Biosorption of Ni (II) ions from aqueous solution using leaves of Araucaria cookii

Factors influencing the Biosorption of Nickel

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ABSTRACT

The aim of the present study was to reduce the Ni (II) ions present in the waste water which is highly toxic to the environment. Biosorption experiments were carried out in a batch process which includes the factors like pH, contact time, size variation, adsorbent dose and metal ion concentration. The maximum percentage removal of Ni (II) ions in the aqueous solution is 96.95 % at pH 6 and contact time 40 min. Langmuir and Freundlich isotherm models were applied to describe the equilibrium data. Kinetic models like Pseudo first order and Pseudo – second order both fit well for the biosorption process. The results show that the leaves of Araucaria cookii can be efficiently used for the removal of Ni (II) ions as low cost biosorbent.

KEY WORDS  Biosorption, Araucaria cookii, Nickel, Langmuir, Freundlich.

I. INTRODUCTION

In the global technological progress the discharge of heavy metals from different industries into the natural environment suffers the detrimental effects of water pollution. The natural process of transportation of metal ions between soil and water consolidates metal contamination in high concentrations that affect the areas of natural ecosystems [1].
of Ni (II) into inland water is 0.1 and 3.0 mg L\(^{-1}\), respectively [6,7].

Nickel is released into the environment by a large number of industrial processes, such as electroplating, leather tanning, wood preservation, pulp processing and steel manufacturing [8]. The most common application of nickel is the use as an ingredient of steel and other metal products such as jewellery [9].

Higher concentrations of nickel cause cancer of lungs, nose and bone. Dermatitis (Ni itch) is the most frequent effect of exposure to Ni, such as coins and jewellery. Acute poisoning of Ni (II) causes headache, dizziness, nausea and vomiting, chest pain, tightness of the chest, dry cough and shortness of breath, rapid respiration, cyanosis and extreme weakness [10, 11 & 12]. Although nickel is not considered to be at low levels, like other pollutant metals, it accumulates in the food chain and once adsorbed into the body cannot be easily excreted [13].

A number of methods exist for the removal of heavy metal pollutants from liquid wastes when they are in high concentrations [14]. Many processes are used to remove heavy metals from industrial effluents, including chemical precipitation, coagulation, solvent extraction, membrane separation, ion exchange, and adsorption [15, 16].

The new technology is based on the utilization of low cost biological materials as adsorbent of heavy metals in a process called biosorption [17, 18]. Biosorption is a term that describes the removal of heavy metals by the passive binding to non-living biomass from an aqueous solution [19]. Living or dead biomass can be used to remove metals, but maintaining a living biomass during metal biosorption is difficult because it requires a continuous supply of nutrients and toxicity of metal for microorganisms might take place. On the other hand, the use of dead biomass can avoid these problems and the used cells can be easily regenerated [20, 21].

In recent years, the search for low-cost adsorbents that have metal binding capacities has intensified. Agricultural by-products have been widely studied for metal removal from water. These include peat, wood, banana pith, soybean and cotton seed hulls, peanut shells, hazelnut shell, rice husk, saw dust, wool, orange peel, compost and leaves [22].

In the present study the dried leaves powder of A. cookii has been used as biosorbent for the removal of Ni (II) ions in the aqueous solution. The various parameters like pH, contact time, dosage, size variation and metal ion concentration have been studied. Experimental data is obtained by using Langmuir and Freundlich isotherms. Kinetic studies of Pseudo first order and Pseudo second order reaction have been carried out.

II. MATERIAL AND METHODS

**PREPARATION OF METAL ION SOLUTION:**

Metal ion solution of Ni\(^{2+}\) was prepared using Nickel Ammonium sulphate purified A.R. grade. Standard stock solution was prepared by dissolving 6.727g in 1000mg/L using double distilled water. The pH of the solution was adjusted using 0.1 M HCl and 0.1 M NaOH. The final concentrations of metal ions were analysed by AAS.

**PREPARATION OF ADSORBATE:**

**BIOSORPTION EXPERIMENTS /BATCH EXPERIMENTS:**

Batch process experiments were carried out using aqueous solution of Ni\(^{2+}\) at room temperature. Different parameters were used for the removal of Ni (II) ions such as pH, size variation, contact time, dosage and metal ion concentration. 2g of biosorbent with 20 ml of 1000 mg/L of Ni (II) solution was taken in a pre cleaned conical flask and it was adjusted to different pH range from 1-7 and was kept in a rotary shaker at stirring speed of 200 rpm. The time intervals were from 5-90 min stirred in a rotary shaker at speed of 200 rpm then the solution was filtered and supernatant solution was collected and analysed by AAS. The percentage of heavy metal removal is calculated by the following formula:

\[
\text{Percentage of Removal} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad \text{(1)}
\]

The metal uptake of A. cookie was calculated for the initial and final concentrations of metal in the aqueous solution. The metal uptake capacity is calculated using following formula:

\[
q_e = \frac{(C_0 - C_e)}{M} \times V \quad \text{(2)}
\]

Where, \(q_e\) is the metal uptake (mg/g), \(C_0\) and \(C_e\) are the initial and final equilibrium metal concentrations in the solution (mg/L), respectively, \(V\) is the solution volume (ml) and \(M\) is the mass of the Biosorbent (g).
III. RESULTS AND DISCUSSION

EFFECT OF PH:

The pH of the aqueous solution is an important controlling parameter in the heavy metals adsorption processes [23]. The pH was ranged using Equip- Tronics EQ- 610 digital pH meter for Ni (II) ions from pH 1 - 7. 20 ml of 1000 mg/L of Ni (II) ions was taken in a capped tubes, using 0.1N Hcl and 0.1N NaOH. The capacity of the biosorption increased with increasing pH of metal ions solution. In the solution, the pH increases from 2.0 - 6.0, Nickel ions show an increase in binding to the adsorbent with optimum binding occurring at pH 6 at percentage removal from 39-96.95 % Fig 1. Furthermore at higher pH poorly soluble hydroxyl ions were formed and precipitation of Nickel would occur [24]. Sorption studies were meaningless above pH 7 due to the formation of insoluble products in investigated solution, what is in accordance with the solubility products of metal hydroxide as follows: Ksp (Ni (OH)2) = 10^-14 [25]. The results with the effect of pH have been shown in Fig.1. The present results coincide with [26] who has reported using protonated rice bran.

![Fig. 1.Effect of pH on biosorption of Ni (II) ions onto A.C.](image1)

EFFECT OF SIZE VARIATION:

In order to find out the adsorption capacity of Ni^{2+}, experiments was conducted using different size variation. The granular size was 100, 200, 300, and 400 µm and percentage of the removal of Nickel ions were at 98.7%, 85.3%, 73.5% and 70% respectively. The dose of the biosorbent shows great influence in the biosorption process. The dose shows number of binding sites in the adsorption. The maximum removal of Ni^{2+} was at 100 µm. As the size increased there was decrease in the percentage of removal. According to [27] the breaking of larger particles tends to open tiny cracks and channels on the particle surface of the material resulting in more accessibility to better diffusion, owing to the smaller particle size. The removal of adsorbate by smaller particles coincides during a study onto removal of colour by Silica [28]. The results are shown in.

![Fig. 2. Effect of size variation on biosorption of Ni (II) ions onto A.C.](image2)

EFFECT OF CONTACT TIME:

The adsorption capacity of Ni^{2+} onto A.cookie was studied with effect of contact time. The time interval was from 5 to 90 min. Equilibrium time is a crucial parameter for an optimal removal of metal ions in the waste water [29]. The maximum adsorption was attained at 40 min. After 40 min it was static throughout the experiment. The results are as follows in Fig 3. The uptake of heavy metal ions by biosorbent has often been observed to occur in two stages: i) rapid and quantitatively predominant and ii) slower and quantitatively insignificant. The rapid stage is probably due to abundant availability of active sites on the biomass, with gradual occupancy of these sites, the sorption becomes less efficient in slower stages [30].

![Fig.3. Effect of time on biosorption of Ni (II) ions onto A.C.](image3)
EFFECT OF DOSAGE:

Dosage is one of the important parameters for determining the adsorption of Ni$^{2+}$ onto A. cookii. Different dosages ranging from 0.1 to 4g of the biomass was taken for the removal of Ni$^{2+}$. The maximum adsorption with respect to dosage was at 2g/L, at desired pH-6, contact time 40 min and agitation speed at 200 RPM. The percentage removal was at 96.95%. High concentrations of adsorbent can act like a screen to prevent the conjunction of metal ions and adsorption sites. The lower utilization of the adsorbents absorptive capacity results in less commensurate increase in biosorption capacity [31, 32]. The results with effect of dosage are shown in.

EFFECT OF METAL ION CONCENTRATION:

The effect of Ni$^{2+}$ ion concentration is shown in onto leaves of A. cookii. The fig shows that there is increase in the initial stage and goes on decreasing as the concentration was varied from 25- 300 mg/L$^{-1}$. The maximum percentage of Ni (II) in aqueous solution was at 20 mg/L$^{-1}$ at desired pH-6, contact time 40 min and it was stagnant throughout the experiment.

At higher concentration low adsorption yield due to the saturation of adsorption sites which is a consequence of increase in the number of ions competing for available binding sites in the biomass [33]. The metal uptake mechanism is particularly dependent on the initial heavy metal concentration: at low concentrations, metals are adsorbed by specific sites, while with increasing metal concentrations the specific sites are saturated and exchange sites are filled [34].

<table>
<thead>
<tr>
<th>Biosorbents</th>
<th>$Q_{\text{max}}$</th>
<th>Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Protonated rice bran</td>
<td>44.90 mg/g</td>
<td>Muhammad Nadeem Zafar et al., 2006 [26].</td>
</tr>
<tr>
<td>Ficus Religiosa (peepal) leaves</td>
<td>25.71 mg/g</td>
<td>Muhammad Zaheer Aslam et al., 2010 [35].</td>
</tr>
<tr>
<td>Potato peel</td>
<td>13.09 mg/g</td>
<td>Devi Prasad and M.A. Abdullah, 2009 [36].</td>
</tr>
<tr>
<td>Tamarind bark</td>
<td>15.34 mg/g</td>
<td>M.A. Abdullah And A.G. Devi Prasad, 2010 [37].</td>
</tr>
<tr>
<td>Rice straw</td>
<td>35.08 mg/g</td>
<td>G.O.EI- Sayed et al., 2010 [29].</td>
</tr>
<tr>
<td>Chitosan-immobilized Brown Algae</td>
<td>38.4 mg/g (algal beads)</td>
<td>W. Fan and Z. Xu, 2011 [38].</td>
</tr>
<tr>
<td>Loquot bark (Eriobotrya japonica)</td>
<td>29.54 mg/g 313(k)</td>
<td>Nida M. Salem, Akl M. Awwad, 2011 [39]</td>
</tr>
</tbody>
</table>
IV. KINETIC STUDY

Kinetics of heavy metal ions is used to analyse the Biosorption process with effect of contact time. Kinetic sorption of heavy metals from wastewater has been studied using mostly pseudo first order [40] and pseudo second order [41] models.

**PSEUDO FIRST ORDER REACTION:**

The first order rate equation of Lagergren is one of the most widely used for the sorption of a solute from Liquid solution [42] and the formula is given by

\[
\ln (q_e - q_t) = \ln q_e - K_{1ad} t \quad \text{....(3)}
\]

Where, \( q_e \) is the mass of metal adsorbed at equilibrium mg/g, \( q_t \) is the mass of metal adsorbed at time mg/g, \( K_{1ad} \) is the first order reaction rate constant, and the linearized form is:

\[
\log (q_e - q_t) = \log q_e - K_1 t / 2.303 \quad \text{....(4)}
\]

A graph is plotted between log (qe-qt) versus t at the rate constant \( K_1 \) can be obtained by slope and intercept. The slope is calculated from the Pseudo first order rate constant \( K_1 \). The calculated values of \( K_1 \) and their corresponding linear correlation coefficient values are shown in Table 2. The correlation coefficient \( R^2 \) value is 0.9496 for 25-300 mg/L of Ni (II) in aqueous solutions. This model shows the \( R^2 \) value can be applied for the adsorption process.

**PSEUDO SECOND ORDER REACTION:**

The Pseudo second order model considers that the rate of occupation of biosorption sites is proportional to the square of the number of unoccupied sites [43].

\[
dq_t / dq_e = K (q_{eq} - q_t)^2 \quad \text{....(5)}
\]

Where, \( t \) (min) shows time, \( q_e \) (mg/g) shows uptake capacity at t and \( K \) (g mg\(^{-1}\) min\(^{-1}\)) shows the equilibrium rate constant of pseudo- second order adsorption and in the integrated form, it is represented as \( n \)t/\( dt = 1 / kq_{eq}^2 + t / q_e \) \( \text{....(6)}\)

The sorption rate, \( h \) (mg/g. min) is defined as

\[
h = K_2 q_e^2 \quad \text{....(7)}
\]

Where, \( K_2 \) and \( h \) values were determined in fig 7 for the slope and intercept of the plots t/q against t. The linear pseudo- second order equation show good agreement of experimental data for different initial metal ion concentrations. The values of pseudo second order equation parameters together with correlation coefficients are shown in Table 2 and Fig.7. The correlation co-efficient for the equation was \( R^2 = 0.999 \) and this was true for all concentrations. The \( q_e \) values also agree very well with the experimental data. Thus pseudo second order models suitably describe the adsorption of kinetic data in the present study. For evaluation of sorption rate, h has been widely used. In the present study, the value of h is 0.3624 and \( K^2 \) is 0.1200(g/mg/min). Similar performances have been observed in the biosorption of Pb2+ Cu2+ on pomegranate peel [44].

<table>
<thead>
<tr>
<th>Metal</th>
<th>Pseudo first order</th>
<th>Pseudo second order</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( q_e ) (mg/g-1)</td>
<td>( K_1 ) (min(^{-1}))</td>
</tr>
<tr>
<td>Ni (II)</td>
<td>1.511</td>
<td>0.0069</td>
</tr>
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<td></td>
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Table 2: Pseudo First-Order And Pseudo Second-Order Constants For Ni (II) Biosorption By A. Cookii.

V. ADSORPTION ISOTHERMS

The equilibrium of the biosorption process is often described by fitting the experimental points with models which are used to represent the equilibrium adsorption isotherm [45]. A batch sorption experiment was conducted to characterize the interaction of Ni (II) for isotherm curves with the leaves of A. Cookii [38].

In order to describe the adsorption mechanism of low-cost adsorbents used for water and waste water treatment experimental equilibrium data are most frequently modelled by the relationship developed by Langmuir isotherm [46]. The Langmuir models is based on the assumptions that maximum adsorption occurs when a saturated monolayer of solute molecules is present on the adsorbent surface, the energy is constant, and there is no migration of adsorbate molecules in
the surface plane [47]. Langmuir model is represented as follows:

\[ C_e / q_e = 1 / (b q_{\text{max}}) + C_e / q_{\text{max}} \]  

Where, \( C_e \) is the equilibrium concentration (mg/L), \( q_e \) and \( q_{\text{max}} \) are the equilibrium and maximal adsorption capacity (mg/g), respectively and \( b \) is the equilibrium constant [48].

The graph of \( C_e / q_e \) vs. \( C_e \) was plotted on contact time where, intercept and the slope can be obtained. The Coefficient correlation \( R^2 \) is 0.996 and \( q_{\text{max}} \) 37.03 is shown in. The Freundlich adsorption isotherm is an empirical model that is based on sorption on a heterogeneous surface [49]. The equation is as follows:

\[ \ln q_e = \ln K_r + 1/n \ln C_e \]  

The constant \( n \) is an empirical parameter that with the degree of heterogeneity and \( K_r \) is a constant related to adsorption capacity. The values of \( n \) and \( K_r \) which is constant can be determined by the plot \( C_e \) and \( q_e \) (Slope = 1/n, Intercept = \( K_r \)) .

The results are represented in Table 3.

![Graph showing the relationship between Ce/qe and Ce](image)

Table 3: Langmuir And Freundlich Constants For Ni (II) Biosorption By A. Cookie

<table>
<thead>
<tr>
<th>Metal</th>
<th>Langmuir</th>
<th>Freundlich</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni (II)</td>
<td>( q_{\text{max}} )</td>
<td>( b )</td>
</tr>
<tr>
<td></td>
<td>37.03</td>
<td>0.026</td>
</tr>
</tbody>
</table>

VI. CONCLUSION

The present study shows the effective removal of Ni (II) ions from the aqueous solution using the leaves of Araucaria cookie. The study shows effect of biosorption process like pH, contact time, size variation, adsorbent dose and metal ion concentration. The metal uptake was effective for the removal of Ni (II) at pH 6. The maximum percentage removal attained was 96.95% at initial concentration of 200 mg/L. The adsorption isotherms onto Araucaria cookie easily fitted with Langmuir and Freundlich equations. Kinetics was described best by pseudo-first order and Pseudo-second order models.

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REFERENCES