Removal of Heavy Metals from Waste Water Using Low Cost Adsorbent

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Abstract: Heavy metal toxicity due to industrial wastewater has been a threat to the environment for the past many decades, especially in the developing countries such as India, China and Thailand, where cost effectiveness of the removal process is a major factor. In this work, adsorption experiments were carried out using rice straw as an agricultural residue was assessed for heavy metals (Cr & Ni) adsorption from aqueous solutions. The effects of pH, contact time, and adsorbent dosage were studied in batch process. Rice straw was treated in order to increase their metal-binding capacity. The adsorption data has been correlated and found that date is well fitted with the Langmuir, Freundlich and Temkin isotherms. Results indicated that rice straw appeared to be the most practical use for adsorption of Cr & Ni from waste water. The modified rice straws could adsorb faster than unmodified one.

Keywords: Rice Straw (RS), Adsorption, Sodium Hydroxide, Isotherms.

I. INTRODUCTION

Environmental pollution is currently one of the most important issues facing humanity. It was increased exponentially in the past few years and reached alarming levels in terms of its effects on living creatures. Toxic heavy metals are considered one of the pollutants that have direct effect on man and animals. Rapid growth in human population is one of the major causes of environmental pollution. Increased industrialization and urbanization throughout the world results in consistent release of toxic effluents, several industrial processes generate metal containing wastes. One of these pollutants is heavy metals. They are introduced into the biological cycle through drinking water, food and air. Heavy metals are dangerous as they bioaccumulate.

Heavy metals are released from industries such as metal plating, mining, batteries, PCB manufacturing etc. Nickel is a non-biodegradable toxic heavy metal ion present in wastewater. Acute nickel toxicity effects are gastrointestinal symptoms like nausea, vomiting, abdominal discomfort and diarrhea. Nickel also affects the blood, liver kidney and immune system. Metallic nickel is teratogenic and carcinogenic to mammals.

The commonly used procedures for removing heavy metals from aqueous streams include chemical precipitation, coagulation, ion exchange, reverse osmosis etc. [1&2]. The disadvantages like incomplete removal, high reagent cost and energy requirements, generation of toxic sludge that require careful disposal have made it imperative for a cost effective treatment method capable of removing heavy metals from aqueous effluents [3&10]. Adsorption is one in which certain adsorptive are selectively transferred from the fluid phase to the surface of particles suspended [14]. Adsorption has advantages over other methods because of simple design with sludge free environment and can involve low investment in terms of both initial cost and land required [6&9].

Rice straw is one of the abundant lignocellulosic naturally available materials in the world. In terms of total production, rice is the third most important grain crop in the world. Some of the advantages of using agricultural residues [17&19] such as rice straw include simple technique [17,15&20], little processing requirement, good adsorption capacity, low cost and easy regeneration [12]. The rice straw contains cellulose, hemicellulose and lignin. Rice straw has several characteristics that make it a potential adsorbent with binding sites capable of removing metals from aqueous solution [5&11].

The aim of this study is to find out the effectiveness of rice straw to be used as an adsorbent for the removal of chromium. In this work, the adsorption behavior was studied by a set of experiments at various conditions including pH, contact time and various adsorbent amounts.

II. MATERIALS AND METHODS

A. Analytical Method

The concentration of chromium was determined from a wastewater using Inductively Coupled Plasma Spectrophotometer (ICP).

B. Preparation of Synthetic Waste Water

Standard Nickel solution was prepared by adding 1g of nickel metal in 20ml of nitric acid and was allowed to dissolve completely and was diluted to 1 liter. The
initial nickel concentration (85 mg/l) was prepared by dilution.

C. Materials

Rice straw which is an agricultural by product has been used as low cost adsorbent. Untreated rice straw was prepared by cutting the straw into small pieces, washed with distilled water, dried in an oven over a period of 24 hrs and then grind into fine powder. Treated rice straw was prepared by using sodium hydroxide solution. 16 g of powdered rice straw was treated with 240 mL of sodium hydroxide solution and dried in oven at 100°C over a period of 24 hrs.

D. Experimental Procedure

Adsorption experiments were conducted in batch process, that is, the solution was kept in separate beakers and was stirred continuously for a particular time and finally samples were analyzed in batches for residual chromium concentration.

E. Batch Adsorption

The influence of rice straw on metal ions removal was investigated under the following experimental conditions. Batch experiments were conducted for varied pH, adsorbent dose, initial chromium concentration and contact time. At desired intervals, effluent samples were collected, filtered using whatman filter paper and analyzed for concentration of chromium. The amount of metal ion adsorbed was calculated as:

\[
\% \text{ Adsorption} = \frac{(C_i - C_f)}{C_i} \times 100 \tag{1}
\]

Where \( C_i \) and \( C_f \) are the initial and final concentrations of the metal ions in the solution (ppm).

III. RESULTS AND DISCUSSIONS

Adsorption studies have been conducted for the removal of chromium and nickel from synthetic wastewater. In order to design any adsorption system, optimization of various operating parameters such as adsorbent dose, pH and contact time are of vital importance. To ascertain the above parameters batch adsorption studies were conducted. Based on the objectives of the present study, laboratory adsorption tests were conducted and the results have been discussed in the following sections.

Batch adsorption technique is widely used for water and wastewater treatments. In batch adsorption process the various operating parameters such as adsorbent dose, pH and contact time have been investigated. The batch adsorption data has been used in the adsorption isotherm models such as Freundlich, Langmuir and Tempkin equations.

A. Effect of pH:

The pH of the aqueous solution plays a vital role in controlling the adsorption process. The pH of aqueous solution governs the adsorption of metal ions. The effect of pH on the adsorption capacity of raw and modified rice straw may be attributed to the combined effect of the nature of the surface and the amount of adsorbed species. The minimal adsorption at very low pH may be due to the higher concentration and high mobility of \( H^+ \), which are preferentially adsorbed rather than metal ions. The effect of pH on chromium and nickel removal using both treated and untreated rice straw has been studied. At very low pH, the percentage adsorption decreased due to the involvement of less number of anions on the positive surface. At higher pH due to more OH \(^-\) ions adsorbent surface carrying net negative charges, which tend to repulse the metal anions. Therefore, maximum removal from aqueous solution was achieved at higher pH. From the Fig.1, it is seen that adsorption rate for chromium increases with increase in pH for both treated and untreated rice straw from pH 2 to pH 6 and pH 2 to pH 4 respectively and there onwards chromium removal was found to be gradual.

![Effect of pH on the Removal of Chromium and Nickel](image)

B. Effect of Adsorbent Dosage

The adsorbent dosage is an important parameter in adsorption studies because it determines the capacity of adsorbent for a given initial concentration of metal ion solution. To study the effect of adsorbent dose on adsorption of chromium, a plot is drawn for percent removal versus adsorbent dosage for fixed initial concentrations of 20mg/l for chromium for both untreated and treated adsorbent shown in Fig.2. From these figure, it is evident that the percent removal of chromium for both treated and untreated adsorbent increases with increase in adsorbent dosage. This may be due to some of the adsorption sites remaining unsaturated during the adsorption process. In the present study adsorbent dosage was varied and equilibrated at an initial chromium ion concentration of 20 mg/l. The removal efficiency decreased with increase in adsorbent dosage for a given initial metal
concentration. The percent removal of chromium concentration for both treated and untreated adsorbent increased with increase in adsorbent dosage. The increase in the adsorbent dosage leads to a greater availability of the exchangeable sites or surface area of the adsorbent. For chromium, the optimum dosage for untreated and treated rice straw was found to be 8g/100ml.

Freundlich adsorption isotherm is obeyed by the adsorptions where the adsorbate forms a monomolecular layer on the surface of the adsorbent.

\[ \frac{x}{m} = kp^{1/n} \]  

(Freundlich adsorption isotherm) \hspace{1cm} (2)

The linear form of Freundlich isotherm can be represented as:

\[ \log \frac{x}{m} = \log k + \frac{1}{n} \log C_e \]  

(3)

where \( x \) is the weight of the adsorbate adsorbed by \( m \) gm of the adsorbent, thus \( x/m \) represents the amount of adsorbate adsorbed by the adsorbents per gm (unit mass), \( k \) and \( n \) are constants at a particular temperature and for a particular adsorbent and adsorbate. The magnitude of the exponent, \( 1/n \), gives an indication of the favorability of adsorption. Values of \( n > 1 \) represent favorable adsorption condition.

\[ \frac{x}{m} = q_e \]  

(4)

In the present study the values of Freundlich constants ‘\( k_f \)’ and ‘\( 1/n \)’ for chromium were determined from linear plots of \( \log q_e \) against \( \log C_e \) as depicted in Fig 4. The values of ‘\( k_f \)’ and ‘\( 1/n \)’ were found to be 8.317 and 0.830 for untreated rice straw, 2.606 and 0.208 for treated rice straw respectively (Table-1). The values of \( k_f \) and \( 1/n \) for nickel was found to be 93.325 and 0.871 for untreated rice straw and 40.36 and 0.534 for treated rice straw as shown in Fig 5.

C. Effect of Contact Time:

Equilibrium time is a crucial parameter for an optimal removal of metal ions in the wastewater. From the Fig 4.5, it is observed that at 40 min the chromium removal was found to be maximum of 65% at 50 min, it was found to be 91% for untreated and treated rice straw (Fig.3).

D. Adsorption Isotherms

Adsorption isotherm is a quantitative relationship describing the equilibrium between the concentration of adsorbate in solution and its adsorbed concentration. In the present study adsorption isotherms have been used to describe adsorption behavior and to estimate the adsorption capacity of rice straw on the removal of heavy metals from wastewaters. In this, adsorption equilibrium data has been fitted with Langmuir, Freundlich, and Temkin adsorption isotherm equations.

E. Freundlich Isotherm:

Figure 2: Effect of Adsorbent Dosage on the Removal of Chromium and Nickel

Figure 3: Effect of Contact Time on the Removal of Chromium and Nickel

Figure 4: Freundlich Isotherm for Chromium Removal Using Rice Straw

Figure 5: Freundlich Isotherm for Nickel Removal Using Rice Straw
Table 1: Freundlich Isotherm Constants for Chromium and Nickel

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Freundlich Constants</th>
<th>1/n</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chromium</td>
<td>K_f</td>
<td>1/n</td>
<td>R²</td>
</tr>
<tr>
<td>Untreated rice straw</td>
<td>8.317</td>
<td>0.83</td>
<td>0.979</td>
</tr>
<tr>
<td>Treated rice straw</td>
<td>2.606</td>
<td>0.208</td>
<td>0.954</td>
</tr>
<tr>
<td>Nickel</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Untreated rice straw</td>
<td>93.325</td>
<td>0.871</td>
<td>0.994</td>
</tr>
<tr>
<td>Treated rice straw</td>
<td>40.36</td>
<td>0.534</td>
<td>0.928</td>
</tr>
</tbody>
</table>

**Langmuir adsorption isotherm**

The Langmuir[8] adsorption model is valid for single layer adsorption. The Langmuir isotherm is represented by Eqn. (5):

\[ q_e = \frac{q_m b C_e}{(1 + b C_e)} \]  

Where \( q_e \) = amount adsorbed per unit weight of adsorbent, \( b \) = Langmuir’s constant related to the enthalpy of the process, \( q_m \) = adsorption capacity to form the single layer, \( C_e \) = equilibrium concentration of adsorbate in solution after adsorption in mg/L.

The linear form of Langmuir isotherm can be represented in Eqn. (6) as:

\[ \frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{1}{q_m} C_e \]  

In the present study, removal of chromium using untreated and treated rice straw as adsorbent has been attempted and the Langmuir constant \( q_m \) and \( b \) are determined from the linear plot of \( C_e/q_e \) versus \( C_e \). The plots of \( C_e/q_e \) versus \( C_e \) for the untreated and treated rice straw have been made, is presented in Fig 6. From the Fig 7, the values of adsorption intensity ‘\( q_m \)’ and adsorption capacity ‘\( b \)’ were found to be 1.984 and 0.153; and 3.921 and 0.089 for untreated and treated rice straw, respectively.

The essential feature of the Langmuir isotherm can be expressed in terms of Separation factor (\( R_L \)) which is a dimensionless constant also referred to equilibrium parameter. \( R_L \) can be calculated by using Eqn. (7).

\[ R_L = \frac{1}{1 + b C_o} \]  

where, \( C_o \) is the initial adsorbate concentration (mg/L), \( b \) can be obtained from Langmuir plot of \( C_e/q_e \) versus \( C_e \). The separation factor \( R_L \) indicates the isotherm shape as:

- \( R_L > 1 \) Unfavorable
- \( R_L = 1 \) Linear
- \( 0 < R_L < 1 \) Favorable
- \( R_L = 0 \) Irreversible

In the present study the value of \( R_L \) was found to be 0.5252 for untreated rice straw and 0.0331 for the treated rice straw for chromium and 0.285 and 0.152 for nickel respectively (Table-2). From the result, it is evident that the values of \( R_L \) obtained for the removal of chromium and nickel using untreated and treated rice straw as adsorbents are between 0 and 1, the adsorption process was found to be favorable and best fitted to Langmuir isotherm.

Similar study was conducted by Khaldoun Al-Sou'od, [6], for the adsorption of chromium by Jordanian pottery material and it was found that Langmuir was the best with average \( R^2 \) value of 0.998 and the maximum value of monolayer adsorption capacity was found. Another study by Nameni et al.[13], showed that the Langmuir adsorption isotherm was the best model for the chromium removal on wheat bran with a correlation coefficient (\( R^2 \)) of 0.997.
Table 2: Langmuir Isotherm Constants for Chromium and Nickel

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Langmuir constants</th>
<th>( R_L )</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated rice straw</td>
<td>0.2852 0.1452</td>
<td>0.5252</td>
<td>0.898</td>
</tr>
<tr>
<td>Treated rice straw</td>
<td>1.6103 1.603</td>
<td>0.0331</td>
<td>0.993</td>
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</table>

### Nickel

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Langmuir constants</th>
<th>( R_L )</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated rice straw</td>
<td>1.984 0.153</td>
<td>0.285</td>
<td>0.996</td>
</tr>
<tr>
<td>Treated rice straw</td>
<td>3.921 0.089</td>
<td>0.152</td>
<td>0.966</td>
</tr>
</tbody>
</table>

**Temkin adsorption isotherm:**

Temkin\(^{[18]}\) adsorption isotherm equation assumes that heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent-adsorbate interaction, and adsorption is characterized by a uniform distribution of the binding energies, up to certain maximum binding energy. Temkin isotherm can be expressed using the Eqn. (8)

\[
\theta = \frac{RT}{\Delta Q} \log k_o C_e \tag{8}
\]

where, \( \theta = (q/q_m) \) = Fractional coverage, \( R \) = Universal gas constant (KJ/mol/K), \( T \) = Temperature (K), \( \Delta Q \) = Variation of adsorption energy (KJ/mol), \( k_o \) = Temkin equilibrium constants (L/mg)

The linear form of Temkin adsorption isotherm can be represented by Eqn. (9).

\[
\theta = \left(\frac{RT}{\Delta Q}\right) \log k_o + \left(\frac{RT}{\Delta Q}\right) \log C_e \tag{9}
\]

The variation of adsorption energy (\( \Delta Q \)) is positive for all the phenolic compounds studied, which indicates that the adsorption reaction is exothermic. However, in the present study the value of Temkin constants ‘\( \Delta Q \)’ and ‘\( k_o \)’ were determined from linear plots of \( \theta \) versus log \( C_e \) as shown in figs. 8 & 9 for chromium and nickel respectively. It is observed that the variation of adsorption energy (\( \Delta Q \)) values for chromium is -16.172KJ/mol and -58.158KJ/mol for untreated and treated rice straw respectively. Similarly, the values for nickel are -13.465KJ/mol and -25.850KJ/mol for untreated and treated rice straw respectively (Table 3). The values are negative for untreated and treated rice straw for both chromium and nickel, which indicates that adsorption reactions are endothermic.

### Figure 8: Tempkin Isotherm for Chromium Removal Using Rice Straw

### Figure 9: Tempkin Isotherm for Nickel Removal Using Rice Straw

### Table 3: Tempkin Isotherm Constants For Chromium and Nickel

<table>
<thead>
<tr>
<th>Parameter</th>
<th>TempinkinIsotherm</th>
<th>( k_o )</th>
<th>( \Delta Q )</th>
<th>( R^2 )</th>
</tr>
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<tbody>
<tr>
<td>Chromium</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Untreated rice straw</td>
<td>0.968 -16.172</td>
<td>0.981</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Treated rice straw</td>
<td>0.941 -58.158</td>
<td>0.972</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nickel</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Untreated rice straw</td>
<td>0.952 -13.465</td>
<td>0.998</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Treated rice straw</td>
<td>0.948 -25.850</td>
<td>0.948</td>
<td></td>
<td></td>
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</tbody>
</table>

### CONCLUSIONS

Batch adsorption tests were conducted on the removal of Nickel present in the wastewaters. Effects of adsorbent dosage depend upon initial solute concentrations. It is seen from the results that at 8 g/100mL and 8 g/100mL of untreated and treated rice straw could remove about 65 % at 40 min contact time and 80% at 50 min contact time of nickel respectively.
The optimum pH for untreated rice straw was 4 and for treated rice straw it was found to be 4. From the Temkin adsorption isotherm studies, the value of variation of adsorption energy (ΔQ) was found to be -13.465KJ/mol and -25.850KJ/mol for untreated and treated rice straw, respectively. The value of variation of adsorption energy (ΔQ) is negative for untreated and treated rice straw, which indicates, the adsorption reaction is endothermic. Among the various adsorption isotherms studied, the adsorption process fits well with the Langmuir isotherm.

**References**


