ABSTRACT
The removal of divalent nickel from aqueous solutions on modified holly sawdust was studied at varying contact
times, pH, initial divalent nickel concentrations and adsorbent dose. Results showed the removal efficiency by
increasing of pH increased and decreased with initial nickel divalent concentration. By increasing pH from 2 to
12 (equilibrium time = 240 min, adsorbent dose = 0.6 g/100 mL, divalent nickel concentration = 60 mg/L), the
removal efficiency increased from 17.47% to 81.76%. Also removal efficiency was decreased from 98% to 19.3%
% by increasing of initial divalent nickel concentrations from 20 mg/L to 100 mg/L. Also the results showed the
removal efficiency was increased by increasing of adsorbent dose and contact time. By increasing of adsorbent
dose from 0.2 g/100CC to 1 g/100CC, the removal efficiency increased from 32.78% to 99.98%. The removal
efficiency increased from 34.7% to 83.67% by increasing of contact time from 5 min to 240 min. Experimental
equilibrium and kinetics data were fitted by Langmuir and Freundlich isotherms and pseudo-first-order and
pseudo-second-order kinetics models, respectively. The results show that the equilibrium data follow Langmuir
isotherm and the kinetic data follow pseudo-second-order model. The obtained maximum adsorption capacity was
22.47 mg/g at a pH 7. The results show that the modified holly sawdust can be used for the treatment of aqueous
solutions containing nickel as a low cost adsorbent.

Key word: Divalent nickel; Sawdust; Kinetic models; Isotherm models; Adsorption

INTRODUCTION
The removal of toxic heavy metal ions from wastewater has been widely studied in recent years, because they may be toxic toorganisms including humans (Meena et al., 2008; Mirbagheri and Saleh, 2006; Choksi and Joshi, 2007; Khellaf and Zerdaoui, 2009). Nickel occurs in two oxidation states in nature namely Ni0 and Ni2+. Divalent nickel is toxic to most organisms for concentrations higher than 0.05 mg/L. It is carcinogenic in animals (Demirbas et al., 2002) and is one frequently encountered in raw wastewater effluent from industries, such as non-ferrous metal, mineral processing, electroplating, porcelain enameling, copper sulfate manufacturing, and battery and accumulator manufacturing. The maximum permissible concentration of nickel in drinking water is 0.02 mg/L according to US-EPA report. Higher concentrations of nickel cause cancer of lungs nose and bone relate. Acute poisoning of divalent nickel causes headache, dizziness, sickness and vomiting, chest pain, tightness of
the chest, dry cough and shortness of breath, rapid respiration, cyanosis and extreme weakness (Malkoc and Nuhoglu, 2005).

Various methods have been used for removal of divalent nickel from industrial wastewater, including: filtration, chemical precipitation, adsorption, electrodeposition and membrane systems or even ion exchange process (Meena et al., 2008; Ramezankhani et al., 2009). Chemical precipitation and reduction process needs other separation techniques for the treatment and disposal of high quantities of waste metal residual sludge produced. These techniques also require a lot of treatment chemicals. The application of membrane systems for the wastewater treatment has major problems such as membrane scaling, fouling and blocking.

The disadvantage of the ion exchange process is the high cost of the resin while the electrodeposition method requires more intensive energy than other methods (Kadirvelu et al., 2001b,a; Kobya et al., 2005). Adsorption with activated carbon can also be highly efficient for the removal of numerous trace elements from water and wastewater, but the high cost of activated carbon inhibits its large scale use as adsorbent (Shukla et al., 2002). To solve these problems, in recent years, investigations have been carried out for the effective removal of large quantities of divalent nickel from wastewater using low cost adsorbents (Yu et al., 2001).

Sawdust is a waste by-product of the timber industry that is either used as cooking fuel or a packing material. Alemayehu and Lennartz studied the removal of nickel onto volcanic rocks (Alemayehu and Lennartz, 2010); Shukla and Pai studied the removal of Cu(II), Ni(II) and Zn(II) on dye loaded groundnut shells and sawdust (Shukla and Pai, 2005); Malkoc and Nuhoglu studied the removal of nickel(II) onto tea factory waste (Malkoc and Nuhoglu, 2005). It can be economically used for the removal of heavy metals in wastewater (Shukla et al., 2002; Ajmal et al., 1998). Hence, research on the application of holly sawdust as an alternative low cost adsorbent for the removal of divalent nickel in contaminated wastewater is very important.

In this paper, the possibility of using holly sawdust to remove divalent nickel from aqueous solution was investigated using batch adsorption studies. The effect of various factors such as contact time, pH, initial divalent nickel concentrations and adsorbent dose on the removal efficiency of holly sawdust was also studied. Adsorption isotherm and kinetic studies were also investigated in order to understand the adsorption mechanism and efficiencies of holly sawdust.

MATERIALS AND METHODS

Preparation of modified Holly sawdust

Holly sawdust from a timber mill in the city of Hamadan was washed with deionized water and dried at sunlight. The sawdust washed several times with distilled water and then decolorized with 1% formaldehyde in the ratio of 1:5 (sawdust:formaldehyde, w/v) at 50°C for 4hr. The sawdust was filtered out, washed with deionized water to remove free formaldehyde and then activated at 80°C in a hot air oven for 24hr. Then one part of as-prepared sawdust was mixed with one part of concentrated sulfuric acid and heated in a oven for 24hr at 150°C. The heated material was washed with distilled water and soaked in 1% sodium bicarbonate solution overnight to remove residual acid (Baral et al., 2006). The obtained material was dried in an oven at 105°C for 24hr, and sieved in the size range of 70 mesh ASTM. The specific surface area (BET) of the modified sawdust was determined as 365 m²/g by Research Institute of Petroleum Industry (RIPI).

Preparation of divalent nickel solution

The stock solution (100 mg/L) of Ni(II) was prepared by the following method: 0.1 g Ni (Nickel metal) was dissolved in 10 mL conc-HNO₃ solution at 60-70°C and deionized water (Andrew, 2005). The initial solution pH was adjusted by adding 1 M NaOH and HNO₃. The experiments were carried out at room temperature (25 ± 2°C).

Adsorption experiments

The equilibrium time (4hr) was determined from kinetic data at conditions (pH=7, adsorbent dosage = 0.6 g/100CC, initial divalent nickel concentration = 60 mg/L). In each adsorption experiment, 100 mL of divalent nickel solution of known concentration and pH was added to 0.6
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3.66 g of modified sawdust in a 250 mL Erlenmeyer flaks and the mixture was mixed by a rotary mixer (H1-190M) at 160 rpm for 4 hours. The aqueous samples were centrifuged (Sigma-301) at 4000 rpm for 10 min to removed adsorbent and then analyzed for divalent nickel. The residual divalent nickel was analyzed by using flame atomic absorption spectrometry (AA) (Andrew, 2005). The experiments were conducted by various amounts of adsorbent (2 to 10 g/100CC), initial divalent nickel concentrations (20 to 100 mg/100CC) and initial pH 2 to 12. The removal efficiency of divalent nickel was by:

\[
\text{removal efficiency (\%)} = \frac{(C_0 - C)}{C_0} \times 100 \quad (1)
\]

where \(C_0\) and \(C\) are the original and residual divalent nickel concentrations in solution, respectively.

**RESULTS**

**Effect of contact time on divalent nickel removal**

Effect of contact time on divalent nickel removal by modified holly sawdust was studied by variation of the contact time (5 to 240 min) for different initial divalent nickel concentrations.

The relationship between the contact time and the percentage removal of divalent nickel is shown in Fig. 1.

**Effect of pH on divalent nickel removal**

The relation between the initial pH of the solution and the percentage removal of divalent nickel is shown in Fig. 2. The removal percentage of divalent nickel increased from 17.47% to 81.76% with increasing the initial pH from 2 to 12.

**Effect of initial divalent nickel concentration on removal efficiency**

A series of divalent nickel solution (20, 40, 60, 80 and 100 mg/L) were prepared by adding 20.0–80.0 mL of 100 mg/L stock solution into 100 mL volumetric flasks. The relationship between the initial divalent nickel concentration of the solution and the percentage removal of divalent nickel is shown in Fig. 3. Removal efficiency was significantly affected by the initial concentration of divalent nickel in aqueous solutions. Percentage removal of divalent nickel decreased from 98 % to 19.3 % with increasing the initial divalent nickel concentration from 20 to 100 mg/L.

![Fig. 1: Effect of contact time on divalent nickel removal by modified holly sawdust; (pH=7, adsorbent dose= 0.6 g/100 CC)](image)
Effect of Adsorbent Dose on divalent nickel removal
divalent nickel solution (60 mg/L) was prepared by adding 60 mL of stock divalent nickel solutions
into deionised water in 100 mL volumetric flasks. The pH was adjusted to 7.0 using 1 M HNO3 or
1 M NaOH before being transferred into 100 mL Erlenmeyer flasks. The concentration of adsorbent (modified holly sawdust) was varied between 0.2-1 g/100CC. The mixture was mix
for 240 min at 160 rpm in room temperature. The relationship between the adsorbent dose of the solution and the percentage removal of divalent nickel is shown in Fig. 4. The percentage removal of divalent nickel increased from 32.78% to
99.98% with increasing the adsorbent dose from 2 to 10 g/100CC.

Adsorption Isotherm and Kinetics
Adsorption isotherm studies were conducted with 60 mg/L initial concentration of divalent nickel and adsorbent dose of 0.04-0.5 g/100CC. Each experiment was repeated three times but the mean values were reported. After equilibration, the samples were separated and analyzed for their residual divalent nickel concentration. The equilibrium adsorption capacity was calculated by Eq. (2) (Ajmal et al., 2000).

\[ q_e = \frac{(C_0 - C_e)V}{M} \]  \hspace{1cm} (2)

Where: \( q_e \) (mg/g) is equilibrium adsorption capacity, \( C_0 \) and \( C_e \) are initial and equilibrium concentrations (mg/L) of divalent nickel, respectively. \( V \) (L) is the volume of solution and \( M \) (g) is the weight of the adsorbent.

For modeling of equilibrium data, both Langmuir and Freundlich isotherms were applied (Liu and Liu, 2008). Langmuir isotherm is:

\[ q_e = \frac{K_L q_m C_e}{1 + K_L C_e} \]  \hspace{1cm} (3)

Where \( K_L \) is the Langmuir constant and is related to the adsorption affinity and \( q_m \) is the maximum adsorption capacity.

The Logarithmic form as Freundlich isotherm is:

\[ \log q_e = \log K + \frac{1}{n} \log C_e \]  \hspace{1cm} (4)

Where: \( K \) and \( 1/n \) are the Freundlich constant.

Fig. 5 (b) shows the linear plot of \( (C_e/q_e \) versus \( C_e \) of Langmuir isotherm. The calculated values of \( q_m \) and \( K_L \) are listed in Table 1. The applicability of the Freundlich sorption isotherm was analyzed by plotting \( \log(q_e) \) versus \( \log(C_e) \), Fig. 5 (a). The obtained Langmuir and Freundlich constants and related correlation coefficients are listed in Table 1. From the obtained correlation values it is clear that the obtained equilibrium data follow Langmuir equation.

The kinetics of adsorption describes the rate of uptake of nickel ions onto the modified holly sawdust. Kinetic studies were conducted in a series 250 mL Erlenmeyer flasks filled with 100 mL of initial divalent nickel concentrations (40, 60, 80 mg/L) and adsorbent dose 0.6 g/100mL and pH=7±0.2. At specified time interval, the samples were separated and analyzed for their residual divalent nickel concentrations. The kinetics of divalent nickel onto the modified holly sawdust were analyzed by pseudo first-order and pseudo
second-order models at various initial divalent nickel concentrations (Azizian, 2004).
The pseudo first-order rate equation for adsorption expressed by Eq. (5):

\[
\frac{dq_t}{dt} = K_1 (q_e - q_t)
\]  

(5)

After integration and then rearrangement:

\[
\ln \left(1 - \frac{q_t}{q_e}\right) = -K_1 t
\]  

(6)

where \(q_e\) (mg/g) and \(q_t\) denote the concentration of adsorbed Ni(II) per unit mass of adsorbent in equilibrium and any time, respectively. \(K_1(1/\text{min})\) is the pseudo first-order rate constant.
The pseudo second-order rate equation is:

\[
\frac{dq_t}{dt} = K_2 (q_e - q_t)
\]  

(7)

where after integration and rearrangement to the linear form, one arrives:

\[
\frac{t}{q_t} = \frac{1}{K_2 q_e} + \frac{1}{q_e} t
\]  

(8)

Where: \(K_2\) (g/mg/min) is the pseudo second order rate constant. The obtained values of \(K_1, K_2\) and \(q_e\) are summarized in Table 2.

**DISCUSSION**

It is evident from Fig.1 that time is an important parameter for the adsorption of divalent nickel on sawdust. While increasing the divalent nickel concentration from 40 to 80 mg/L, the percentage removal decreases from 48.37% to 40.45% for initial 15 min of contact time. After that, the percentage removal of divalent nickel reaches slowly to 86% and 80.67% till 240 min for the initial divalent nickel concentration of 40 to 80 mg/L, respectively. A further increase in the contact time has a negligible effect on the rate of adsorption of divalent nickel. The percentage removal of divalent nickel increased from 34.7% to 83.66% with increasing the contact time from 5 to 240 min for initial divalent nickel concentration of 60 mg/L.

Fig. 1 shows that the optimal removal efficiency was reached within about 90 min. The favorable removal of divalent nickel at higher pH was related with increasing negative charge density onto holly sawdust (Pradhan et al., 2005; Rao et al., 2002). Similar observations have also been reported from other research groups (Meena et al., 2008; Gupta and Babu, 2009).

**Table 2: Calculated kinetic parameters for pseudo first-order and pseudo second-order models for removal of divalent nickel by modified holly sawdust**

<table>
<thead>
<tr>
<th>Initial concentration (mg/L)</th>
<th>(C_0)</th>
<th>(K_1) (L/min)</th>
<th>(q_e) (mg/g)</th>
<th>(R^2)</th>
<th>(K_2) (g/mg/min)</th>
<th>(q_e) (mg/g)</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>0.072</td>
<td>5.74</td>
<td>0.9371</td>
<td></td>
<td>0.0149</td>
<td>5.95</td>
<td>0.995</td>
</tr>
<tr>
<td>60</td>
<td>0.0278</td>
<td>8.37</td>
<td>0.9073</td>
<td>0.994</td>
<td>0.009</td>
<td>8.69</td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>0.0278</td>
<td>10.76</td>
<td>0.9073</td>
<td>0.994</td>
<td>0.005</td>
<td>11.36</td>
<td>0.99</td>
</tr>
</tbody>
</table>

(185)
The decrease in the percentage removal of divalent nickel by increasing initial divalent nickel concentration can be explained with the fact that the adsorbent had a limited number of active sites, which would have become saturated above a certain concentration (Shukla and Pai, 2005; Shukla et al., 2005). Similar observations have also been reported from other research groups (Bulut and Tez, 2007; Acar and Eren, 2006). The increase in divalent nickel removal with an increase in the sawdust amount is due to the increase in surface area and adsorption sites available for adsorption (Meena et al., 2008). Similar observations have also been reported from other research groups (Bulut and Tez, 2007; Malkoc, 2006; Rafatullah et al., 2009). The value of correlation coefficient \( R^2 = 0.9734 \) indicates that there was a good agreement between the experimental equilibrium data and the Langmuir isotherm. The monolayer saturation capacity is 22.47 mg/g. The values of nickel(II) uptake found in this work is higher than other reported values; for example \( q_m \) is 7.49 for removal nickel onto groundnut shells and sawdust (Shukla and Pai, 2005), \( q_m \) is 2.68 for nickel adsorption on the Modified Pine Tree Materials (Argun et al., 2005), \( q_m \) is 15.26 for nickel(II) removal by using of tea factory waste (Malkoc and Nuhoglu, 2005). The comparison of sorption capacity of modified holly sawdust used in this study with those obtained in the literature shows that the modified holly sawdust is an effective adsorbent for the removal of Nickel(II) from aqueous solution. The value of correlation coefficient \( R^2 = 0.9945 \) indicates that there was a good agreement between the kinetic data of adsorption and the pseudo second-order model.

The present work shows that partially modified Holly sawdust can be used to achieve nickel ion...
adsorption successfully. Sawdust is found to be a better adsorber for the removal of divalent nickel as compared to many other low cost and commercially available adsorbents. The metal ion concentration gradient is a fundamental force that transfers metal ion from solution to adsorbent surface and diffuses metal ion into the inside of adsorbent. The adsorption isotherms do not match Freundlich isotherms very well, and can be better described by Langmuir isotherms which indicates a homogeneous surface of adsorbent. The results show that the modified holly sawdust can be used for the treatment of aqueous solutions containing nickel as a low cost adsorbent.

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