Removal of Nickel from Industrial Wastewater Using Date Seeds


1,4,5 Department of Engineering, College of Applied Sciences, Suwar, Sultanate of Oman
2Department of Mechanical and Industrial Engineering, Caledonian college of Engineering, Al Hail, Sultanate of Oman
3Petroleum and Chemical Engineering Programme area, Faculty of Engineering, Universiti Teknologi Brunei, Gadong, Brunei Darussalam
6Department of Chemical Engineering, Sathyabama Institute of Science of Technology, Chennai, India

Abstract- Many studies discussed the treatment of waste water that includes chemical method to remove nickel. But present studies carried out using raw date seeds which is environmental friendly method. Removal of Nickel ions from aqueous solutions using raw date seeds was achieved using batch adsorption experiments The effect of initial Ni(II) concentration, particle size and effect of pH was studied. Results showed that the equilibrium adsorption was described by the Freundlich model. FTIR analysis confirmed the involvement of –OH− and aromatics− groups in Ni(II) adsorption by date seed adsorbent.

Keywords-Nickel, absorbent, date seed carbon, Langmuir and Freundlich equation, Activated carbon.

I. INTRODUCTION

Many heavy metals in waste water introduced in various industries released into the environment. The bad effect caused by these heavy metals is a major concern for the environment. The heavy metals are accumulate and not biodegradable in living organism and causing various diseases and disorder. Nickel is commonly used in industrial processes like the galvanizing metal, plating industry, tanneries and mining operations, which is normally provided in a high concentration in the liquid waste. it is directly released to the environment without doing for it any treatment. Nickel is a toxic metal and has been known to prevent the sperm, the enzymes amylase, and the formation of insulin and the formation of the kidney. Given the very highly toxicity of these metal, and the interest in development of the technologies to remove nickel from wastewater before it disposed in the environment is increased (Bailey et al.[1990])

Some of techniques which are used to extract metals from the liquid waste include chemical precipitation, ion exchange, electrolysis, cementation and reverse osmosis. Those methods are an expensive method and have no ability to remove the metals at the low concentration. Compared with the above techniques has proven to be a substitute for economic adsorption more favorable conditions for the removing of the heavy metals from the aqueous solution (Namasivaysm et al, 1999). The commonly used is the activated carbon capacitor. Garments used as adsorbents activated carbon to remove the minerals in the components of a single-component and multiple of two solutions and has been shown to have kinetics adsorption is about 2 -20 times higher than those granular activated carbon (Faur-Brasquet et al, 2002).

Due to the high cost of the activated carbon adsorbent and cost effective to treatment of wastewater contaminated with minerals. It is proved that some agricultural residues are capable of absorbing and low cost. Because of its low cost, after the exchange of these materials can be eliminated without the renewal of faces (Bailey et al, 1999). some studies have been on the use of the intensive, such as coconut shells, bark, tea waste, teak wood and mulch, dried plant to remove the metals from the aqueous solutions (Olayinka et al , 2005; .. Olayinka et al, 2007; Benhima et al, 2008). It was found that the absorption capacity of these materials, since it depends on the experimental condition like the contact time, pH and the concentration of the metals and loading of adsorbent.

II. EXPERIMENTAL PROCEDURE

2.1Material-
The objective of this project work is to remove the nickel from industrial waste water. Many adsorbents such as activated carbon, algae have been used for the removal of nickel but in this project the activated carbon from the date seeds are used as adsorbent since it are on hand and available in a very large quantities in Oman as a waste so it is low cost adsorbent. Date seeds are collected, washed and dried and it is soaked in phosphoric acid for 24 hrs. Then it is washed and dried again and kept it Oven for 5 hrs to convert into activated carbon. This is again crushed
and ground into small particles and sieved by using mesh to get various particle size. Then these particles are used for the experiment for the removal of nickel.

2.2 Preparation Of Adsorbate-
The Nickel Chloride used of analytical grade. A stock solution of 1000 ppm was prepared by dissolving 4.05 g of nickel chloride on 100 ml of distilled water to obtain solution of some different concentration 20, 40, 60, 80 and 100 ppm the stock solution was diluted as it is required.

2.3 Analysis of nickel(II) ions-
The concentration of nickel(II) ion in the sample solution was determined spectrophotometrically. 20ml of sample solution containing less than 10 mgNi/l was treated with 0.5 ml of 25% HCl and bromine solution (2–4 drops). After 10 min, 1 ml of ammonical solution was added to the sample solution followed by the addition of dimethylglyoxime (1 g dissolved in 100ml methanol) and the volume made upto 50 ml with distilled water. The absorbance of the wine red to brown coloured complex of nickel(II) ion with dimethylglyoxime was read at a wavelength of 440 nm within 15 min of mixing (V. Padmavathy,2002).

2.4 Adsorption -
Adsorption experiments will be done in the rotary shaker at 100 rpm using 250 ml Erlenmeyer flask which is containing desired adsorbent in 100 ml Nickel metal concentration. The metal content in the supernatant will be determined Spectrophotometrically using Analysis of nickel(II) ions method discussed previously. The amount of metal which is biosorbed can be calculated from the difference between the metal quantity which is added initially and the metal content of the supernatant using following equation:

\[ Q = V(C_0 - C_f) / M \]  
Where the Q is metal uptake (mg/g); C0 and Cf are the initial and equilibrium metal concentration in the solution (mg/l), respectively; V is solution volume (l); and M is mass of biosorbent (g).

2.5 Batch and data modeling-
Langmuir sorption model is chosen for estimating of the maximum metal biosorption by biosorbent. Langmuir isotherm can be expressed as following

\[ Q = \frac{Q_{max} bC_f}{1 + bC_f} \]  
Where Qmax is maximum metal uptake (mg/g) and b is Langmuir equilibrium constant (l/mg).
The adsorption data of nickel is also analyzed by Freundlich model. The logarithmic form of Freundlich model is given by the following equation:

\[ \log qe = \log K_F + \frac{1}{n} \log C_e \]  
where qe is the amount adsorbed (mg/g) , Ce the equilibrium concentration of the adsorbate (mg/g) and KF and n are Freundlich constants related to adsorption capacity and adsorption intensity, respectively.

2.6 Kinetic model-
Kinetic studies were conducted by varying the initial nickel(II) ion concentration and the date seeds activated carbon amount 0.3 g of was suspended in 100 ml of nickel(II) solution (20, 40, 60, 80 and 100 PPM ) and the pH of solutions was adjusted to a value of 4. The mixture was continuously stirred at 100 rpm. Studies on the effect of activated carbon on nickel(II) ion sorption were carried out at different initial concentration of at pH 4, and at an agitation speed of 100 rpm. Samples were withdrawn at pre-determined time intervals, filtered and analysed for residual nickel(II) ion concentration. the results reading were fitted to Pseudo first order and Pseudo second order to know the order of the reaction.

2.7 Pseudo first order-
A simple kinetic analysis of biosorption is the Pseudo-first order model in the form (Ho and McKay 1998),

\[ \frac{dQ}{dt} = K_1(Q_e - Q_t) \]  
where Qe is the amount of metal sorbed at equilibrium per unit weight of sorbent (mg/g); Qt is the amount of metal sorbed at any time (mg/g) and K1 is the rate constant (1/min).
Integrating and applying boundary conditions, t = 0 and Qt = 0 to t = t and Qt = Qt, takes the form
log(\(Q_e - Q_t\)) = log \(Q_e\) - \(K_1 t / 2.303\) \hspace{1cm} (5)

The values of \(K_1\) and \(Q_e\) can be determined experimentally by plotting \(log(Qe-Qt)\) versus \(t\).

2.8 Pseudo second order-
Pseudo-second order model may be tested using the experimental data. The kinetic rate equation is (Ho and McKay 1998),

\[
d\frac{Q_t}{dt} = K_2 (Q_e - Q_t)^2
\hspace{1cm} (6)
\]

where \(K_2\) is the equilibrium rate constant (g/mg min). Integrating the above equation and applying boundary conditions \(t = 0\) and \(Q_t = 0\) to \(t = t\) and \(Q_t = Q_e\), gives,

\[
t / Q_t = 1 / K_2 Q_e^2 + t / Q_e
\hspace{1cm} (7)
\]

The values of \(K_2\) and \(Q_e\) can be determined experimentally by plotting \(t/Q_t\) versus \(t\) of Equation

**III. EXPERIMENT AND RESULT**

3.1. Effect of pH-
The uptake of nickel(II) ion using Date seeds Activated Carbon was affected by pH as seen in Fig. 4.2.1 The experiments were not conducted beyond pH 7.0 to avoid possible nickel hydroxide precipitation. The nickel(II) ion adsorption capacity of Activated Carbon has increased with the increasing of pH, and it shows the best performance at pH of 4 sorption capacities of nickel was 16.651 mg.g^{-1} with initial concentration of 50 PPM. The fact that the pH influences the binding of metal ions by Activated carbon indicates that there is an interaction of biomass binding sites with protons. With an increase in the pH the sorption uptake increases as the degree of ionization of negative groups present on the biomass would increase. Metal adsorption is brought about by ionization of negative functional molecular groups which serve as the binding sites [7].

![Figure 1. Effect of pH on nickel(II) removal using Activated Carbon (A.C dose 0.3 g- 50 PPM)](image)

3.2. Influence of particle size-
The particle size can have a strong influence on the sorption properties of the adsorbent. Experiments were performed using different particle sizes of the adsorbent (150-212 and 300 um) with different initial concentrations (20-40-60-80 and 100) . Generally, the smaller the adsorbent particles, the greater the amount of metal ions could be adsorbed. Comparatively higher adsorption with smaller adsorbate particles may be due to the fact that smaller particles give a larger external surface area.

![Figure 2. Effect of particle size on nickel(II) removal using Activated Carbon (A.C dose 0.3 g- 90 PPM)](image)
Experimental results showed in Figure 4.2.2.1. that 150μm particles performed well with high removal efficiencies and uptakes of 56.13. Other particle sizes (212 μm - 300μm) performed very closely to that of 150 μm particles. Therefore, considering the rigidity and strength, 300 μm particles were selected for all further biosorption studies.

3.3 Effect of biosorbent dosage

The effect of biosorbent dosage was examined by varying dosages from 0.1 to 0.3 g/l. The figure presents the typical set of results obtained by varying adsorbent dosages during Nickel adsorption. It was observed that the percentage of removal increases with an increase in adsorbent dosage. An increase in biomass concentration generally increases the adsorbed metal ions because of an increase in surface area of the adsorbent, which in turn increases the binding sites. Whereas the adsorbed metal quantity per unit weight of adsorbent (Q) decreases by increasing the adsorbent dosage, this may be due to complex interactions of several factors. The important factor being that at high sorbent dosages, the available metal ions are insufficient to cover all the exchangeable sites on the adsorbent, usually resulting in low metal uptake.

![Figure 3. Effect of Dosage on nickel(II) removal using Activated Carbon (A.C dose 0.1, 0.2 and 0.3 g - 90 PPM)](image)

3.4 Kinetics of Sorption Reaction

3.4.1 Effect Of initial Concentration

The effect of initial concentration on adsorption Nickel on DSC was studied by changing the concentration of solution from 20 to 100 PPM. From this study it can be seen that the total amount of Nickel adsorbed increases with the increase in concentration of nickel. The rate uptake of adsorbate is found to increase non-linearly with an increasing concentration of solute. Similar results showed in the literature[3].

It is observed that the experimental data obtained with varying concentrations of nickel follows pseudo-second-order equation with a regression constant greater than 0.98. Pseudo-second-order plots of adsorption of nickel on date seeds activated carbon at different initial concentrations.

![Figure 4. Effect of initial concentration on nickel(II) removal using Activated Carbon (A.C dose 0.3 g)](image)

The prediction of batch biosorption kinetics is necessary for the design of industrial columns. Biomass were found to increase with time and attain a maximum value at about 300 min. The sorption capacities was increased from 17.28 to 78.14 mg g⁻¹. The model constants, along with predicted uptake values for both models are summarized in Table 4.1.

The pseudo-first-order kinetic model has been widely used to predict the sorption kinetics, which can be expressed as,

\[ \ln(Q_e - Q_t) = \ln Q_e - k_1t \]

Thus the rate constant k1 (1/min) can be calculated from the slope of the plot of ln (Qe – Qt) versus time t. The calculated k1 values and the corresponding linear regression coefficient values are shown in Table 1. Even though,
reasonably high correlation coefficients were obtained pseudo first order module, but it did not predict the equilibrium uptake values in any of the cases examined.

The kinetic data were further analyzed using pseudo-second-order kinetics, which can be represented as,

\[
\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t
\]

where \( k_2 \) is the pseudo-second-order rate constant (g/mg min), \( Q_e \) and \( Q_t \) represent the metal uptake at equilibrium and at any time \( t \), respectively. The rate constant \( k_2 \) and predicted \( Q_e \) can be calculated from the plot of \( t/Q_t \) versus time \( t \) using the equation. Good fits were generally observed for pseudo-second order model, with correlation coefficients always greater than 0.99. The model also predicted the equilibrium uptake values, which is in close agreement with the experimental values. The model constants, along with predicted uptake values for both models are summarized in Table1.

### Table-1 Kinetic Parameters for the Nickel(II) biosorption by date seeds at different initial metal concentrations.

<table>
<thead>
<tr>
<th>Metal</th>
<th>C0 (mg/l)</th>
<th>(Qe)exp (mg/g)</th>
<th>Pseudo first order</th>
<th>Pseudo second order</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>K1 (1/min)</td>
<td>Qe (mg/g) R2</td>
</tr>
<tr>
<td>Nickel</td>
<td>20</td>
<td>17.28571</td>
<td>0.0043</td>
<td>4.87 0.9138 0.1358</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>35.28571</td>
<td>0.0031</td>
<td>13.969 0.9831 0.0312</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>53</td>
<td>0.0035</td>
<td>20.546 0.9151 0.0313</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>70.14286</td>
<td>0.0034</td>
<td>32.191 0.949 0.016</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>78.14286</td>
<td>0.0034</td>
<td>32.191 0.949 0.016</td>
</tr>
</tbody>
</table>

The pseudo-first order model was widely applied to data modeling, but no adsorption mechanisms could be reasonably available. The pseudo-second order model is based on chemical adsorption and conforms to the adsorption of Nickel on the activated carbon adsorbent in this study. according to the high correlation coefficient \( R^2 \), adsorbent showed the highest adsorption capacity for Nickel. The pseudo-second order model assumes that the adsorption rate is controlled by chemical adsorption, and it has been successfully used in many adsorption processes.

### 3.5 Sorption isotherm-
#### 3.5.1 Langmuir isotherm-
When \( 1/q_e \) was plotted against \( 1/C_e \), straight lines with slope \( 1/bQ_o \) were obtained (Fig. 4.5.1), which shows that the adsorption of nickel followed the Langmuir isotherm. The Langmuir constants, \( b \) and \( Q_o \); were calculated and the values of these are given in Table 4.5.1. The values of constants indicate favourable conditions for adsorption.

![Figure 5. Langmuir isotherm](image)

#### 3.5.2 Freundlich isotherm-
The adsorption data of nickel is also analysed by Freundlich model. The plots of \( \log Q_e \) against \( \log C_e \); for the adsorption data of nickel are given in Fig.4.5.2 which clearly shows that the data is fitting well to the Freundlich model. However, the Freundlich constants, \( K_F \) and \( n \); were calculated. The data are given in Table 4.5.1.

### Table-2 Langmuir and Freundlich model parameters at different pH conditions for nickel biosorption by date seeds

<table>
<thead>
<tr>
<th>Metal</th>
<th>pH</th>
<th>Langmuir parameters</th>
<th>Freundlich parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel</td>
<td>4</td>
<td>Qmax (mg/g) 0.336008</td>
<td>2.9741 0.5373</td>
</tr>
<tr>
<td></td>
<td></td>
<td>b (l/mg) 0.8979</td>
<td>KF (l/g) 0.137187</td>
</tr>
<tr>
<td></td>
<td></td>
<td>R2 0.8979</td>
<td>n 0.9065</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Fourier transform IR spectroscopy (FTIR) was used for functional group analysis of the activated carbon, before and after adsorption. Figure 8 FTIR spectra analysis

Peaks for aromatics disappeared and new sharp peaks were formed. This shows that it is the only responsible groups for metal ion adsorption. The results of a typical FTIR analysis of the activated carbon confirm the ion exchange process.

FTIR spectra analyses for the activated carbon before and after adsorption of nickel(II) were undertaken and results are illustrated in Fig.4.6.1. activated carbon FTIR analysis shows main absorption bands of activated carbon at 3417.04, 2923.76 and 1618.08 cm$^{-1}$. The current results are in good agreement with the absorption frequencies, demonstrated by previous researchers [8]. bands around 3440 cm$^{-1}$ are related to the presence of bonded hydroxyl groups (OH). The band of 2923.76 is from C-H (alkanes) The band at 1618.08 cm$^{-1}$ is from C=C Aromatic group. The FTIR spectra confirm that there is a shift of some functional group bands. Differences in the spectra would indicate bonding between the metal with active sites on the activated carbon due to adsorption or a chemical reaction (Ahmad B. Albadarina et al. 2011). Changes occurring on the activated carbon after adsorption of Ni (II) are reflected in the broad band present. The intensity of the peak representing the $\pi$ group increased and shifted from 1618.08 (C=C Aromatic group) to 1644.69 cm$^{-1}$ (C=C Alkene Group) and Some peaks are disappeared as it is shown in Fig.8
IV. CONCLUSION
There are so many methods of removing heavy metals from industrial waste water. The effective method of removal of nickel using date seeds activated carbon has been investigated from the literature and experiments were conducted. The various factors influencing the removal of nickel are; pH, particle size, concentration and dosage. All the factors were optimized and results validated using standard models.

The Date Seed Activated Carbon adsorbents was effective for Nickel removal from water

The sorption capacities of Nickel on the adsorbent increased with increasing solution pH.
The pseudo-second order model fitted the kinetic data reasonably well for the adsorbent

The adsorption equilibrium data of Nickel on adsorbent was fitted to Freundlich with a regression constant greater than 0.97.

FTIR analysis confirmed the involvement of –OH− C=C Alkene − groups in Ni(II) adsorption by date seed adsorbent.

V. REFERENCE