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Research Note

Fixed Bed Column Study for the Removal of Zn(II) from Aquatic Waste by Sodium Carbonate Treated Rice Husk

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Abstract: The fixed bed of sodium carbonate treated rice husk (NCRH) was used for the removal of Zn(II) from water environment. The NCRH was found to be a efficient media for the removal of Zn(II) from wastewater. The column having a diameter of 2 cm, with bed depth 10 cm can treat 2.28 litre of Zn(II) bearing wastewater with Zn(II) concentration 10 mg/l and flow rate 9.5 ml/min. A method has been shown to predict the theoretical breakthrough curve using the data obtained from the batch isotherm studies and theoretical breakthrough curve was compared with experimental breakthrough curve.

Key words: Zinc, sodium carbonate treated rice husk (NCRH), adsorption, column study, breakthrough curve.

Introduction

Zinc is mostly released by man-made activities through surface water release, from the discharge of metal manufacturing and chemical industries. Metallic zinc is used to prevent corrosion and it is used in the dry cell batteries. Zinc is mixed with other metals to form alloys such as brass and bronze and is used to make paints, wood protective dyes, ceramics, rubbers, fertilizers and drugs. Surface water releases can also result from runoff after precipitation falls on soils with high zinc concentration either naturally or due to human application of fertilizer in the agricultural fields. Symptoms of zinc toxicity include nausea, vomiting, cough, fever, diarrhea and dehydration. Eating large amount of zinc can cause anemia, damage the pancreas, and lower level of high-density lipoprotein cholesterol. Infertility or low birth rate and skin irritation have been observed in laboratory animals such as rats, rabbits and mice given high doses of zinc. Hence it is important to eliminate trace of zinc from drinking water, or to remove zinc from wastewaters before they are discharged into receiving bodies. 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 world wide 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 zinc, Corncob (Vaughan et al., 2001), Sugar beet pulp (Reddad et al., 2002) and Petiolar felt-sheath of palm (Iqbal et al., 2002) to name a few.

Rice husk, an abundant biomaterial, is capable of removing heavy metals and can be considered as an efficient and low cost adsorbent for heavy metals. The data obtained under batch conditions are generally not applicable to most treatment system (such as column operations) where contact time is not sufficiently long for the attainment of equilibrium (Low and Lee, 1991). Hence, there is a need to perform fixed bed columns studies. Some of the researchers have reported the removal of Zn(II) in fixed bed columns using different adsorbent (Gupta and Ali, 2000; Chen and Wang, 2000; Monser and Adhoum, 2002). Reports regarding the removal of Zn(II) in continuous mode using fixed bed column are only a few. Thus, the present study aims towards the removal of Zn(II) from Zn(II) bearing wastewater in fixed bed column filled with sodium carbonate treated rice husk (NCRH).

Materials and Methods

Reagents, instrumentation and preparation of sodium carbonate treated rice husk (NCRH) is similar and is in accordance with our earlier research work (Kumar and Bandyopadhyay, 2006).

Experimental Methods

Fixed bed column studies were conducted using columns of 2 cm diameter and 55 cm length. The column was packed with NCRH between two supporting layers of pre-equilibrated glass wool. The bed depths were taken as 10 cm. The column was charged with Zn(II) bearing wastewater in the upflow mode with a volumetric flow rate of 9.5 ml/min (~ 1.72 $m^3/m^2/hr$). The initial concentration of Zn(II) was 10 mg/l. The samples were collected at certain time intervals and were analyzed for Zn(II) using atomic absorption spectrophotometer (AA-6650, Shimadzu). The temperature was 28 ± 2°C and the pH was 6.0 ± 0.2 for all studies.

Results and Discussion

Behaviour of Adsorption Column

The breakthrough curves of S-shaped as obtained were shown in Figure 1. The breakthrough times and the exhaust times correspond to $C/C_o = 0.1$ and $C/C_o = 0.9$ respectively. The breakthrough time and volume of Zn(II) treated were obtained as 4.0 hours and 2.28 litres. It was calculated that about 3.70 gm of NCRH is required per litre of Zn(II) removal.

Theoretical Breakthrough Curve

Using the data obtained from the batch isotherm studies, it is possible to predict the theoretical breakthrough curve, which can be well compared with the experimental curve. The theoretical breakthrough was generated with the initial concentration of 10 mg/l, following the concepts of Michaels (1952) as follows:

1. The equilibrium line was prepared using Freundlich adsorption isotherm in batch isotherm studies. The

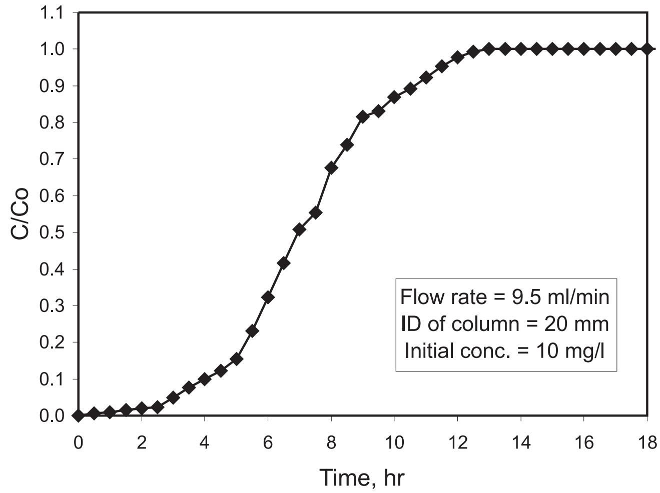

Figure 1: Breakthrough curves for Zn(II) at bed depth of 10 cm.

equilibrium adsorption data were fitted to Freundlich model as shown below.

$$q_e = K_F\,(C_e)^{1/n} \qquad (1)$$

where q_e is the amount of adsorbate adsorbed (X, mg) per unit weight of adsorbent (M, g) and C_e is the equilibrium concentration of the adsorbate remaining in solution (mg/l). Linearised form of Freundlich equation, reported below, was applied to the sorption equilibria at different adsorbent doses in batch studies (Kumar and Bandyopadhyay, 2006).

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \qquad (2)$$

In the above equation, K_F and $1/n$ are constants, which are considered to be the relative indicators of adsorption capacity and adsorption intensity. The values of K_F and $1/n$ were obtained by the Freundlich isotherm as shown in Figure 2.

$$\therefore\ q_e = X/M = 2.16\,(C_e)^{0.3991} \qquad (3)$$

The equilibrium and operating lines were then plotted on an arithmetic graph as shown in Figure 3.

2. An operating line was drawn which is passing through the origin and through the point given by the co-ordinates C_0 and $(X/M)_0$. The significance of this operating line was that the data of continuously mixed batch reactor (CMBT) and the data of fixed bed reactor (FBR) are identical at these two points, first at the initiation and other at the exhaustion of the reaction (Michaels, 1952).

3. According to Weber (1972), the rate of transfer of the adsorbate from the solution over a differential depth of column dh is given by:

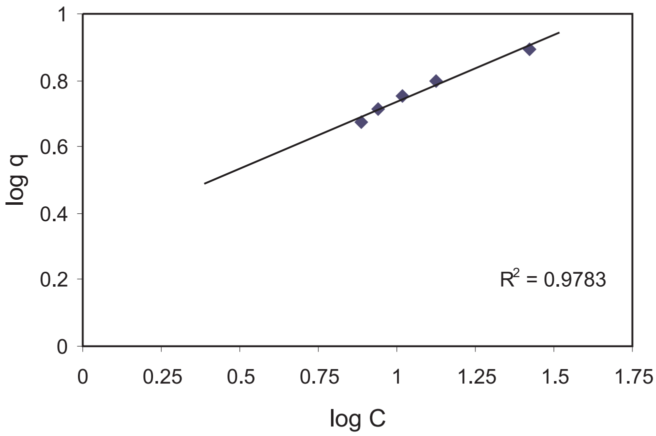

Figure 2: Freundlich isotherm of Zn(II)–NCRH system.

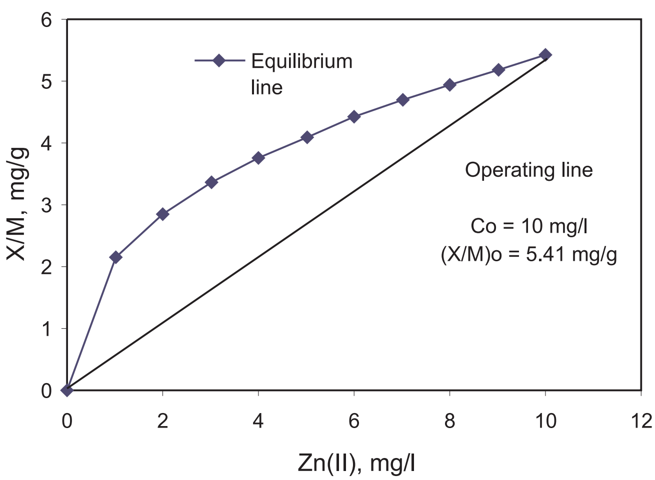

Figure 3: Plot of equilibrium and operating lines for determination of theoretical breakthrough curve of Zn(II).

$$F_w . dC = K_m(C - C^*)\, dh \tag{4}$$

where F_w is the flow rate, K_m is overall mass transfer coefficient which includes the resistances offered by film and pore diffusions, C^* is the equilibrium concentration of the adsorbate in the solution corresponding to a adsorbed concentration (*X/M*) and *C* is the concentration of the adsorbate at a given instant of time *t*.

The term $(C - C^*)$ is the driving force for adsorption and is equal to the difference between the operating line and equilibrium curve at any given (*X/M*) value. Integrating the equation (4) and solving for the height of adsorption zone at saturation,

$$h_z = \frac{F_w}{K_m}\int_{C_B}^{C_E}\frac{dC}{(C - C^*)} \tag{5}$$

where C_B and C_E are the concentrations of adsorbate in effluent at breakthrough and at exhaustion respectively. 4. The plot of $(C - C^*)^{-1}$ versus C is shown in Figure 4. The area under the curve represented the value of the above integration.

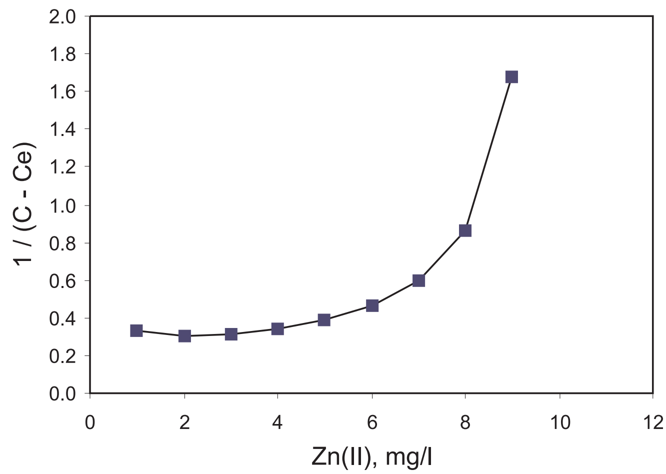

Figure 4: Curve to evaluate equation 5 for determination of theoretical breakthrough curve of Zn(II).

Since $(C - C^*)^{-1}$ approaches infinity as C approaches C_0, it is necessary to terminate the plot of C at a value somewhat less than C_0. Generally, a value of $C_E = 0.90C_0$ is selected, which is frequently considered to be the point of exhaustion for adsorption beds. For any value of h less than h_z corresponding to a concentration C between C_B and C_E, equation (5) can be written as

$$h = \frac{F_w}{K_m}\int_{C_B}^{C}\frac{dC}{(C - C^*)} \tag{6}$$

Dividing equation (6) by equation (5) results in

$$\frac{h}{h_z} = \frac{\int_{C_B}^{C}\frac{dC}{(C - C^*)}}{\int_{C_B}^{C_E}\frac{dC}{(C - C^*)}} = \frac{V - V_B}{V_E - V_B} \tag{7}$$

(h/h_z) is equal to the ratio $(V - V_B) / (V_E - V_B)$. Where V_B and V_E are total volume of water treated till breakthrough and up to the point of exhaustion respectively and V is the volume of water treated within V_E for an effluent concentration C within C_E.

5. The values of $(V - V_B)/(V_E - V_B)$ were calculated by dividing the values of $\int_{C_B}^{C} \frac{dC}{(C - C^*)}$ by the value of $\int_{C_B}^{C_E} \frac{dC}{(C - C^*)}$. Finally the theoretical breakthrough curves that were generated by plotting $(V - V_B)/(V_E - V_B)$ versus (C/C_0), are shown in Figure 5. The experimental and theoretical breakthrough curves followed the same trend. So using the data obtained from the batch isotherm studies, it is possible to predict the theoretical breakthrough curve, which can be well compared with the experimental curve.

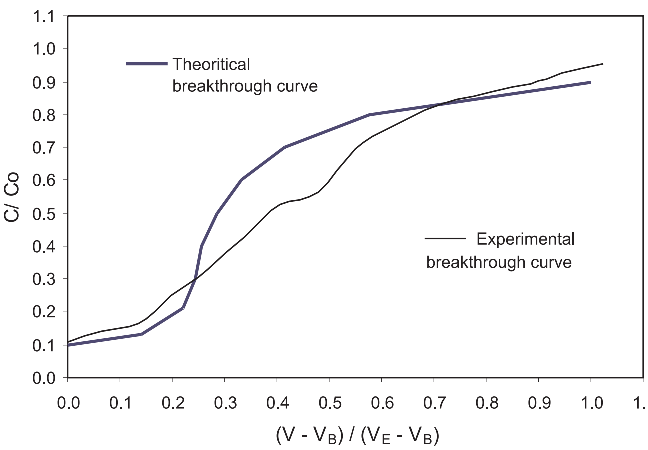

Figure 5: Theoretical and experimental breakthrough curve of Zn(II).

Conclusions

NCRH was found to be efficient media for the removal of Zn(II) from wastewater. The column with 2 cm diameter, and bed depth 10, 20 and 30 cm could treat 2.28 litre of Zn(II) at breakthrough, at initial concentration 10 mg/l. Theoretical breakthrough curve was developed from the batch isotherm data and it followed almost same pattern of experimental breakthrough curve.

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