BIOSORPTION OF Ni(II) IONS FROM AQUEOUS SOLUTIONS USING MELIA AZEDARACH BIOMASS

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ABSTRACT. Biosorption is a cost effective tool for removing heavy metals from aqueous solutions. In the present study, M. azedarach biomass has been used for the biosorption of Ni(II) ion from aqueous solution. The effect of pH, contact time, concentration and temperature were separately studied. The optimum pH was found to be 6.0. 92% biosorption of Ni(II) ion was founded, when 25 mg/L of initial Ni(II) ion concentrations was used at room temperatures in 60 min. It was also observed that percent biosorption of Ni(II) increases with increase in temperature. The equilibrium biosorption data were analyzed by the Langmuir and Freundlich isotherms both were best fitted to our data. The maximum biosorption capacity (qmax) of 9.345 mg/g for Ni(II) according to Langmuir model. The kinetics of Ni(II) ion revealed that present biosorption process proceeds according to pseudo second order kinetics. From Thermodynamic parameters including Gibbs free energy change (∆G), enthalpy change (∆H) and entropy change (ΔS), it was concluded that biosorption of Ni(II) ion using M. azedarach biomass is feasible, spontaneous and endothermic in nature.

KEY WORDS: Ni(II) ions, Melia azedarach, Biosorption, Kinetics, Thermodynamics

INTRODUCTION

The rapid industrialization and urbanization are discharging industrial wastewater, which are responsible for the degradation of aquatic environment [1]. Among them contamination by heavy metals has been a great concern, because of their nondestructive nature, toxicity, bio-accumulation and subsequent bio-magnifications [2].

Nickel (Ni(II)) is an essential micronutrient and also act as co-factor for the urease enzyme in plants, however its elevated concentrations cause adverse health effects [3]. Ni(II) is the 24th most abundant element (two times as compared to copper (Cu)) and contributes about 0.008% to the content of the earth’s crust, so it is a natural component of soil and water [4]. It is released into aquatic environment by many industries like electroplating, battery manufacturing, mineral processing, steam–electric power plants, paint formulation and steel manufacturing [5]. The maximum permissible limit prescribed by the U.S. Environmental Protection Agency (EPA) for Ni(II) discharged with industrial effluent is less than 1.0 mg/L [7]. General population are exposed to Ni(II) through drinking water and food [8]. Exposure to Ni(II) causes inhibition of enzymes, pain in chest, diarrhea, vomiting and dizziness, skin, kidney diseases, rapid respiration and severe weakness in the body [9 – 10]. Lung, nose and bone cancer are also caused when exposed to its high concentration [11, 12].

Many conventional approaches for removing heavy metals ions from aqueous solutions include electrochemical treatment, chemical oxidation or reduction, ion exchange, phytoremediation, chemical precipitation, filtration, reverse osmosis and membrane technologies.
But several disadvantages including high operating costs, production of large quantities of wastes and lack of complete removal of metal ions are associated with these methods. Moreover, these approaches are also ineffective when concentration of metals in solutions is in the range of 1-100 mg/L [14]. Therefore, there is an urgent need for highly efficient, eco-friendly and cost effective separation processes, which could be provide biosorption phenomena [15]. Biosorption, which involves the use of biological materials as biosorbents, presents an attractive technique for the removal of toxic heavy metals from aqueous solutions. Many functional groups like carboxyl, imidazole, sulphydryl, amino, phosphate, sulfate, thioether, phenol, carbonyl, amide and hydroxyl moieties are present on the surface of biosorbent, which act as metal ions binding sites [16]. Different types of biosorbents such as microorganisms (bacteria, fungi, algae and yeast), plant by products (wheat straw and husk, rice straw and husk, chick pea husk, mango leaves) and waste materials (fallen leaves and peels) have been investigated for the biosorption of heavy metals from aqueous solutions [17]. However, according to our knowledge, the bark of *Melia azedarach* in biosorption is not exploited.

*Melia azedarach* locally called Darek but its common name is Chinaberry tree/White Cedar. It belongs to family *Meliaceae* which is a shrub or small evergreen, medium sized deciduous tree. The adult tree commonly attain a height of 45 feet while leaves are up to 50 cm long. It has purplish dotted bark with stout branches. *M. azedarach* grows in temperate and tropical countries like India, China, and Japan and also found in Pakistan [18].

**EXPERIMENTAL**

**Chemicals**

Analytical grade chemicals were used in all experiments. Nickel sulfate hexahydrate (NiSO₄·6H₂O) was used. Different concentrations (0.01, 0.1, 0.5 and 1 M) of hydrochloric acid (HCl) and sodium hydroxide (NaOH) were used for pH adjustment. All aqueous solutions were prepared in deionized (DI) water.

**Preparation of standard solutions and biosorbent**

Initially 1000 mg L⁻¹ stock solution of Ni(II) ion was prepared from its salt. The stock solution was diluted to prepare desired concentrations.

The bark biomass of *M. azedarach* was locally collected and rinsed with DI water to remove dust particles and water soluble impurities. The material was first sundried and then in oven at 70 °C. The dried material was obtained as fine brown powder through locally prepared grinder, sieved to 70 and 100 mesh sizes. This sample was labeled as *M. azedarach* biosorbent and stored for further use.

**Scanning electron microscopy/energy dispersive X-ray (SEM/EDX)**

The morphological analysis of *M. azedarach* biomass was performed using scanning electron microscopy by SEM model JSM-5910 JEOL. Elemental analysis was carried out using EDX model INCA – 200.

**Biosorption studies**

The biosorption studies of Ni(II) ion was conducted using batch experiments and the effects of experimental parameters: Initial pH (2–9), contact time (5–300 min), initial Ni(II) ion concentration (5–100 mg L⁻¹) and temperature (288-325 K) on the adsorptive removal of Ni(II) ion at 30 mL of each Ni(II) solutions with 0.1 g of biosorent in 100 mL Erlenmeyer flasks. These
flasks were shaken in a temperature controlled orbital shaker at a constant speed of 120 rpm. Suspensions were then filtered and the filtrates of each experiment were analyzed by Perkin Elmer Analyst 800 atomic absorption spectrometer.

The biosorption efficiency (% biosorption) and biosorption capacity was calculated by using the following equations:

\[
\text{% biosorption} = \left( \frac{C_i - C_f}{C_i} \right) \times 100 \\
Q = \frac{(C_i - C_f)V}{m}
\]

where \(Q\) is biosorption capacity (mg/g), \(C_i\) and \(C_f\) are initial and final concentrations (mg/L) of metal ion (Ni(II)), respectively, \(V\) is the volume (L) of the solution, and \(m\) is the mass (g) of biosorbent used.

RESULTS AND DISCUSSION

Scanning electron microscopy/energy dispersive X-ray (SEM/EDX)

Biosorption capacity is directly related to the nature of biosorbent surface. For this purpose, morphological study of \(M.\) azedarach biomass was performed using SEM at magnification of 1000Xs and 2000Xs (Figure 1A and B). The SEM surface morphology indicates that the presence of pores and rough surface of \(M.\) azedarach biosorbent is an evidence for the water detoxification with respect to metal ions. The surface of \(M.\) azedarach by EDX (Figure 1C) clearly revealed the presence of carbon (48.97%) and oxygen (44.98%) in addition to K, Ca, P, Mg and Si. The results of elemental analysis are presented in the Figure 1D.

Effect of pH

Biosorption of Ni(II) ion using biomass of \(M.\) azedarach as a function of pH (Figure 2A) was carried out in the range of 2.0–9.0. It was observed that (%) biosorption of Ni(II) ion was low when the pH of solution was low and increased linearly with the increase in the pH of solution. More than 60% biosorption was achieved at pH 6.0, after which, there occurs decline in the % biosorption with a further raise in pH. The variation in the pH affects not only metal precipitation and ionization degree but also activity of the functional groups [19, 20]. With increasing pH levels from 3 to 6, the adsorbent surface charge became negative which in turn increased nickel uptake. The adsorption in basic region is declined due to the unavailability of the Ni(II) ion. At lower pH, there was competition between hydrogen ions (H\(^+\)) and nickel ions for the binding sites present on biosorbent surface. Hence, the surface of biosorbent was surrounded by more H\(^+\) ions and decreasing the interaction between adsorbent and absorbate cations. Moving towards high pH of solution, the Ni(II) ion become more competitive for binding in comparison with hydrogen ions and thus resulting in the increase in % biosorption. In contrast, at higher pH values (above pH 6), Ni(II) ions precipitates (the dominate form of nickel are Ni(OH)\(_2\)) as insoluble hydroxides starts thus resulting reduction in biosorption [21].

Effect of contact time

The effect of contact time on the % biosorption of Ni(II) ion was investigated (Figure 2B) at room temperature at various time intervals (5–300 min), while keeping all other parameters (pH, metal ion concentration and biosorbent amount) constant. The result is shown in Figure 2B. The % biosorption of Ni(II) ion increased rapidly in the beginning (52%, at t = 60 min) and then remained independent of contact time up to the end (t > 60 min). The initial fast rate of biosorption can be explained in terms of availability of active sites, so binding portability is large and consequently
biosorption proceeds with high rate. On the other hand, the slow biosorption rate at the end \((t > 60 \text{ min})\) indicated that most of the binding sites on biosorbents surface are covered with metal ions. Therefore, a period of 60 min was considered sufficient for biosorption to attain equilibrium and was used in further experiments.

Figure 1. (A and B) SEM image of \textit{M. azedarach} biomass at 1000Xs and 2000Xs, (C) energy dispersion X-rays of \textit{M. azedarach} biomass and (D) table of elemental analysis of \textit{M. azedarach}.

\textit{Effect of initial metal ion concentration}

The impact of initial Ni(II) ion concentration on biosorption using \textit{M. azedarach} biomass was studied in the range of 5–100 mg/L (Figure 2C). The equilibrium time (60 min), temperature (298 K), pH (pH 6) and adsorbent amount (0.1 g) were maintained constant throughout this study. It has been observed that metal uptake (% biosorption) was linearly increased from 53.52% to 91.74% while increasing initial Ni(II) concentration from 5 to 25 mg/L. Further increase in initial Ni(II) concentration (above 25 mg/L), there occurs decline in the %biosorption of Ni(II) ion. It is implied that surface area of biosorbent available to Ni(II) ion was high at is low Ni(II)
concentration, and hence more chances for the binding at the available sites at a given biosorbent dose. While at higher concentration more Ni(II) ions were left unabsorbed in solution because of the saturation of the binding sites. Similar mechanism was also observed previously in biosorption of Ni (II) ions using Potato peel [22].

Effect of temperature

To study the effect of temperature in order to evaluate the thermodynamics parameters for Ni(II) ion biosorption, experiments were carried in the temperature in the range 288–325 K at pH 6 (Figure 2D). The % biosorption of Ni(II) was increased with a raise in temperature in temperature of the solution/system. Maximum biosorption of 68.67% was achieved at a temperature of 318 K. This might be due to swelling of internal structure of biosorbent with raise in temperature and thus enabling the metal ions to penetrate more deeply into the bulk of the sorbent. Similarly, raise in temperature might also be responsible for the increase in the number of surface binding sites due to rupture of bonds such as physical/van der Waals interaction among functional groups of biosorbent surface as well as in the bulk. Moreover, the results also provide a more important clue about the biosorption of Ni(II) ions using M. azedarach biomass is endothermic process and physical adsorption in nature [23–24].

Biosorption isotherm modeling

Several isotherm models have been reported in the literature for the description of equilibrium biosorption systems however two most common Langmuir and Freundlich isotherm models was applied for the current experimental biosorption data. The obtained data for this purpose was at constant experimental conditions (pH = 6, temperature = 298 K, amount of biosorbent = 0.1 g) and using 30 mL of Ni(II) solutions with varied the initial concentrations in the range 10-75 mg/L.
Langmuir model

Linear form of the Langmuir equation can be represented as;

\[
\frac{C_e}{X} = \frac{1}{K_bX_m} + \frac{C_e}{X_m}
\]

(3)

where \( C_e (\text{mg/L}) \) is the equilibrium concentration of adsorbate after biosorption, \( X (\text{mg/g}) \) is the amount adsorbed per unit mass of biosorbent, \( X_m (\text{mg/g}) \) is the maximum adsorbed amount, \( K_b (\text{L/g}) \) is the binding energy or Langmuir constant. The graph was plotted between \( C_e/X \) vs. \( C_e \) which gave a straight line (Figure 3a). The values of \( X_m \) and \( K_b \) was calculated from the slope and intercept, respectively.

Figure 3. (a) Langmuir isotherm plot for Ni(II) biosorption using \( M. azedarach \) biomass (L S). (b) Freundlich isotherm plot for Ni(II) biosorption using \( M. azedarach \) biomass (R S)

Freundlich model

Freundlich Isotherm is expressed as:

\[ X_e = K_f C_e^{\frac{1}{n}} \]

(4)

The logarithmic form of the equation is:

\[ \log X_e = \log K_f + \frac{1}{n} \log C_e \]

(5)

where \( X_e (\text{mg/g}) \) is the amount of Ni(II) adsorbed per unit mass of biosorbent, \( C_e (\text{mg/L}) \) is the equilibrium concentration of adsorbate (Ni(II) solutions) after biosorption, \( K_f (\text{mg/g}) \) and \( n \) are Freundlich constants which indicates biosorption capacity and intensity of biosorption, respectively, and which vary with temperature and nature of biosorbent. By plotting \( \log X_e \) versus \( \log C_e \) gave a straight line (Figure 3b), with slope = \( 1/n \) and intercept \( K_f \). When applied Langmuir equation, the data produced a straight line with a good correlation coefficient (\( R^2 = 0.999 \)), which clearly indicates the acceptability of Langmuir’s model to the current biosorbent Ni(II) system. The values of adsorption capacity \( (X_m) \) and Langmuir constant \( (K_b) \) obtained are 9.345 mg/g and 0.0746 mg\(^{-1}\), respectively. Similarly the values of \( R^2 \), \( K_f \) and \( n \) obtained when experimental data was fitted in Freundlich equation were 0.997, 0.748 mg/g and 1.1173 g/L, respectively. For biosorption of Ni(II) using \( M. azedarach \) biomass, the correlation coefficient \( (R^2) \) of both models was greater than 0.95 and closed to 1, which indicates that our experimental data of Ni(II) biosorption fit well to both models. The values of isotherm constants obtained are given in Table 1. The maximum biosorption capacity \( (X_m) \) of Ni(II) ions found in the present study was compared with those of the other biosorbent is presented in Table 2. It is clearly observed that the maximum
biosorption capacity of the sludge was fairly high as compared to some of the already reported biosorbents.

Table 1. Langmuir and Freundlich isotherm parameters for the biosorption of Ni(II) using *M. azedarach* biomass.

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Langmuir parameters</th>
<th>Freundlich parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(II)</td>
<td>X&lt;sub&gt;m&lt;/sub&gt; (mg/g)</td>
<td>K&lt;sub&gt;b&lt;/sub&gt; (L/mg)</td>
</tr>
<tr>
<td>9.345</td>
<td>0.0746</td>
<td>0.999</td>
</tr>
</tbody>
</table>

Table 2 Comparison of maximum biosorption capacities (X<sub>m</sub>) for Ni(II) ion removal by various biosorbents.

<table>
<thead>
<tr>
<th>Biosorbent</th>
<th>X&lt;sub&gt;m&lt;/sub&gt; (mg g&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Cocos nucifera</em></td>
<td>0.09</td>
<td>[26]</td>
</tr>
<tr>
<td><em>Streptomyces noursei</em></td>
<td>0.8</td>
<td>[27]</td>
</tr>
<tr>
<td>Sugarcane bagass</td>
<td>2.23</td>
<td>[28]</td>
</tr>
<tr>
<td>Rice husk</td>
<td>5.52</td>
<td>[29]</td>
</tr>
<tr>
<td>Carrot residue</td>
<td>6.51</td>
<td>[30]</td>
</tr>
<tr>
<td>Banana peel</td>
<td>6.60</td>
<td>[31]</td>
</tr>
<tr>
<td><em>Melia azedarach</em> biomass</td>
<td>9.345</td>
<td>Present study</td>
</tr>
</tbody>
</table>

Kinetic modeling

To trace out the mechanism of biosorption as a function of the physical and chemical characteristics of the biosorbent, a suitable kinetic model is needed to describe the kinetic data. Kinetic data of Ni(II) biosorption using *M. azedarach* biomass were applied to commonly used pseudo first and pseudo second order kinetic models.

Pseudo second order kinetic model

The pseudo second order kinetic model is given in the following form;

\[
\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{t}{q_e}
\]  

\[(6)\]

where \(k_2\) (g min<sup>-1</sup> mg<sup>-1</sup>) is the rate constant of the second order equation. \(q_e\) (mg/g) is the maximum adsorption capacity. \(q_t\) (mg/g) is the amount of adsorption at time t. Plot of \(t/q_t\) vs. \(t\) gave straight line (Figure 4a), with R<sup>2</sup> value > 0.99 indicating pseudo second order model is more suitable to the current kinetic data. The calculated values of \(q_e\) were much close to the experimental values of \(q_e\) given in table 03. The applicability of pseudo second order kinetic model provide a strong evidence for the chemical nature [25] of the biosorption process of Ni(II) ion onto *M. azedarach* biomass.

Table 3. Kinetics parameters for the biosorption of Ni(II) using *M. azedarach* biomass.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>X&lt;sub&gt;e&lt;/sub&gt; (mg/g) (experimental)</th>
<th>First order</th>
<th>Second order</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>X&lt;sub&gt;e&lt;/sub&gt; (mg/g) (calculated)</td>
<td>k&lt;sub&gt;t&lt;/sub&gt; (min&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>R&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
<tr>
<td>298</td>
<td>8.676</td>
<td>2.228</td>
<td>0.0322</td>
</tr>
</tbody>
</table>

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Figure 4. (a) Pseudo second order plot for Ni(II) biosorption using *M. azedarach* biomass (LS) and (b) Plot of $\ln k_d$ vs $T^{-1}$ ($10^{-3}$) for Ni(II) ion biosorption on *M. azedarach* biomass (RS).

**Thermodynamic studies**

The changes in thermodynamic parameters like Gibbs free energy ($\Delta G$) and enthalpy ($\Delta H$), entropy ($\Delta S$) were calculated according to equations;

$$K_d = \frac{C_a}{C_e}$$ \hspace{1cm} (7)

where $C_a$ (mg/L) and $C_e$ (mg/L) are concentrations of Ni(II) ion on the biosorbent surface and in the solution at equilibrium, respectively and $K_d$ is equilibrium constant (dimensionless) calculated at different temperatures.

$$\Delta G = -RT\ln K_d$$ \hspace{1cm} (8)

$R$ is ideal gas constant (8.314 J/molK) and $T$ is absolute temperature (K).

$$ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$$ \hspace{1cm} (9)

The plot of $\ln K_d$ vs $T^{-1}$ ($10^{-3}$) (Figure 4b), the values of $\Delta H$ and $\Delta S$ were obtained from the slope and intercept. The values of thermodynamic parameters are listed in Table 4. It reflects that the process is feasible and spontaneous in nature as $\Delta G$ values are negative at all the temperature. Ni(II) ion biosorption using *M. azedarach* biomass is endothermic in nature as confirmed from the positive value of $\Delta H$. The positive value of $\Delta S$ (J K$^{-1}$ mol$^{-1}$) indicates the affinity of biosorbents for the metal ions. It was also noted that Ni(II) ion biosorption using *M. azedarach* biomass is physical adsorption since $\Delta G$ for Ni(II) ion biosorption is in the range of $-1.12$ to $-1.83$ kJ mol$^{-1}$. Generally for physical adsorption the $\Delta G$ range from $-20$ to $0$ kJ mol$^{-1}$ and for chemical adsorption the $\Delta G$ range from $(-80$ to $-400)$ kJ mol$^{-1}$ [32].

<table>
<thead>
<tr>
<th>Temp (K)</th>
<th>$\Delta G$ (kJ mol$^{-1}$)</th>
<th>$\Delta S$ (J mol$^{-1}$K$^{-1}$)</th>
<th>$\Delta H$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>$-1.12$</td>
<td>34.4</td>
<td>9.54</td>
</tr>
<tr>
<td>308</td>
<td>$-1.59$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>318</td>
<td>$-1.83$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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CONCLUSION

*M. azedarach* bark biomass was selected to study biosorption so as to utilize its waste biomass to eradicate metal pollution from aqueous solution. SEM analysis confirmed the homogenous and porous nature of *M. azedarach* with high surface area which made it an excellent biosorbent. The biosorption of Ni(II) was rapid and equilibrated within 60 min and increased linearly with increase in pH. Optimum pH was found to be 6. Equilibrium isotherm data was in good agreement to both Langmuir and Freundlich isotherm models. The maximum biosorption capacity of Ni(II) ion calculated from Langmuir model was found to be 9.345 mg/g. The kinetic studies revealed that biosorption process followed pseudo-second order kinetics. Thermodynamics study indicate that process biosorption of Ni(II) ion on waste biomass *M. azedarach* was spontaneous, physical and endothermic in nature.

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