Fixed Bed Column Study for the Removal of Copper from Aquatic Environment by NCRH

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Abstract - This paper reports the results of the study on the performance of low-cost adsorbent such as NCRH in removing copper. The adsorbent materials adopted were found to be an efficient media for the removal of heavy metals in continuous mode using fixed bed column. The fixed bed column experiment was conducted in a column having a diameter of 2 cm with 10 mg/l Cu(II) solution at a bed depth of 10 cm maintaining a constant flow rate of 10 ml/min. The breakthrough and exhaust time were found to be 3.583 and 10.500 h, respectively. Height of adsorption zone was found to be 10.21 cm and the rate at which the adsorption zone was moving through the bed was 1.48 cm/h. The percentage of the total column saturated at breakthrough was found 44.95%. The value of adsorption rate coefficient (K) and adsorption capacity coefficient (N) were obtained as 0.056 l/(mg h) and 1623 mg/l, respectively.

Keywords : copper, NCRH, breakthrough curve, adsorption rate coefficient, adsorption capacity coefficient.

GJRE-C Classification : FOR Code: 030504

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Abstract - This paper reports the results of the study on the performance of low-cost adsorbent such as NCRH in removing copper. The adsorbent materials adopted were found to be an efficient media for the removal of heavy metals in continuous mode using fixed bed column. The fixed bed column experiment was conducted in a column having a diameter of 2 cm with 10 mg/l Cu(II) solution at a bed depth of 10 cm maintaining a constant flow rate of 10 ml/min. The breakthrough and exhaust time were found to be 3.583 and 10.500 h, respectively. Height of adsorption zone was found to be 10.21 cm and the rate at which the adsorption zone was moving through the bed was 1.48 cm/h. The percentage of the total column saturated at breakthrough was found 44.95%. The value of adsorption rate coefficient (K) and adsorption capacity coefficient (N) were obtained as 0.056 l/(mg h) and 1623 mg/l, respectively.

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I. Introduction

Water pollution due to toxic heavy metals has been a major cause of concern. The industrial and domestic wastewater is responsible for causing several damages to the environment and adversely affecting the health of the people. Metals can be distinguished from other toxic pollutants, since they are nonbiodegradable and can accumulate in living tissues, thus becoming concentrated throughout the food chain. As one of the important toxic heavy metals, copper finds its way to the water stream from industries like electroplating, mining, electrical and electronics, iron and steel production, the non-ferrous metal industry, the printing and photographic industries and metalworking and finishing processes. Moreover, copper sulfate has been used in eutrophic lakes to kill the algae since the early 1990s and is still widely used today. Trace amounts of copper are essential to human and many other living species. However, the intake of excessively large doses of Cu(II) by human may lead to severe mucosal irritation, a central nervous system irritation, possible necrotic changes in the liver and kidney, etc., and the recommended maximum acceptable concentration of Cu(II) in drinking water by the World Health Organization (WHO) is 1.5 mg/L. As per U.S. Environmental Protection Agency (EPA) maximum acceptable concentration in drinking water is 1.3 mg/L.

Various treatment techniques have been employed to eliminate or reduce heavy metals in wastewater including precipitation, adsorption, ion exchange and reverse osmosis. As of now, adsorption by activated carbon is accepted to be the best available technology for the reduction of heavy metals, except that its manufacturing cost is quite high. Hence, a search is on worldwide for a low-cost alternative. Research in the recent years has indicated that some natural biomaterials including agricultural products and by-products can accumulate high concentration of heavy metals. Adsorbent generated from these biomass are cost effective and efficient. Low-cost agricultural products and by-products have been reported to be effective in removing heavy metals. Adsorption process of heavy metals present in aqueous solution by low-cost adsorbents from plant wastes can be carried out with or without chemical modifications. In general, chemically modified plant wastes exhibit higher adsorption capacities than unmodified forms.

In our continued study on the use of low-cost material for the removal of organic and heavy pollutants from water and wastewater we investigated rice husk as a sorbent for the removal of Cu(II). Some simple and low-cost chemical modifications resulted in increasing the sorption capacity of raw rice husk. The highly efficient low cost and the rapid uptake of Cd(II) by NCRH indicated that it could be an excellent alternative for the removal of heavy metal by sorption process.

Agricultural products and by-products have been reported to be effective in removing copper. Rice husk consists of cellulose (32.24%), hemicelluloses (21.34%), lignin (21.44%) and mineral ash (15.05%) as well as high percentage of silica in its mineral ash, which is approximately 96.34%. Rice husk is insoluble in water, has good chemical stability, has high mechanical strength and possesses a granular structure, making it a good adsorbent material for treating heavy metals from wastewater. Rice husk, an abundant agricultural product, is capable of removing heavy metals and can be considered as an efficient and low-cost adsorbent for heavy metals. The present study has been undertaken to report the Cu(II) adsorption in the fixed bed column process. In recent years, attention has been taken on the utilization of unmodified or modified rice husk as a sorbent for the removal of pollutants.

II. Materials and Methods

a) Equipments and Chemicals

All chemicals used were of analytical grade (BDH, India). Stock solutions of 100 mg/l were prepared...
using metal nitrate salts, which were diluted with distilled water to prepare working solutions. Cyberscan 510 model pH meter was used for the measurement of pH of the solution. A peristaltic pump (Miclins India Limited, PP 30) was also used for providing constant flow of metal and desorbing solution in fixed bed column. The metal ion concentrations in the solution were analyzed using atomic absorption spectrophotometer (AA-6650, Shimadzu).

b) Preparation of adsorbent

Fresh rice husk was obtained from a local rice mill and was passed through different sieve size. The fraction of particle between 425 and 600 micron (geometric mean size: 505 micron) was selected. The rice husk was washed thoroughly with distilled water. It was dried at 60°C. The sorbent thus obtained was designated Raw Rice Husk (RRH). Rice husk was treated with 0.1 M sodium carbonate solution at room temperature for 4 h. Excess of sodium carbonate was removed with distilled water and the material was dried at 40°C. This material was designated as sodium carbonate treated rice husk (NCRH).

c) Experimental Studies

Fixed bed column study for Cu(II) removal from wastewater by NCRH was conducted using a column of 2 cm diameter and 55 cm length. The column was packed with NCRH between two supporting layers of pre-equilibrated glass wool. The bulk density of NCRH packed in the column was 0.267 g/cm$^3$. The column bed depth was kept 10 cm. The schematic diagram of column study is shown in Fig. 1. The study was conducted at temperature of 28 ± 2°C and the pH of the Cu(II) solution as 6.0 ± 0.2 for the present study. The column was charged with Cu(II) bearing wastewater with a volumetric flow rate of 10 ml/min (~ 2.10 m$^3$/m$^2$/h). The initial concentration of Cu(II) was 10 mg/l. The samples were collected at certain time intervals and were analyzed for Cu(II) using atomic absorption spectrophotometer (AA-6650, Shimadzu).

III. Results and Discussions

a) Behavior of adsorption column

The fixed bed column experiment was conducted with 10 mg/l Cu(II) solution at a bed depth of 10 cm maintaining a constant flow rate of 10 ml/min. The breakthrough curve of S-shaped was obtained as shown in Fig. 2. The breakthrough time (corresponding to C/Co = 0.1) and exhaust time (corresponding to C/Co = 0.9) were found to be 3.583 and 10.500 h respectively. The corresponding volumes of wastewater treated were 2.15 and 6.30 liters respectively. About 8.39 gm of NCRH were used in the 10 cm column. The volume of metal effluent treated and the requirement of NCRH up to breakpoint have been shown in Table 1. The market price of activated carbon for industrial grade is US $ 20-22 (Rs. 1000 – 1100) per kg depending on the quality. The cost of NCRH is in India was estimated as only Rs. 4 per Kg (US $ 0.08). Hence, by cost comparison the cost, NCRH is about 250 times cheaper than activated carbon. Cost for volume of metal effluent treated up to breakpoint per kg of NCRH has been calculated and has been presented in Table 6.2.

The formation and movement of the adsorption zone has been described mathematically. The time required for the exchange zone to move the length of its own height up/down the column once it has become established is

$$t_z = \frac{V_E - V_R}{Q_w}$$

(1)
Where,

\[ V_E = \text{volume of wastewater treated to the point of exhaustion (l)} \]

\[ V_B = \text{volume of wastewater treated to the point of breakthrough (l)} \]

\[ Q_w = \text{wastewater flow rate (l/h)} \]

The time required for the exchange zone to become established and move completely out of the bed is

\[ t_E = \frac{V_E}{Q_w} \]  

(2)

Rate at which the exchange zone is moving up or down through the bed is

\[ U_z = \frac{h_z}{t_z} = \frac{h}{t_E - t_f} \]

(3)

where,

\[ h = \text{height of exchange zone (cm)} \]

\[ h = \text{total bed depth (cm)} \]

\[ t_f = \text{time required for the initially form (h)} \]

Rearranging Eq. 3 provides an expression for the height of the exchange zone as given below.

\[ h_z = \frac{h(t_z)}{t_E - t_f} \]  

(4)

The value of \( t_f \) can be calculated as follows.

\[ t_f = (1 - F)t_z \]  

(5)

At breakthrough the fraction of adsorbate present in the adsorption zone still possessing ability to remove solute is

\[ F = \frac{S_z}{S_{\text{max}}} = \frac{\int (C_0 - C) dV}{V_E - V_B} \]

(6)

Where,

\[ C_0 = \text{initial solute concentration (mg/l)} \]

\[ S_z = \text{amount of solute that has been removed by the adsorption zone from breakthrough to exhaustion} \]

\[ S_{\text{max}} = \text{amount of solute removed by the adsorption zone if completely exhausted} \]

The percentage of the total column saturated at breakthrough is

\[ \% \text{saturation} = \frac{h + (F - 1)h_z}{h} \times 100 \]  

(7)

The values of the important design parameters were calculated using the data from breakthrough curve. Height of adsorption zone was found to be 10.21 cm and the rate at which the adsorption zone was moving through the bed was 1.48 cm/h. The percentage of the total column saturated at breakthrough was found to be 44.95 %.

b) Evaluation of adsorption column design parameters

Data collected during laboratory and pilot plant tests serve as the basis for the design of fullscale adsorption columns. A number of mathematical models have been developed for the use in design. In the present research work the fixed bed column was designed by logit method \(^{14,15} \). The logit equation can be written as:

\[ \ln \left( \frac{C / C_o}{1 - C / C_o} \right) = -\frac{K N_o X}{V} + K C_o t \]  

(8)

Where,

\[ C = \text{concentration at any time t} \]

\[ C_o = \text{initial Cu(II) concentration (10 mg/l)} \]

\[ V = \text{approach velocity (210 cm/h)} \]

\[ X = \text{bed depth (10 cm)} \]

\[ K = \text{adsorption rate constant (l/mg-h)} \]

\[ N_o = \text{adsorption capacity constant (mg/l)} \]

Rearranging Eq. 8

\[ \ln \left( \frac{C}{C_o - C} \right) = -\frac{K N_o X}{V} + K C_o t \]  

(9)

Plot of \( \ln C/(C_0 - C) \) vs. t gives a straight line with slope \( KC_o \) and intercept \( -KN_o X /V \) from which \( K \) and \( N_o \) could be calculated. Plot of \( \ln C/(C_0 - C) \) vs. t was shown in Fig. 3. The values of adsorption rate constant (K) and adsorption capacity constant (N_o) were obtained as 0.056 l/mg.h and 1623 mg/l (1.623 kg/m\(^3\)) respectively. These values could be used for the design of adsorption columns. The adsorption capacity was found to be good. Hence, it could be concluded that NCRH is effective for Cu(II) removal.
NCRH was found to be efficient media for the removal of Cu(II) from aquatic environment. The column with 2 cm diameter, and bed depth 10 cm could treat 2.15 liters of Cu(II) at breakthrough, at initial concentration 10 mg/l. About 3.90 g of NCRH was required per liter of Cu(II) treatment. Height of adsorption zone was found to be 10.21 cm and the rate at which the adsorption zone was moving through the bed was 1.48 cm/h. The values of adsorption rate constant (K) and adsorption capacity constant (N_o) were obtained as 0.056 l/mg.h and 1623 mg/l respectively.

**References**


**Table 1**: Volume of effluent treated and the mass of NCRH required up to breakthrough

<table>
<thead>
<tr>
<th>Bed depth (cm)</th>
<th>10% Breakthrough time (hr)</th>
<th>Treated volume (lts)</th>
<th>Total mass of NCRH (gm)</th>
<th>Mass per litre (gm/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>3.583</td>
<td>2.15</td>
<td>8.39</td>
<td>3.90 gm</td>
</tr>
</tbody>
</table>

**Table 2**: Cost for volume of metal effluent treated up to breakpoint per kg of NCRH

<table>
<thead>
<tr>
<th>Metal</th>
<th>Volume of metal effluent treated per kg of NCRH</th>
<th>Cost per kg NCRH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(II)</td>
<td>256 litres</td>
<td>@ Rs. 4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>@ US $ 0.08</td>
</tr>
</tbody>
</table>