

Continuous fixed bed adsorption of Cu(II) by halloysite nanotube–alginate hybrid beads: an experimental and modelling study

Yanyan Wang, Xiang Zhang, Qiuru Wang, Bing Zhang and Jindun Liu

ABSTRACT

We used natural resources of halloysite nanotubes and alginate to prepare a novel porous adsorption material of organic–inorganic hybrid beads. The adsorption behaviour of Cu(II) onto the hybrid beads was examined by a continuous fixed bed column adsorption experiment. Meanwhile, the factors affecting the adsorption capacity such as bed height, influent concentration and flow rate were investigated. The adsorption capacity (Q_0) reached 74.13 mg/g when the initial inlet concentration was 100 mg/L with a bed height of 12 cm and flow rate of 3 ml/min. The Thomas model and bed-depth service time fitted well with the experimental data. In the regeneration experiment, the hybrid beads retained high adsorption capacity after three adsorption–desorption cycles. Over the whole study, the new hybrid beads showed excellent adsorption and regeneration properties as well as favourable stability.

Key words | alginate, column adsorption, Cu(II), halloysite nanotube

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INTRODUCTION

With the development of industry and technology, more attention has been paid to pollution caused by heavy metals which are not biodegradable and can persist and accumulate in the environment and living organisms, posing a serious threat to lives (Petrangeli Papini *et al.* 2004; Li *et al.* 2009). Copper ions especially are discharged from the industrial waste streams of the pulp, fertilizer and paint industries, water run-off, etc. Recently, various technologies have been developed to remove copper ions from effluent, such as chemical precipitation, ion exchange, adsorption, solvent extraction, membrane filtration, and electrochemical methods (Ghassabzadeh *et al.* 2010). However, numerous studies show that adsorption is one of the most effective alternatives for its low investment, simple operation, and potential recovery and reuse of metals.

In recent years, many biopolymer adsorbents have been widely used in the recovery of valuable metals and removal of toxic metal contaminants as they are biodegradable, environmentally friendly, efficient, and inexpensive (Hasan *et al.* 2006). Such materials include cellulose, alginates, carrageenans, proteins, and chitin derivatives (Seki & Suzuki 1996). In these materials, alginate mainly

extracted from brown seaweed has many carboxylic groups which offer metal-binding sites and are favourable for adsorption processes. Several studies reveal that the alginate beads can be used to remove some metal ions from wastewater (Papageorgiou *et al.* 2008; Rocher *et al.* 2008). However, the use of pure alginate beads on a practical scale has been limited because of low rigidity, high mass transfer resistance and poor mechanical strength (Zhang *et al.* 2008). To improve the properties of alginate beads is a challenge.

Halloysite nanotubes (HNTs) with layered hollow structure and large specific surface area have been proven to be attractive adsorbents for various metal ions and organic pollutants (Luo *et al.* 2010; Wang *et al.* 2010). More importantly, HNTs can be used as reinforcing nanofibre instead of expensive carbon nanotubes in composites. Thus, the present study was devoted to fabricating halloysite nanotube–alginate (HNT–alginate) hybrid beads with high adsorption capacity and mechanical strength in aqueous solution by using halloysites as the supporting matrix. The column adsorption experiments for Cu(II) were applied to evaluate the adsorption performance of the hybrid beads. The results indicated that HNT–alginate hybrid beads could be used as

an economical and efficient adsorbent for removal of Cu(II) from wastewater and were valuable for further application in heavy metal ion removal.

MATERIALS AND METHODS

Materials and instruments

Sodium alginate (chemical grade) was received from Painsi Chemical Reagent Co. Ltd (Zhengzhou, China). HNTs were obtained by shattering and sieving clay minerals (Henan, China). Other chemicals were all analytical reagent grade and used as received. Distilled water was used in the whole process.

Using an ultraviolet and visible spectrophotometer (UV-2450, Shimadzu) with the sodium diethyldithiocarbamate spectrophotometric method, the concentration of Cu(II) in the effluent was analyzed. The morphology of hybrid beads was examined by a scanning electron microscope (SEM, JSM-7500F).

Preparation of HNT-alginate hybrid beads

The steps to prepare HNT-alginate hybrid beads were as follow. Firstly, HNTs, sodium alginate and distilled water were added to a beaker followed by stirring of the solution for 12 h at room temperature to a homogeneous mixture. Under continuous stirring, the mixture was slowly dropped into a solution of calcium chloride (2%) by syringe. Then HNT-alginate hybrid beads were formed by Ca^{2+} crosslinking the sodium alginate to form hydrogel microspheres and embedding the uniformly dispersing HNTs into the microspheres. The obtained hybrid beads were left in the solution for 24 h and washed with distilled water several times and dried at 50 °C for 12 h. To obtain uniform and porous beads, a series of experiments was performed and the results showed that the optimal mass ratio of HNT and sodium alginate was 1:1.

Continuous fixed bed column adsorption experiments

The continuous fixed bed adsorption experiments were conducted in a glass column with different amounts of HNT-alginate hybrid beads (Figure 1). Before operation, the bed was rinsed with distilled water and left for 6 h to ensure a closely packed arrangement of beads with no voids, channels or cracks. In down-flowed mode the Cu(II)

solutions with known initial concentration and volumetric flow rate flowed through the fixed bed. The effluent solution was collected as a function of designed time at the bottom of the column. The effects of bed height, influent concentration and volumetric flow rate were studied, and all experiments were carried out at room temperature.

Regeneration of adsorbents

In the regeneration experiment 1 M HCl solution was used as an eluent. When adsorption equilibrium was achieved, the eluent was pumped into this column with the same volumetric flow rate as in the adsorption process. When the concentration of Cu(II) in the effluent solution reached zero, the desorption process finished. Then distilled water was sent through the column to remove HCl until the effluent was close to neutral. The next adsorption process was conducted under the same conditions. In this study, three adsorption–desorption cycles were performed.

RESULTS AND DISCUSSION

Figure 2(a) shows a digital photograph of the HNT-alginate hybrid beads in the wet state. It reveals that the beads possessed an average diameter of about 1.5 mm with a smooth and uniform surface, and the beads were light yellow or gray due to the presence of HNTs. To examine the fine morphology, the hybrid beads were observed by scanning electron microscopy. Figure 2(b) shows clearly that the bead was comprised of HNTs and alginate, and the HNTs overlapped loosely together in the interior of the hybrid beads. This loose structure may be more beneficial to the mass transfer of adsorbate molecules during adsorption.

The Thomas model of dynamic adsorption

A very important characteristic for an adsorption column is the breakthrough curve, whose shape determines the dynamic response and operation. The Thomas model based on Langmuir adsorption–desorption kinetics is one of the most generally used methods to describe the breakthrough curves in the study of column performance (Unuabonah *et al.* 2010; Barron-Zambrano *et al.* 2010; Song *et al.* 2011).

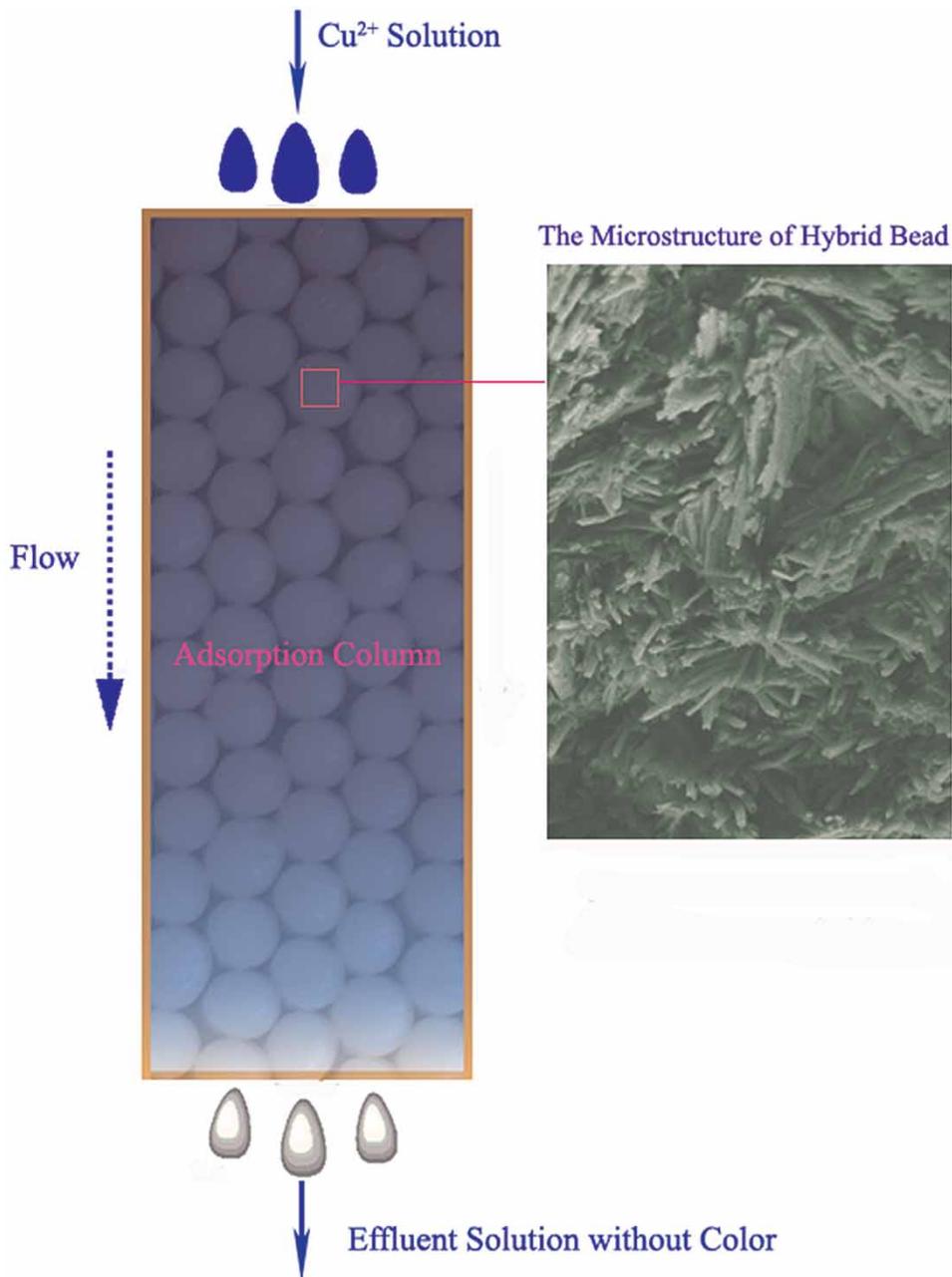


Figure 1 | The schematic of the fixed-bed column of HNT-alginate hybrid beads for Cu(II) adsorption.

The nonlinear and linear equations of the Thomas model are shown as follows:

$$\frac{C_t}{C_0} = \frac{1}{1 + \exp(K_{th}Q_0M/v - K_{th}C_0t)} \quad (1)$$

$$\ln\left(\frac{C_0}{C_t} - 1\right) = \frac{K_{th}Q_0M}{v} - K_{th}C_0t \quad (2)$$

where K_{th} ($\text{ml mg}^{-1} \text{min}^{-1}$) is the Thomas rate constant; C_t (mg/L) is the effluent concentration at any time; C_0 (mg/L) is the influent concentration; Q_0 (mg/g) is the maximum solid phase concentration of Cu(II) per weight of adsorbent; M (g) is the mass of the adsorbent; v (ml/min) is the volumetric flow rate.

According to Equation (2), the Q_0 and K_{th} under different conditions, such as bed height, initial inlet concentration

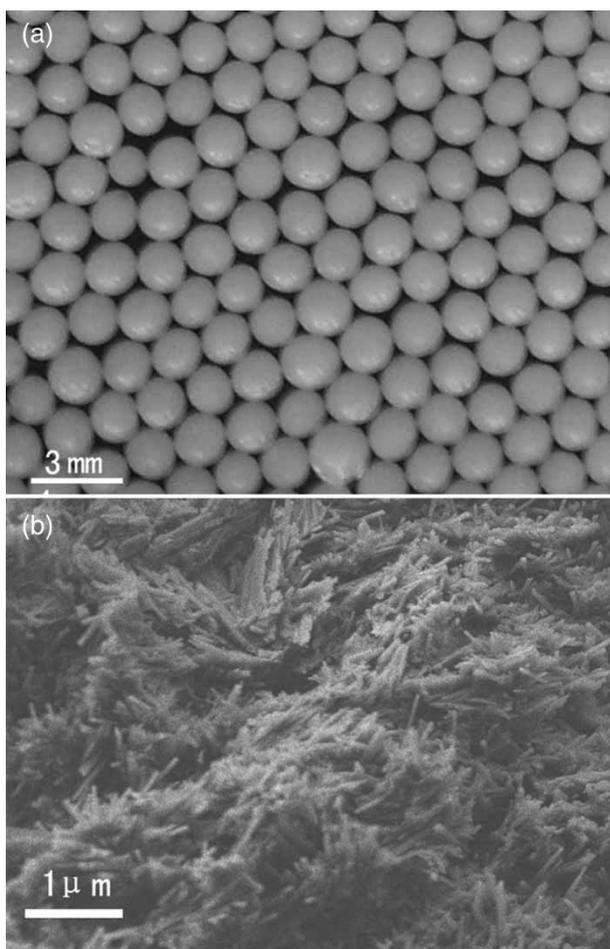


Figure 2 | (a) Digital photograph and (b) SEM image of HNT-alginate hybrid beads.

and flow rate, can be obtained from the slope and intercept of plots of $\ln[(C_0/C_t)-1]$ versus t . The values of R^2 , Q_0 and K_{th} are listed in Table 1. The R^2 of the linear plots of $\ln[(C_0/C_t)-1]$ versus t at different conditions are all above 0.992, which suggest that the adsorption of Cu(II) onto the hybrid beads predominantly fits the Thomas model.

Effect of bed height

The influence of bed height was studied at different bed heights (6, 9, 12 cm) with the constant initial concentration of 50 mg/L and flow rate of 3 ml/min. All three breakthrough curves are shown in Figure 3(a) with a similar trend. As indicated in Table 1, the breakthrough time increased from 256 to 1,240 min, and the exhaustion time increased from 2,270 to 4,100 min as the bed height increased from 6 to 12 cm. And as the bed height increased, the Q_0 calculated via the Thomas model increased from 46.41 to 63.07 mg/g. For the column with greater bed height has more adsorbents which

Table 1 | The data and the Thomas model of column adsorption under different reaction conditions

C_0 (mg/L)	H (cm)	v (ml/ min)	t_b (min)	t_e (min)	K_{th} (ml $\text{mg}^{-1} \text{min}^{-1}$)	Q_0 (mg/ g)	R^2
50	6	3	256	2700	0.039	46.41	0.995
50	9	3	693	3414	0.034	59.59	0.996
50	12	3	1240	4100	0.035	63.07	0.998
50	12	3	1240	4100	0.035	63.07	0.998
75	12	3	658	3438	0.023	72.68	0.996
100	12	3	400	2384	0.023	74.13	0.997
50	12	3	1240	4100	0.035	63.07	0.998
50	12	4.5	511	3489	0.031	62.34	0.992
50	12	6	353	2837	0.041	53.89	0.995

can provide more adsorption sites for Cu(II). In addition, in the higher column the effluent would have enough contact time for Cu(II) to be adsorbed on the hybrid beads, while in the lower column the opposite phenomenon occurred. The result means the bed height is an important factor for the column adsorption process.

Effect of initial inlet concentration

The effect of initial inlet concentration was studied at different initial concentrations (50, 75 and 100 mg/L) with a bed height of 12 cm and flow rate of 3 ml/min. All three breakthrough curves are shown in Figure 3(b), and the breakthrough time, exhaustion time and the total adsorption capacity are shown in Table 1. As the table shows, with the increase of initial concentration from 50 to 100 mg/L, the breakthrough time decreased from 1,240 to 400 min, and similarly, the exhaustion time decreased from 4,100 to 2,384 min, while the Q_0 increased from 63.07 to 74.13 mg/g. That may be attributed to the higher driving force provided by the greater concentration. The driving force for sorption is the concentration difference between the solute on the sorbent and in the solution (Uddin *et al.* 2009; Ahmad & Hameed 2010). The change of concentration gradient affects the saturation rate and breakthrough time. Therefore, the higher initial concentration provides a higher adsorption rate, and the column can reach exhaustion more quickly.

Effect of flow rate

To study the influence of different flow rates (3, 4.5 and 6 ml/min), the experiments were performed with a constant initial concentration of 50 mg/L and bed height of 12 cm.

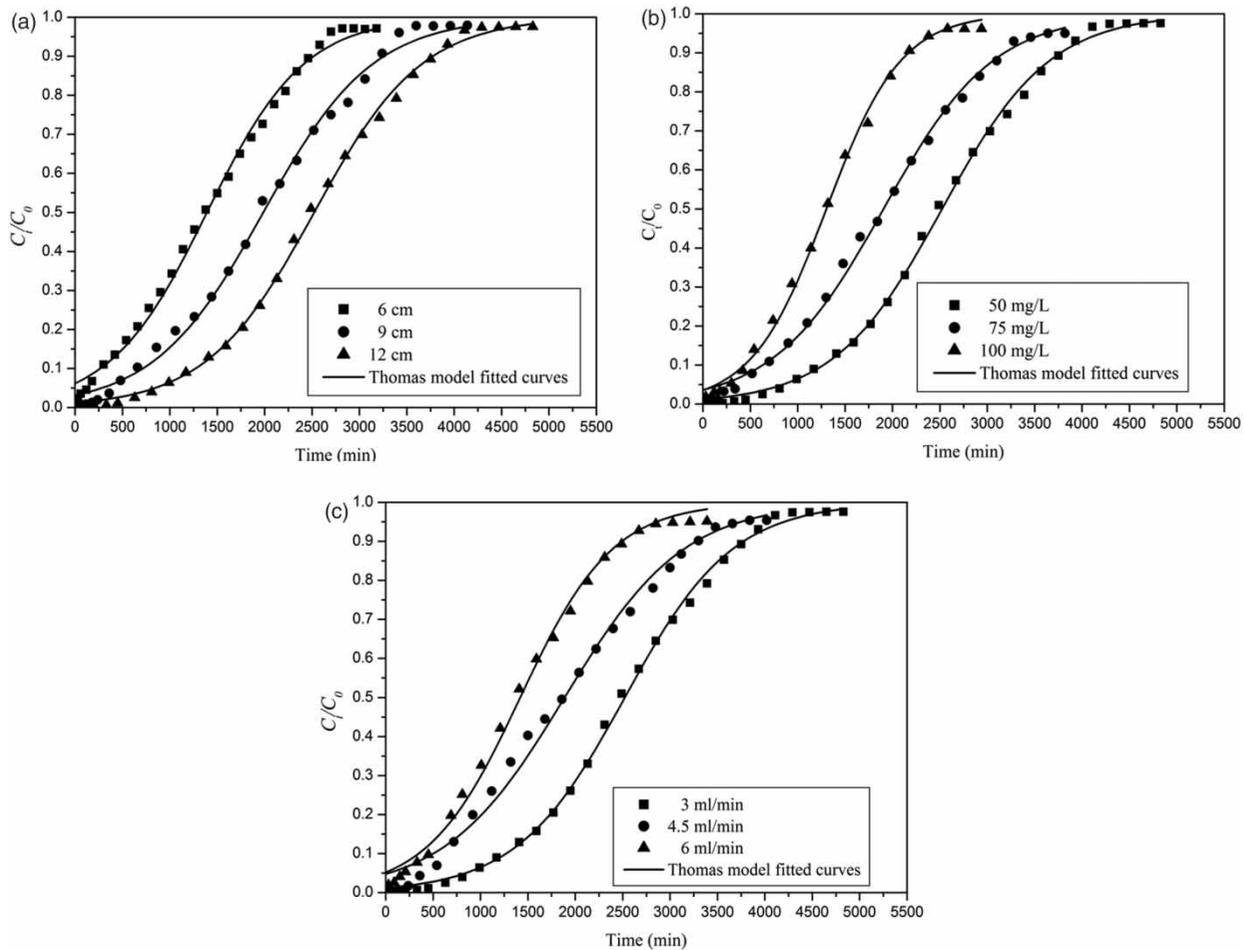


Figure 3 | Effects of (a) bed height, with initial concentration of 50 mg/L and flow rate of 3 ml/min; (b) initial inlet concentration, with bed height of 12 cm and flow rate of 3 ml/min; and (c) flow rate, with initial concentration of 50 mg/L and bed height of 12 cm for adsorption of Cu(II) on HNT-alginate hybrid beads.

The breakthrough curves are shown in Figure 3(c), and the other parameters are shown in Table 1. As expected, the breakthrough time increased from 353 to 1,240 min, and the exhaustion time increased from 2,837 to 4,100 min with the flow rate decreasing from 6 to 3 ml/min. Similarly, the Q_0 increased from 53.89 to 63.07 mg/g. It is considered that at higher flow rate, the adsorbates and adsorbents do not have enough contact time for interaction and Cu(II) does not have more chances to be adsorbed on the hybrid beads. While at lower flow rate, the Cu(II) can fully contact with the adsorbents. In brief, the lower flow rate the effluent has, the greater adsorption capacity the column has.

The bed-depth service time model of dynamic adsorption

The bed-depth service time (BDST) model is a simple model for predicting the relationship between bed depth

and service time at a certain concentration and flow rate. The equation of the BDST model can be expressed as follows (Abu-Lail et al. 2010; Maiti et al. 2008):

$$t = \frac{N_0 Z}{C_0 u_0} - \frac{1}{K_a C_0} \ln \left(\frac{C_0}{C_t} - 1 \right) \quad (3)$$

where C_0 (mg/L) is the influent concentration; C_t (mg/L) is the Cu(II) concentration at breakthrough; N_0 (g/L) is the adsorption capacity of the bed; u_0 (cm/min) is the linear velocity; K_a ($\text{L g}^{-1} \text{min}^{-1}$) is the BDST rate constant; Z (cm) is the bed depth; and t (min) is the service time at breakthrough. According to the model, the breakthrough time can be predicted under different bed heights, which can provide reference for the column design in practical applications.

The times when C_t/C_0 reached 0.1, 0.2 and 0.3 were selected as column service times and Figure 4 shows the fitted curves. It can be seen that the breakthrough time

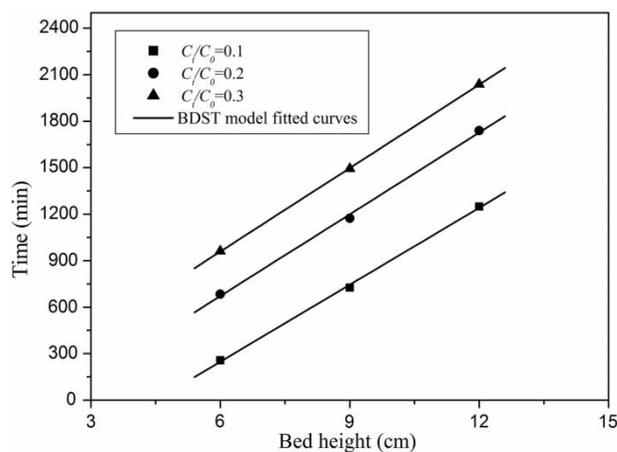


Figure 4 | The BDST model for adsorption of Cu(II) on HNT-alginate hybrid beads. Reaction conditions: initial concentration: 50 mg/L, flow rate: 3 ml/min.

increased with the increase of bed height at the same C_i/C_0 . As indicated in Table 2, the related coefficients almost reached 0.999, which means the results fitted well with the BDST model. As the C_i/C_0 increased from 0.1 to 0.3, N_0 increased from 24.83 to 26.92 g/L, and K_a increased from 0.058 to 0.143. This indicates that the adsorption capacity per unit volume increased with the increase of C_i/C_0 , and the amount of Cu(II) which was adsorbed on the beads also increased. So enhancing the bed height can advance the removal of Cu(II).

Regeneration of the adsorbents

It is critically significant for an adsorbent to possess favourable reusability in practical application. Adsorption–desorption cycle experiments were performed to evaluate the reusability of HNT-alginate hybrid beads. In this study, the column with the constant initial concentration of 50 mg/L, bed height of 9 cm, and flow rate of 3 ml/min was used for the experiments. The breakthrough curves plotted by the adsorption process of the three cycles are shown in Figure 5, and the breakthrough time, exhaust time and Q_e of the three cycles are exhibited in Table 3. It

Table 2 | The constants of the BDST model for Cu(II) adsorption on HNT-alginate hybrid beads

C_i/C_0	U_0 (cm/min)	C_0 (g/L)	N_0 (g/L)	K_a (L g ⁻¹ min ⁻¹)	R^2
0.1	3	0.05	24.83	0.058	0.999
0.2	3	0.05	26.37	0.072	0.998
0.3	3	0.05	26.92	0.143	0.999

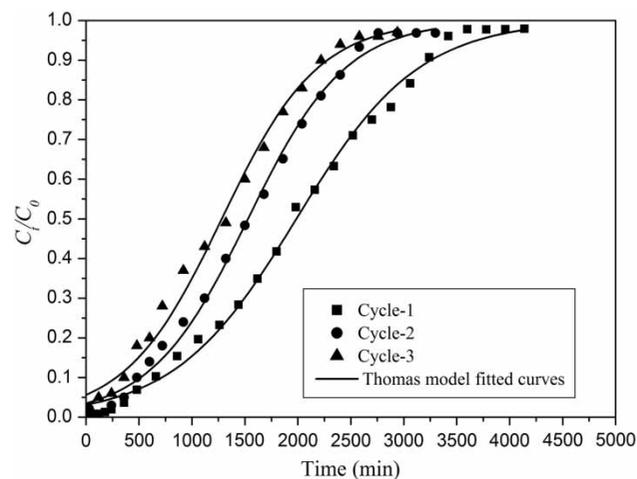


Figure 5 | The adsorption process of the adsorption–desorption cycles. Reaction conditions: initial concentration: 50 mg/L, bed height: 9 cm, flow rate: 3 ml/min.

can be seen that, t_b , t_e and Q_e decreased from 693 to 278 min, 3,414 to 2,561 min, and 59.59 to 38.45 mg/g respectively with the number of the cycles increasing. After three cycles, the adsorption capacity Q_e still remained about 40 mg/g, which was relatively high for the adsorption of Cu²⁺ ions from wastewater and indicated the good adsorption property of the prepared adsorbent. That means the hybrid beads can be regenerated and reused in practical application.

Furthermore, the experiment with three cycles had lasted more than 150 hours, and in the whole process, the adsorbents were washed by 1 M HCl more than once. Even so, the morphology and size of the hybrid beads did not change. But generally, pure alginate beads easily swell and rupture during the comparison experiments. So the HNT-alginate hybrid beads show excellent mechanical strength and stability in the aqueous solution.

In addition to good adsorption of Cu²⁺ ions from wastewater, the HNT-alginate hybrid beads showed good adsorption performance for other heavy metal ions, such as Ag⁺ ions and Cd²⁺ ions.

ADSORPTION MECHANISM

In this study, the main mechanism of the adsorption of Cu(II) on HNT-alginate hybrid beads can be attributed to ion exchange and complexation reactions (Chen *et al.* 2002; Saxena & Bajpai 2009). Alginates possess large amounts of functional groups (represented as R), such as carboxylic groups. In aqueous solution of Cu²⁺ ions,

Table 3 | The data from column adsorption over three cycles

Cycle	C_0 (mg/L)	H (cm)	V (ml/min)	t_b (min)	t_e (min)	K_{th} (ml mg ⁻¹ min ⁻¹)	Q_e (mg/g)	R^2
1	50	9	3	693	3414	0.034	59.59	0.996
2	50	9	3	470	2933	0.043	45.87	0.996
3	50	9	3	278	2561	0.044	38.45	0.991

exchange between Cu^{2+} ions and calcium ions inside the hybrid beads takes place as shown in Equation (4). In addition, there may be some free functional groups (R^{2-}) in the hybrid beads, leading to a complexation reactions with Cu^{2+} ions as shown in Equation (5):



Furthermore, HNTs have been proven to have a layered hollow structure and surface negative charge (Wang *et al.* 2010). The layered hollow structure with large specific surface is conducive to the physical adsorption of Cu^{2+} ions. At the same time, the surface negative charge of HNTs can generate electrostatic attraction with Cu^{2+} ions, which is also favourable for adsorption (Luo *et al.* 2010).

CONCLUSION

In this study, the adsorbent HNT–alginate hybrid beads showed good adsorption and regeneration properties and were prepared by simply immobilizing alginate onto a nanotubular structure. They also had favourable mechanical and chemical stability. In the column adsorption, the experimental data fitted well with both the Thomas and BDST models. Meanwhile, the regeneration experimental results showed that the adsorbent still exhibited a good adsorption capacity after three cycles. To summarize, the prepared HNT–alginate hybrid beads have excellent prospects for application in the wastewater treatment field.

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