# Ni(II) removal from aqueous solutions using cone biomass of *Thuja orientalis*

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## Abstract

The biomass of terrestrial-plant materials has high removal capacities for a number of heavy metal ions. The Ni(II) biosorption capacity of the cone biomass of *Thuja orientalis* was studied in the batch mode. The biosorption equilibrium level was determined as a function of contact time, pH, temperature, agitation speed at several initial metal ion and adsorbent concentrations. The removal of Ni(II) from aqueous solutions increased with adsorbent concentration, temperature and agitation speed of the solution were increased. The biosorption process was very fast; 90% of biosorption occurred within 3 min and equilibrium was reached at around 7 min. It is found that the biosorption of Ni(II) on the cone biomass was correlated well ($R^2 > 0.99$) with the Langmuir equation as compared to Freundlich, BET Temkin and D–R isotherm equation under the concentration range studied. According to Langmuir isoterm, the monolayer saturation capacity ($Q_o$) is 12.42 mg g$^{-1}$. The pseudo-first-order, pseudo-second-order and intraparticle diffusion kinetic models were applied to test the experimental data for initial Ni(II) and cone biomass concentrations. The pseudo-second-order kinetic model provided the best correlation of the used experimental data compared to the pseudo-first-order and intraparticle diffusion kinetic models. The activation energy of biosorption ($E_a$) was determined as 36.85 kJ mol$^{-1}$ using the Arrhenius equation. This study indicated that the cone biomass of *T. orientalis* can be used as an effective and environmentally friendly adsorbent for the treatment of Ni(II) containing aqueous solutions.
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*Keywords:* Nickel; Biosorption; Cone biomass of *Thuja orientalis*; Kinetics; Isotherm; Activation energy

## 1. Introduction

Metals are among the main environmental concerns because of their unique characteristics: unlike organic pollutants, they are non-biodegradable and hence are accumulated by living organisms. Heavy metal ions such as $Cu^{2+}$, $Zn^{2+}$, $Mn^{2+}$, $Fe^{2+}$, $Ni^{2+}$ and $Co^{2+}$ are essential for plant and animals but when present in excess, these, and non-essential metals such as $Cd^{2+}$, $Hg^{2+}$, $Ag^{2+}$ and $Pb^{2+}$, can become extremely toxic [1]. The heavy and toxic metal contaminants in aqueous waste streams can cause serious water pollution problems being faced the world over. Nickel is one of the toxic heavy metals which are common pollutants of the environment. In humans, nickel can cause serious problems, such as dermatitis, allergic sensitization, lung and nervous system damages. It is also a known carcinogen [1]. The maximum permissible concentration of nickel in effluents in the U.S. for plants discharging 38,000 L or more per calendar day of electroplating process wastewater the following limitations shall apply: maximum for any 1 day is 4.1 mg L$^{-1}$ and average of daily values for 4 consecutive monitoring days shall not exceed 2.6 mg L$^{-1}$ [2]. In drinking water, nickel may cause health problems if found in amounts greater than the health standard set (MCLG: 0.1 mg L$^{-1}$) by the United States Environmental Protection Agency (EPA). The MCLG for nickel has been set at 0.1 parts per million (ppm) because EPA believes this level of protection would not cause any of the potential health problems [3]. According to World Health Organization (WHO) guidelines for drinking water, the permissible level $Ni^{2+}$ is 5 ppm. Therefore, it is necessary to decrease the concentration of heavy metals to their permissible limits before their discharge to the environment [4].

Nickel is one of the heavy metals present in raw wastewater streams from industries such as electroplating, nonferrous metals mineral processing, dye industries, porcelain enameling, and steam-electric power plants [5]. A number of technologies

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have been used to remove Ni(II) from wastewater streams, such as adsorption onto activated carbon [6–8], filtration of precipitate [9] and by crystallization in the form of nickel carbonate [10]. However, these technologies are most suitable in situations where the concentrations of the heavy metal ions are high. They are either ineffective or expensive when heavy metals are present in the wastewater at low concentrations or when very low concentrations of heavy metals in treated water are required [5]. Alternative technologies of treating diluted wastewater streams have been studied in recent years [9–11]. Biosorption of heavy metals is an effective separation process for the removal and recovery of heavy metal ions from aqueous solutions. It utilizes the ability of biological materials to accumulate heavy metals from waste streams by either metabolically mediated or purely physicochemical pathways of uptake [5,12,13]. Biosorption of metals by biomass has been much explored in recent years. This novel approach is competitive, effective and cheap [14,15]. The biomass of terrestrial-plant materials has been reported to have high removal capacities for a number of heavy metal ions. Different form of inexpensive, non-living plant material such as peat and pith [15], plant wood, root, leaves and bark [16–18], sawdust [18], papaya wood [19], *Capsicum annuum* seeds [20], cork biomass [21], dehydrated wheat bran [22], tea-industry waste [23,24], grape stalks waste [25] have been widely used and the cone biomass newly investigated [14], as potential adsorbents for heavy metals.

*Thuja orientalis* is an exotic tree planted in Turkey. It is grown in the garden and parks for esthetical (landscape) purposes. The cones of *T. orientalis* caused a visual and litter pollutant impact after patching off on the ground [26]. For this reason, as a novel approach, the Ni(II) biosorption from aqueous solutions through cone biomass of *T. orientalis* was evaluated as environmentally friendly treatment for the biosorption of Ni(II) ions from wastewaters.

Cones of other conifers such as the cone biomass of *T. orientalis* are readily available adsorbents in nature. Each cone is composed of an axis upon which are borne, in a spiral fashion, a large number of woody scales. Two megasporangia, in ovules, develop on the upper surface of each scale. Upon maturity they become seeds; the ovulate cone is, therefore, a seed-bearing cone. The scales of the mature cone are composed of epidermal and sclerenchyma cells which contain cellulose, hemicellulose, lignin, resin and tannins in their cell walls [26,27].

In this study, the cone biomass of *T. orientalis* as an adsorbent for Ni(II) was used to determine biosorption efficiency as a function of pH, temperature, agitation speed, contact time, adsorbent and adsorbate concentrations. The pseudo-first-order, pseudo-second-order and intraparticle diffusion kinetic models were applied to data as well as the Langmuir, Freundlich, BET, Temkin and D–R isotherm models.

## 2. Material and methods

### 2.1. Adsorbent preparation

In this study, *T. orientalis* L. (Chinese arbor vitae) cones, a low-cost adsorbent, were used for its biosorption capacity for removal of Ni(II) from aqueous solutions. Cones were collected in June of 2002 on the garden of Engineering Faculty at Atatürk University. Fresh cones of *T. orientalis* were dried at 90 °C for 48 h and cut into small pieces, ground in a warring blender to powder and sieved to constant size (between 35–60 meshes or 250–500 μm). Certain size and portions of the samples were taken for biosorption. Adsorption experiments were carried out 250–500 μm at adsorbent particle size.

### 2.2. Batch biosorption studies

Metal ion solutions were prepared by dissolving of NiCl$_2$·6H$_2$O analytical grade in deionized water. The pH of the solution was adjusted with diluted sulfuric acid and diluted ammonia solutions. Experiments were conducted in 250 mL Erlenmeyer flasks containing known Ni(II) synthetic solutions. Flasks were agitated on a shaker at 300 rpm constant shaking rate for 30 min to ensure equilibrium was reached and filtered through (Schleicher & Schüll589). Samples (5 mL) were taken after mixing the adsorbent and Ni(II) solution bearing solution and at pre-determined time intervals (1–30 min) for the determination of residual Ni(II) concentration. The initial pH adjustments were carried out either by sulfuric acid and sodium hydroxide. The amount of filtrate Ni(II) concentrations was analyzed complexometrically [28].

The amount of metal adsorbed was calculated using the Eq. (1):

$$q_e = \frac{(C_0 - C_e)V}{M} \tag{1}$$

where $C_0$ and $C_e$ are the initial and equilibrium concentrations of Ni(II) (mg L$^{-1}$), $M$ the mass of cone biomass (g) and $V$ is the volume of solution (L).

The zeta potential of cone particles in deionized water and nickel solutions were measured with a Zeta-Meter (ZETAMETER 3:0/542, USA).

## 3. Results and discussion

### 3.1. Fourier transform infrared spectroscopy (FTIR) analysis

The infrared spectra of the adsorbent sample was measured as potassium bromide pellets using a Perkin-Elmer 1600 series FTIR spectrometer. The FTIR spectra before and after adsorption of the cone biomass of *T. orientalis* are shown in Fig. 1a and b, and the FTIR spectroscopic characteristics are shown in Table 1.

As shown in the figure, the spectra display a number of absorption peaks, indicating the nature of the cone biomass of *T. orientalis*. The bands observed at 3441 and 2925 cm$^{-1}$ representing bonded –OH group and aliphatic C–H group. The peak around 1627 cm$^{-1}$ correspond to the C=O stretch. Symmetric bending of CH$_3$ is observed to 1451 cm$^{-1}$. The peaks observed at 1054 and 551 cm$^{-1}$ could be assigned to –C–C– group and –CN stretching, respectively. There were clear band shifts and intensity decrease of the band at 3441 and 1627 cm$^{-1}$.

Table 1
The FTIR spectral characteristics of cone biomass of *Thuja orientalis* before and after adsorption

| IR peak | Frequency (cm$^{-1}$) | | | Assignment |
|---|---|---|---|---|
| | Before adsorption | After adsorption | Differences | |
| 1 | 3441 | 3418 | −23 | Bonded —OH groups |
| 2 | 2925 | 2925 | 0 | Aliphatic C—H group |
| 3 | 1627 | 1618 | −9 | C=O stretching |
| 4 | 1452 | 1457 | +6 | Symmetric bending of CH$_3$ |
| 5 | 1054 | 1057 | +3 | —C—C— group |
| 6 | 551 | 596 | +45 | —CN stretching |

The hydroxyl groups of the cone biomass of *T. orientalis* (Fig. 1a and b) are effective binding sites for metal ions, forming stable complexes by coordination. As seen in Table 2, the spectral analysis before and after metal adsorption indicated that especially the bonded —OH groups and C—O stretching were especially involved in Ni(II) biosorption [24]. The interaction between the functional groups in the cone biomass and Ni(II) ions may be responsible for pH increase in the initial stages and as the saturation of the bed proceeds, the pH decreased. Decrease in biosorption at higher pH is due to the formation of soluble hydroxyl complexes.

It has been well documented that several biomolecules, proteins, polysaccharides and extracellular polymers contain different surface functional groups, such as carboxyl, carbonyl, hydroxyl, amino, phosphoryl and sulfide groups. The different functional groups have a high affinity towards heavy metals so that they can complex the metal ions [29].

Because of the complexity of most cell walls, several different mechanisms have been proposed to explain the uptake of metals by non-living biomass, including microprecipitation, ion exchange and complexation. Untreated biomass generally contains light metal ions such as K$^+$, Na$^+$, Ca$^{2+}$ and Mg$^{2+}$ [24,34]. The biosorption process of nickel, copper and cadmium can be mainly accounted for by ion exchange with calcium [29]. There was a significant release of Ca$^{2+}$, Mg$^{2+}$, K$^+$ and H$^+$ from the biosorbent due to the uptake of Cu(II) and Ni(II). This might indicate the displacement of these cations by the metals [25].

### 3.2. Effect of adsorbent dose on biosorption

The effects of cone dosage on the removal of Ni(II) from aqueous solutions were investigated using five different adsorbent concentrations since biosorption is highly dependent on the initial adsorbent concentration. The extent of biosorption
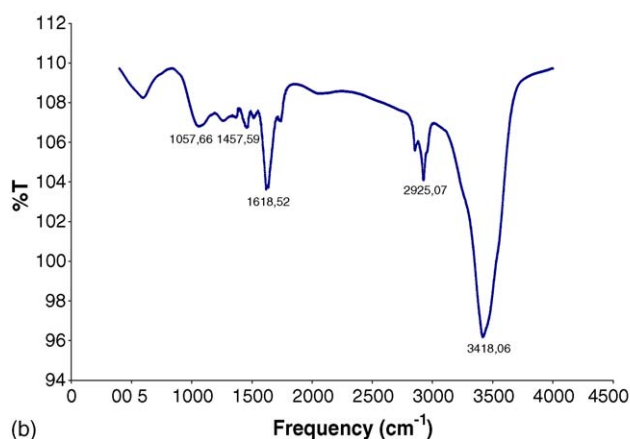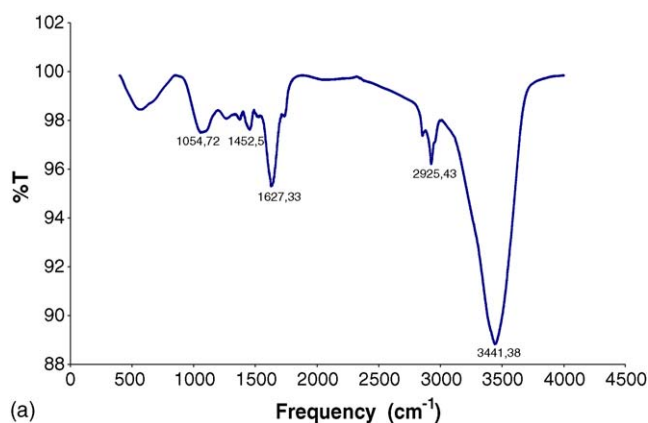


Fig. 1. (a) The FTIR spectra of cone biomass before adsorption. (b) The FTIR spectra of cone biomass after Ni(II) adsorption.

Table 2
Isotherm constants for Ni(II) sorption on cone biomass of *Thuja orientalis*

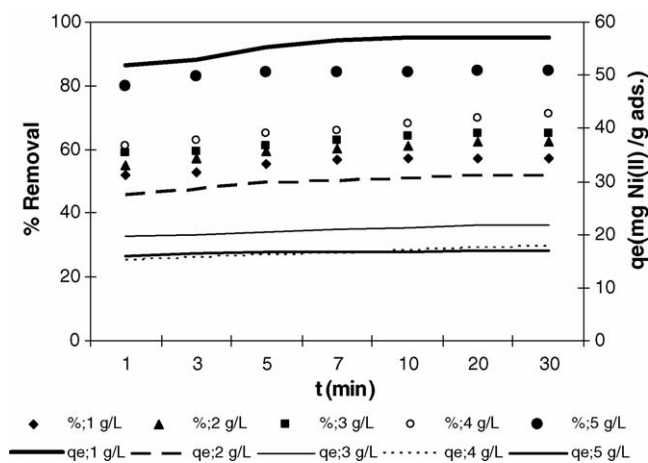| Type | Ni(II) |
|---|---|
| Langmuir isotherm | |
| $Q_o$ (mg g$^{-1}$) | 12.42 |
| $b$ (L g$^{-1}$) | 3.06 |
| $R^2$ | 0.9915 |
| Freundlich isotherm | |
| $K$ (L g$^{-1}$) | 29.48 |
| $n$ | 4.76 |
| $R^2$ | 0.9344 |
| BET isotherm | |
| $Q$ (mg g$^{-1}$) | 0.0027 |
| $B$ | 10.71 |
| $R^2$ | 0.6491 |
| Temkin isotherm | |
| $A$ (L g$^{-1}$) | 1936 |
| $B$ | 3.42 |
| $R^2$ | 0.9553 |
| D–R isotherm | |
| $K$ (mol$^2$/kJ$^2$) | 0.0031 |
| $q_m$ (mg g$^{-1}$) | 14.58 |
| $E$ (kJ mol$^{-1}$) | 12.70 |
| $R^2$ | 0.6962 |

Fig. 2. Effect of adsorbent concentration on Ni(II) removal ($C_0$: 100 mg L$^{-1}$, pH 4.0, agitation speed: 300 rpm, temperature: 25 °C).



Fig. 3. Effect of adsorbate concentration on Ni(II) biosorption efficiency (pH 4, agitation speed: 300 rpm, temperature: 25 °C, adsorbent concentration: 5 g L$^{-1}$).

is proportional of specific area. Specific area can be defined as that portion of the total area that is available for biosorption. Cone dosage was varied from 1 to 5 g L$^{-1}$. The effect of cone biomass on the sorption kinetics of Ni(II) ion was studied at pH of 4.0 and 100 mg L$^{-1}$ initial Ni(II) concentration. The results are presented in Fig. 2 which indicated that the equilibrium concentration of Ni(II) decreases with increasing cone doses for a given initial Ni(II) concentration. This result was anticipated because increasing adsorbent doses provides greater surface area. When the adsorbent concentration was increased from 1 to 5 g L$^{-1}$, the removal increased from 57.2 to 84.5%. This may be due to the fact that the higher doses of the adsorbent, the more sorbent surface and pore volume will be available for the biosorption [14–18,30].

### 3.3. Effect of metal ion concentration on biosorption

The initial metal ion concentration provides an important driving force to overcome all mass transfer resistances of Ni(II) between the aqueous and solid phases. The initial metal ion concentration was varied from 50 to 400 mg L$^{-1}$. The results are presented in Fig. 3, which shows that the equilibrium concentration of Ni(II) increased with increasing adsorbate concentration.

The higher the initial metal ion concentration, the larger the metal ion sorbed per unit weight of adsorbent at equilibrium. It showed a decrease in percent removal efficiency at increasing concentration. When the initial Ni(II) concentration was increased from 50 to 400 mg L$^{-1}$, the removal decreased from 93.25 to 68%. This was due to the saturation of the sorption sites on the adsorbent as the concentration of the metal increased. However, higher biosorption yields were observed at lower metal concentration [31].

### 3.4. Biosorption time

The effect of the contact time on biosorption of Ni(II) on the cone biomass was studied and the results are presented in Figs. 3, 6 and 7, where the biosorption occurred in two steps; an initial very fast step, maximum biosorption was occurred,
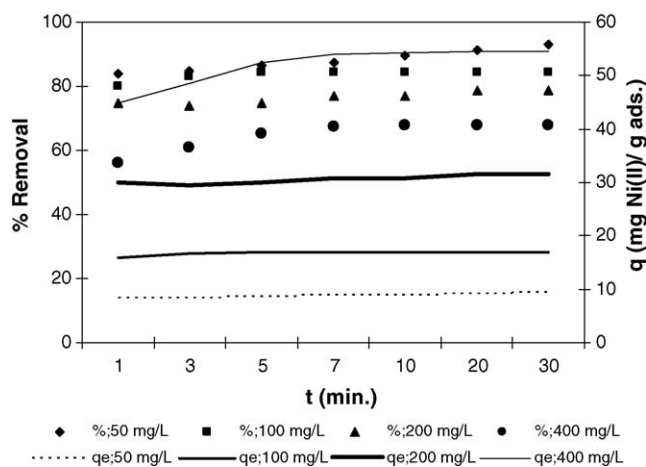
which lasted for 3 min, the slow second phase which continued until 20 min. The equilibrium was reached within 7 min. Further increase in contact time did not show an increasing in biosorption. Thus, 7 min shaking time was considered to be the optimum contact time for biosorption of Ni(II) on the cone biomass.

### 3.5. Effect of pH on biosorption

It is well known that the pH of the aqueous solution is an important controlling parameter in the adsorption process [6,8,32–34]. In order to establish the effect of pH on the biosorption of Ni(II) on the cone biomass, batch equilibrium experiments were carried out 100 mg L$^{-1}$ initial Ni(II) concentration and 5 g L$^{-1}$ adsorbent at various pH values. The pH of the samples was kept constant by addition of 0.2N sulfuric acid or 0.2N NaOH as needed and the studies were carried out at pH 2–6. The results are presented in Fig. 4 and show the greatest increase in the biosorption yield. The maximum biosorption capacity of *T. orientalis* was determined as 16.95 mg g$^{-1}$ at pH 4. Thus, all the biosorption experiments were conducted at this optimum pH value.
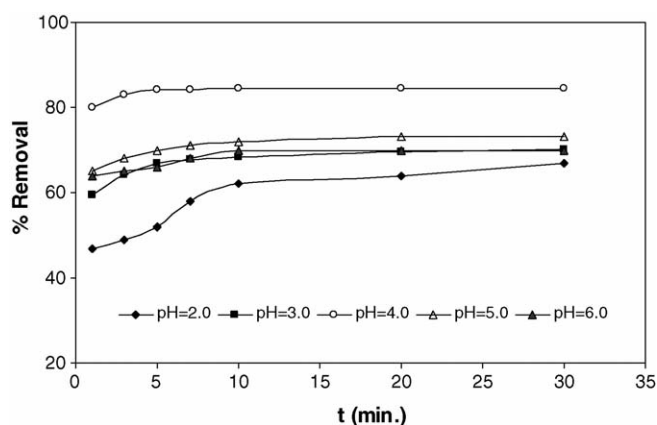


Fig. 4. Efffect of pH on Ni(II) biosorption efficiency ($C_0$: 100 mg L$^{-1}$, adsorbent concentration: 5 g L$^{-1}$, agitation speed: 300 rpm, temperature: 25 °C).
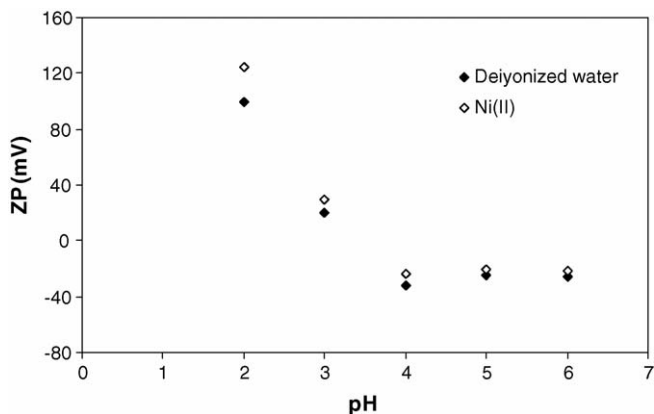
Fig. 5. The zeta potential of cone particles of *Thuja orientalis* in deionized water and nickel solutions ($C_0$: 100 mg L$^{-1}$, adsorbent concentration: 5 g L$^{-1}$, agitating rate: 300 rpm, agitating time: 30 min).



Fig. 6. Effect of agitating speed on Ni(II) biosorption efficiency ($C_0$: 100 mg L$^{-1}$, adsorbent concentration: 5 g L$^{-1}$, temperature: 25 °C, pH 4).

Solution pH influences both metal binding sites on the biosorbent surface and metal chemistry in aqueous solutions. At low pH values, adsorbent surfaces were closely associated with the hydronium ions ($H_3O^+$) and restricted the approach of metal cations as a result of repulsive force. In contrast, when the pH values increased, adsorbent surfaces were more negatively charged with subsequent attraction of metallic ions with positive charge and the biosoption process was favored [13,14] until a maximum was reached around pH 4. Decrease in biosorption at higher pH is due to the formation of soluble hydroxyl complexes. The heavy metal cations are completely released under circumstances of extreme acidic conditions.

In order to assure the optimal performance of the biomass, ionic form should be used for removing heavy metals, and what chemicals should be selected for desorbing the metals [35].

For values of pH higher than the optimum, the formation of hydroxilated complexes of the metal would also compete with the active sites, and as a consequence, the retention would decrease again. The percent removal of Ni(II) onto cone biomass of *T. orientalis* was found to be 67.72, 70.10, 84.74, 73.01 and 73.6% for solution of pH 2, 3, 4, 5 and 6, respectively.

The zeta potential of cone particles in deionized water and nickel solutions are presented in Fig. 5. Fig. 5 shows that the pH decreased, the surface of cone biomass exhibits an increasing positive charge. H$^+$ ions present at a higher concentration in the reaction mixture and compete with Ni(II) ions for the biosorption sites resulting in the reduced removal of Ni(II) ions. In contrast, the pH increased, the adsorbent surface became more negatively charged and therefore the biosorption of positively charged Ni(II) particles were more favorable. Zeta potential values of the cone particles at pH (2–6 and especially 4) in the deionized water were bigger than Ni(II) solution concentration. The zeta potential of the cone particles were decreased while Ni(II) were adsorbing by the cone particles. The decrease in the zeta potential values of cone particles was an indicator of biosorption of Ni(II) from aqueous solutions.
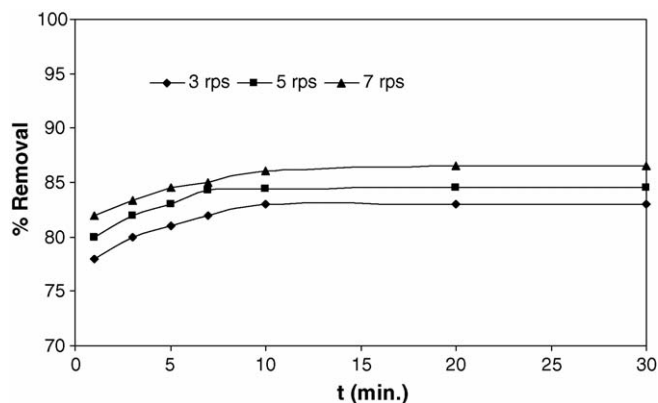
### 3.6. Effect of agitating speed on biosorption

Biosorption studies were carried out with a magnetic shaker at pH 4. In order to determination of the optimal agitating speed, the experiments were studied at 180, 300 and 420 rpm. According to Fig. 6, as agitating rate on adsorption increased from 180 to 420 rpm, Ni(II) adsorption of cone biomass increased from 81 to 86.5%. This suggests that the diffusion of nickel ions from the solution to the surface of adsorbent and into the pores has increased with the increase of agitation rate. At time of 30 min, the efficiency of phosphate removal at 300 rpm was approximately 84.5%.

### 3.7. Effect of temperature on biosorption

The effect of temperature on the removal of Ni(II) was investigated as a function of contact time. The results are shown in Fig. 7. From this figure, it has been determined that the contact time 7 min is sufficient to remove a considerable amount of Ni(II) at 25, 45 and 60 °C temperatures from aqueous solutions, respectively. The biosorption of metal ions has been found to increase with an increase in temperature from 25 to 60 °C.
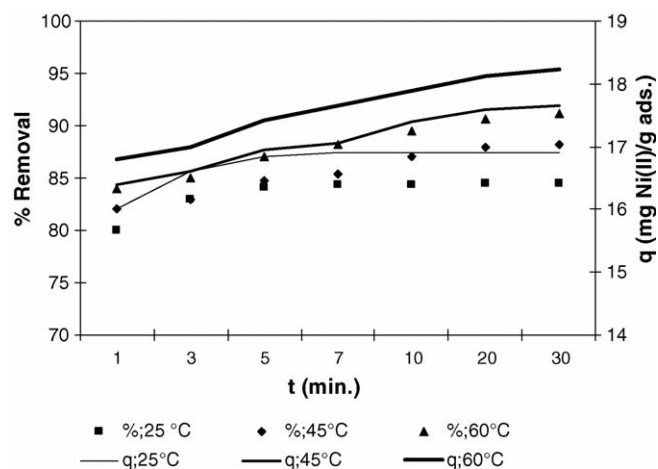


Fig. 7. Effect of temperature on Ni(II) biosorption efficiency and biosorption uptake ($C_0$: 100 mg L$^{-1}$, adsorbent concentration: 5 g L$^{-1}$, agitation speed: 300 rpm, pH 4).

Fig. 6, also shows that the removal of Ni(II) depends on temperature. The increase in biosorption capacity of cone biomass with temperature indicates an endothermic process. The increase in biosorption with temperature may be attributed to either increase in the number of active surface sites available for biosorption on the adsorbent or the desolvation of the adsorbing species and the decrease in the thickness of the boundary layer surrounding the adsorbent with temperature, so that the mass transfer resistance of adsorbate in the boundary layer decreases. Since diffusion is an endothermic process, greater biosorption will be observed at higher temperature. Thus, the diffusion rate of ions in the external mass transport process increases with temperatures [36].

As seen in Fig. 7, the biosorption of Ni(II) on cone biomass increased from 16.9 mg g$^{-1}$ (84.5% removal) to 18.24 mg g$^{-1}$ (91.2% removal) when temperature was increased from 25 to 60 °C at an initial concentration of 100 mg L$^{-1}$.

### 3.8. Isotherm data analysis

The two most widely accepted surface adsorption models for single-solute systems used in the literature are the Langmuir and Freundlich models [14,32,37,38]. The correlation with the amount of adsorption and the liquid-phase concentration was tested with the Langmuir, Freundlich, BET, Temkin and Dubinin–Radushkevich (D–R) isotherm equations.

### 3.8.1. Langmuir isotherm
The most widely used isotherm equation for modeling the equilibrium is the Langmuir equation [38], which is, valid for monolayer sorption on to a surface a finite number of identical sites and is given by Eq. (2):

$$q_e = \frac{Q_o b C_e}{1 + b C_e} \tag{2}$$

Eq. (2) is usually linearized to obtain the following form:

$$\frac{C_e}{q_e} = \frac{C_e}{Q_o} + \frac{1}{b Q_o} \tag{3}$$

where $C_e$ is the equilibrium concentration (mg L$^{-1}$), $q_e$ the maximum amount of the nickel per unit weight of the cone biomass to form a complete monolayer on the surface bound at high $C_e$ and $b$ is a constant related to the affinity of the binding sites. $Q_o$ represents a practical limiting biosorption capacity when the surface is fully covered with nickel and assists in the comparison of biosorption performance, particularly in cases where the sorbent did not reach its full saturation in experiments. $Q_o$ and $b$ can be determined from the linear plot of $C_e/q_e$ versus $C_e$ [38]. The values of $Q_o$ and $b$ constants and the correlation coefficient for the Langmuir isotherm are presented in Table 2.

### 3.8.2. Freundlich isotherm
The Freundlich model has been widely adopted to characterize the adsorption experiments [6,30,32,37,38]. The Freundlich isotherm is also more widely used adsorption experiments but provides no information on the monolayer adsorption capacity, in contrast to the Langmuir model [38]. This model assumed

that the uptake of metal ions occur on a heterogeneous adsorbent surface [6]. The Freundlich equation is given by (Eq. (4))

$$q_e = \frac{x}{m} = K_F C_e^{1/n} \tag{4}$$

where the parameters $K_F$ and $n$ can be obtained using the linear form of Eq. (4);

$$\log \frac{X}{m} = \log K_F + \frac{1}{n} \log C_e \tag{5}$$

where in our specific case, $X$ is amount of metal ion adsorbed, $m$ the weight of biomass used, $K_F$ and $n$ the Freundlich constants characteristic on the system and $C_e$ is the amount of the residual Ni(II) concentration in the solution. The values of $K_F$ and $n$ constants, and the correlation coefficient for the Freundlich isotherm are presented in Table 2.

### 3.8.3. BET isotherm
The linearized BET isotherm is shown in Eq. (6) [14]:

$$\frac{C_e}{(C_s - C_e)(X/M)} = \left(\frac{1}{BQ}\right) + \left(\frac{B-1}{BQ}\right)\left(\frac{C_e}{C_s}\right) \tag{6}$$

where $C_e$ is the concentration of solute remaining in solution at equilibrium (mg L$^{-1}$), $C_s$ the saturation concentration of solute (mg L$^{-1}$), $X/M$ the amount of solute adsorbed per unit weight of adsorbent (mg g$^{-1}$), $Q$ the amount of solute adsorbed per unit weight of adsorbent in forming a compete monolayer on the surface (mg L$^{-1}$) and $B$ is the constant expressive of energy of interaction with the surface. The $B$ and $Q$ values, and the correlation coefficient for the BET isotherm are presented in Table 2.

### 3.8.4. Temkin isotherm
The derivation of the Temkin isotherm assumes that the fall in the heat of sorption is linear rather than logarithmic, as implied in the Freundlich equation. The Temkin isotherm has generally been applied in the following form [39].

Temkin isotherm model is shown in Eq. (7):

$$q_e = \frac{RT}{b} \ln(A C_e) \tag{7}$$

$$q_e = B \ln A + B \ln C_e \tag{8}$$

where $B = (RT)/b$, $q_e$ (mg g$^{-1}$) and $C_e$ (mg L$^{-1}$) are the amounts of adsorbed Ni(II) per unit weight of adsorbent and unadsorbed Ni(II) concentration in solution at equilibrium, respectively. Also, $T$ the absolute temperature in K and $R$ is the universal gas constant, 8.314 J mol$^{-1}$ K$^{-1}$. The constant $b$ is related to the heat of biosorption [40,41].

### 3.8.5. Dubinin and Radushkevich isotherm
The D–R isotherm is more general than the Langmuir isotherm, because it does not assume a homogeneous surface or constant sorption potential [42]. The D–R Eq. (9) is:

$$q_e = q_m \exp(-K \varepsilon^2) \tag{9}$$

The linear form is shown in Eq. (10);

$$\ln q_e = \ln q_m - K\varepsilon^2 \tag{10}$$

where $q_e$ is the amount of the metal ion adsorbed at the equilibrium, $K$ a constant related to the adsorption energy, $q_m$ the theoretical saturation capacity, $\varepsilon$ is the Polanyi potential, equal to $RT\ln(1 + 1/C_e)$. The slope of the plot of $\ln q_e$ versus $\varepsilon^2$ gives $K\,(\text{mol}^2\,(\text{kJ}^2)^{-1})$ and the intercept yields the sorption capacity, $q_m\,(\text{mol g}^{-1})$. The mean free energy of adsorption ($E$), defined as the free energy change when one mole of ion is transferred from infinity in solution to the surface of the solid, was calculated from the $K$ value using the following relation [43]:

$$E = (2K)^{-0.5} \tag{11}$$

The calculated value of $E$ is given in Table 2.

The calculated results of the Langmuir, Freundlich, BET, Temkin and Dubinin–Radushkevich (D–R) isotherm constants are given in Table 2. It is found that the biosorption of Ni(II) on the cone biomass were correlated well ($R > 0.99$) with the Langmuir equation as compared to Freundlich, BET, Temkin, and Dubinin and Radushkevich (D–R) equation under the concentration range studied. According to Langmuir isotherm, the monolayer saturation capacity is 12.42 mg g$^{-1}$.

The essential features of a Langmuir isotherm can be expressedin terms of a dimensionless constant separation factor or equilibrium parameter, $R_L$ that is used to predict if an adsorption system is "favorable" or "unfavorable". The separation factor, $R_L$ is defined by Eq. (12):

$$R_L = \frac{1}{1 + bC_0} \tag{12}$$

where $C_0$ is the initial Ni(II) concentration (mg L$^{-1}$) and $b$ is the Langmuir adsorption equilibrium constant (L g$^{-1}$). $R_L$ values are 0.0065, 0.0032, 0.0016 and 0.00082 while initial Ni(II) concentrations are 50, 100, 200 and 400 mg L$^{-1}$, respectively. All $R_L$ values obtained using Eq. (12) for Ni(II) biosorption are greater than zero and less than unity showing favorable biosorption of Ni(II) onto cone biomass.

Also, from Table 2, the magnitude of $K$ showed a high Ni(II) adsorptive capacitiy of cone biomass from aqueous solution at 25 °C. Table 2 also indicated that $n$ is greater than 1.0, indicating that Ni(II) is favorably adsorbed by cone biomass at 25 °C. The magnitude of $E$ is useful for estimating the type of sorption reaction. The $E$ values obtained are 12.70 kJ mol$^{-1}$, which are in the energy range of an ion-exchange reaction, i.e., 8–16 kJ mol$^{-1}$.

Table 3 shows a comparison between the results of this work and others found in the literature. The values of Ni(II) specific uptake found in this work were significantly higher, with two exception [34,44], than reported elsewhere. The comparison of sorption capacities of cone biomass used in this study with those obtained in the literature shows that the cone biomass is the most effective for the removal of Ni(II) from aqueous solution.

Table 3
Maximum capacity, $Q_o$ (mg g$^{-1}$) for biosorption of Ni(II) by various adsorbents

| $Q_o$ (mg g$^{-1}$) | Adsorbent | Reference |
|---|---|---|
| 18.42 | Waste of tea factory | [34] |
| 31.08 | PAC | [44] |
| 0.03 | Fly ash | [44] |
| 0.001 | Bagasse | [44] |
| 11.40 | Baker's yeast | [45] |
| 7.20 | Sheep manure waste | [46] |
| 9.18 | Sphagnum moss peat | [47] |
| 8.5 | Succinated alfalfa biomass | [48] |
| 10.5 | Calcium-alginate | [49] |
| 12.42 | Cone biomass of *Thuja orientalis* | This study |

### 3.9. Kinetic studies

There have been several reports [15,45,50,51] on the use of different kinetic models to describe the experimental data of heavy metals adsorption on biomass.

The pseudo-first-order rate Lagergren model is:

$$\frac{dq}{dt} = k_1(q_e - q_t) \tag{13}$$

where $q_t$ (mg g$^{-1}$) is the amount of adsorbed uranium on the adsorbent at time $t$ and $k_1$ (min$^{-1}$) is the rate constant of first-order adsorption. The integrated form of Eq. (13) is

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{14}$$

A straight line of $\log(q_e - q_t)$ versus $t$ suggests the applicability of this kinetic model. $q_e$ and $k_1$ can be determined from the intercept and slope of the plot, respectively [45].

The pseudo-second-order kinetic model (Ho equation) is expressed as:

$$\frac{dq}{dt} = k_2(q_e - q_t) \tag{15}$$

where $k_2$ (g mg$^{-1}$ min$^{-1}$) is the rate constant of second-order adsorption. Eq. (15) can be rearranged and linearized to obtain:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{16}$$

The plot $t/q_t$ versus $t$ should give a straight line if second-order kinetics are applicable and $q_e$ and $k_2$ can be determined from the slope and intercept of the plot, respectively.

$$h = k_2 q_e^2 \tag{17}$$

where $h$ is the initial sorption rate (mg g$^{-1}$ min$^{-1}$) [51].

External mass transfer resistance cannot be neglected even for a high agitation speed, but in a well-agitated batch system, the boundary layer surrounding the particle is much reduced, or the stirring rate is uneffective on the equilibrium as present adsorption system, reducing the external mass transfer. The intraparticle diffusion equation [41] can be written as follows:

$$q_t = k_p t^{1/2} + C \tag{18}$$

Table 4
Parameters for the effects of cone doses, initial Ni(II) concentrations and pH on sorption of Ni(II) onto cone biomass of *Thuja orientalis*

| Parameters | $q_{e,exp}$ (mg g$^{-1}$) | Second-order kinetic model | | | | First-order kinetic model | | | Intraparticle diffusion | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $R^2$ | $q_{e2,cal}$ (mg g$^{-1}$) | $k_2$ (mg g$^{-1}$ min$^{-1}$) | $h$ (mg g$^{-1}$ min$^{-1}$) | $R^2$ | $q_{e1,cal}$ (mg g$^{-1}$) | $k_1$ (L min$^{-1}$) | $R^2$ | $k_p$ (mg (g min$^{1/2}$)$^{-1}$) | $C$ (mg (g min$^{1/2}$)$^{-1}$) |
| Initial Ni(II) concentartion (mg L$^{-1}$) | | | | | | | | | | | |
| 50 | 18.36 | 0.999 | 18.48 | 0.194 | 66.22 | 0.952 | 15.00 | 0.132 | 0.945 | 0.377 | 16.46 |
| 100 | 16.90 | 1.000 | 16.92 | 0.230 | 65.84 | 0.937 | 10.23 | 0.428 | 0.501 | 0.349 | 16.27 |
| 200 | 15.72 | 0.999 | 15.84 | 0.251 | 62.97 | 0.926 | 8.47 | 0.178 | 0.856 | 0.309 | 14.25 |
| 400 | 13.60 | 0.999 | 13.73 | 0.312 | 58.9 | 0.965 | 4.24 | 0.445 | 0.625 | 0.471 | 11.55 |
| Cone dose (g L$^{-1}$) | | | | | | | | | | | |
| 1.0 | 57.20 | 1.000 | 57.47 | 0.116 | 383.12 | 0.931 | 39.52 | 0.366 | 0.683 | 1.151 | 52.11 |
| 2.0 | 31.20 | 1.000 | 31.44 | 0.122 | 120.69 | 0.978 | 15.13 | 0.212 | 0.825 | 0.811 | 27.43 |
| 3.0 | 21.67 | 0.999 | 21.88 | 0.177 | 84.73 | 0.945 | 10.65 | 0.208 | 0.850 | 0.497 | 19.31 |
| 4.0 | 17.75 | 0.999 | 17.95 | 0.125 | 40.27 | 0.956 | 5.02 | 0.122 | 0.950 | 0.567 | 14.89 |
| 5.0 | 16.90 | 1.000 | 16.92 | 0.139 | 39.79 | 0.937 | 4.21 | 0.084 | 0.501 | 0.149 | 14.27 |

where $C$ is the intercept and $k_p$ is the intraparticle diffusion rate constant (mg (g min$^{1/2}$)$^{-1}$). Consistent with Eq. (18), the values of $q_t$ correlated linearly with values of $t^{1/2}$ and the rate constant $k_p$ directly evaluated from the slope of the regression line.

For evaluating the biosorption kinetics of Ni(II) ions, the pseudo-first-order and pseudo-second-order kinetic and intraparticle diffusion models were used to fit the experimental data. Using Eq. (14), a $\log(q_e - q_t)$ versus $t$ was plotted at different Ni(II) concentrations and cone dose. The first-order model data do not fall on straight lines indicating that this model is less appropriate. The Lagergren first-order rate constant ($k_1$) and $q_{e,cal}$ determined from the model are presented in Table 4 along with the corresponding correlation coefficients. It is important to note that for a pseudo-first-order model, the correlation coefficient is always less than 0.978 at different initial Ni(II) and adsorbent concentrations, which is indicative of a bad correlation. Moreover, from Table 4, it can be seen that the experimental values of $q_{e,exp}$ are not in good agreement with the theoretical values calculated ($q_{e,cal}$) from Eq. (14). Therefore, the pseudo-first-order model is not suitable for modeling the biosorption of Ni(II) onto cone biomass of *T. orientalis* at different initial Ni(II) and adsorbent concentrations.

By plotting $t/q_t$ against $t$ for the studied different initial Ni(II) concentration and cone dose, a straight line is obtained in all cases and using Eq. (16) the second-order rate constant ($k_2$) and $q_e$ values were determined from the plots. The values of correlation coefficient were very high ($R^2 > 0.999$) and the theoretical $q_{e,cal}$ values were closer to the experimental $q_{e,exp}$ values at different initial Ni(II) and adsorbent concentrations (Table 4). In the view of these results, it can be said that the pseudo-second-order kinetic model provided a good correlation for the biosorption of Ni(II) onto cone biomass at different initial Ni(II) and adsorbent concentrations in contrast to the pseudo-first-order model and intraparticle diffusion model.

Moreover, values for the product $h$ (initial sorption rate) that represents the rate of initial sorption, is practically decreased from 66.22 to 58.9 mg g$^{-1}$ min$^{-1}$ with the increase in initial Ni(II) concentrations from 50 to 400 mg L$^{-1}$. Also, initial sorption rate decresed from 383.12 to 39.79 mg g$^{-1}$ min$^{-1}$ with the increase in cone dose concentrations from 1 to 5 g L$^{-1}$.

The values of intercept $C$ in Table 4 provide an information about the thickness of the boundary layer, i.e. the resistance to the external mass transfer. The larger the intercept is the higher the external resistance [52]. Table 4 shows that the $C$ values or the boundary layer decreased with the increased initial Ni(II) concentration and adsorbent concentrations. Intra particle diffusion model equation was applied to the experimental data for different initial Ni(II) concentrations, different cone biomass doses. The rate constant values for intraparticle diffusion were obtained from the slopes of the linear portions of the plots of $q_t$ versus $t^{1/2}$ for different initial Ni(II) and cone biomass concentrations and results were presented in Table 4. $k_p$ values decreased with increased adsorbent concentrations and increased with increased initial Ni(II) concentrations.

### 3.10. Activation energy of Ni(II) uptake on cone biomass

The activation energy $E_a$ was determined using the Arrhenius equation [53]:

$$\ln k_1 = \ln A - \frac{E_a}{RT} \quad (19)$$

where $k_1$ is the rate constant value for the metal adsorption, $E_a$ the activation energy in kJ mol$^{-1}$, $T$ the temperature in Kelvin and $R$ is the gas constant (=8.314 kJ mol$^{-1}$ K$^{-1}$). As seen in Fig. 8, a plot of $\ln k_1$ versus $1/T$ was found to be linear.

The rate constants $k_1$ values determined from Fig. 8 and Eq. (14) at 25, 45 and 60 °C. The correlation coefficients obtained are than greater 0.986 for 100 mg L$^{-1}$ Ni(II) at all temperatures studied. Fig. 9 shows the corresponding linear plot of $\ln k_1$ against $1/T$ with a high correlation coefficient of 0.989. The activation energy for the biosorption system of Ni(II) onto cone biomass of *T. orientalis* was 36.85 kJ mol$^{-1}$ derived from the slope of this plot. This value is of the same magnitude as the activation energy of activated chemisorption. These findings showed that Ni(II) biosorption process by cone biomass of *T. orientalis* is endothermic and involves chemical sorption [53]. As is known, chemical adsorption is a type of adsorption occurring with a single layer. Some authors have reported similar results, for instance Aksu [53], who when studying
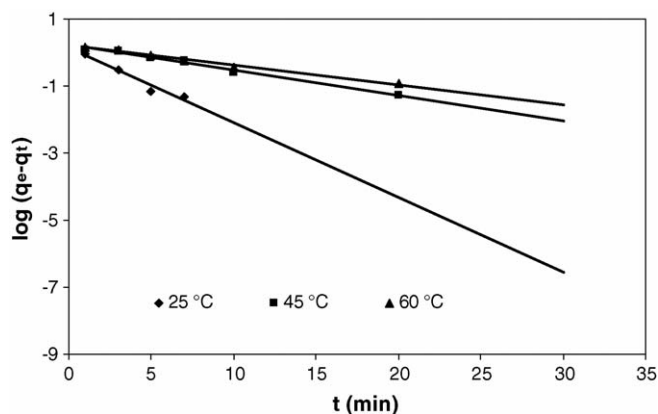
Fig. 8. Linearized pseudo-first-order kinetic model Ni(II) uptake by cone biomass of *Thuja orientalis* at different temperatures.
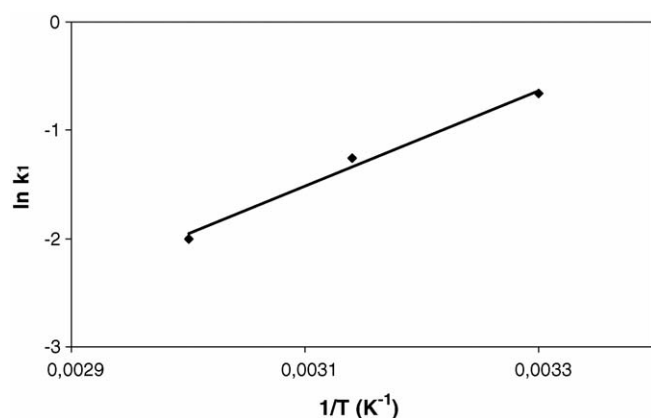


Fig. 9. $\ln k_1$ vs. $1/T$ plot.

Ni(II) sorption on *Chlorella vulgaris*, reported a value for $E_a$ of $25.92\,\mathrm{kJ\,mol^{-1}}$.

## 4. Conclusion

The present investigation aimed the heavy metal biosorption from synthetic wastewaters with another pollutant matter. The cones of *T. orientalis* have been caused visual and litter pollution impact on the parks and gardens after patching off cones. For this reason, the Ni(II) removal from aqueous solutions through cone biomass of *T. orientalis* may be evaluated as an environmentally friendly and extra economic treatment.

The present investigation shows that the cone biomass of *T. orientalis* is an effective and inexpensive adsorbent for the removal of Ni(II) ions from aqueous solutions. The cone biomass of *T. orientalis* exhibited high biosorption capacity. The biosorption process is a function of the adsorbent concentration, adsorbate concentration, pH, agitation rate and temperature of solution. The highest Ni(II) biosorption onto cone biomass was obtained at pH 4.0. In the result of this work, Ni(II) biosorption in excess of 91.8% was obtained for $50\,\mathrm{mg\,L^{-1}}$ Ni(II) and it was found that the cone biomass of *T. orientalis* is a favorable adsorbent for removal of Ni(II) from aqueous solutions. While sorption of Ni(II) onto the cone biomass of *T. orientalis* was best fitting to Langmuir isotherm compose to Freundlich,

BET, Temkin, and Dubinin and Radushkevich (D–R) biosorption isotherm models was best fit. Using the first-order kinetic constant, the activation energy of biosorption was determined as $36.85\,\mathrm{kJ\,mol^{-1}}$ showing that the biosorption process is endothermic. The pseudo-first-order, pseudo-second-order kinetic and intraparticle diffusion kinetic models were used to describe the kinetic data for initial Ni(II) and adsorbent concentrations and the rate constants were evaluated. The used experimental data were fitted by the second-order kinetic model, which indicates that chemicalsorption is the rate limiting step, inside of mass transfer.

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