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Kinetics and Equilibria of Cd(II) Adsorption onto a Chemically Modified Lawny Grass with H[BTMPP]

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ABSTRACT: Removing Cd(II) by a modified lawny grass adsorbent (RG) containing H[BTMPP] (Cyanex272) has been investigated in this paper. The grass sorbents were characterized by SEM, FTIR, and elemental analysis, confirming that carboxylic groups were introduced onto the grass by chemical modification (citric acid (1CG)) and H[BTMPP] was successfully immobilized onto the grass (H-RG and H-1CG). H[BTMPP] played an important role in improving the maximum adsorption capacities to 133.2 $mg \cdot g^{-1}$ from 89.26 $mg \cdot g^{-1}$ and shortened the equilibration time from (40 to 20) min. From the batch experiments, the optimum pH is in the range of 5.5−6.0 for all adsorbents. H-1CG always had a higher ability to adsorb cadmium ions and the removal rate could be up to 99.54%. The kinetic equilibria could be explained as pseudosecond-order. Column experiments showed that breakthrough began at 160 bed volumes (BV) with H-1CG. A selection of 0.1 $mol \cdot L^{-1}$ HCl was used as the optimum desorption agent and elution is completed within 25 BV. Thermodynamic results indicated the adsorption of Cd(II) is spontaneous and endothermic. An ion exchange mechanism is involved in the adsorption process. This modified method can be regarded as an efficient strategy to improve the adsorption of cadmium from aqueous solution.

1. INTRODUCTION

Nowadays heavy metal pollution is one of the most important environmental problems. Heavy metals are stable and persistent environmental contaminants since they cannot be degraded or destroyed. These metal ions can be harmful to aquatic life, and water contaminated by toxic metal ions remains a serious public health problem. Finding practical and efficient methods to remove heavy metals from industrial wastewater is necessary for protecting the quality of aquatic systems and ground waters and has received much more attention over the past decade.[1−5] In particular, cadmium exposes human health to severe risks, due to its high toxicity, and can exert its toxic effect even at low concentrations. It can provoke cancer, kidney damage, mucous membrane destruction, vomiting, diarrhea, bone damage, and itai−itai disease, as well as affect the production of progesterone and testosterone.[6] The increasing presence of cadmium in the environment derives mainly from industrial activities, such as electroplating, paint pigments, plastics, alloy preparation, and silver−cadmium batteries. Therefore, it is necessary to remove cadmium from industrial effluents. The removal of heavy metals using a passive binding process with biomaterials that are capable of efficiently collecting heavy metals is termed bisorption. The major advantages of biosorption over conventional treatment methods include low cost, high efficiency, minimization of chemical or biological sludge, no additional nutrient requirement, and regeneration of biosorbents and possibility of metal recovery.[7,8] Many biomaterials are used to remove cadmium form wastewater, such as chitosan,[9] orange peel,[10] *Saccharomyces cerevisiae*,[11] and wheat bran.[12] However, the exploration and development of new adsorbents is endless.

Cellulose grass is a remarkable pure organic polymer, consisting solely of units of anhydroglucose held together in a giant straight chain molecule,[13] which is a crystalline homopolymer of glucose with β1−4 glycosidic linkages and intramolecular and intermolecular hydrogen bonds.[14] Cellulose grass includes alcohols, aldehydes, ketones, carboxylic, phenolic, and ether groups, which have the ability to some extent to bind heavy metals by donation of an electron pair from these groups to form complexes with the metal ions in solution.[15] Excess lawny grass is left as a solid waste during the process of city beautifying or garden building. Based on the above-mentioned advantages, lawny grass seemed to be a viable option for heavy metal remediation. This promising biomaterial has been used in the removal of metal ions either in their natural form or after some physical or chemical modification.[7]

H[BTMPP], called Cyanex272 commercially, is a kind of acidic organophosphorus extractant, which has good chemical stability for heat and hydrolysis and can be completely dissolved in aliphatic and aromatic diluents. H[BTMPP] has been used widely in separation and purification of rare earth elements and other metals.[16−19] In order to reduce the use of toxic volatile organic solvents, H[BTMPP] was immobilized onto some supports. Karve and co-workers reported that Amberlite XAD-2 resin was impregnated with Cyanex272 and Cyanex302 to separate uranium(VI) from rare earth elements.[20] Sun and co-workers developed a method where Cyanex923 was fixed on Amberlite XAD-7 with assistance of ionic liquids to extract yttrium from rare earths.[21] Draa and co-workers

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reported extraction of Pb(II) by XAD7 impregnated resins with organophosphorus extractants (DEHPA, IONQUEST801, Cyanex272).[22]

In our work, first, a biomass material with a macroporous structure, high surface area, and good mechanical stability was chosen as a support. Cellulosic grass is suitable. Second, in order to improve the performance of the grass, it was modified with citric acid to introduce a lot of functional carboxyl groups. Third, H[BTMPP] was immobilized on the grass by a solid−liquid grinding method for enhancing the uptake of Cd(II) from aqueous solution. Herein, in view of cost, the dosage of H[BTMPP] is very small in this work. Ultimately, a new biosorbent, chemically modified grass containing H[BTMPP] is prepared. Although there is a little loss of H[BTMPP] during the adsorption process, its applicability for the removal of Cd(II) is well proven by the experimental facts.

2. EXPERIMENTAL SECTION

2.1. Materials and Chemicals. Grass obtained from the lawn of our campus (Northeast Normal University, China) was washed with water to remove mud, sand, and other contaminants and then oven-dried at about 60 °C for 12 h. The dried grass was milled in a mull and sieved to smaller particles by a boult with the diameter of 0.25 mm. H[BTMPP] (American Cyanamid Company) was used without further purification. A stock solution of Cd(II) was prepared by dissolving a weighed quantity of $CdCl_2$ (Shanghai Reagents Four Factory) in 25 mL of 0.1 $mol \cdot L^{-1}$ NaCl (Beijing Chemical Works) and 10 mL of hexamethylenetetramine (Tianjin Huadong Reagents Factory) buffer solution (pH 6.4) and then diluted to 250 mL with distilled water. Herein, 0.1 $mol \cdot L^{-1}$ NaCl was used to control the ionic strength and hexamethylenetetramine buffer solution was used to keep a proton balance. The initial pH of each solution was adjusted with 0.1 $mol \cdot L^{-1}$ HCl and/or NaOH (Beijing Chemical Works) and measured with a pHs-3C model acidity meter (Shanghai Precision & Scientific Instrument Co. Ltd. China). All chemicals used in this study were analytical grade, and all solutions were prepared with distilled water.

2.2. Preparation of Adsorbents. *2.2.1. Raw Material.* A total of 30 g of dried grass was mixed with 700 mL of 20% isopropyl alcohol for 24 h at room temperature to remove some organic components like chlorophyll pigments and other low molecular-weight compounds such as limonene. The sample was then filtered and washed with distilled water until the filtrate had no color. The residue was dried in an oven at 60 °C for 12 h and used in our experiments as raw materials, hereafter named as RG.

2.2.2. Modified with Citric Acid. A total of 4 g of RG and 100 mL of 1.0 $mol \cdot L^{-1}$ citric acid solution were mixed in a beaker and stirred at 60 °C for 2 h, then filtered and dried in a convection oven at 60 °C for 12 h. The temperature was then increased up to 120 °C for 3 h. After that, the product was washed thoroughly with distilled water until the pH was neutral. Finally, it was dried in an oven at 60 °C for 12 h. Hereafter abbreviated as 1CG.

2.2.3. Modified with H[BTMPP]. A total of 3 g of RG or 1CG was placed into two porcelain mortars, and then 1.5 mL of H[BTMPP] was added. The solid−liquid mixture was fully grinded and then dried for 12 h at 60 °C after aging for 24 h at room temperature. The adsorbents were abbreviated as H-RG and H-1CG.

2.3. Batch Adsorption Studies. Batch adsorption tests were carried out at room temperature and used to investigate the effects of various parameters on Cd(II) adsorption by the adsorbents. A total of 0.15 g of each adsorbent was mixed with 15 mL of Cd(II) aqueous solution in Erlenmeyer flasks and then shaken for 2 h to reach equilibrium in a rotary shaker (HY-5, Jiangsu, Huarong Instrument Manufacturing Co. Ltd. China). After filtering by filter paper, 1 mL of filtrate was placed in a conical flask, and then two drops of 0.1 % xylenol orange were added, one drop saturated sulfosalicylic acid and approximately 10 mL of 30 % hexamethylene tetramine solution. The concentration of Cd(II) in the filtrate was determined by titration using EDTA standard solution. The adsorption amount (q) and removal efficiency (E %) were calculated according to eqs 1 and 2:

$$q = \frac{(C_0 - C_e)V}{W} \tag{1}$$

$$E\,\% = \frac{C_0 - C_e}{C_0} \times 100 \tag{2}$$

where C_0 and C_e are the initial concentration and equilibrium concentrations of cadmium in the aqueous phase, respectively ($mg \cdot L^{-1}$), q is the amount adsorbed of metal ion per unit mass adsorbent ($mg \cdot g^{-1}$), W is the mass of adsorbent (g), and V represents the volume of the aqueous phase (L).

2.4. Desorption Process. Batch desorption tests were conducted by using different concentrations of HCl, H_2SO_4, and HNO_3 in order to select the optimal desorption agent as an eluent in the column tests. A total of 0.025 g of adsorbent loaded with cadmium ions was mixed with 15 mL of (0.005, 0.01, 0.05, 0.1, and 0.2) $mol \cdot L^{-1}$ desorption agents solution in Erlenmeyer flasks, then shaken for 4 h to reach equilibrium in a rotary shaker. After filtering by filter paper, the concentration of Cd(II) in the filtrate was titrated using the same method as the adsorption process. The desorption process can also be considered as a very efficient medium to concentrate and recover cadmium.

2.5. Column Test. Adsorption in fixed-bed columns is widely used and considered as fundamental in further studies involving the scaling-up of the process under actual conditions. Appropriate amounts of 1CG or H-1CG were filled into two glass columns with a 1.1 cm diameter and 21.5 cm length. A small amount of glass wool was placed at the bottom and top of the column to prevent any loss of the adsorbent particles during the loading of cadmium. Two columns were fixed at the height of 5.0 cm and then conditioned by passing water of pH 6.0 before metal ion loading. A solution of 112.4 $mg \cdot L^{-1}$ of Cd(II) with an initial pH 6.0 was pumped downflow through the fix-bed column at a constant volume velocity of 2 $mL \cdot min^{-1}$. Effluent was collected regularly and the concentration of Cd(II) in this effluent was analyzed. After the adsorption reached saturation, the columns were prewashed with distilled water so as to expel any unbound metal ions. A 0.1 $mol \cdot L^{-1}$ HCl solution was used as eluent and percolated into the adsorbed columns at the same constant flow rate. Elution samples from the outlet were collected and analyzed by the same procedure used in the adsorption experiments. After elution, the columns were rinsed with distilled water until the pH reached the value of initial Cd(II) solution in the process of adsorption. The regenerated columns were reused for the next adsorption−desorption recycle.

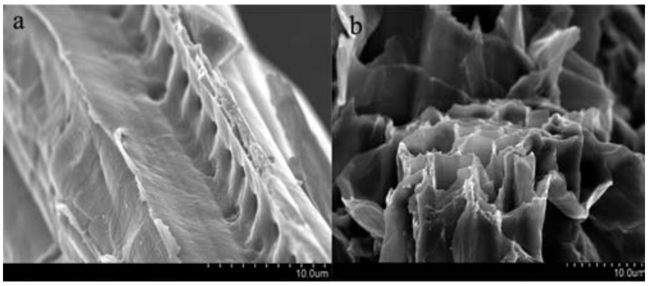


Figure 1. SEM images of (a) RG and (b) 1CG.

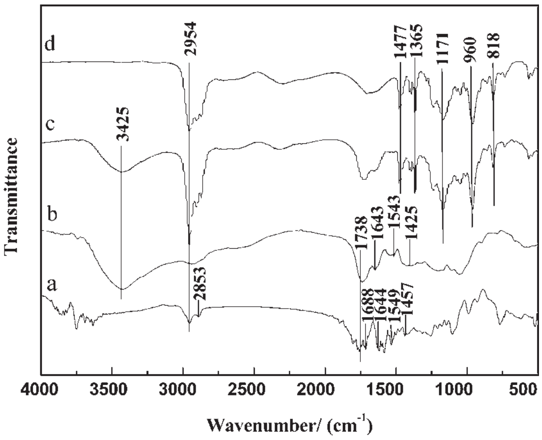


Figure 2. The FTIR spectra of (a) RG, (b) 1CG, (c) H-1CG, and (d) H[BTMPP].

3. RESULTS AND DISCUSSION

3.1. Characterization of Biosorbents. *3.1.1. SEM Image of Lawny Grass.* The morphology of the samples was observed using a field-emission scanning electron microscope (FE-SEM, HITACHI S-4800). Figure 1 shows SEM images of (a) RG and (b) 1CG. As compared to RG, the surface of 1CG is more irregular and porous, and indicates that the surface area and pore volume increased. These large pores and increased surface area are important factors to enhance uptake of Cd(II). Besides, this structural feature indicates that lawny grass can be used as a supporting biomaterial to fix H[BTMPP].

3.1.2. Elemental Analysis. Elemental analysis of raw lawny grass was carried out using a GmbH Elementar. The sample was heated in an oven from (25 up to 1000) °C at a heating rate of 10 °C·min^{-1}. The gases generated from heating were analyzed by an electrical conductivity detector. Elemental analysis results show that the raw lawny grass is composed of 43.69 % carbon, 5.63 % hydrogen, and 3.64 % nitrogen.

3.1.3. FTIR Analysis. FTIR spectra of the raw, modified lawny grass adsorbents and H[BTMPP] were measured with a Fourier Transform Infrared Spectrometer (Nicolet MagNAIR 560-spectrophotometer) under ambient conditions. The spectra were recorded from (4000 to 500) cm^{-1} using KBr. To better understand the immobilization of H[BTMPP] onto the grass biosorbents, a comparison of the FTIR spectrum of RG, 1CG, H-1CG and H[BTMPP] is shown in Figure 2. The FTIR spectra of RG as illustrated in Figure 2a, shows that the doublet peaks at wave numbers of (2954 and 2853) cm^{-1} are due to the asymmetric and symmetric stretch of aliphatic chains (−CH), the three peaks at (1738, 1688, and 1644) cm^{-1} are the adsorption band of carbonyl (C=O) stretching and hydroxyl (−OH) deformation vibration of carboxylic groups, the peak at 1549 cm^{-1} corresponds to the amide and the peak at 1457 cm^{-1} is the symmetric C=O stretching. For 1CG (Figure 2b), it is observed that the peak at 1738 cm^{-1} stayed in position, but the peak at 1688 cm^{-1} disappeared. The amide vibration shifts from (1549 to 1543) cm^{-1}, hydroxyl (−OH) of carboxylic groups shifted a little from (1644 to 1643) cm^{-1}, alkyl (−CH) shifted from (2923 to 2929) cm^{-1} and became a broad peak, and hydroxyl (−OH) appeared at a wavenumber of 3425 cm^{-1}. The appearance and disappearance of different peaks indicates that some functional groups (−COOH and −OH) have been successfully introduced into the surface of the biomaterial grass after chemical modification. These functional groups are very effective in capturing Cd(II) ions from aqueous solution. In addition, from comparison of panels a and d in Figure 2, it can be found that the FTIR spectra of H-1CG is very similar to that of H[BTMPP]. H-1CG possesses the characteristic adsorption peak of H-[BTMPP], the adsorption band at 2954 cm^{-1} is attributed to −CH stretching of CH_3 contained in the 3-methyl-amyl of H[BTMPP], and two peaks appeared at (1477 and 1365) cm^{-1} are due to the deformation vibration of −CH of H[BTMPP]. The peak at 1171 cm^{-1} corresponds to the P=O group of H[BTMPP]. The adsorption stretching bands of P−O−C in H-1CG and H[BTMPP] appear at (960 and 818) cm^{-1}, which remain unaltered. However, the only difference is that H-1CG has an adsorption band at 3425 cm^{-1}, which is attributed to hydroxyl (−OH) of 1CG, and H[BTMPP] does not. This suggested that the H[BTMPP] is fixed on 1CG.

The IR spectra suggested that the physical adsorption of the acidic organophosphorus extractant H[BTMPP] by the lawny grass is achieved partly through hydrophobic interaction between the hydrophobic alkyl part of H[BTMPP] and the aliphatic chain (methyl) of the support and partly through other mechanisms such as polar or electrostatic forces.[22] During the preparation process, H[BTMPP] can be fixed on both the surface and pores, and fills the pore space gradually from the smallest pores of the grass up to the large pores.

3.2. Immobilization and Determination of H[BTMPP] Content in Biosorbents. The method of solid−liquid grind was used to prepare the biosorbents in our study. Adsorptive materials can be prepared by chemical processes, such as with sol−gel sorbents[23] and Levextrel resins,[24−26] or the physical linkage of extractant and supporting material with a macroreticular network, namely, solvent-impregnated resins (SIR).[21,27,28] Like solvent-impregnated resins, H[BTMPP] was immobilized to the biosorbents through physical connection in our work. Determination of the H[BTMPP] content in H-RG and H-1CG was similar to the measurement of Cyanex923 content in IL-SIR[21] and in 923SG.[23] A total of 0.1 g of H-RG (or H-1CG) was immersed into 10 mL of ethanol for 24 h and shaken for 1 h to ensure that H[BTMPP] was completely dissolved in ethanol and then separated by centrifuging for 5 min. Finally, 1 mL of H[BTMPP] ethanol solution was titrated by a NaOH standard solution, with two drops of 0.1 % bromothymol blue used as indicator. In order to eliminate the effects of other acidic substances, we have also carried out blank tests of RG and 1CG under the same conditions. The results of the blank tests and measurement of H[BTMPP] on H-RG and H-1CG are shown in Table 1. It is obvious that a great mass of H[BTMPP] was fixed on RG (80.56 %) and 1CG (86.55 %).

Table 1. Determination of H[BTMPP] Content in H-RG and H-1CG[a]

	added sequence		data and analytical results		
sorbents type	dosage/(g)	ethanol/(mL)	NaOH[b]/(mL)	concentration of H[BTMPP]/(mol·g^{-1})	percentage of fixed H[BTMPP]/(%)
RG	0.10	10	0.05		
1CG	0.10	10	0.11		
H-RG	0.10	10	0.32	1.26×10^{-3}	80.56
H-1CG	0.10	10	0.40	1.35×10^{-3}	86.55

[a] Density of H[BTMPP]: 0.91 g·mL^{-1}; relate molecular mass: 290 g·mol^{-1}. [b] The volume of titration with NaOH (0.0468 mol·L^{-1}).

Table 2. Concentration of Active Sites and PZC

sorbents type	acidic sites/(mol·kg^{-1})	basic sites/(mol·kg^{-1})	PZC
RG	0.75	2.25	6.38
1CG	6.20	1.70	3.60
H-RG	2.12	2.05	4.24
H-1CG	6.25	1.62	3.43

3.3. Determination of the Point of Zero Charge and Active Sites. The point of zero charge (PZC) of the adsorbents was determined by the following procedure: 100 mL of distilled water was added to an Erlenmeyer flask, which was then capped with cotton. The distilled water was heated until boiling for 20 min to eliminate CO_2 dissolved in the water. Once heating was stopped, this flask was capped immediately to prevent CO_2 dissolving in the water again. A total of 0.2 g of adsorbent was placed in a 25 mL Erlenmeyer flask to which 15 mL of the CO_2-free water was added. The flask was sealed with a rubber stopper and left in continuous agitation for 48 h at room temperature. Then the pH of the filtrate was measured and this value is the PZC. This method has been used satisfactorily by Moreno-Castilla et al.[29] and Leyva-Ramos et al.[30]

Acidic and basic sites on the biosorbents were determined by the acid−base titration method proposed by Boehm.[31] The total acid sites were neutralized using 0.1 mol·L^{-1} NaOH solution, whereas the basic sites were neutralized with 0.1 mol·L^{-1} HCl solution. The acidic and basic sites were determined by adding 50 mL of 0.1 mol·L^{-1} titration solutions and 0.2 g of lawny grass biosorbents to a 50 mL flask. These flasks were left for 5 days at room temperature and agitated manually twice a day. Finally, a 10 mL sample was titrated with 0.1 mol·L^{-1} HCl or NaOH.

The active sites and PZC of different adsorbents are also shown in Table 2. It can be seen that the concentrations of acid sites are higher than that of basic sites for all of the adsorbents, hence the surfaces of these adsorbents are acidic and the number of acidic sites indicated the number of functional groups.[32] This would lead to electrostatic attractions between positively charged cations [Cd(II)] and negatively charged binding sites. The lower the PZC is, the more Cd(II) ions are attracted to the surface while increasing pH above PZC, because the surface of the adsorbents become more negative.[30] The concentrations of acidic sites are different due to different chemical modification, which lead to their differences in adsorption capability.

3.4. Effect of pH on Adsorption. The effect of pH on metal biosorption has been studied by many researchers previously, and the results indicated that the pH of solution exerts a great effect on the uptake of metal ions.[33−35] In this work, we investigated the effect of pH on adsorption of cadmium onto the different adsorbents, and the experimental results are shown in Figure 3.

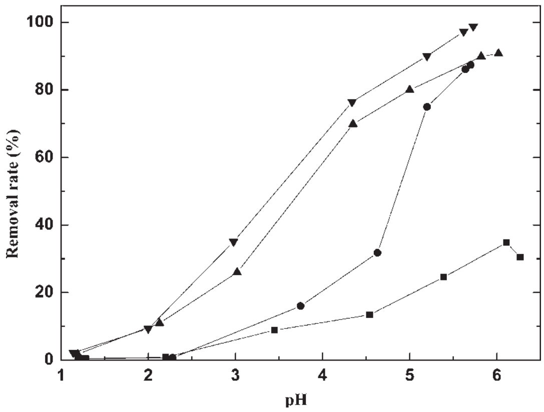


Figure 3. Effect of pH on Cd(II) uptake by different adsorbents. Initial Cd(II) concentration = 224.8 mg·L^{-1}; s/l ratio = 10 g·L^{-1}; contact time = 2 h; ▼, H-1CG; ▲, 1CG; ●, H-RG; ■, RG.

From Figure 3 we can see that the uptake of cadmium was small at pH < 2. The reason for this phenomenon is that hydrogen ions tend to occupy the surface active sites and resist cadmium ions due to electrostatic forces, which leads to fewer binding sites being available to bind cadmium ions, so the adsorption of Cd(II) is negligible. With increased pH, there are fewer protons in solution, which means that there is less competition for binding sites and more binding sites are released, which leads to greater adsorption of Cd(II). The adsorption reaches a maximum of a pH of 5.5−6.0. With a further pH increase, because of the formation of hydroxyl complexes and precipitation of cadmium hydroxide, the adsorption efficiency of Cd(II) decreases. Figure 3 shows that the removal rate of Cd(II) on H-1CG is close to 100 %. It is clear that the removal percentage of Cd(II) on RG is low (38 %), which increases substantially to 88 % on H-RG. This suggested that H[BTMPP] played an important role in the removal of cadmium ions from aqueous solution.

The PZC also can be used to explain the effect of pH on Cd(II) adsorption. At pH = PZC, the surface charge of adsorbents is neutral, and there is negligible electrostatic attraction existing between the adsorbent surface and Cd(II) in solution. When pH is > or < the PZC, the balance is broken. At pH < PZC, the surface charge of the adsorbents is positive, which inhibits the approach of positively charged Cd(II). At pH > PZC, the surface charge of the adsorbents is negative, and functional groups such as carboxyl, hydroxyl and amino are free so as to promote interaction with Cd(II). The maximum sorption is likely to occur at pH values greater than the PZC when adsorbents have a net negative charge.[36] As can be seen from Table 2, the PZC of H-1CG is 3.43, which is the lowest PZC, so it has the maximum adsorption capacity. The PZC value of RG is 6.38, which is higher than the optimal pH, so its adsorption capacity is the lowest.

3.5. Adsorption Kinetic Models. The contact time was also evaluated as an important factor of the biosorption efficiency. Two popularly used kinetic models (pseudofirst-order[37] and pseudosecond-order[38]) have been employed to fit the experimental data in this work.

The pseudofirst-order kinetic model is generally expressed as eq 3

$$\ln \frac{q_e - q_t}{q_e} = -K_1 t \qquad (3)$$

where q_e is the equilibrium adsorption amount of metal ion per unit weight of adsorbent (mg·g^{-1}), q_t is the amount of metal ions adsorbed (mg·g^{-1}) at time t (min), and K_1 is the pseudo-first-order rate constant (min^{-1}).

The pseudosecond-order kinetic model is expressed as the following formulation:

$$\frac{t}{q_t} = \frac{1}{K_2 {q_e}^2} + \frac{t}{q_e} \qquad (4)$$

where K_2 is the pseudosecond-order rate constant (g·(mg·min)$^{-1}$).

The kinetic model parameters are obtained from fitting results and are presented in Table 3. The pseudosecond-order kinetic model provides much better R^2 values (0.9820, 0.9975, 0.9754, and 0.9989) than that of the pseudofirst-order kinetic model (0.9523, 0.8854, 0.9224, and 0.7938), which indicates that the pseudosecond-order kinetic model provided a good correlation of the biosorption of Cd(II) onto the grass adsorbents in contrast to the pseudofirst-order model.

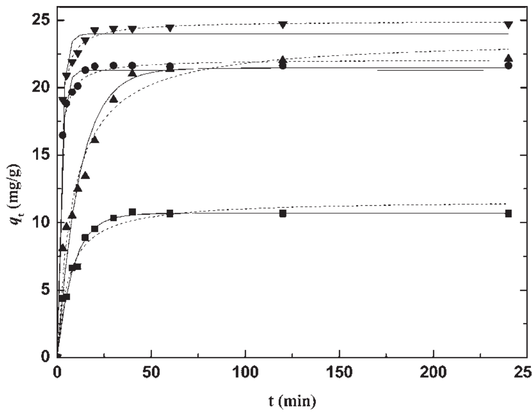


Figure 4. Effect of contact time on Cd(II) uptakes by different adsorbents. Initial pH 6.0; initial Cd(II) concentration = 224.8 mg·L^{-1}; s/l ratio = 10 g·L^{-1}; ▼, H-1CG; ▲, 1CG; ●, H-RG; ■, RG; —, Pseudofirst-order model; ···, Pseudosecond-order model.

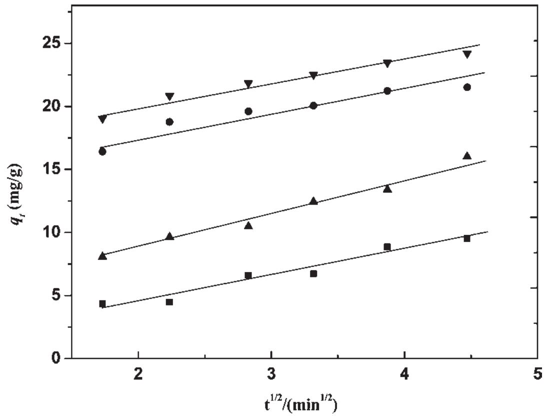


Figure 5. Intraparticle diffusion plot on Cd(II) adsorption by different adsorbents. Initial pH 6.0; initial Cd(II) concentration = 224.8 mg·L^{-1}; s/l ratio = 10 g·L^{-1}; ▼, H-1CG; ▲, 1CG; ●, H-RG; ■, RG.

Figure 4 shows the effect of contact time on adsorption of Cd(II) onto the grass adsorbents. It is obvious that more than 40 min was needed to attain equilibrium by RG and 1CG; however, the equilibrium time was shortened to 20 min by H-RG and H-1CG, which may be attributed to the additional ion exchange capacities and fast mass transfer. The time dependent adsorption data demonstrate that the adsorption of Cd(II) rapidly occurred within the first 15 min. The adsorption process of Cd(II) onto grass adsorbents seemed to have a second adsorption phase, and it is suspected that the uptake of heavy metals onto the lawny grass was probably not only due to cell-surface binding, but also via intracellular accumulation.[39] This possibility is explored by plotting q_t versus $t^{1/2}$, according to the Weber–Morris model, $q_t = K_{id}\, t^{1/2}$,[40] where K_{id} is the intraparticle diffusion coefficient. According to this model, a plot of uptake (q_t), versus the square root of time ($t^{1/2}$) should be linear if intraparticle diffusion is involved in the adsorption process and if these lines pass through the origin then intraparticle diffusion is the rate controlling step. When the plots do not pass through the origin, this is indicative of some degree of boundary layer control and further shows that the intraparticle diffusion is not the only rate-limiting step, but also other kinetic models may control the rate of adsorption, all of which may be operating simultaneously.[41] The plots of q_t versus $t^{1/2}$ are presented in Figure 5. It can be seen that these plots do not pass through the origin, which indicates that intraparticle diffusion is not the only rate controlling step.

3.6. Adsorption Isotherms. The capacity of an adsorbent can be described by sorption isotherms, which can help to explore

Table 3. Pseudofirst-Order and Second-Order Kinetics Models for the Adsorption of Cd(II)

	pseudofirst-order model			pseudosecond-order model		
sorbents type	R^2	q_e/(mg·g^{-1})	K_1/(min^{-1})	R^2	q_e/(mg·g^{-1})	K_2/(g(mg min)$^{-1}$)
RG	0.9523	10.67	115.8×10^{-3}	0.9820	11.65	14.61×10^{-3}
H-RG	0.8854	21.30	455.9×10^{-3}	0.9975	22.11	47.55×10^{-3}
1CG	0.9224	21.45	83.43×10^{-3}	0.9754	23.66	4.970×10^{-3}
H-1CG	0.7938	23.99	468.4×10^{-3}	0.9989	24.96	41.82×10^{-3}

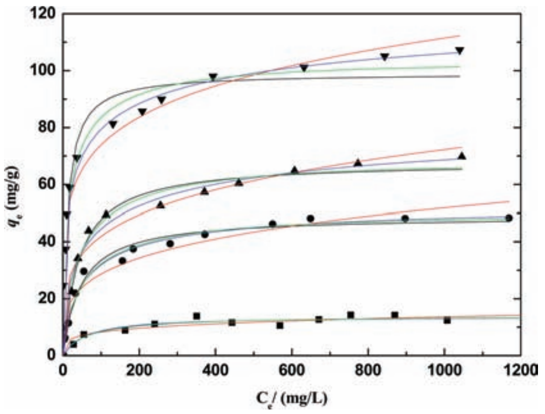


Figure 6. Adsorption isotherms of Cd(II) onto different adsorbents. Initial pH 6.0; s/l ratio = 10 $g \cdot L^{-1}$; contact time = 2 h; ▼, H-1CG; ▲, 1CG; ●, H-RG; ■, RG; black line, Langmuir; red line, Freundlich; blue line, Langmuir−Freundlich; green line, Dubinin−Radushkevich.

Table 5. Biosorption Results for Cd(II) Ions by Various Sorbents from the Literature

sorbent material	sorption capacity/($mg \cdot g^{-1}$)	refs
rice husk	103.1	46
grape stalk	27.88	47
sugar beet pulp	17.20	48
wheat bran	15.71	12
tea-industry waste	11.29	49
rice polish	9.720	50
Saccharomyces cerevisiae	6.710	11
peanut hulls	5.960	51
H-1CG	133.2	this study

the adsorption mechanism much more thoroughly. Sorption isotherm equations can explain the adsorption process at equilibrium conditions and provide an easier solution to the complex problem. The Langmuir and Freundlich models are the most commonly used isotherms to fit experimental data. In addition, an attempt to test other available isotherm models was also done in our work, such as the Langmuir−Freundlich model (also known as the Sips model) and the Dubinin−Radushkevich (D-R) model. The fitting curves of relationship between q_e and the equilibrium concentration of Cd(II) by the four isotherms are shown in Figure 6, and the various parameters of the isotherm equations are listed in Table 4.

The Langmuir isotherm describes monolayer coverage of adsorbate over specific homogeneous sites, which was assumed to be identical, energetically equivalent and distant from each other, and there are no interactions between molecules adsorbed on neighboring sites:[42]

$$q_e = \frac{q_m b C_e}{1 + bC_e} \qquad (5)$$

where q_e and q_m ($mg \cdot g^{-1}$) are the equilibrium and maximum adsorption amount of metal ion per unit weight of adsorbent, respectively, b represents the equilibrium constant of the adsorption reaction ($L \cdot mg^{-1}$), and c_e ($mg \cdot L^{-1}$) is the concentration of adsorbate at equilibrium. R^2 values of the Langmuir isotherms were 0.9299, 0.9839, 0.9754, and 0.9625 for Cd(II) adsorption on RG, H-RG, 1CG, and H-1CG, respectively (Table 4). These results indicate that the biosorption of Cd(II) onto grass adsorbents fitted the Langmuir model well. In other words, this adsorption process took place at the functional groups/binding sites on the surface of adsorbents which is regarded as monolayer biosorption.

The Freundlich isotherm[43] is an empirical equation assuming that the adsorption process takes place on heterogeneous surfaces and the adsorption capacity is related to the concentration of cadmium at equilibrium.

$$q_e = K_f C_e^{1/n} \qquad (6)$$

where K_f and n are the Freundlich constants. K_f is roughly an indicator of the adsorption capacity ($L \cdot g^{-1}$) and $1/n$ is an empirical parameter relating the adsorption intensity. The values of n were found to be 4.603, 3.891, 4.231, and 5.602 for Cd(II) adsorption on RG, H-RG, 1CG, and H-1CG, respectively. They were all between 1 and 10, indicating that the adsorption performance of Cd(II) onto grass biomass was favorable in the studied conditions.[38]

The Langmuir−Freundlich (L-F) isotherm[44] is given by

$$q_e = q_m \frac{bC_e^{1/n}}{1 + bC_e^{1/n}} \qquad (7)$$

Table 4. Comparison of Four Isotherm Models for Cd(II) Adsorption on Adsorbents

isotherm models		RG	H-RG	1CG	H-1CG
Langmuir	R^2	0.9299	0.9839	0.9754	0.9625
	$b/(L \cdot mg^{-1})$	16.54×10^{-3}	21.65×10^{-3}	23.62×10^{-3}	84.21×10^{-3}
	$q_m/(mg \cdot g^{-1})$	13.84	48.99	67.923	99.07
Freundlich	R^2	0.8808	0.9450	0.9741	0.9790
	$K_f/(L \cdot g^{-1})$	3.039	8.784	14.11	32.48
	n	4.603	3.891	4.231	5.602
L-F	R^2	0.9299	0.9888	0.9855	0.9894
	$b/(L \cdot mg^{-1})$	15.23×10^{-3}	42.04×10^{-3}	88.64×10^{-3}	21.11×10^{-3}
	n	0.9780	1.297	1.906	2.369
	$q_m/(mg \cdot g^{-1})$	13.76	53.76	89.26	133.2
D-R	R^2	0.8517	0.9819	0.9676	0.9749
	$k/(mol^2 \cdot J^{-2})$	5.371×10^{-9}	5.203×10^{-9}	5.067×10^{-9}	5.943×10^{-9}
	$q_m/(mg \cdot g^{-1})$	13.66	49.29	67.80	102.9

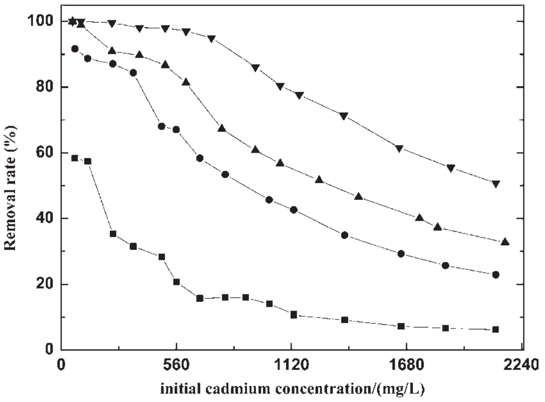


Figure 7. Effect of initial Cd(II) concentration on removal rate by different adsorbents. Initial pH 6.0; s/l ratio = 10 g·L^{-1}; contact time = 2 h; ▼, H-1CG; ▲, 1CG; ●, H-RG; ■, RG.

in which n is the Sips constant. On the basis of a comparison study of a number of isotherm equations applied to the sorption of Cd(II) and Pd(II) onto brown seaweed, Basha and Jha[45] concluded that the Sips isotherm provided the better fitting of the experimental data ($R^2 = 0.9747$). In our study, the values of R^2 were 0.9299, 0.9888, 0.9855, and 0.9894 for Cd(II) adsorption on RG, H-RG, 1CG, and H-1CG, respectively, indicating that the experimental data fitted the L-F best, and the order of maximum capacities q_m of Cd(II) onto different adsorbents was H-1CG > 1CG > H-RG > RG. A comparison between our adsorbents and others has been listed in Table 5, and the biosorption capacity of H-1CG obtained for Cd(II) ions in our study was found to be higher than that of other sorbents in the literature.

The Dubinin−Radushkevich (D-R) model[52] is given by

$$\ln q_e = \ln q_m - k\varepsilon^2 \tag{8}$$

in which q_m is the Dubinin−Radushkevich constant representing the theoretical monolayer saturation capacity (mg·g^{-1}),[53] k is the constant of the adsorption mean energy (mol^2·J^{-2}), $\varepsilon$is the Polanyi potential and is further defined by[54]

$$\varepsilon = RT \ln(1 + 1/C_e) \tag{9}$$

Inserting eq 9 into eq 8, we obtain the following equation:

$$\ln q_e = \ln q_m - kR^2T^2 \ln^2(1 + 1/C_e) \tag{10}$$

where R is the gas constant and T is the absolute temperature in Kelvin. The values of R^2 were 0.8517, 0.9819, 0.9676, and 0.9749 for the adsorption of Cd(II) onto RG, H-RG, 1CG, and H-1CG, respectively. It suggested that the mechanism of adsorption of Cd(II) onto modified grass adsorbents could also be explained by the D-R isotherms.

Then, the mean adsorption energy (E) can be calculated as follows:

$$E = 1/\sqrt{2K} \tag{11}$$

In general, the D-R isotherm equation has often been used to determine the mean adsorption energy (E) which may provide useful information with regard to whether or not biosorption is subject to a chemical or physical process. If E value is between (8 and 16) kJ·mol^{-1}, the biosorption process follows chemical ion-exchange and if $E < 8$ kJ·mol^{-1}, the adsorption process is of a physical nature.[55] In our study, E values were calculated as (9.650, 9.803, 9.935, and 9.173) kJ·mol^{-1} for biosorption of cadmium on RG, H-RG, 1CG, and H-1CG, respectively. These results indicate that the biosorption of cadmium onto all adsorbents could be described by a chemical ion-exchange mechanism.

In addition, the relationship between the removal percentage and the initial concentration of cadmium are shown in Figure 7. When the initial cadmium concentration was lower than 562.1 mg·L^{-1}, the removal percentages of cadmium on H-1CG were more than 95 %, but there was a sharp decline of cadmium adsorption on 1CG (99−82 %), H-RG (92−68 %), and RG (59−20 %) at higher concentrations. When the initial cadmium concentration reached the maximum (2248 mg·L^{-1}), the removal percentage of cadmium on H-1CG was still more than 50 %, compared with 40, 25, and 9 % on 1CG, H-RG, and RG, respectively.

3.7. Effects of Temperature on Cd(II) Adsorption. The effect of temperature on the adsorption rate of Cd(II) on H-1CG was investigated at (278, 288, 298, 308 and 318) K, respectively. Increasing the temperature is known to increase the rate of diffusion of adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent, owing to a decrease in the viscosity of the solution. In addition, changing temperature will change the equilibrium capacity of the adsorbent for a particular adsorbate.[56] The adsorption capacity increased from (49.71 to 54.77) mg·g^{-1} when temperature of the solution was increased from (278 to 318) K, indicating the process to be endothermic (Table 6). This may be a result of an increase in the mobility of cadmium ions with increasing temperature. An increasing number of molecules may also acquire sufficient energy to undergo an interaction with active sites at the surface. Furthermore, increasing the temperature may produce a swelling effect within the internal structure of the H-1CG enabling large cadmium ions to penetrate further.[57] Figure 8 shows the plot of $1/T$ versus $\ln K_d$. The distribution coefficient K_d can be calculated from the following equation:

$$K_d = \frac{(C_0 - C_e)V}{C_eW} \tag{12}$$

Thermodynamic parameters namely Gibbs energy ΔG, enthalpy changeΔH and entropy change ΔS are calculated from the slopes and intercepts of a linear variation plot of $1/T$ versus $\ln K_d$ according to the following equations[58] and the results are shown in Table 6.

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{13}$$

$$\Delta G = \Delta H - T\Delta S \tag{14}$$

where R is the gas constant (8.314 J·(mol K)$^{-1}$) and T is the temperature (K).

As illuminated in Table 6, values of ΔH and ΔS are 41.32 kJ·mol^{-1} and 160.8 J·(mol K)$^{-1}$ for H-1CG. The positive value of ΔH indicated the endothermic nature of adsorption process. The positive value of ΔS show an affinity of these adsorbents and the increasing randomness at the solid−solution interface during adsorption process of Cd(II). The negative value of ΔG indicates a feasible and spontaneous nature of this adsorption process. The values of ΔG are found to increase as temperature increases, indicating more driving force and hence resulting in higher adsorption capacity.

Table 6. Thermodynamic Parameters for Cd(II) Adsorption on H-1CG

				ΔG (kJ·mol^{-1})			
sorbent type	ΔH (kJ·mol^{-1})	ΔS (J·(mol·K)$^{-1}$)	278 K	288 K	298 K	308 K	318 K
H-1CG	41.32	160.8	−3.382	−4.991	−6.598	−8.206	−9.814

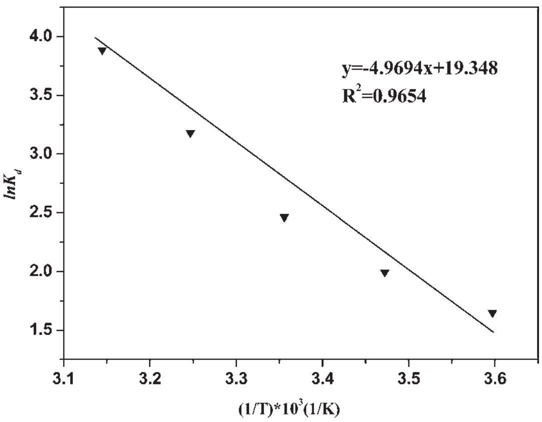
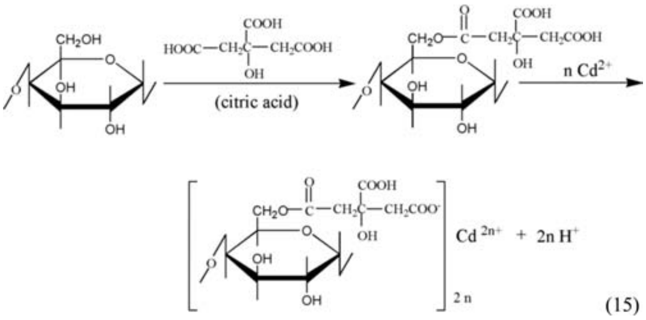


Figure 8. Plots of $1/T$ vs ln K_d on Cd(II) uptake by H-1CG. Initial pH 6.0; s/l ratio = 1.6 g·L^{-1}; contact time = 60 min; initial Cd(II) concentration = 112.4 mol·L^{-1}.

3.8. Column Study. The experimental breakthrough curves of Cd(II) are presented in Figure 9a, It can be seen that the breakthrough point for Cd(II) adsorption on H-1CG begins at 160 BV which is higher than that on 1CG (130 BV) under the same conditions. Here, BV is defined as a volume ratio of metal solution which passes through the column (cm^3) to the packed adsorbents (cm^3). This suggests that adsorption capability of H-1CG was larger than that of 1CG, which coincides with the results of the batch tests. The columns of H-1CG and 1CG are completely saturated at 310 BV and 280 BV respectively.

Solutions of (0.005, 0.01, 0.05, 0.1, and 0.2) mol·L^{-1} HCl, H_2SO_4, and HNO_3 were used as desorption agents for the regeneration of adsorbents in batch tests. The results showed that the desorption percentages for 0.1 mol·L^{-1} H_2SO_4 (95.13%) and 0.1 mol·L^{-1} HNO_3 (93.09%) is similar to 0.1 mol·L^{-1} HCl (95.2%) under the same conditions. Considering the cadmium chloride ($CdCl_2$) was used as initial substance in our experiments; therefore, the 0.1 mol·L^{-1} HCl solution was selected as the eluent to regenerate the adsorption column with a constant volume velocity of 2 mL·min^{-1}. The elution curve of H-1CG is presented in Figure 8 b. It can be seen that the adsorption column is easily regenerated by a small amount of 0.1 mol·L^{-1} HCl and elution is complete within 25 BV.

3.9. Adsorption Mechanism. The study of the mechanism on cadmium biosorption by lawny grass in this work is based on ion exchange. Functional groups such as −COOH and −OH of cellulose can react with Cd(II) to form complexes by releasing protons.[59] The reaction equation can be described as



(15)

The reactive anhydride is combined with cellulosic hydroxyl groups so as to form an ester linkage and introduce carboxyl groups to the cellulose. The addition of carboxylic function groups increases the adsorbents ability to binding with positively charged metal ions.[60,61] Additionally, adsorption capacities are further enhanced due to ion exchange between cadmium ions and H[BTMPP] fixed on the adsorbents. The mechanism of the reaction has also been deduced. It may be expressed by

$$Cd^{2+} + 2HA \leftrightarrow CdA_2 + 2H^+ \qquad (16)$$

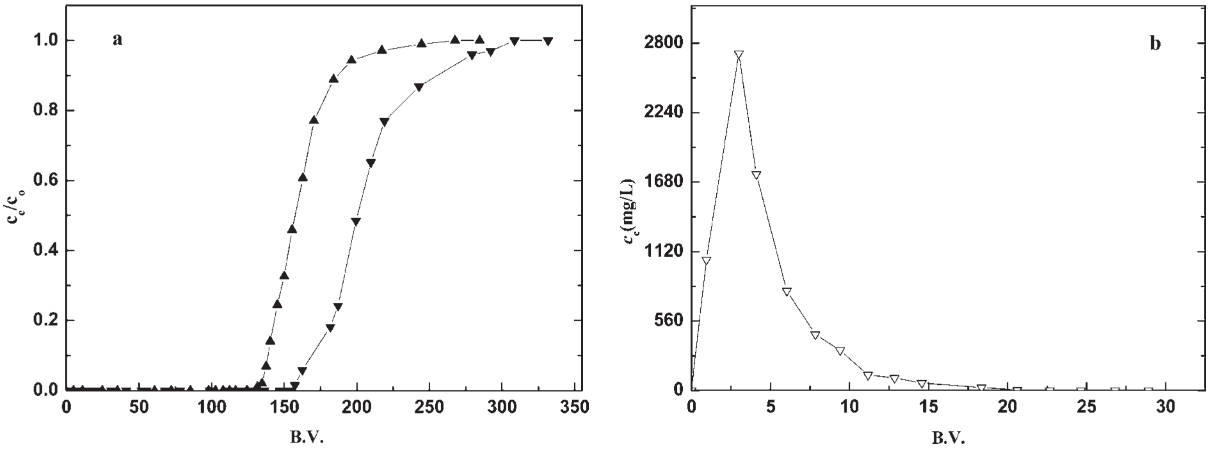


Figure 9. Breakthrough curves of (a) Cd(II) adsorption onto 1CG and H-1CG and (b) elution curve onto H-1CG. Initial pH 6.0; initial Cd(II) concentration = 112.4 mg·L^{-1}; ▼, H-1CG; ▲, 1CG; ▽, H-1CG (desorption by 0.1 M HCl).

where HA was used to represent monomeric species of H[BTMPP] in the grass biosorbent.[62]

In conclusion, the ion-exchange capacities of biosorbents have been greatly enhanced. It is attributed to both chemical modification and fixed extractant H[BTMPP]. The pH of the Cd(II) solution diminishes after adsorption and HCl is used as the desorption agent, which also indicates that the ion exchange mechanism is maybe involved in the adsorption process.

4. CONCLUSION

In conclusion, a newly developed biosorbent containing extractant H[BTMPP] has been prepared via solid−liquid grinding. Grass biosorbents were characterized by SEM, FTIR and elemental analysis, confirming that carboxylic groups were introduced to the grass by chemical modification and H[BTMPP] was successfully immobilized on the grass biosorbents. Ion exchange mechanism is involved in the adsorption process. The experimental results showed that H-1CG always had a higher ability to adsorb cadmium ions and the removal rate could be up to 99.5 % in the pH range of 5.5−6.0. Kinetic equilibrium could be explained by a pseudosecond-order kinetic model and the experimental data fitted Langmuir−Freundlich isotherm model best. H[BTMPP] played an important role in improving the maximum adsorption capacities from (89.26 to 133.2) $\text{mg}\cdot\text{g}^{-1}$ and shortening the equilibration time from (40 to 20) min. Column experiments show that breakthrough begins at 160 BV by H-1CG. Thermodynamic results indicated the adsorption of Cd(II) is spontaneous and endothermic. The desorption percentage when 0.1 $\text{mol}\cdot\text{L}^{-1}$ HCl solution was used as eluent was high (up to 95.2 %) and elution was complete within 25 BV.

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