Removal of Zn$^{2+}$ Ions from Aqueous Solution Using Rice (Oryza Sativa) Husk in a Sequential Bed Adsorption Column

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ABSTRACT

The rapid growth of industrialization in the world has caused changes in the chemical and biological properties of both surface and ground water which constitute a health hazard. Heavy metals find their way into water bodies mainly from the refuge of electroplating, tannery, paint and power generation industries. The heavy metals render the water unsuitable for drinking and are also highly toxic to human beings. Removal of these materials is therefore essential. Adsorption on activated carbon is the most widely used method for removal because of the simplicity of the procedure in comparison to other methods. However, the use of activated carbon is not economical for small scale industries and studies pertaining to the use of inexpensive agro-based adsorbents, such as tree bark, saw dust, corn cob, straw, and fly ash etc. for heavy metal ion removal are gaining a lot of importance. In the present study removal of Zn$^{2+}$ ions has been investigated using a sequential bed adsorption column and results compared to those obtained by using a vertical column.

Batch adsorption studies have shown that removal is dependent upon process parameters like contact time, metal ion concentration and pH. Maximum removal of Zn$^{2+}$ (to the extent of 75%) has been achieved at pH 8 in 2.5 h in the concentration range 30 to 300 mgL$^{-1}$. The use of sequential bed adsorption column has been investigated at the optimized conditions, to study the feasibility of the process for application in small scale industries.

The sorption data obtained from batch studies at optimized conditions have been subjected to Freundlich and Langmuir isotherm studies. The data fits well to both the Freundlich and Langmuir isotherm models indicating favourable and monolayer adsorption. Freundlich and Langmuir constants have been calculated. The Langmuir constant, $b$, has been used to calculate the dimensionless factor, $R_L$ in the concentration range studied.

Keywords : adsorption, Langmuir isotherm studies, intraparticle diffusion, batch studies.

INTRODUCTION

Removal of heavy metals from industrial waste water is of primary importance because they not only cause contamination of water bodies but are also toxic to many life forms. Since most of heavy metals are non-degradable and toxic (Calace et al 2002) so their concentration must be reduced to acceptable levels before discharging into environment, otherwise these can pose a threat to public health. The metals of most immediate concern are zinc, chromium, iron, nickel, mercury, cadmium and lead (Kadirvelu et al 2001). Most zinc enters the environment as a result of human activities such as mining, purifying zinc, lead and cadmium ores, steel production, coal burning, galvanizing and from the waste water of pharmaceuticals, paints, pigments, insecticides, cosmetics and industries (Bhattacharya 2006). Technologies generally used for the removal of heavy metals such as ion exchange, chemical precipitation, ultra-filtration, reverse osmosis, electrochemical dispersion etc. do not seem to be economically feasible because of their high cost (Axtell et al 2003: Kandah 2004). As a result, recent research has been focused on development of cost effective alternatives. Adsorption is one of the physico-chemical treatment process found to be effective in removing heavy metals from aqueous solution using low cost adsorption (Bailey et al (1999). Most commonly used adsorbents are untreated plants wastes such as teak leaf powder (King et al 2006), rubber leaf powder (Hanafiah 2006), papaya wood (Saeed et al 2005), newspaper pulp (Chakravarthy et al 2007), baggage fly ash (Gupta and Sharma 2003), banana and orange peels (Annadurai et al 2003), carrot residue (Eslamzadah 2004), tea waste (Mahvi et al 2005), etc.

The objective of the present study is to investigate the sequential bed adsorption column in order to study the feasibility of the process for application in small scale industries. The results are compared to those obtained by using a vertical column. Batch adsorption studies have been carried out to study the effect of pH, contact time, metal ion concentrations, different particle sizes of adsorbent as well as temperature effects. Experimental
The rice husk (variety PR 106) was procured from the agricultural land of Sangrur, Punjab, India. This was crushed, sieved, washed with distilled water and dried at ∼ 80°C. The particles retained on 20, 40 and 60 mesh number were used for the experiment. Stock solution of the metal ions was obtained by dissolving the required amount of metal sulphate (Merk, A.R. grade) is distilled water. Different initial metal ion concentrations were prepared by making suitable dilutions.

**Batch adsorption studies**

Batch experiments were carried out by agitating a known weight of rice husk placed in contact with 100 ml of metal ion solutions of different concentrations. The suspension was continuously stirred in a shaker, the effect of pH and initial metal ion concentration have been studied for pH range 4-9 and for initial metal ion concentrations ranging from 30-300 mg/L of zinc, which corresponds to the concentration of the metal ion found in effluents from related industries. The pH of the solution was adjusted by the addition of ammonium chloride and ammonium hydroxide or H₂SO₄ solutions. The contact time was varied from 0.5 to 3.0 hrs, the Zn²⁺ ion concentration was determined titrimetrically by the standard method using EDTA solution (Vogel, 1978).

**Column adsorption studies**

The sequential bed column was constructed by connecting glass tubes to contain the adsorbent (figure 1) without using other materials that could affect the adsorbate speed. The use of feed pumps was also avoided by taking into account the flow under gravity. The first tube, filled with solid adsorbent, received the influent (controlled by a valve) which flowed through the second tube and so on. The flow rate was controlled in such a way that contact time in the column is in the range of 2 to 3 h (hours). At the end of the column a container was collecting the treated solution.

![Figure 1. Sequential bed adsorption column](image)

**RESULT AND DISCUSSIONS**

**Effect of pH**

Effect of pH on the adsorption characteristics of rice husk was determined in the pH range 4-9, studies indicate that the system is strongly pH dependent. The rate of adsorption is maximum at pH 8, as is apparent from figure 2. The sorption rate is lower in acidic ranges because at low pH, due to high positive charge density there is electrostatic repulsion resulting in lower rate of adsorption (Bhattacharya et al 2006). With increasing pH, electrostatic repulsions decrease due to reduction of positive charge density on the sorption sites of adsorbent resulting in increase in rate of adsorption.

<table>
<thead>
<tr>
<th>SEQUENTIAL COLUMN</th>
<th>VERTICAL COLUMN</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. of Beds used = 4</td>
<td>Length of the column = 60 cm</td>
</tr>
<tr>
<td>Bed diameters = 2.5 cm</td>
<td>Diameter of the column = 4 cm</td>
</tr>
<tr>
<td>Bed depth = 3 cm.</td>
<td>Bed height = 50 cm</td>
</tr>
</tbody>
</table>

Removal efficiency % = \[ \frac{C_0 - C_i}{C_0} \times 100 \]

where \( C_0 \) and \( C_i \) are metal concentration in sample solution before and after treatment respectively. The column parameters for sequential bed as well as vertical columns have been presented in table 1.
Effect of contact time

Contact time is also an important factor affecting removal, most of adsorption occurs in the initial half hour and increases very slowly later similar results have been reported by Sharma and Kareer (2006) for adsorption of cobalt on rice husk. A further increase in contact time tends to decrease adsorption (Figure 2), probably due to desorption. Variation of time of contact from 0.5 to 3.0 hours shows that maximum removal occurs at 2.5 hours.

Effect of metal concentration

The concentrations of Zn(II) ranging from 30-300 mg/L were used in the experiment, this corresponds to the concentration of the metal ion found in effluents from related industries. The amount of metal ion adsorbed increases with concentration, however, percentage removal increases with decrease in the concentration of Zn ions . The increase in percentage adsorption with dilution is explained on the basis of availability of larger number of surface sites of the adsorbent for a relatively small number of adsorbing species at high dilution (Parekh et al., 2002; Raji et al., 1997).

Effect of particle size

Adsorption of Zn(II) has been studied on rice husk particles of varying sizes----those retained on 20 mesh, 40 mesh and 60 mesh respectively. The experimental data shows that amount of Zn(II) adsorbed decreases with increase in particle size of the adsorbent. The percentage adsorption on 20 mesh is 75%, on 40 mesh is 72% and on 60 mesh is 68.3%. Higher rate of removal by adsorbent with smaller particle size is due to availability of more surface area on the adsorbent (Karthikeyan et al 2004).

Effect of temperature

The temperature dependence of adsorption studies of Zn(II) by rice husk was studied over the range of 25°C to 45°C (298K – 318K). Increase of temperature from 25°C to 45°C increases the sorption, indicating the process is endothermic, similar observations have been reported by Pandey et al (1985) for adsorption of Cu(II) onto flyash and Karthikeyan et al (2004) for adsorption of Zn(II) onto chitosan. The increase in uptake of Zn(II), with temperature may be due to desolvation of the adsorbing species, the change in pore size and enhanced rate of intraparticle diffusion of adsorbate as diffusion is an endothermic process.

Adsorption isotherm studies

The data for the uptake of Zn(II) by rice husk has been analyzed in the light of Freundlich model of adsorption and adsorption of Zn(II) on rice husk was also found to confirm to Freundlich adsorption isotherm at all the temperatures studied. The linearised form of the Freundlich equation can be given as :

$$\log q_e = \frac{1}{n} \log C_e + \log K_f$$

where $C_e$ is the equilibrium concentration (mg/L) and $q_e$ is the amount adsorbed (mg/g). The values of $n$ and $K_f$ at different temperatures were determined from slope and intercept of the linear plots of $\log q_e$ vs. $\log C_e$ (Figure 3). The values of $n$ are 1.109,1.200, 1.198 and those for $k$ are 0.0462, 0.0465 and 0.0471 at temperatures 25°C, 35°C and 45°C respectively. (The values of 1<n<10 indicate the
The data also are also in consistence with the Langmuir model; the Langmuir equation may be described as $C_e/q_e = 1/Q_0b + C_e/Q_0$ where $C_e$ is the equilibrium concentration mg/L, $q_e$ is the amount adsorbed at equilibrium mg/g and $Q_0$ and $b$ are Langmuir constants related to adsorption capacity and energy of adsorption, respectively. The plot of $C_e/q_e$ vs. $C_e$ gives straight line at each temperature as shown in figure 4, showing the applicability of Langmuir isotherm (Hu et al., 2006). The applicability of the isotherm models and the high values of the correlation coefficients ($r^2$ values are in the range 0.9321 to 0.9872) suggests favourable and monolayer adsorption (Hu et al 2006). The values of $Q_0$ and $b$ at different temperatures as determined from slope and intercept of the Langmuir plot and are given in table 2. The essential characteristics of Langmuir isotherm can be described by the dimensionless parameter $R_L$;

$$R_L = \frac{1}{bC_0}$$ where $C_0$ is the initial metal ion concentration. The factor $R_L$ indicates whether adsorption is favourable or not. The values of $R_L$ have been found to be between 0 and 1 which suggests favourable adsorption (Sharma et al 2007, Meena and Rajagopal 2003).

The free energy change ($\Delta G^0$) for the process has been calculated using the following equation (Meena et al 2005).

$$\Delta G^0 = -RT \ln K_c$$ where

$$K_c = \frac{C_{Ad}}{C_e}$$

$K_c$ is equilibrium constant and $C_{Ad}$ and $C_e$ are the equilibrium concentrations (mg/L) of the metal ion on the adsorbent and in the solution respectively. The negative values of $\Delta G^0$ (table 2) indicate feasibility and spontaneous nature of adsorption of metal ions on the adsorbent.

![Freundlich adsorption isotherm](image)

Figure 3. Freundlich adsorption isotherm for adsorption of Zn on Rice Husk at different temperatures at pH 8 and metal concentration 300mg/L

<table>
<thead>
<tr>
<th>Temperature, ºC</th>
<th>Langmuir constants</th>
<th>$K_c$</th>
<th>$\Delta G^0$, KJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>84.03</td>
<td>3.67 x 10^-4</td>
<td>1.01</td>
</tr>
<tr>
<td>35</td>
<td>71.42</td>
<td>4.38 x 10^-4</td>
<td>1.12</td>
</tr>
<tr>
<td>45</td>
<td>75.18</td>
<td>4.15 x 10^-4</td>
<td>1.25</td>
</tr>
</tbody>
</table>
Intraparticle diffusion study

Besides adsorption at the outer surface of rice husk there is also possibility of intraparticle diffusion from the outer surface into the pores of the material. The possibility was explored by plotting amount of Zn(II) adsorbed vs. $t^{1/2}$ for different dosages and particle sizes, according to Weber and Morris equation, $q_t = K_p t^{1/2}$ (Sharma and Kareer 2006) where $q_t$ is amount of Zn adsorbed at time $t$ in mg/g , $t$ is time of contact (min) and $K_p$ is intraparticle diffusion constant (mg/g/min$^{1/2}$)

Figure 5 describes the plots of $q_t$ against time with half power (i.e. $t^{1/2}$) for different particle sizes of the adsorbent. The $K_p$ values for three different particle sizes i.e. 20 Mesh, 40 Mesh and 60 Mesh are 0.2845, 0.2818 and 0.2678 respectively. This shows that decreasing particle size increases the adsorption of Zn(II) on rice husk. For large particles the diffusional resistance to mass transport is higher and most of the internal surface of the particle may not be utilized for adsorption and consequently the amount of Zn(II) adsorbed is small. Earlier studies for adsorption of Zn(II) onto Chitosan have reported (Karthikeyan et al 2004) similar conclusions . The values of $K_p$ for different metal ion concentrations are 0.0264, 0.0852, 0.1991, 0.1053 and 0.1748 for metal ion concentrations of 30, 60, 90, 120, 150 mg/L respectively (Figure 6). $K_p$ values give an idea about the surface porosity, higher the value of $K_p$, more porous is the surface.
Figure 6. Intraparticle diffusion plot for the adsorption of zinc on rice husk at different Zn\textsuperscript{2+} concentrations at pH 8

Figure 7. Removal efficiency at different flow rates for sequential bed and vertical columns at metal ion concentration of 200 mg/L

**Column studies**

In case of sequential column studies concentrations viz. 200 mg/L, 250 mg/L and 300 mg/L were used in the experiment, maximum removal was observed at 200 mg/L concentration. Removal efficiency decreases with increase in concentration of zinc ions. This can be explained by the fact that as the concentration of zinc ions increases which causes the metal loading on adsorbent i.e. influent concentration 300 mg/L has higher surface loading as compared to 200 mg/L concentration, because it causes an equal increase in no. of zinc ions coming in contact with rice husk increasing during same interval of time while on the other hand the number of the adsorbing sites available for adsorption are constants for all concentrations. However at higher concentrations, the available sites of adsorption becomes fewer hence the percentage of metal ions removed is dependent upon initial concentrations (Parekh et al., 2002). In batch studies maximum adsorption upto 75% decreased to 42% in concentration ranging (30-300 mg/L) while in sequential column studies maximum adsorption upto 85% decreases to 75% then to 66% in concentration ranging (200 mg/L, 250 mg/L and 300 mg/L). In vertical column studies maximum adsorption upto 76% decreases to 65% then 57% in concentration ranging (200 mg/L, 250 mg/L & 300 mg/L) Figure 7.
Figure 8. Removal efficiency at different metal ion concentrations for sequential bed and vertical columns at a flow of 1.2 L/h

**Effect of flow rate**

It is observed that removal efficiency increases with low injection rate and goes on decreasing with increasing injection rate. The maximum removal efficiency up to 85% at the flow rate 1.2 L/hr, removal efficiency decreases to 80.4% when the flow rate is increased to 1.5 L/hr and further removal efficiency decreases to 76% when the flow rate is increased to 1.8 L/hr. In vertical column maximum removal efficiency up to 76% has been observed when the flow rate is 1.2 L/hr and decreases to 69.4% when the flow rate is increased to 1.5 L/hr and further decreases to 65.3% when the flow rate is increased to 1.8 L/hr (Figure 8).

**REFERENCES**


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