

Fixed bed column study for heavy metal removal using phosphate treated rice husk

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Received 12 August 2006; received in revised form 7 August 2007; accepted 8 August 2007
Available online 12 August 2007

Abstract

This paper reports the results of the study on the performance of low-cost adsorbent such as raw rice husk (RRH) and phosphate treated rice husk (PRH) in removing the heavy metals such as lead, copper, zinc and manganese. 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 column studies were conducted with 10 mg/l of individual and combined metal solution with a flow rate of 20 ml/min with different bed depths such as 10, 20 and 30 cm. The breakthrough time was also found to increase from 1.3 to 3.5 h for Pb(II), 4.0 to 9.0 h for Cu(II), 12.5 to 25.4 h for Zn(II) and 3.0 to 11.3 h for Mn(II) with increase in bed height from 10 to 30 cm for PRH. Different column design parameters like depth of exchange zone, adsorption rate, adsorption capacity, etc. were calculated. It is found that the adsorption capacity and adsorption rate constant were increased and the minimum column bed depth required was reduced when the rice husk is treated with phosphate, when compared with that of RRH.

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Keywords: Heavy metal removal; Adsorption study; Continuous experiments; Breakthrough curve

1. Introduction

Heavy metals get distinguished from other toxic pollutants, due to their non-biodegradability and can accumulate in living tissues, thus becoming concentrated throughout the food chain and can be readily absorbed into the human body. Even a very small amount can cause severe physiological or neurological damage to the human body [1].

Lead as a pollutant is a major concern as it has been used as one of the raw materials for battery manufacturing, printing, pigments, fuels, photographic materials and explosive manufacturing [2]. The presence of lead in drinking water even at low concentration may cause diseases such as anemia, encephalopathy, hepatitis and nephritic syndrome [3].

Copper is an essential nutrient, required by the body in very small amounts. Short periods of exposure can cause gastrointestinal disturbance, including nausea and vomiting. Use of water that exceeds the permissible level over many years could

cause liver or kidney damage. Copper is rarely found in source water, but copper mining and smelting operations and municipal incineration may be sources of contamination.

Zinc, even though is an essential mineral, but when it is excess, it is highly harmful. Symptoms of zinc toxicity include nausea/vomiting, fever, cough, diarrhea, fatigue, neuropathy and dehydration. Further signs include growth retardation, altered iron function, anemia, copper deficiency, decreased immune function, decreased high density lipoprotein (HDL), and increased low density lipoprotein (LDL). The uptake of manganese by humans mainly takes place through food, such as spinach, tea and herbs. The foodstuffs that contain the highest concentrations of manganese are grains and rice, soya beans, eggs, nuts, olive oil, green beans and oysters. After absorption in the human body, manganese will be transported through the blood to the liver, the kidneys, the pancreas and the endocrine glands.

Manganese effects occur mainly in the respiratory tract and in the brains. Symptoms of manganese poisoning are hallucinations, forgetfulness and nerve damage. Manganese can also cause Parkinson, lung embolism and bronchitis. When men are exposed to manganese for a longer period of time, there is

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likelihood that they may become impotent. A syndrome that is caused by manganese has symptoms such as schizophrenia, dullness, weak muscles, headaches and insomnia. Thus, it is imperative that heavy metals are removed from effluent before being discharged into the sewage system or into the aquatic environment.

Rice husk is the outer covering of paddy and accounts for 20–25% of its weight. It is removed during rice milling and is used mainly as fuel generating CO₂ and other forms of pollution to the environment. The annual generation of rice husk in India is in the range of 18–22 million tons. In recent years, attention has been focused on the utilization of unmodified or modified rice husk as a sorbent for the removal of pollutants. Unmodified rice husk has been evaluated for their ability to bind metal ions. Various modifications on rice husk have been reported in order to enhance sorption capacities for metal ions and other pollutants [4,5].

There is a need to carryout the columns studies to assess the required contact time for the adsorbate to achieve equilibrium as the results obtained from the batch studies for the heavy metal adsorption studies may not be directly applied for field applications in the treatment of wastewater [6]. In this reported study, an effort has been made to study the removal of heavy metals in fixed bed column with RRH and PRH and arrive at the adsorption column design parameters.

A preliminary analysis of the leachate samples indicates that the concentration of heavy metal ions such as Pb(II), Cu(II), Zn(II) and Mn(II) are ranging from 0.2 to 9.8 mg/l, 0.07 to 9 mg/l, 0.7 to 16 mg/l, and 0.8 to 15 mg/l, respectively. Even though, many authors performed column study for various metal ions, this paper was initially started with the aim of treating the leachate from an existing open solid waste dumping site in the Chennai city, India with locally available rice husk.

2. Materials and methods

2.1. Reagents

All chemicals used were of analytical grade. Stock solutions of 10 mg/l was prepared based on the results of the analysis of the leachate samples from Chennai solid waste dumping site for Pb(II), Cu(II), Zn(II) and Mn(II) using lead nitrate (Pb(NO₃)₂), copper sulphate pentahydrate (CuSO₄·5H₂O), Zinc chloride (ZnCl₂) and MnSO₄·H₂O, respectively, according to the procedures stipulated in the APHA [7].

2.2. Preparation of adsorbent

Crushed Rice husk was obtained from local rice mill and sieved through 1 mm IS sieve to have the uniform size of adsorbent for the whole study. Before pretreatment, it was washed with distilled water for several times to remove the impurities. This rice husk is referred herein after as raw rice husk (RRH). After complete washing with distilled water, it was dried at 60 °C for 2 h and preserved at room temperature. 45 g of dried-husk was treated with 900 ml of 1.0 M K₂HPO₄ for 24 h. The mixture was filtered and washed several times with distilled water to

remove the excess phosphate from the treated husk. The resultant adsorbent was finally dried at 70 °C for 2 h and preserved at room temperature. This treated rice husk is herein after referred as phosphate treated rice husk (PRH). Trial runs were carried out with 0.5, 1.0 and 1.5 M of K₂HPO₄. The results indicated that the almost equal efficiency was observed with 1.0 and 1.5 M of K₂HPO₄ and the efficiency was higher than that of 0.5 M K₂HPO₄. Hence, it is decided to use 1.0 M K₂HPO₄ treatment for further study.

2.3. Characterization of rice husk

Unmodified and modified rice husk were characterized by using X-ray diffraction (XRD) and scanning electron microscope (SEM). The X-ray diffraction spectra were obtained by using a Shimadzu XRD 6000 X-ray diffractometer. XRD analysis was carried out to identify the mineral composition and morphological features of adsorbents. The prepared rice husk samples were exposed to X-ray ($k=1.54060 \text{ \AA}$) with the 2θ angle varying between 10 and 40 with Cu K_α radiation. The applied voltage and current were 40 kV and 30 mA, respectively. Scanning electron microscopy (SEM) investigations of the rice husk samples were conducted in a JEOL JMT-300 operated at 30 kV and linked with an energy dispersive X-ray spectrometry (EDXS) attachment. The SEM analysis was done at 500× magnification to examine the morphological characteristics of both the adsorbents. Table 1 shows the physicochemical characteristics of the raw rice husk used in this study.

To identify the functional group responsible for the adsorption in the RRH, Fourier transform infrared spectroscopy (FTIR) analysis was carried out. The ratio between the sample and potassium bromide (KBr) was at about 1:100 prior to compacting into thin pellet using an 8 tons force hydraulic press for 5 min. Infrared spectrum was obtained in transmission and was set to operate in the range of 400–4000 cm⁻¹.

2.4. Column studies

The adsorption with rice husk was studied with the aim of treating the leachate collected from the open dumping site. The heavy metal concentration in the leachates was observed as around 10 mg/l and thus this concentration level has been selected for column study. The fixed bed column experiments were conducted with 10 mg/l synthetic single metal solutions using the columns at a constant flow rate of 20 ml/min. The samples were collected from the ports at bed depths of 10, 20 and

Table 1
Physicochemical characteristics of rice husk studied

| Characteristics | Values |
|----------------------------------|----------|
| Bulk density (g/ml) | 0.249 |
| Dry density (g/ml) | 0.236 |
| Moisture content (%) | 7.04 |
| Ash content (%) | 33.9 |
| Particle size (mesh) | 0.6–1 mm |
| Surface area (m ² /g) | 0.69 |

Table 2
Specifications of packed column

| S. no. | Parameters | Sample water |
|--------|--------------------------------|------------------------|
| 1 | Column bed height | 30 cm |
| 2 | Diameter of the column | 2.5 cm |
| 3 | Area of the column | 4.91 cm ² |
| 4 | Volume of the column | 245.43 cm ³ |
| 5 | Weight of adsorbent taken | 36 g |
| 6 | Bulk density | 0.244 g/cc |
| 7 | Volume of the wastewater taken | 50 l |
| 8 | Initial concentration | 10 mg/l |
| 9 | Flow rate | 20 ml/min |

30 cm at 1 h regular time interval. The preparation of the columns for the continuous study and the calculation of the column design parameters are discussed below.

2.5. Preparation of column

The effective column height, area, initial concentration of metal ion, diameter of the column, weight of adsorbent taken and flow rate are listed in Table 2.

The column was packed with adsorbent between two supporting layers of glass wool. The adsorbent was added from the top of the column and allowed to settle by gravity force. The upper portion of the adsorbent was covered with glass beads. 50 l of synthetic wastewater was taken in a bucket and a peri-

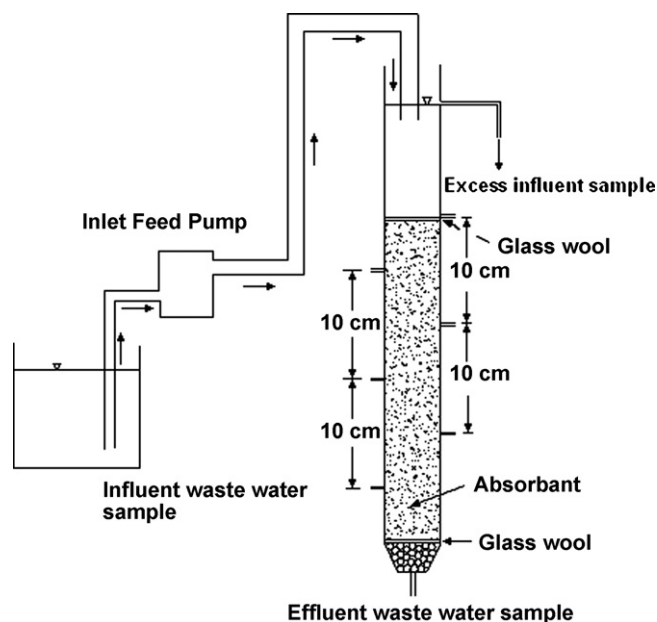


Fig. 1. Schematic diagram of lab-scale column study.

static pump controlled the inlet flow rate. The bottom of the column was connected with rubber tubing with flow adjustable clamp. Thus, the outflow rate was controlled by adjusting the clamp. The samples were collected in regular time intervals and

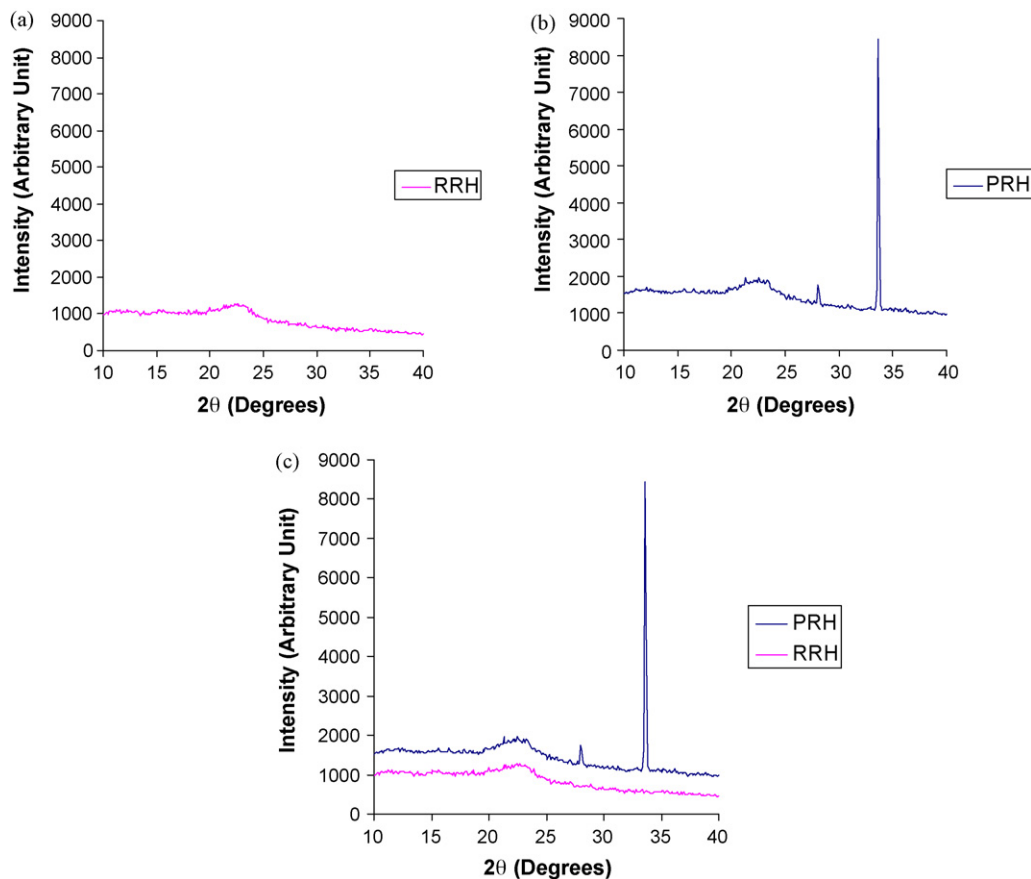


Fig. 2. X-ray spectra of both RRH and PRH.

stored for analysis. The schematic diagram of the column study is shown in Fig. 1.

3. Results and discussion

3.1. Characterization of rice husk

The techniques used in the study for the characterization of rice husk are XRD and SEM, to compare the modification to the RRH due to the treatment. The XRD plots for both the adsorbents are shown in Fig. 2. The phases were identified by comparing the peak positions and intensities with those in the Joint Committee on Power Diffraction Standards (JCPDS) data files. XRD analysis indicated that RRH does not show any large peak, thereby indicating the amorphous nature of the product. The XRD chart for the RRH is shown in Fig. 2a. A broad peak from 15 to 35 - 2θ diffraction angles indicates the presence of amorphous silica. In fact, the result obtained confirms those already reported in the literature for rice husk ash [8]. In the Fig. 2b the sharp peak at 37 - 2θ diffraction angles indicates the presence of Phosphate ions on the surface of treated rice husk. Fig. 2c represents the similar morphology for both modified and unmodified rice husk except the phosphate ions on the PRH and is observed that the phosphate treatment process to the RRH does not damage the surface of the RRH.

The effect of treatment on the rice husk on the morphology of the RRH and PRH has been verified with the SEM and the results are shown in Fig. 3 and the bar in the figure indicates the magnification that is represented by the first number (in μm). Some

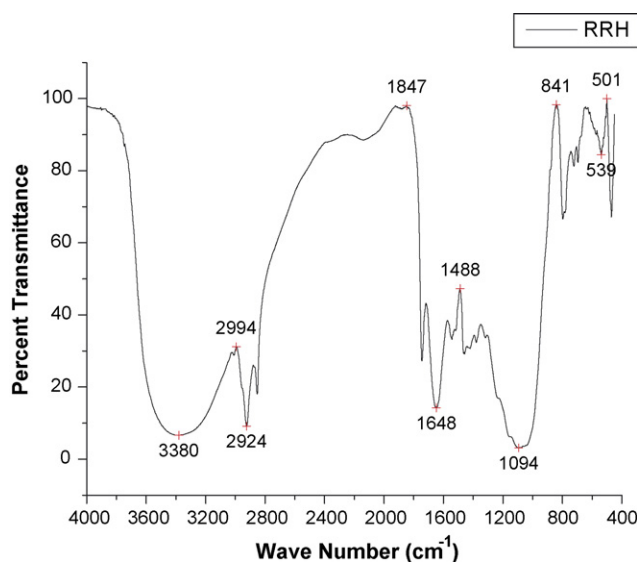


Fig. 4. Results of FTIR analysis.

imperfections on the surface of the vegetable wall are verified after treatment. It can be inferred that the essential mechanism of adsorption in this case is by chemisorption. These figures also reveal that the treatment process does not cause any damage to the inner and outer surface of the RRH as visualized from these figures (Fig. 3a and b).

The FTIR analysis of RRH (Fig. 4) shows a broad band at 3380 cm^{-1} that represents bounded $-\text{OH}$ groups. An absorption band corresponding to $\text{Si}-\text{O}$ stretching at 1094 cm^{-1} dominates

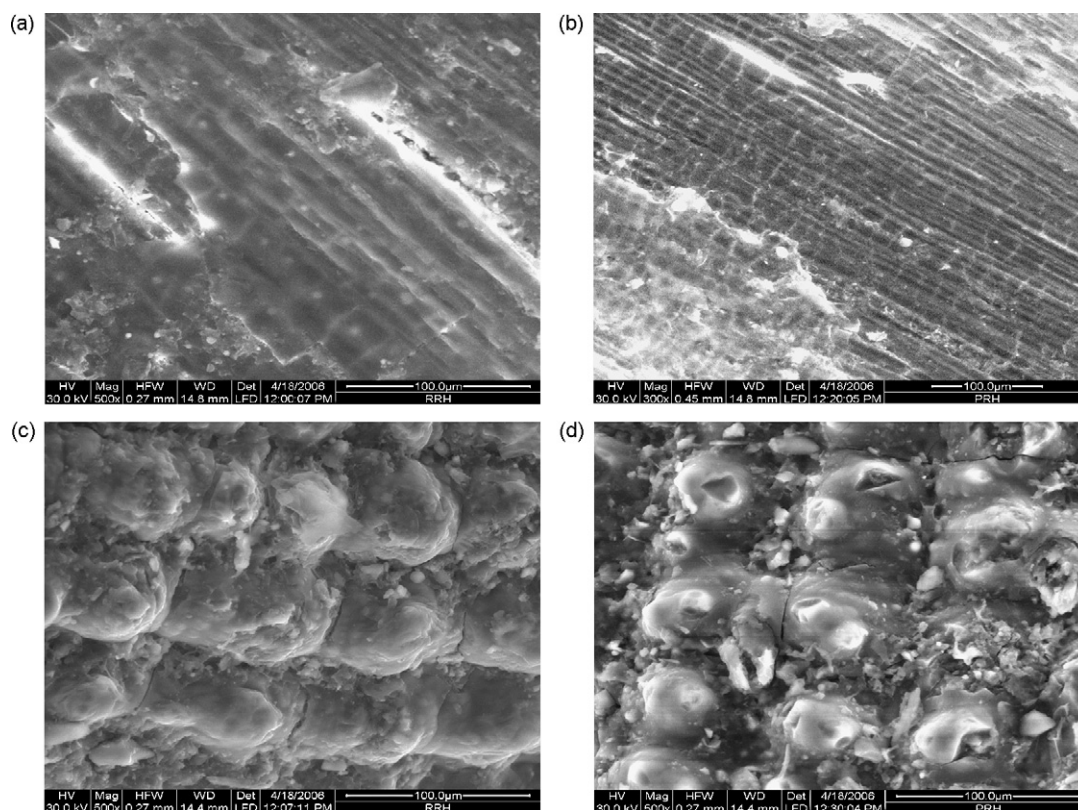


Fig. 3. Scanning electron micrographs of rice husk: (a) for inner side of RRH, (b) for inner side of PRH, and (c) for outer side RRH and (d) for outer side of PRH.

and the band at wave number 800–850 cm^{-1} corresponding to Si–C stretching was found. –CH stretch could be ascribed to the band that appeared at 2924 cm^{-1} . A weak absorption at the wave number 790–800 cm^{-1} were also observed, the peak could be corresponded to the Si–O vibration from the silica existing in the sample. On the other hand, –CH stretch could be ascribed to the band that appeared at 2924 cm^{-1} . The presence of Si–OH groups and phosphate groups on the rice husk surface are responsible for adsorption. Thus, it can be concluded that modified rice husks present an adequate morphological profile to retain metal ions.

3.2. Behavior of adsorption column for individual metal solutions

From the results obtained by the columns experiments for RRH and PRH the breakthrough curves are plotted for various metal ions and are shown in the Figs. 5 and 6, for the RRH and PRH, respectively. From Figs. 5 and 6, it can be observed that, the uptake of heavy metals increased with the increase in the bed depth from 10 to 30 cm. The increase in the metal uptake capacity with the increase of bed height in the column was due to the increase in the contact time. Service time corresponds to the

Table 3
Drinking water standards

| S. no. | Metal ion | BIS 10500: 1991 | USEPA |
|--------|-----------------------------|-----------------|-------|
| 1 | Lead (as Pb) mg/l, Max | 0.05 | 0.015 |
| 2 | Copper (as Cu) mg/l, Max | 0.05 | 1.0 |
| 3 | Zinc (as Zn) mg/l, Max | 5 | 0.5 |
| 4 | Manganese (as Mn) mg/l, Max | 0.10 | 0.05 |

effluent concentration of 0.05 mg/l for Pb(II), Cu(II) and Zn(II) and 0.1 mg/l for Mn(II) were adopted according to the drinking water standards. It may also be noted that the service time of the bed for various metal ions followed the order $\text{Zn} > \text{Mn} > \text{Cu} > \text{Pb}$. It may be due to the adsorbent affinity towards metal ions. It will vary depending on the ionic radius and the electro positive charges on the ions [9]. Desorption and regeneration study has been performed for batch experiments and was observed a maximum decrease in the efficiencies was 8%.

USEPA and Indian standards of toxicity limit of studied metal ions in the drinking water were shown in Table 3. The service time was also increased with an increase in bed height. All the metals showed a similar trend of breakthrough profiles with varying the time of breakthrough.

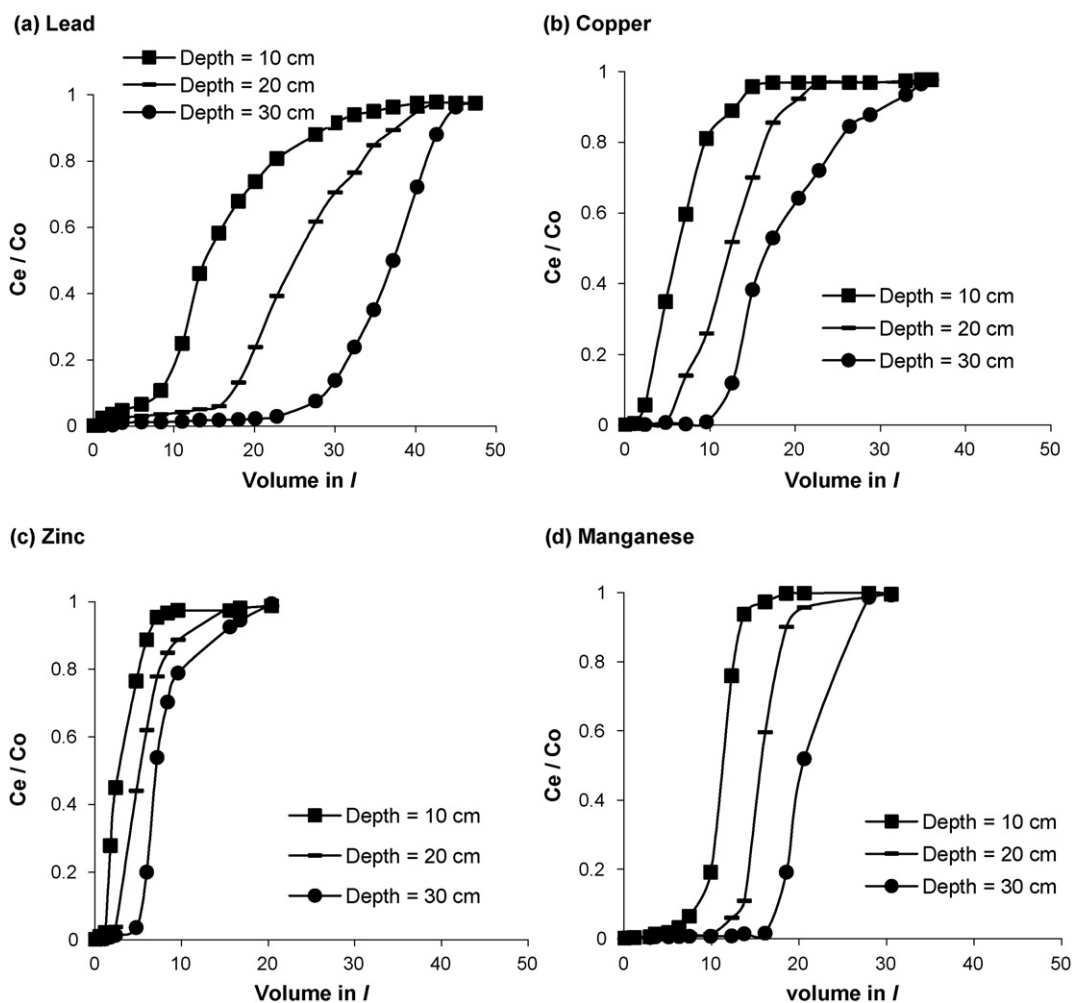


Fig. 5. Breakthrough curves for different metal ions with RRH.

Table 4
Service time for RRH and PRH at different bed heights

| Metal | Depth in cm | Service time (h) | |
|--------|-------------|------------------|-------|
| | | RRH | PRH |
| Pb(II) | 10 | 0.24 | 1.32 |
| | 20 | 1.72 | 2.36 |
| | 30 | 2.40 | 3.50 |
| Cu(II) | 10 | 1.02 | 4.02 |
| | 20 | 3.82 | 6.28 |
| | 30 | 6.97 | 9.06 |
| Zn(II) | 10 | 2.21 | 12.52 |
| | 20 | 4.23 | 23.16 |
| | 30 | 5.83 | 25.35 |
| Mn(II) | 10 | 1.01 | 2.98 |
| | 20 | 2.61 | 10.25 |
| | 30 | 5.30 | 11.31 |

From Fig. 5 and Fig. 6, the service time for both adsorbents for each heavy metal at 10, 20 and 30 cm bed depth are calculated and are given in the Table 4. From Table 4, it can be observed that the service time of adsorption with PRH is more when compared to that of RRH. The increase in the metal uptake capacity for the treated rice husk is due to the increase in the surface charge of adsorbent, which provided more binding site for the adsorption.

3.3. Evaluation of adsorption column design parameters

Data collected during laboratory tests serve as the basis for the design of full-scale adsorption columns. A number of mathematical models have been developed for the use in design. Among various design approaches, bed depth service time (BDST) approach based on Bohrat and Adams equation is widely used [6]. This approach, herein after be referred as the BDST approach. The equation of Bohrat and Adams, which is based on surface reaction rate theory, can be represented as follows:

$$t = \frac{N_0}{C_0 V} X - \frac{1}{C_0 K} \ln \left(\frac{C_0}{C_B} - 1 \right) \quad (1)$$

where C_0 is the initial concentration of solute (mg/l), C_B the desired concentration of solute at breakthrough (mg/l), K the adsorption rate constant (l/mg h), N_0 the adsorption capacity (mg/l), X the bed depth of column (cm), V the linear flow velocity of feed to bed (cm/h), t is the service time of column under above conditions (h).

The form of the Bohart–Adams equation, shown as Eq. (1) can be used to determine the service time, t , of a column of bed depth, X , given the values of N_0 , C_0 and K which must be determined for laboratory columns operated over a range of velocity values, V . Setting $t=0$ and solving Eq. (1) for X yields

$$X_0 = \frac{V}{KN_0} \ln \left(\frac{C_0}{C_B} - 1 \right) \quad (2)$$

where X_0 is the minimum column height necessary to produce an effluent concentration C_B , also known as critical bed depth. At least nine individual column tests must be conducted to col-

Table 5
Fitted equations between the service time and the bed depth

| Heavy metal | RRH | | PRH | |
|-------------|----------------------|-------|----------------------|-------|
| | Fitted equation | R^2 | Fitted equation | R^2 |
| Pb | $Y=0.1082X - 0.822$ | 0.999 | $Y=0.109X + 0.2145$ | 0.999 |
| Cu | $Y=0.2973X - 2.011$ | 0.999 | $Y=0.2521X + 1.4075$ | 0.996 |
| Zn | $Y=0.1811X + 0.4673$ | 0.996 | $Y=0.6413X + 6.4643$ | 0.991 |
| Mn | $Y=0.2146X - 1.3178$ | 0.979 | $Y=0.4161X - 0.8083$ | 0.977 |

lect the laboratory data required for the original Bohart–Adams approach, an expensive and time-consuming task. With the modified Bohart–Adams equation, it is necessary to have only three-fixed bed tests to collect the necessary data instead of nine. The Bohart–Adams Eq. (1) can be expressed as

$$t = aX + b \quad (3)$$

where

$$a = \text{slope} = \frac{N_0}{C_0 V} \quad (4)$$

and

$$b = \text{intercept} = -\frac{1}{KC_0} \ln \left(\frac{C_0}{C_B} - 1 \right) \quad (5)$$

This approach, herein after be referred as the BDST approach. In order to develop a BDST relation, the data of breakthrough curves plotted for different bed depths by recording the operating time to reach a certain removal at each bed depth. The slope of the line is equal to the reciprocal of the velocity of the adsorption zone and the intercept on abscissa is the critical depth defined as the minimum bed depth required to obtain the desired effluent quality at time equal to zero. The plots of service time versus bed height for RRH and PRH for the sorption of Pb(II), Cu(II), Zn(II) and Mn(II) are shown in Figs. 7 and 8. The details of fitted equations between the service time (Y) and the bed depth (X) and their corresponding R^2 values are given in Table 5. These fitted curves can be used for predicting the service time (h) given the bed depth (cm) both for RRH and PRH as the R^2 values are quite high.

From Figs. 7 and 8, it can be seen that the variation of the service time with bed depth is highly linear, thus indicating the validity of BDST model when applied to the continuous column studies. From the slope and intercept of the fitted lines, the BDST parameters namely the adsorption rate constant (K), the adsorption capacity (N_0) the minimum column height (X_0) are calculated using BDST equations [6]. The X_0 is calculated for standard effluent concentration of 0.05 mg/l for Pb(II), 0.05 mg/l for Cu(II), 5 mg/l for Zn(II) and 0.1 mg/l for Mn(II). The BDST model parameters for four metals are calculated and are listed in Table 6.

From Table 6, the values of K and N_0 indicated that both the adsorbents are highly efficient for removal of all heavy metals from water environment. The above results show an increase in the adsorption capacity (N_0) and adsorption rate constant (K) after the treatment for all the four heavy metals. The minimum

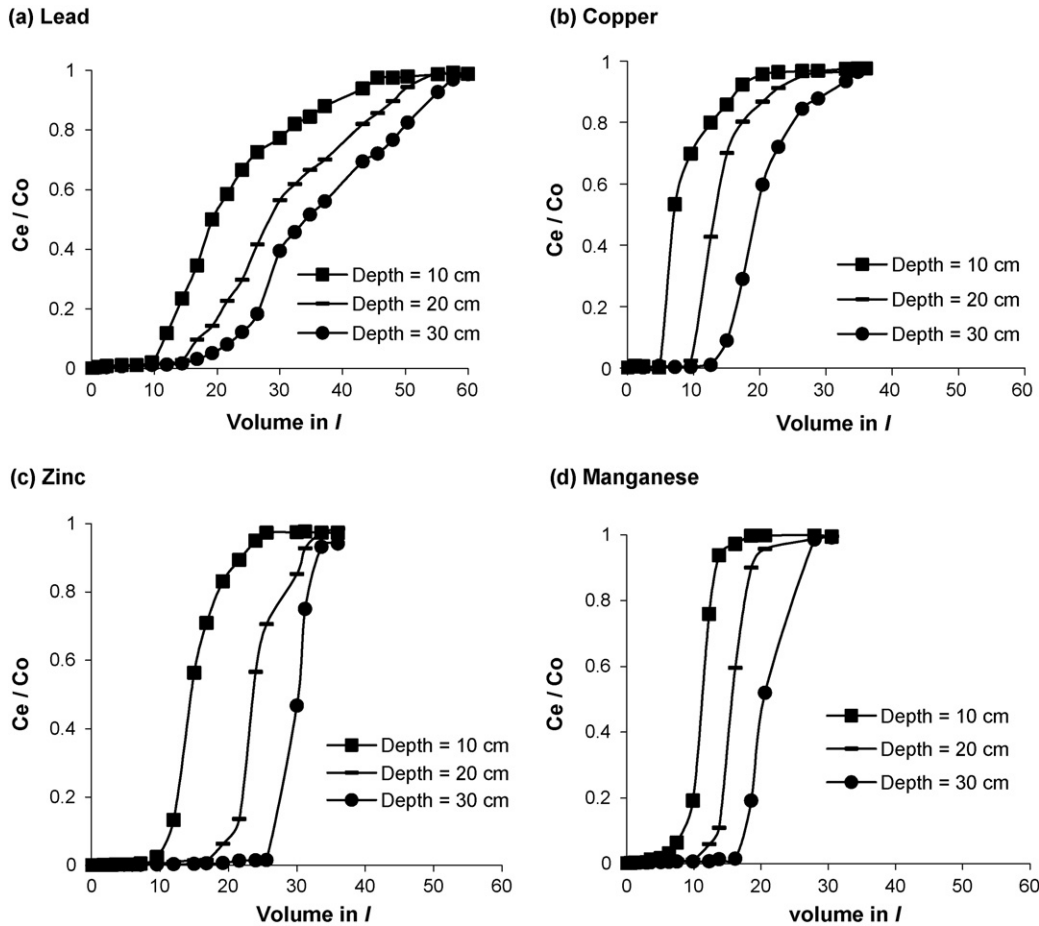


Fig. 6. Breakthrough curves for different metal ions with PRH.

column height (X_0) required to produce the corresponding effluent standard is reduced from 6.5 to 2 cm for Pb(II), 6.8 to 5.5 cm for Cu(II), 11 to 2.1 cm for Zn(II) and 6.25 to 2 cm for Mn(II). The above results conclude that modified rice husk is more efficient than unmodified rice husk with the increase in the surface charge of the RRH. The values of K and N_0 of the BDST model indicate that both the adsorbents could be used for removal of

heavy metals from synthetic single metal solutions. The N_0 and K values are doubled for PRH, when compared to RRH for all metals. The minimum column height (X_0) required is reduced by three times for PRH when compared to RRH except for Cu(II). Once the column design parameters are calculated, fixed bed columns can be designed for different flow rates and different initial concentrations.

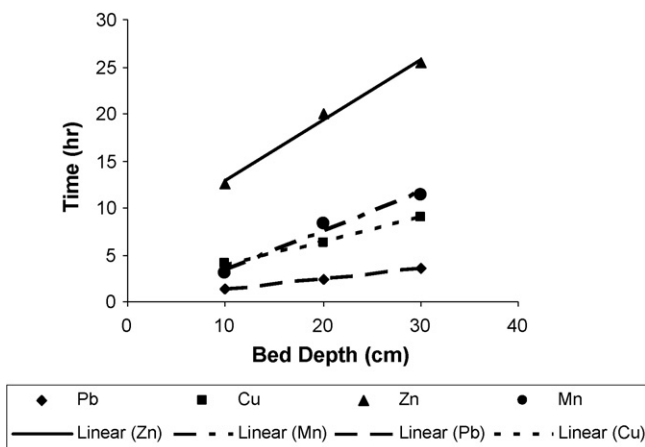


Fig. 7. BDST plot for different heavy metal for RRH.

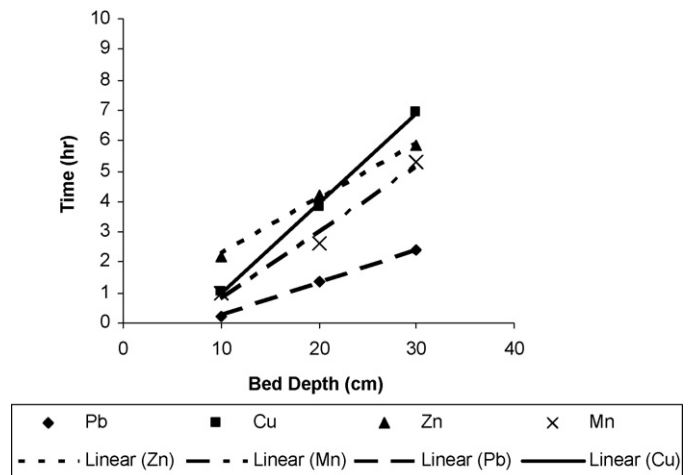


Fig. 8. BDST plot for different heavy metal for PRH.

Table 6
BDST parameters for sorption of Pb(II), Cu(II), Zn(II) and Mn(II)

| Metal | Adsorbent | N_0 (mg/cc) | K (cc/mg h) | X_0 (cm) |
|--------|-----------|---------------|---------------|------------|
| Pb(II) | RRH | 0.22 | 863 | 6.53 |
| | PRH | 0.52 | 2837 | 2.0 |
| Cu(II) | RRH | 0.64 | 290 | 6.8 |
| | PRH | 0.98 | 414 | 5.6 |
| Zn(II) | RRH | 0.451 | 17.3 | 11 |
| | PRH | 1.36 | 291 | 2.2 |
| Mn(II) | RRH | 0.42 | 4.2 | 6.3 |
| | PRH | 0.81 | 668 | 2 |

4. Conclusions

From the study on adsorption of heavy metals in fixed bed columns, the following conclusions have been arrived at:

1. From the column studies for individual metal ions, it is observed that the increase in the metal uptake capacity with the increase of bed height is due to the increase in the contact time.
2. From the values of K and N_0 from the BDST model indicate that both the adsorbents could be used for removal of heavy metals from synthetic single metal solutions.
3. From the column design parameters, it can be observed that the adsorption capacity (N_0) and the rate of adsorption (K)

are doubled for PRH when compared to RRH for all metals and

4. It can be found that the minimum column height (X_0) required for the removal of all heavy metal ions was reduced to three times with PRH when compared to RRH.

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