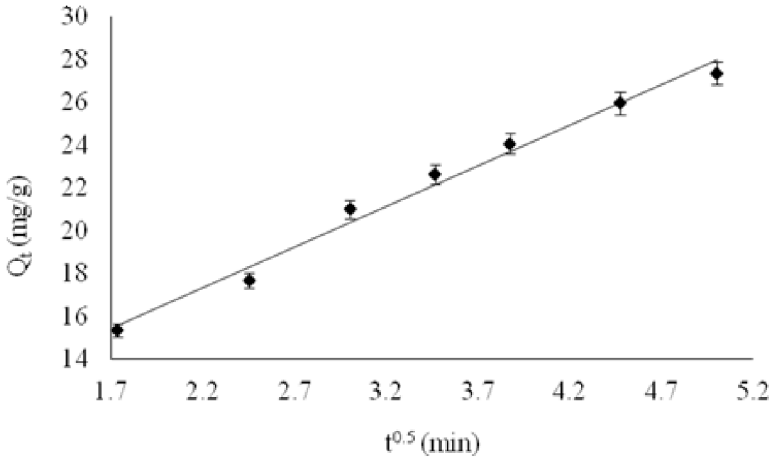

Fig. 6. Application of intraparticle diffusion model in Ni(III) biosorption on *Bacillus sphaericus* biomass

fact that the high concentration may enhance the interaction between Ni(II) ions and *Bacillus sphaericus* biomass surface binding sites (Aryal and Liakopoulou-Kyriakides, 2013). The effect of sorption data as the function of contact time was used to investigate the biosorption mechanism using pseudo-first order and pseudo-second order kinetic models. The kinetic constants and correlation coefficients of pseudo-first order and pseudo-second order kinetic models are listed in Table 1. The lower value of the correlation coefficient (R^2) and higher value of the error function (χ^2) as well as the higher value of difference between $Q_{e,exp}$ and $Q_{e,cal}$ suggested that Ni(II) sorption on *Bacillus sphaericus* biomass is not a pseudo-first order

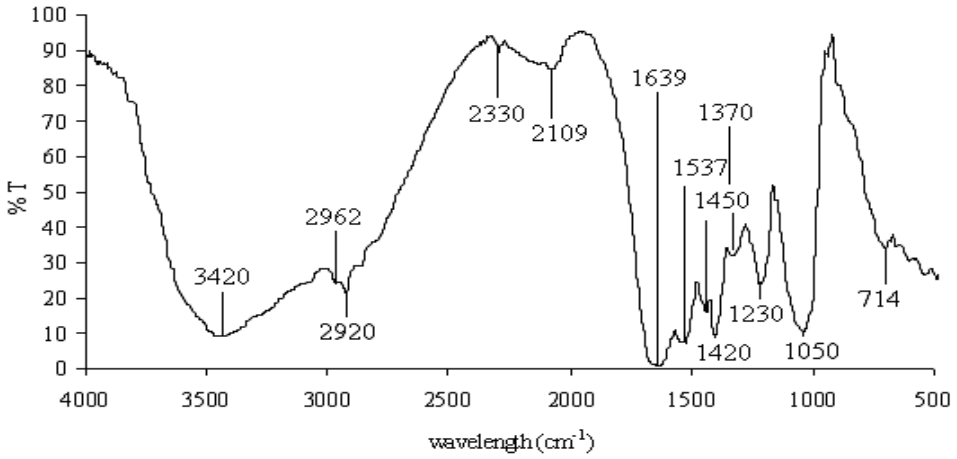

Fig. 7. FT-IR spectrum of Ni(II)-loaded *Bacillus sphaericus* biomass

Table 3. Thermodynamic parameters of Ni(II) biosorption onto *Bacillus sphaericus* biomass

ΔG^o (kJ/mol)				ΔH^o (kJ/mol)	ΔS^o(J/mol/K)	ΔH_r (kJ/mol)
10 °C	20 °C	30 °C	40 °C	10-40 °C	10-40 °C	10-40 °C
-27.10	-27.12	-27.61	-28.08	-17.30	33.53	-8.00

Table 4.Subsequent sorption-desorption cycles using *Bacillus sphaericus* biomass with 0.1 M HNO_3

No. of cycles	$Q_{e,sorption}$ (mg/g)	$Q_{e,desorption}$ (mg/g)	Desorption efficiency (%)	Lost in sorption efficiency (%)
1	28.06	27.43	97.76	–
2	25.23	23.56	93.41	10.08
3	22.16	19.40	87.56	12.16
4	18.16	14.35	79.06	18.05
5	13.20	10.06	72.56	27.31

reaction. On the other hand, it was observed that pseudo-second order kinetic model explains better Ni(II) sorption with a relatively higher value of correlation coefficient and the lower value of the error function compared to pseudo-first order kinetic model, indicating the applicability of pseudo-second order kinetic model for Ni(II) sorption. The calculated $Q_{e,cal}$ value obtained from this model is almost close with the experimental $Q_{e,exp}$ value, which shows better agreement with kinetic data. Therefore, the best fit of experimental kinetic data with pseudo-second order kinetic model assumes that the chemisorptions is the rate controlling step (Ho and McKay, 1999).

The plot of Q_t versus $t^{0.5}$ at initial Ni(II) concentration 50 mg/L, pH 5.0, temperature 40 °C and biomass concentration 1.0 g/L is given in Fig. 6. When the plot of Q_t versus $t^{0.5}$ gives a straight line, then the sorption process is controlled by intraparticle diffusion. If it does not pass through the origin, the intraparticle diffusion is not the rate-limiting step (Aryal and Liakopoulou-Kyriakides, 2015). As it can be seen from this figure, intraparticle diffusion is not the sole rate-controlling step in the whole sorption process, since the plot does not pass through the origin. However, Ni(II) sorption process of *Bacillus sphaericus* biomass is controlled by intraparticle diffusion, since the plot of Q_t versus $t^{0.5}$ gives a straight line.

The equilibrium data of Ni(II) sorption on *Bacillus sphaericus* biomass were estimated with the widely used Langmuir and Freundlich isotherm models. The calculated isotherm constants, correlation coefficients and error functions for Ni(II) sorption are presented in Table 2. The relatively lower correlation coefficient value (R^2) and higher error function (χ^2) value indicated that Ni(II) biosorption on *Bacillus sphaericus* biomass did not follow the Langmuir isotherm model. However, the maximum monolayer biosorption capacity was calculated at 55.55 mg-Ni(II)/g-*Bacillus sphaericus* biomass. Comparing this value with those reported in literature specifically; 89 mg-Ni(II)/g-*Staphylococcus xylosus* (Gialamouidis *et al*., 2009), 73.9 mg-Ni(II)/g-*Bacillus pumilus*, 65.1 mg-Ni(II)/g-*Pseudomonas fluorescens*

(Wierzba and Latala, 2010), 46.13 mg-Ni(II)/g-Grapefruit peel (Torab-Mostaedi *et al.*, 2013), 32.6 mg-Ni(II)/g-NaOH-treated *Streptomyces rimosus* (Selatnia *et al.*, 2004), 13.60 mg-Ni(II)/g-*Mucor hiemalis* (Shroff and Vaidya, 2011), 12.29 mg-Ni(II)/g-*Rhodococcus opacus* (Cayllahua *et al.*, 2009) and 9.10 mg-Ni(II)/g-*Azadirachta indica* leaf powder (Bhattacharyya *et al.*, 2009). It shows that *Bacillus sphaericus* biomass can be used to remove Ni(II) ions from wastewaters.

The high correlation coefficient value (R^2) and low error function (χ^2) value suggests the best fit of the Freundlich isotherm model to the experimental equilibrium data, revealing the multilayer sorption on biomass surfaces. The value of Freundlich constant, *n* indicates the favorability of the biosorption process. The values of *n* ranging from 2 to10 represent good, from 1 to 2 moderately difficult and less than 1 poor sorption characteristics. In our case, the value of *n* in the range of 2 to10 confirms that Ni(II) biosorption is favorable on *Bacillus sphaericus* biomass. In addition, high value of K_f is an indicative of the biosorption capacity. The calculated value K_f further reveals that higher uptake capacity of *Bacillus sphaericus* biomass for Ni(II) ions (Freundlich, 1906). The values of Gibbs free energy change (ΔG^o), enthalpy change (ΔH^o), entropy change (ΔS^o) and isosteric heat (ΔH_r) for the sorption of Ni(II) on *Bacillus sphaericus* biomass at different temperatures from 10 to 40 °C with initial Ni(II) concentration at 50 mg/L are given in Table 3.

The negative values of ΔG^o at all temperatures used confirm that Ni(II) biosorption was spontaneous and thermodynamically favorable. The decrease in ΔG^o values with increase in temperature corresponds to the decrease in feasibility of Ni(II) biosorption at higher temperatures.

The negative value of ΔH^o indicated the exothermic nature of Ni(II) biosorption. More specifically, ΔH^o values in the range of 2.1 to 20.9 kJ/mol indicated the physisorption, whereas values ranging from 20.9 to 418.4 kJ/mol favored the chemisorption (Sag and Kutsal, 2000). The calculated ΔH^o value for Ni(II) biosorption further supports the physical sorption as the predominant mechanism. The positive value of ΔS^o suggests the increased randomness of Ni(II) ions on *Bacillus sphaericus* biomass surface, reflecting further its affinity for Ni(II) ions.The negative value of ΔH_r shows that Ni(II) sorption on *Bacillus sphaericus* biomass is exothermic in nature. ΔH_r values lower than 80 kJ/mol suggest the physical sorption, whereas those values between 80 and 400 kJ/mol responsible for chemical sorption.

The calculated value of ΔH_r indicates that physical sorption is the main mechanism for Ni(II) biosorption (Aryal *et al.*, 2012). Desorption and regeneration of biomass is an important factor for commercial application. The effect of subsequent sorption-desorption cycles with each regenerating system at 50 mg/L of Ni(II) ions is depicted in Table 4. The first desorption of Ni(II) ions from Ni(II)-loaded *Bacillus sphaericus* biomass was observed at 97.76 %. This result indicates that Ni(II) ions were interacted extracellularly by binding sites present in the bacterial cell wall.

The observed loss of biomass binding efficiency after the first cycle may be attributed to the biomass deterioration caused by subsequent acid treatments and also weight lost by subsequent sorption-desorption cycles (Aryal *et al.*, 2010).In order to investigate the biosorption mechanism of Ni(II) ions, the *Bacillus sphaericus* biomass before and after Ni(II) sorption was studied by FT-IR analyses. According to an earlier publication (Aryal *et al.*, 2012), the strong band in the region of 3300-3500 /cm in raw *Baccilus sphaericus* biomass indicates the N-H stretches in primary -NH_2. The band around 2990-2850 /cm may correspond to alkyl chains. Amide I band is located at 1630 /cm (C=O stretching), whereas amide II band is approximately close to 1535 /cm. C-O-C stretching appeared at 1228 /cm. Peak positions at 1396 /cm may be attributed to COO^- present on the biomass, whereas peaks at 1441 /cm may correspond to -OH bending in carboxyl groups. Band at 1293 /cm also correspond to phosphate groups on the biomass surface. In addition, peaks at 1056 /cm represent C-O stretches in primary alcohols, whereas region around 604 /cm can be assigned to C–H bends. The FT-IR spectrum of *Bacillus sphaericus* biomass after Ni(II) sorption is given in Fig. 7. The results show that transmittance wave numbers of raw *Bacillus sphaericus* biomass at 3369 and 1396 /cm have been shifted to 3420 and 1420 /cm in *Bacillus sphaericus* biomass after Ni(II) sorption, indicating that amine and carboxylic groups are mainly involved in Ni(II) interactions on *Bacillus sphaericus* biomass surface.

CONCLUSIONS

Bacillus sphaericus biomass showed a higher uptake capacity for Ni(II) ions from aqueous solutions. Kinetic data were described by the pseudo-second order kinetic model, whereas equilibrium sorption data were followed by Freundlich isotherm model. The negative values of ΔG^o and ΔH^o showed the spontaneous and exothermic sorption processes, and positive ΔS^o value indicated the increased randomness at the solid/solution interface during

Ni(II) biosorption. The calculated values of change in heat of sorption (ΔH^o) and the isosteric heat of sorption (ΔH_r) suggested the physical sorption mainly involved for Ni(II) biosorption. FT-IR results showed that amine and carboxylic groups are responsible for Ni(II) biosorption. This biomass can be used as an efficient and economic biomass for removal and recovery of the Ni(II) from polluted waters.

REFERENCES

APHA. (1975). Standard methods for the examination of water and wastewater. 14th ed., AWWA, WPCF, Washington, D.C.

Amer, R.A., Ossman, M.E., Hassan, H.S., Ghozlan, H. and Sabry, S.A. (2014). Adsorption of Ni(II) by *Exiguobacterium* sp. 27 and Polyaniline Nanoparticles. International Journal of Environmental Research, **8**, 601-612.

Amiri, M.J., Fadaei, E., Baghvand, A. and Ezadkhasty, Z. (2014). Removal of heavy metals Cr (VI), Cd (II) and Ni (II) from aqueous solution by bioabsorbtion of *Elaeagnus angustifolia*. International Journal of Environmental Research, **8**, 411-420.

Aryal, M. and Liakopoulou-Kyriakides, M. (2015). Bioremoval of heavy metals by bacterial biomass. Environmental Monitoring and Assessment, **187**, 4173.

Aryal, M. and Liakopoulou-Kyriakides, M. (2014). Characterization of *Mycobacterium* sp. strain Spyr1 biomass and its biosorption behavior towards Cr(III) and Cr(VI) in single, binary and multi ion aqueous systems. Journal of Chemical Technology and Biotechnology, **89**, 559-568.

Aryal, M. and Liakopoulou-Kyriakides, M. (2013). Binding mechanism and biosorption characteristics of Fe(III) by *Pseudomonas* sp. Cells. Journal of Water Sustainability, **3**, 117-131.

Aryal, M., Ziagova, M. and iakopoulou-Kyriakides, M. (2012). Cu(II) biosorption and competitive studies in multi-ions aqueous systems by *Arthrobacter* sp. Sphe3 and *Bacillus sphaericus* cells: Equillibrium and thermodynamic studies. Water Air Soil & Pollution, **223**, 5119-5130.

Aryal, M., Ziagova, M. and Liakopoulou-Kyriakides, M. (2011). Comparison of Cr(VI) and As(V) removal in single and binary mixtures with Fe(III)-treated *Staphylococus xylosus* biomass: Thermodynamic studies, Chemical Engineering Journal, **169**, 100-106.

Aryal, M. and Liakopoulou-Kyriakides, M. (2011). Equilibrium, kinetics and thermodynamic studies on phosphate biosorption from aqueous solutions by Fe(III)-treated *Staphylococus xylosus* biomass: Common ion effect. Colloids & Surfces. A: Physicochemical Engineering Aspects, **387**, 43-49.

Aryal, M., Ziagova, M. and Liakopoulou-Kyriakides, M. (2010). Study on arsenic biosorption using Fe(III)-treated biomass of *Staphylococcus xylosus.* Chemical Engineering Journal, **162**, 178-185.

Bhattacharyya, K.G., Sarma, J. and Sarma, A. (2009). *Azadirachta indica* leaf powder as a biosorbent for Ni(II) in aqueous medium. Journal of Hazardous Materials, **165**, 271-278.

Cayllahua, J.E.B., Carvalho, de J.R. and Torem, M.L. (2009). Evaluation of equilibrium, kinetic and thermodynamic parameters for biosorption of nickel(II) ions onto bacteria strain, *Rhodococcus opacus*. Mineral Engineering, **22**, 1318-1325.

Divyasree, P., Braun, J. J. and Subramanian, S. (2014). Comparative Studies on the Bioremediation of Hexavalent and Trivalent Chromium using *Citrobacter freundii*: Part I-Effect of parameters controlling Biosorption. International Journal of Environmental Research, **8**,1127-1134.

Freundlich, H. (1906). Ueber die adsorption in Loesungen. Zeitschrift für Physikalische Chemie, **57**, 385-470.

Gialamouidis, D., Mitrakas, M. and Liakopoulou-Kyriakides, M. (2009). Biosorption of nickel ions from aqueous solutions by *Pseudomonas* sp. and *Staphylococcus xylosus* cells. Desalination, **248**, 907-914.

Ho, Y.S. and McKay, G. (1999). Pseudo-second order model for sorption processes. Process Biochemistry, **34**, 451–465.

Ileri, O., Cay, S., Uyanik, A. and Erduran, N. (2014). Removal of common heavy metals from aqueous solutions by waste *Salvadora persica* L. branches (Miswak). International Journal of Environmental Research, **8**, 987-996.

Kasprzak, K.S., Sunderman, Jr. F. and Salnikow, W.K. (2003). Nickel carcinogenesis. Mutation Research, **533**, 67-97.

Lagergren, S. (1898). Zur theorie der sogenannten adsorption gelöster stoffe, Kungliga Svenska Vetenskapsakad. Handlingar, **24**, 1-39.

Langmuir, I. (1918). The adsorption of gases on plane surfaces of glass, mica, and platinum. Journal of American Chemical Society, **40**, 1361-1367.

Sag, Y. and Kutsal, T. (2000). Determination of the biosorption heats of heavy metal ions on *Zoogloea ramigera* and *Rhizopus arrhizus.* Biochemical Engineering Journal, **6**, 145-151.

Selatnia, A., Madani, A., Bakhti, M.Z., Kertous, L., Mansouri, Y. and Yous, R. (2004). Biosorption of Ni^{2+} from aqueous solution by a NaOH-treated bacterial dead *Streptomyces rimosus* biomass. Mineral Engineering, **1**7, 903-911.

Shroff, K.A. and Vaidya, V.K. (20110. Effect of pre-treatments on biosorption of Ni (II) by dead biomass of *Mucor hiemalis.* Engineering in Life Sciences, **11**, 588-597.

Subbaiah, M.V., Vijaya, Y., Kumar, S.N., Reddy, S.A. and Krishnaiah, A. (2009). Biosorption of nickel from aqueous solutions by *Acacia leucocephala* bark: Kinetics and equilibrium studies. Colloids and Surfaces B:, **74**, 260-265.

Torab-Mostaedi, M., Asadollahzadeh, M., Hemmati, A. and Khosravi, A. (2013). Equilibrium, kinetic, and thermodynamic studies for biosorption of cadmium and nickel on grapefruit peel. Journal of Taiwan Institute of Chemical Engineering, **44**, 295-302.

Webi, T.W. and Chakravort, R. K. (2004). Pore and solid diffusion models for fixed bed adsorbers. AIChE Journal, **20**, 228-238.

Wierzba, S. and Latala, A. (2010). Biosorption lead(II) and nickel(II) from an aqueous solution by bacterial biomass. Polish Journal of Chemical Technology, **12**, 72-78.

World Health Organization (WHO) (2006). Guidelines for drinking-water quality, incorporating first addendum to third edition, Volume 1: Recommendations. World Health Organization, Geneva.