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A novel biodegradable β-cyclodextrin-based hydrogel for the removal of heavy metal ions

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ABSTRACT

A novel biodegradable β-cyclodextrin-based gel (CAM) was prepared and applied to the removal of Cd^{2+}, Pb^{2+} and Cu^{2+} ions from aqueous solutions. CAM hydrogel has a typical three-dimensional network structure, and showed excellent capability for the removal of heavy metal ions. The effect of different experimental parameters, such as initial pH, adsorbent dosage and initial metal ion concentration, were investigated. The adsorption isotherm data fitted well to the Freundlich model. The adsorption capacity was in the order $Pb^{2+} > Cu^{2+} > Cd^{2+}$ under the same experimental conditions. The maximum adsorption capacities for the metal ions in terms of mg/g of dry gel were 210.6 for Pb^{2+}, 116.41 for Cu^{2+}, and 98.88 for Cd^{2+}. The biodegradation efficiency of the resin reached 79.4% for *Gloeophyllum trabeum*. The high adsorption capacity and kinetics results indicate that CAM can be used as an alternative adsorbent to remove heavy metals from aqueous solution.

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1. Introduction

In recent years, with the development of industrialization, heavy metal ion pollution of water is a serious matter. In the environment, heavy metal ions cannot be degraded naturally and accumulate in living organisms through food chain circulation. Furthermore, excessive heavy metal ion accumulation becomes toxic and directly affects the growth and physiological functions of organisms, leading to disease and even death of organisms (Yurtsever & Sengil, 2009).

The typical methods for heavy metal ions removal from industrial wastewater include chemical precipitation, reverse osmosis, membrane systems, solvent extraction, adsorption, electrolytic processes, ion exchange processes, and biological methods. Among these methods, adsorption is one of the most economically favorable and it is technically an easy method (Vismara, Melone, Gastaldi, Cosentino, & Torri, 2009). However, many absorbents, as well as being economically expensive, have disadvantages such as low adsorption capacity and non-biodegradability. Thus, considerable attention has been focused on the removal of heavy metal ions from wastewater using biodegradable adsorbents derived from low-cost materials.

β-Cyclodextrin (β-CD) has many hydroxyl groups on the outside of the cyclic cavity. These hydroxyl groups can enhance the adsorption of heavy metal ions by strong interactions between the hydroxyl groups and metal ions (Chao, Jin, Xu, Zhuang, & Shen, 2008). Another β-CD is the cyclic oligosaccharide formed from seven glucose molecules by α-1–4-glucosidase linkages. β-CD and its derivatives are biodegradable (Del Valle, 2004).

In this paper, a novel biodegradable β-CD based adsorbent (CAM, Fig. 1) was prepared by cross-linking reactions under microwave irradiation. The objective of the study was to search for a biodegradable adsorbent with a high adsorption capacity for heavy metal ions. The chemical structure of CAM was characterized, and the adsorption behavior of CAM for Cd^{2+}, Pb^{2+} and Cu^{2+} was investigated. The possible adsorption mechanisms were also explored by fitting to the isotherm equations.

2. Experimental

2.1. Materials

β-CD, acrylic acid (AA), N,N′-methylene-bis-acrylamide (MBA), and $Ce(NH_4)_2(NO_3)_6$ were purchased from the Chemical Reagent Development Center of Kemiou Engineering (Tianjin, China). *Aspergillus niger* (*A. niger*), *Penicillium* and *Gloeophyllum trabeum* were obtained from the Laboratory of Forest Protection of the Northeast Forestry University. The standard stock solutions (500 mg/L) of Cd^{2+}, Pb^{2+} and Cu^{2+} were prepared from their nitrate salts. The pH of the experimental solutions was adjusted using 0.1 M

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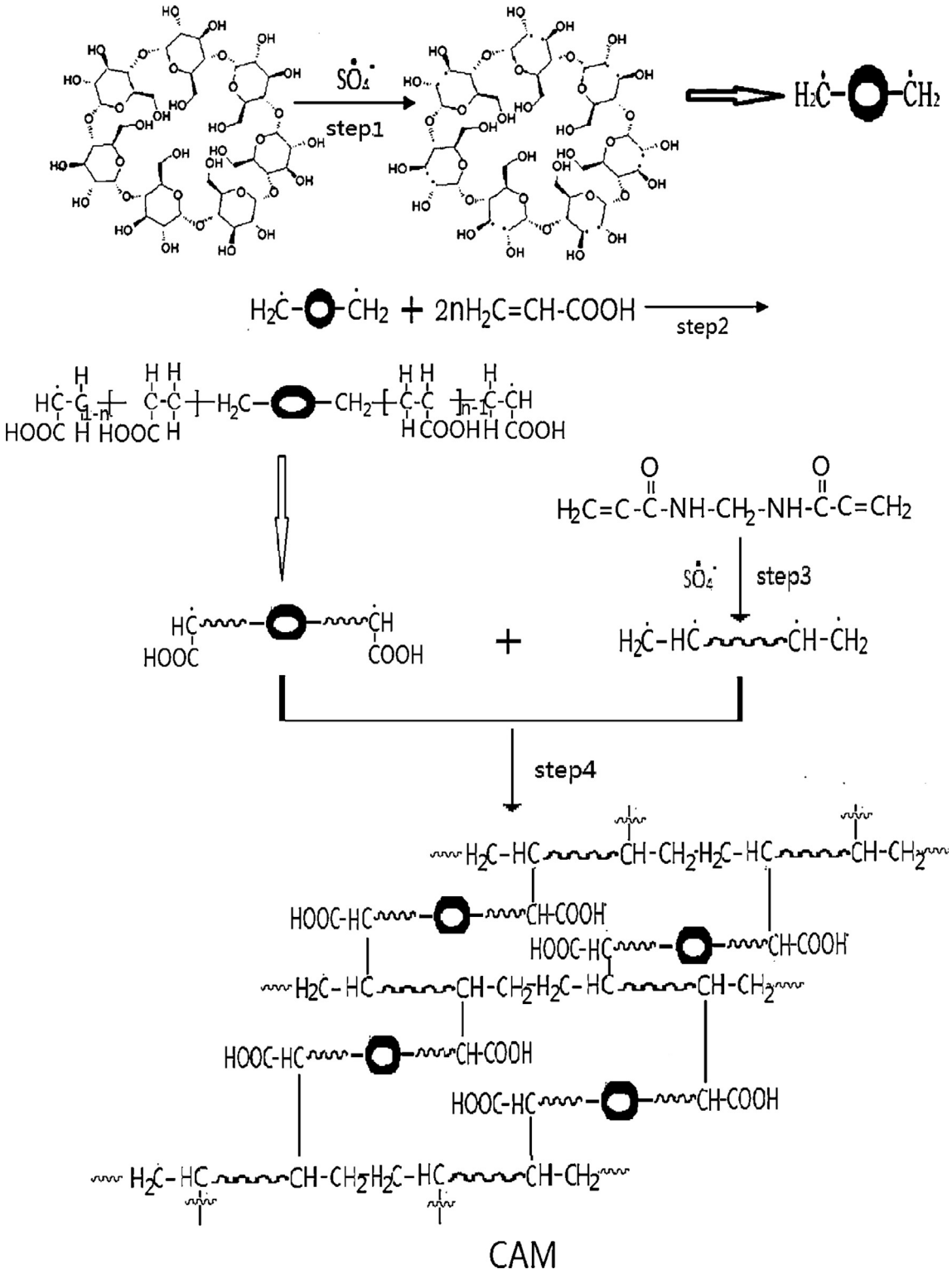

Fig. 1. Main structure of CAM resin.

HCl and 0.1 M NaOH. All reagents used were of analytical grade, and all solutions were prepared with distilled water.

2.2. Microwave preparation of CAM

β-CD, AA, and MBA were mixed in a 250 mL three-neck reaction bottle with a mass ratio of 1:6:3. The resulting mixture was dissolved in 0.01 M NaOH solution with stirring to adjust the mixture to a specified degree of neutralization. The mixture was uniformly mixed to dissolve the solid samples. Then, the three-neck reaction bottle was installed on the microwave synthesizer. Nitrogen flowed through for the whole reaction process. 0.01 g $Ce(NH_4)_2(NO_3)_6$ (quantitative initiator) was then added in the three-neck reaction bottle using a funnel at a constant rate of 1 d/s to 2 d/s with stirring at 60 °C. After then, the microwave irradiated reaction was maintained 15 min exposure time and at 250 W microwave power. Then,

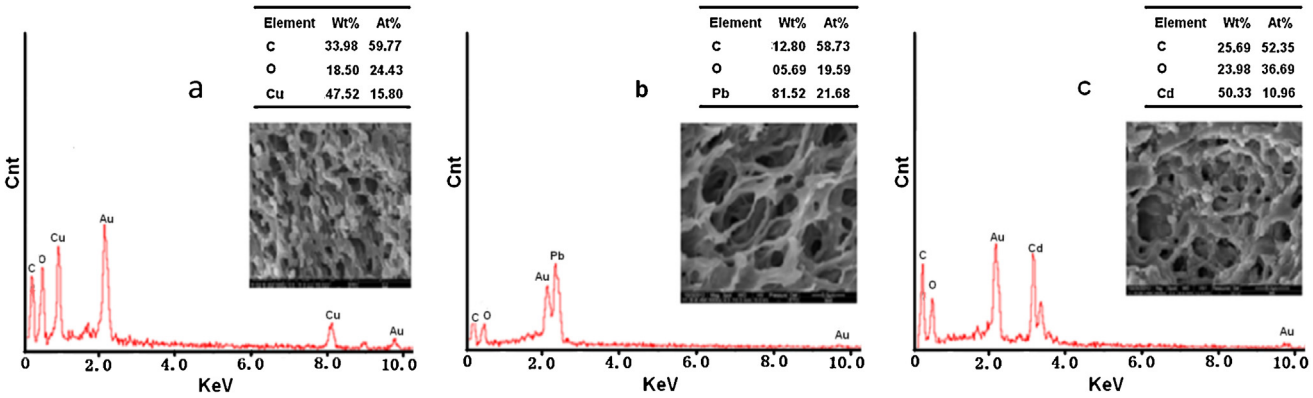

Fig. 2. SEM-EDX spectra of the adsorbent in the Cd^{2+}, Pb^{2+} and Cu^{2+} solutions.

the mixture was passed through a filter, and the filtered cake was extracted for 6–8 h by acetone under 50 °C, filter again, the filtered cake was washed by alcohol for three times in order to remove unreacted monomer. Finally, the filtered cake was dried at 40 °C for 48 h to give CAM.

2.3. Characterization

The Fourier transform-infrared (FTIR) spectra were recorded on a MAGNA 560 FTIR spectrometer (Thermo Nicolet Corporation, USA) using KBr discs in the range 400–4000 cm^{-1}. Scanning electron microscope (SEM) images and energy dispersive X-ray analyses (EDX) were obtained using a FEI QUANTA 200 Microscope (FEI Corporation, Netherlands). Solid-state carbon-13 cross-polarization and magnetic-angle spinning nuclear magnetic resonance (^{13}C CPMAS NMR) spectra were obtained using a Bruker Avance 400 NMR spectrometer (BRUKER Corporation, Germany) with a frequency of 75.47 MHz and a sample spin of 4.0 kHz.

2.4. Adsorption experiments

Cd^{2+}, Pb^{2+} and Cu^{2+} aqueous solutions were prepared from the corresponding standard stock solutions by diluting with deionized water to give different concentrations (25 mg/L, 50 mg/L, 100 mg/L and 150 mg/L). 0.1 g of the CAM was mixed with 200 mL of each salt solution, and the water absorbency was then measured. Buffer solutions with pH values of 2, 4, 6, 8, 10, and 12 were prepared using 0.1 g of the CAM mixed with 200 mL of the buffer solutions of different pH values. After saturation, the solutions were filtered and weighed, the hydrogel characteristics were determined, and the absorbency was calculated. The adsorption capacity (Q) and removal rate (A) were calculated as follows:

$$Q = \frac{C_0V_0 - C_eV_e}{m} \quad (1)$$

$$A = \frac{C_0V_0 - C_eV_e}{C_0V_0} \times 100\% \quad (2)$$

where C_0 and C_e are the initial and equilibrium concentrations of the metal ions, V_0 and V_e are the initial and equilibrium volumes of the solution, and m is the dose of CAM.

2.5. Determination of biodegradability

CAM sheets with size 1 cm × 2 cm were obtained from the CAM products by cutting, and were then weighed and labeled separately. The sheets were placed in 18 PDA plates containing fungi (six plates each of *A. niger*, *Penicillium* and *G. trabeum*), sealed with tape, and incubated at 30 °C. Then, the CAM gels were filtered, dried, weighed, and the biodegradation was observed every 72 h.

3. Results and discussion

3.1. SEM-EDX analysis

0.1 g of CAM was added into saturated solutions of Cd^{2+}, Pb^{2+} and Cu^{2+}. After static adsorption for 6 h, filtering and purifying, three different test samples were obtained. The Cu, Pb and Cd distributions in the samples were studied by SEM-EDX analysis (Jacobson, Dousset, Andreux, & Baveye, 2007). Fig. 2a–c shows the mapping of Cu, Pb and Cd and the corresponding scanning image in the samples. The EDX spectra at single regions of the sample (Fig. 2) indicated the relative proportion of the different atoms. As shown in Fig. 2, Cu, Pb and Cd are present in the test samples with proportions of 50.55 wt%, 81.52 wt% and 47.52 wt%, respectively. The results indicated that the Pb content was significantly higher than Cu and Cd in the respective solutions.

The SEM images of the resin CAM hydrogel in Cd^{2+}, Pb^{2+} and Cu^{2+} saturated solutions are shown in Fig. 2a–c. After adsorption, the internal structure of the CAM hydrogel had an obvious three-dimensional network, and the network size increased with increasing adsorption content of the metal to the CAM adsorbent surface. However, in this study, the SEM-EDX technique was not sensitive enough to identify the differences of metal speciation generated during adsorption.

3.2. FTIR spectra

Fig. 3 shows the FTIR spectra of β-CD and CAM. The characteristic absorption peaks of β-CD (3406, 2928, 1156 and 1028 cm^{-1}), PAA (2830, 1721 and 1450 cm^{-1}) and MBA (1560 and 1450 cm^{-1}) are observed in the spectra. In the FTIR spectra, the peak for the stretching vibration absorption of —NH_2 is 1560 cm^{-1} (Tripathy, Mishra, & Behari, 2009), while the peak at 1450 cm^{-1} corresponds to the C—N stretching vibration of the MBA unit. Moreover, the lack of a characteristic —C=C absorption peak indicates that a polymerization reaction occurred. Based on these results, it can be concluded that —C=O and —NH_2 were introduced to the CAM.

Fig. 4 shows the ^{13}C NMR spectra of β-CD and CAM. Fig. 3 indicates that there is a dissymmetrical β-CD cavity, because of an obvious signal split of characteristic carbon atoms, with the split peaks at 101–104 ppm being the C1 signal peaks connected to the β-CD vertical glycosidic linkage. The chemical shifts at 80–85 ppm are the characteristic signals for C4; the five split peaks at 58–63 ppm are characteristic of the signal for C6; and the chemical shifts at 72–78 ppm are the cyclic carbons C2, C3, C5, which are

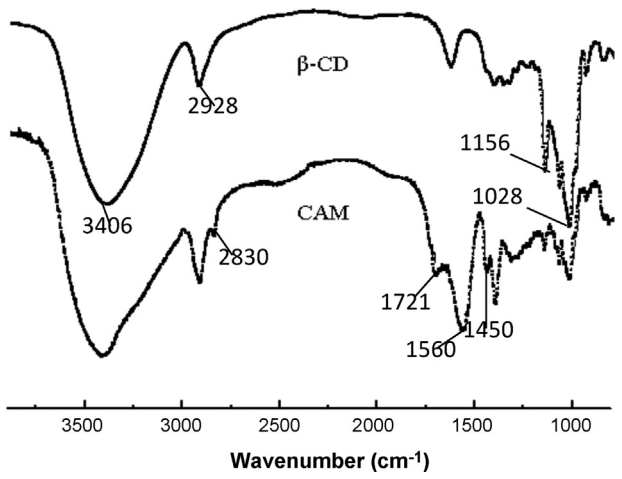

Fig. 3. FTIR spectra of β-CD and CAM.

not connected to the glycosidic bond but have the same characteristics of the separate peaks (Huang, Liu, Zhang, Xu, & Hu, 2012).

It can be seen from the ^{13}C NMR spectra of CAM that the spectrogram was smooth and split peaks were not observed. The characteristic peak at 185.24 ppm represents the carbon signal from C=O. The peaks at 20–50 ppm are characteristic signal peaks for different alkyl group in the polymer chains. The peaks at 104.44 ppm and 82.11 ppm represent C1 and C4 signals of the glucose residues, and the split peaks at 65.06 ppm and 61.41 ppm represent C6 signals of the glucose residues. The peak at 73.55 ppm was identified as the cyclic carbons C2, C3 and C5, which are not connected to the glycosidic linkage. In certain environments, the resonance peaks of C2, C3, and C5 tend to overlap to form a single peak (Lu, Yang, Zhou, & Lei, 2008). The peaks at 20–50 ppm are characteristic signal peaks of alkyl groups in polymer chains. The above results indicate that the cycle cavity of β-CD was open during polymerization.

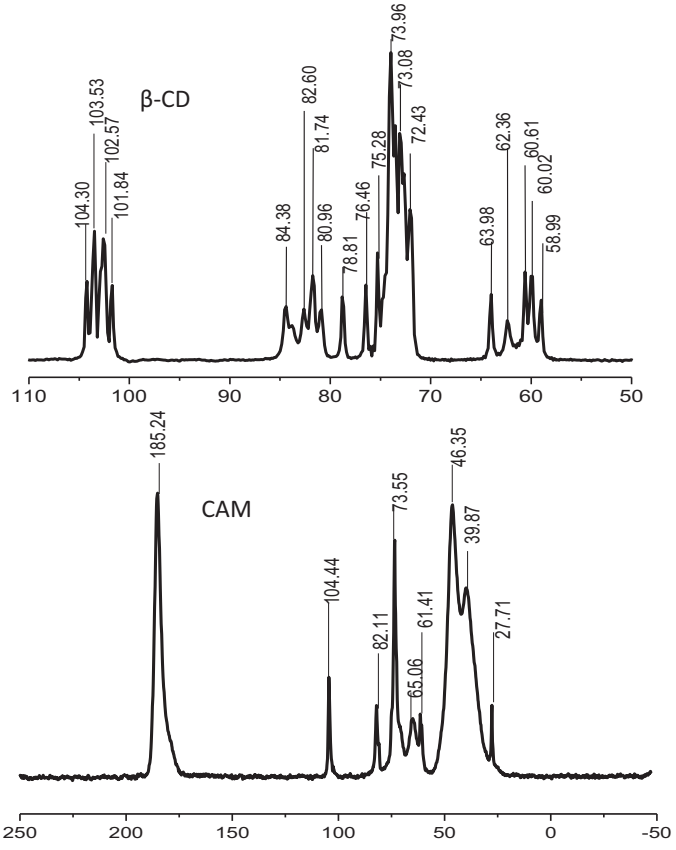

Fig. 4. Solid-state ^{13}C NMR spectra of β-CD and CAM.

3.3. Effect of different experimental parameters on metal ion adsorption to CAM

The effects of adsorbent dosage, initial pH and initial metal ion concentration on the uptake and removal rate of CAM are shown in Fig. 5. As shown in Fig. 5a, the removal rate of Cd^{2+}, Pb^{2+} and Cu^{2+} shows a trend of initial increasing and then decreasing when the CAM dose was increased from 0.01 g/L to 0.2 g/L. In contrast, the uptake of Cd^{2+}, Pb^{2+} and Cu^{2+} gradually decreases from 228.91 mg/g to 49.03 mg/g, 505.60–63.29 mg/g, and 188.25–49.86 mg/g, respectively. A possible reason could be that the increase in adsorbent provides excess active groups beyond the capacity to be accepted by the metal ions. Moreover, the competition for adsorption sites on the adsorbent between water and the metal ions leads to an increase in water uptake and a decrease in the removal rate of the metal ions (Naiya, Bhattacharya, & Das, 2009). As shown in Fig. 5b, the adsorption capacities increased significantly with an increase in solution pH from 2 to 5. At lower solution pH values, H^+ competes with metal ions for the adsorption sites, resulting in the surface of the adsorbent occupied by more H^+ and reducing the complexation of the metal ions on the surface of the adsorbent (Liang, Guo, Feng, & Tian, 2010). At higher solution pH values, the surface of the adsorbent is occupied by more negative charges, which attracts more metal ions. The effect of initial metal ion concentration on the uptake is shown in Fig. 5c. The results indicate that the adsorption capacities increase with increasing initial concentration of metal ions, and the removal rate initially increases and then decreases. When the initial concentration of metal ions increases, the increase in metal ions combining with the active groups on the adsorbent gradually decreases, which results in a gradual increase in the adsorption capacity. In addition, more metal ions are left in solution because of saturation of the adsorption sites (Cao, Tan, Che, & Xin, 2010). Thus, when the concentration of metal ions increase, the increase in metal ions combining with the active groups gradually decreases.

3.4. Adsorption isotherm

The adsorption isotherms were evaluated using the Langmuir and Freundlich isotherm models. The Langmuir isotherm model (Sharma & Mishra, 2010) is given by

$$q_e = \frac{K_L C_e}{1 + a_L C_e}, \tag{3}$$

where q_e (mg/g) and C_e (mg/L) are the amount of metal ion adsorbed per unit weight of adsorbent and the unadsorbed metal ion concentration in solution at equilibrium, respectively. The empirical constants K_L and a_L of the Langmuir model are related to the maximum adsorptive capacity of the adsorbent (L/g) and the bonding strength (L/mg), respectively.

The Freundlich isotherm model (Dabrowski, 2001) is given by

$$\log\ q_e = \log K_F + \frac{1}{n} \log C_e, \tag{4}$$

where q_e is the amount adsorbed at equilibrium (mg/g), C_e is the equilibrium concentration of metal ions (mg/L), and K_F (mg/g) and n (g/L) are Freundlich constants related to the adsorption capacity and the intensity of adsorption, respectively.

The values of the isotherm constants and the correlation coefficients for the isotherm plots of Cd^{2+}, Pb^{2+} and Cu^{2+} are given in Table 1. The highest numerical value of K_F (115.46) was obtained

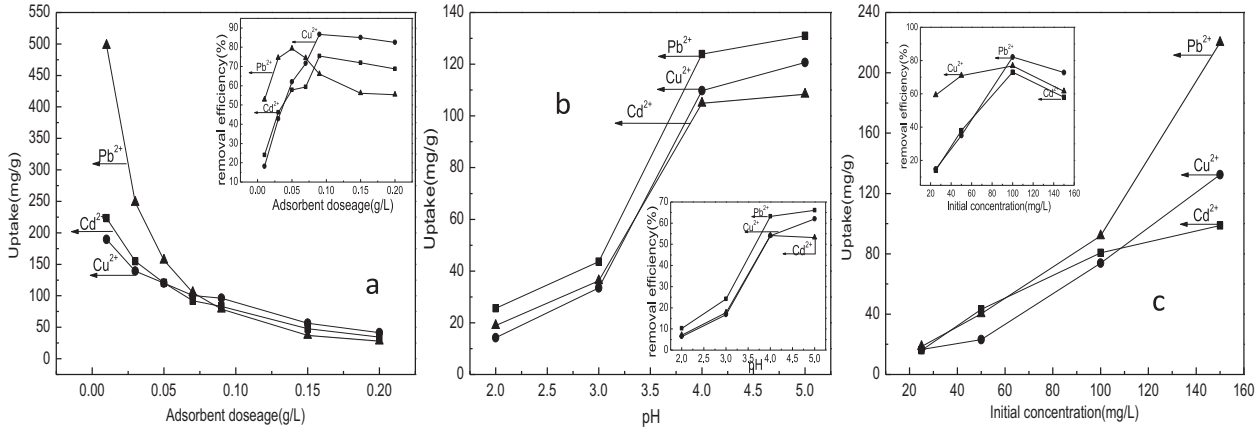

Fig. 5. Effect of the (a) adsorbent dosage, (b) initial pH, and (c) initial metal ion concentration on the adsorption capacities of Cd^{2+}, Pb^{2+} and Cu^{2+}.

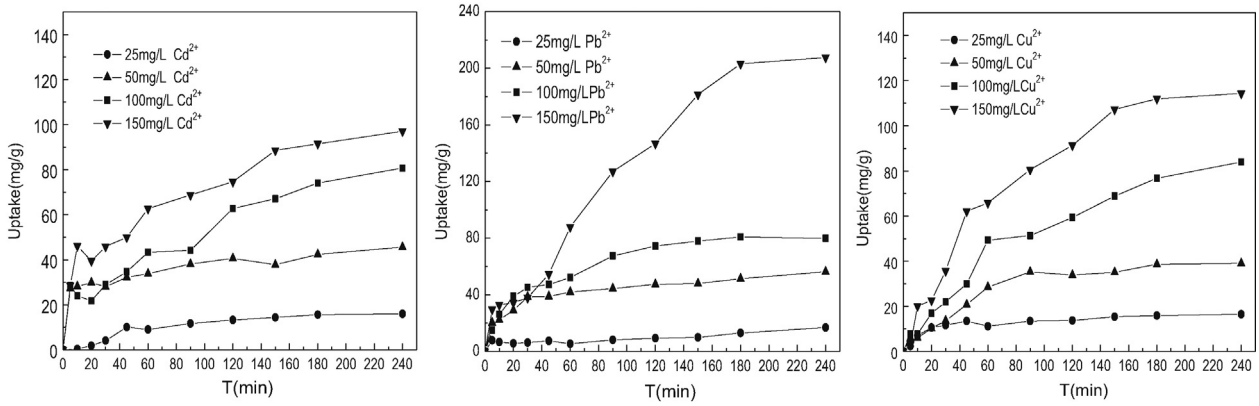

Fig. 6. Effect of adsorption time on the adsorption capacities of CAM for Cd^{2+}, Pb^{2+} and Cu^{2+}.

for Pb^{2+}, followed by Cu^{2+} (18.97) and then Cd^{2+} (11.62). The results indicate that the equilibrium adsorption data for CAM fits the Freundlich isotherm model better than the Langmuir model. Therefore, the adsorption mechanism of metal ions to CAM takes place through an ion exchange process (Homagai, Ghimire, & Inoue, 2010).

3.5. Adsorption kinetics

The adsorption capacities of CAM gel for Cd^{2+}, Pb^{2+} and Cu^{2+} solutions are shown in Fig. 6. The adsorption capacities of the metal ions occurred in the order Pb^{2+} (210.6 mg/g) > Cu^{2+} (116.41 mg/g) > Cd^{2+} (98.88 mg/g). The results indicate that CAM has excellent adsorption performance for heavy metal ions, and the adsorption rate is fast, reaching equilibrium within 60–90 min. A high correlation between the experimental data and the quasi-second order adsorption rate equation was obtained. The results of R^2 for each metal ion are 0.971 (Cd^{2+}), 0.987 (Pb^{2+}), and 0.983 (Cu^{2+}).

Table 1
Adsorption isotherm constants of Langmuir and Freundlich models for Cd^{2+}, Pb^{2+} and Cu^{2+} ions adsorbed by CAM.

Model	Coefficient	Cd^{2+}	Cu^{2+}	Pb^{2+}
Langmuir	q_{max} (mg/g)	98.88	116.41	210.60
	K_L (L/g)	17.53	30.74	42.04
	R^2	0.896	0.909	0.922
Freundlich	K_F (mg/g)	11.62	18.97	115.46
	n	0.174	0.305	0.181
	R^2	0.967	0.995	0.989

3.6. Biodegradation of CAM

The degradation efficiency of CAM resin gel in *A. niger*, *Penicillium* and *G. trabeum* is shown in Fig. 7. The degradation was observed to be very slow with *Penicillium*, with only 6.31% of the

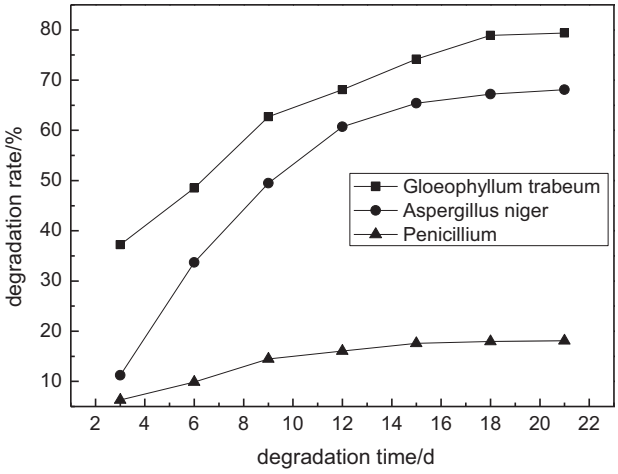

Fig. 7. Fungus degradation of CAM.

CAM gel degraded after 3 days and the degradation efficiency reaching a maximum of 18.11% after 21 days. In *A. niger*, the CAM gel degradation efficiency rapidly increased with time. After 3 days, the degradation efficiency was 11.2%, but after 18 days it reached 68.19%. With *G. trabeum*, the degradation efficiency was 39.26% after 3 days, and 79.4% after 21 days. The CAM block samples turned into fluid in 3 days. These results indicate that the CAM gel is biodegradable by *G. trabeum*. The order of the fungi based on the resin degradation efficiency is as follows: *G. trabeum* > *A. niger* > *Penicillium*.

4. Conclusions

A biodegradable β-cyclodextrin-based hydrogel (CAM) was prepared and shown to be an excellent adsorbent for the removal of Pb^{2+}, Cu^{2+} and Cd^{2+} ions from aqueous solution. The adsorption capacities of CAM were in the order: Pb^{2+} (210.6 mg/g) > Cu^{2+} (116.41 mg/g) > Cd^{2+} (98.88 mg/g). After adsorption, the internal structure of CAM hydrogel had an obvious three-dimensional network structure. The adsorption mechanism of the metal ions with CAM was through an ion exchange process. CAM hydrogel is biodegradable by *G. trabeum*, and the degradation efficiency was 79.4% after 21 days. This study shows that CAM is an eco-friendly adsorption material that is effective in removing heavy metal heavy metal ions from aqueous solution.

Acknowledgments

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