Fixed Bed Column Study for the Removal of Lead 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 lead. The adsorbent materials adopted were found to be an efficient media for the removal of lead 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 Pb(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 3.7 and 11.21 h, respectively. Height of adsorption zone was found to be 10.32 cm and the rate at which the adsorption zone was moving through the bed was 1.38 cm/h. The percentage of the total column saturated at breakthrough was found 47.6 %. The value of adsorption rate coefficient (K) and adsorption capacity coefficient (N) were obtained as 0.0524 l/(mg h) and 1712 mg/l, respectively.

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

Introduction

Water pollution due to toxic heavy metal lead has been a major cause of concern. The industrial 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 non-biodegradable and can accumulate in living tissues, thus becoming concentrated throughout the food chain[1]. Lead is a soft, malleable, bluish gray, heavy metal with comparatively low malting point (327°C). It is widely distributed in lithosphere and is also present in atmosphere and hydrosphere. Its most common form in the environment is Pb(II). Lead exists in the nature mostly in the mineral called galena (PbS). Most of the leads containing minerals are very sparingly soluble in water, which reflects its extremely low concentrations in natural water. The lead concentration in natural waters is increased mainly through anthropogenic activities. A large number of industries such as battery manufacturers, petroleum, paint, ceramics, electric cable insulation, pesticides and plastics uses lead in various operations. These industrial wastewater contains varying quantities of lead and contaminate the water. Some lead is also present in the runoff waters originating from various sources. The runoff in the lead mining areas is very high in lead concentration. Lead accumulates mainly in bone from where it can be excreted only slowly, but at the time of stress or illness it can come in circulation in the body. The toxic responses are anemia and distribution of hemoglobin synthesis, damage to nervous system and kidneys, brain damage; acute lethal dose to Man is 300-700 mg/kg. In mild cases, insomnia, restlessness, loss of appetite and gastrointestinal problems. A concentration of 0.8 mg/l of lead in blood is considered as a threshold for lead poisoning[2]. The presence of high levels of

lead in the environment may cause long-term health risks to humans and ecosystems. It is therefore mandatory that their levels in drinking water, waste water and water used for agricultural and recreational purposes must be reduced to within the maximum allowable concentrations recommended by national and international health authorities such as world health organisation. Its removal from wastewater prior to discharge into environment is, therefore, necessary. Current drinking water standard for lead as per are USEPA, WHO and BIS (Beauro of Indian Standard IS: 10500-1983) are 0.05 mg/l, 0.1 mg/l and 0.05 mg/l respectively; but a level of 0.02 mg/l has been proposed and is under review. According to BIS, the tolerance limit for discharge of lead into inland surface waters is 0.1 mg/l, Public sewer is 1.0 mg/l and discharge in marine costal area is 1.0 mg/l [3].

Several techniques for wastewater treatment including coagulation, sedimentation, lime precipitation, floatation, filtration, electrochemical, ion-exchange, biological and membrane processes have been used for the metal ions removal from wastewaters, but some of these methods have disadvantages as generate toxic sludge, incomplete metal removal, continuous input of chemicals and high cost[4]. Adsorption is an effective, economical and efficient method for the removal of metal ions from wastewaters. The most commonly used solid sorbent is activated carbon but it is expensive and requires chelating agents (for metal containing effluents) to enhance its performance, which results in increases of its cost. Because of high cost of activated carbon, there is a need to explore less expensive cleanup methodology for the eradication of metal ions from aqueous systems[5,6].

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[5]. 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[7].

In our continued study on the use of low-cost material for the removal of organic and organic pollutants from water and wastewater we investigated rice husk as a sorbent for the removal of Pb(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[1,3].

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[6]. 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. In recent years, attention has been taken on the utilization of unmodified or modified rice husk as a sorbent for the removal of pollutants[8,9,10]. The present study has been undertaken to report the Pb(II) adsorption in the fixed bed column process.

Material and Methods

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).

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)[1].

Experimental Studies: Fixed bed column study for Pb(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 figure 1. The study was conducted at temperature of 28 ± 2°C and the pH of the Pb(II) solution as 6.0 ± 0.2 for the present study. The column was charged with Pb(II) bearing wastewater with a volumetric flow rate of 10 ml/min (~ 2.10 m^3/m^2/h). The initial concentration of Pb(II) was 10 mg/l. The samples were collected at certain time intervals and were analyzed for Pb(II) using atomic absorption spectrophotometer (AA-6650, Shimadzu).

Results and Discussion

Behavior of adsorption column: The fixed bed column experiment was conducted with 10 mg/l Pb(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 figure 2. The breakthrough time (corresponding to $C/C_o = 0.1$) and exhaust time (corresponding to $C/C_o = 0.9$) were found to be 3.7 and 11.2 h respectively. The corresponding volumes of wastewater treated were 2.22 and 6.72 liters respectively. About 8.39 gm of NCRH were used in the 10 cm column. The volume of Pb(II) 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[11]. The cost of NCRH in India was estimated as only Rs. 4 per Kg (US $ 0.08). Hence, by comparing the cost, NCRH is about 250 times cheaper than activated carbon. Cost for volume of Pb(II) effluent treated up to breakpoint per kg of NCRH has been calculated and has been presented in table 2.

Table-1
Volume of Pb(II) effluent treated and the mass of NCRH required up to breakthrough

Bed depth (cm)	10% Breakthrough time (hr)	Treated volume (lts)	Total mass of NCRH (gm)	Mass per litre (gm/l)
10	3.7	2.22	8.39	3.74 gm

Table-2
Cost for volume of Pb(II) effluent treated up to breakpoint per kg of NCRH

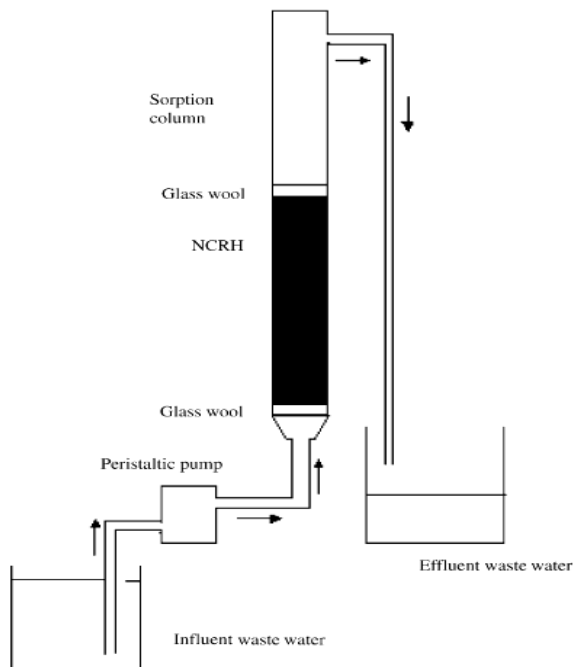| Volume of metal effluent treated per kg of NCRH	Cost per kg NCRH @ Rs. 4 @ US $ 0.08
264 litres	66 litres / Rs. 3300 litres / US $

Figure-1
Schematic diagram fixed bed column experimental set up

The formation and movement of the adsorption zone has been described mathematically[12,13]. 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

$$t_z = \frac{V_E - V_B}{Q_w} \qquad (1)$$

Where, V_E = volume of wastewater treated to the point of exhaustion (l), V_B = volume of wastewater treated to the point of breakthrough (l), Q_w = wastewater flow rate (l/h)
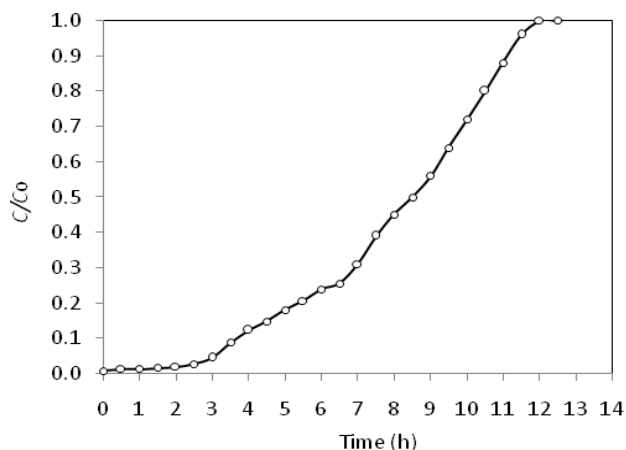

Figure-2
Breakthrough curve for Pb(II) using NCRH

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

$$t_E = \frac{V_E}{Q_w} \qquad (2)$$

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

$$U_z = \frac{h_z}{t_z} = \frac{h}{t_E - t_f} \qquad (3)$$

Where, h = height of exchange zone (cm), h = total bed depth (cm), t_f = time required for the exchange zone to initially form (h)

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

$$h_z = \frac{h(t_z)}{t_E - t_f} \qquad (4)$$

The value of t_f can be calculated as follows.

$$t_f = (1 - F)t_z \qquad (5)$$

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

$$F = \frac{S_z}{S_{max}} = \frac{\int_{V_B}^{V_E}(C_o - C)dV}{C_o(V_E - V_B)} \qquad (6)$$

Where, C_0 = initial solute concentration (mg/l), S_z = amount of solute that has been removed by the adsorption zone from breakthrough to exhaustion, S_{max} = amount of solute removed by the adsorption zone if completely exhausted

The percentage of the total column saturated at breakthrough is

$$\% \, saturation = \frac{h + (F-1)h_z}{h} \times 100 \qquad (7)$$

The values of the important design parameters were calculated using the data from breakthrough curve. Height of adsorption zone was found to be 10.32 cm and the rate at which the adsorption zone was moving through the bed was 1.38 cm/h. The percentage of the total column saturated at breakthrough was found to be 47.6 %.

Evaluation of adsorption column design parameters: Data collected during laboratory and pilot plant 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. In the present research work the fixed bed column was designed by logit method[14,15]. The logit equation can be written as:

$$\ln\left[\frac{C/C_o}{1 - C/C_o}\right] = -\frac{KN_oX}{V} + KC_ot \qquad (8)$$

Where, C = concentration at any time t, C_o = initial Cu(II) concentration (10 mg/l), V = approach velocity (210 cm/h), X =

bed depth (10 cm), K = adsorption rate constant (l/mg-h), N_o = adsorption capacity constant (mg/l)

Rearranging equation 8

$$\ln\left[\frac{C}{C_o - C}\right] = -\frac{KN_o X}{V} + KC_o t \qquad (9)$$

Plot of ln $C/(C_0 - C)$ vs. t gives a straight line with slope KC_o and intercept $-KN_0 X/V$ from which K and N_o could be calculated. Plot of ln $C/(C_0 - C)$ vs. t was shown in figure 3. The values of adsorption rate constant (K) and adsorption capacity constant (N_o) were obtained as 0.0524 l/mg.h and 1712 mg/l (1.712 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 Pb(II) removal.

Conclusion

NCRH was found to be efficient media for the removal of Pb(II) from aquatic environment. The column with 2 cm diameter, and bed depth 10 cm could treat 2.22 liters of Pb(II) at breakthrough, at initial concentration 10 mg/l. About 3.74 g of NCRH was required per liter of Pb(II) treatment. Height of adsorption zone was found to be 10.32 cm and the rate at which the adsorption zone was moving through the bed was 1.38 cm/h. The values of adsorption rate constant (K) and adsorption capacity constant (N_o) were obtained as 0.0524 l/mg.h and 1712 mg/l respectively.
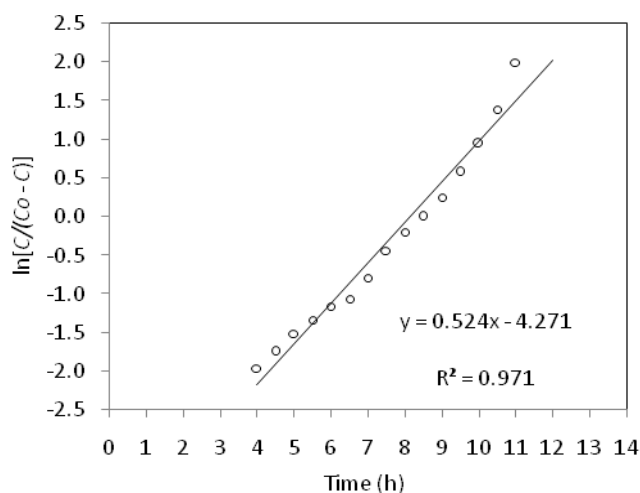

Figure-3
Linearized form of logit model

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