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Bioresource Technology

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Rice husk derived double network hydrogel as efficient adsorbent for Pb(II), Cu(II) and Cd(II) removal in individual and multicomponent systems



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GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords: Adsorption Metal ions Rice husk Chitosan Hydrogel Multicomponent

ABSTRACT

In this study, lignin extracted from rice husk was used to synthesis double network hydrogel adsorbent, named RH-CTS/PAM gel. RH-CTS/PAM gel exhibited macroporous structure and high buried water content, which gave rise to the exceptional adsorption performance. As results, in individual systems, the equilibrium time of Pb(II), Cu(II) and Cd(II) with initial concentration of 200 mg/L could be reached within 10 min, with the theoretical maximum adsorption capacity of 374.32, 196.68 and 268.98 mg/g, respectively. The adsorption rate and capacity of Pb(II), Cu(II) and Cd(II) in multicomponent systems were lower than that of individual systems. However, in a few cases of ternary system, higher adsorption rate and capacity was observed compare to binary systems. Adsorption mechanism indicated that both oxygen-containing and nitrogen-containing functional groups played a dominant role during the adsorption process, and mainly through chemical interaction along with a small amount of physical interaction.

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https://doi.org/10.1016/j.biortech.2019.121793 Received 2 May 2019; Received in revised form 8 July 2019; Accepted 9 July 2019 Available online 11 July 2019 0960-8524/ © 2019 Elsevier Ltd. All rights reserved.

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1. Introduction

The contamination of heavy metal ions in industrial effluents has aroused public concerns owing to its negative impact on human health and ecological security (Zhang et al., 2019). Generally, the components in industrial wastewater are very complex and multifarious, and simultaneous uptake of various heavy metal ions from industrial wastewater is of great significance. Adsorption is viewed as one of the most effective options for heavy metal ions removal due to its simple and cost-efficient operation, and large numbers of materials have been developed for heavy metal adsorption (Ali, 2012). Recently, iron oxychloride (FeOCl) nanosheets have been synthesized and applied on lead removal with great performance, and it is relevant to the exposure of oxygen and chlorine sites (Luo et al., 2019). Biochar materials, substitute for activated carbon, prepared from a variety of biomass feedstock have been used for efficient heavy metal removal, however, the carbonization process generally involves high pressure or high temperature (Liu et al., 2015; Zhou et al., 2017b). Aerogel possesses 3D interconnected macroporous framework with advanced adsorption performance and high separation performance has aroused special attention for being an adsorbent, but the mechanical properties and stability need to be further strengthened (Liang et al., 2018; Zhi et al., 2016). Overall, adsorbents that (i) exhibiting easily exposed active sites, (ii) 3D structure and (iii) high mechanical properties are highly desirable and can be regarded as an ideal adsorbent for efficient heavy metal removal.

Hydrogel adsorbents that can simultaneously fulfill the above advantages have been selected as an ideal adsorbent candidate for efficient heavy metals removal. Buried water in hydrogel has been demonstrated to play combinatorial roles of transport nanochannel, hydrogen bonding and supporting media (Ma et al., 2017a). These characters can largely benefit the free diffusion of water-soluble small molecules, exposure of active sites and recycling of hydrogel (Ma et al., 2017a). In addition, the preparation of hydrogel material is facile (Hou et al., 2017; Sun et al., 2016), the mechanical property is adjustable (Kumru et al., 2017; Zhao et al., 2016), and the source of the monomer is wide (Annabi et al., 2016; Rashad et al., 2017). So far, natural polymers based double network hydrogel has great performance on heavy metals removal (Ma et al., 2018a; Ma et al., 2018b; Ma et al., 2017b; Zhou et al., 2017a), but the use of organic matter in rice husk (RH) has not yet been studied. RH occupies a preeminent position in agricultural wastes or biomasses available in terms of its amount produced worldwide, and which exhibits unique chemistry-related features (Soltani et al., 2015; Vaisanen et al., 2016). Therefore, researches on advanced materials derived from RH have been widely conducted, such as Si (Jung et al., 2013; Liu et al., 2013; Zhang et al., 2017; Zhang et al., 2016), carbon (Naiya et al., 2009; Pode, 2016; Teo et al., 2016) and direct modified materials (Ajmal et al., 2003; Ye et al., 2010). Undesirably, the organic matter in RH (contains 80 wt%) is discarded in the most of these production processes (Soltani et al., 2015). Lignin is one of the main components of organic matter in RH, and cold alkali/ urea pretreatment can be expected for the extraction of lignin from RH for the similar composition of RH and rice straw (Dong et al., 2018). Lignin contains various functional groups (i.e., methoxyl, hydroxyl and carboxyl), which can serve as cost-effective adsorbent. Since the lignin content in RH is limited, modification is necessary for improving the adsorption performance. Chitosan (CTS) and lignin composite exhibit good adsorption properties, indicating the potential of CTS as a functional modifier (Nair et al., 2014). Moreover, CTS can be dissolved in alkali/urea composite solution, and the mechanical strength of hydrogel constructed from the alkaline solution is stronger than which prepared from the acid solution (Duan et al., 2015; Liu & Li, 2018). The enhanced mechanical strength can maintain the structure of hydrogel, which makes it potentially to be applied in the field study.

Hence, in this work, a double network hydrogel based on RH solution, CTS and polyacrylamide (PAM) through one-step free-radical polymerization process, named RH-CTS/PAM gel, was successfully synthesized. The lignin extracted from RH and CTS dissolved in cold alkali/urea solution were mixed in a certain ratio and acted as the first network, which provides reactive functional groups that responsible for heavy metals removal. Meanwhile, the PAM served as the ductile second network, which can form a stable structured hydrogel adsorbent (Ma et al., 2017b). Surface morphology, stability, swellability and shape recovery properties of RH-CTS/PAM gel were comprehensively characterized. Furthermore, the adsorption performance of RH-CTS/ PAM gel toward target heavy metal ions (i.e., lead (Pb(II)), copper (Cu (II)), and cadmium (Cd(II))) in individual, binary and ternary systems under different environmental conditions were investigated. The newly reported RH-CTS/PAM gel adsorbent and the utilization of organic matter in RH can provide a new avenue for the treatment of heavy metals and also the greater use of RH.

2. Materials and methods

2.1. Chemicals and materials

Air-dried rice husk (RH) was obtained from Wugang, Hunan province, China. Chitosan powder (CTS, deacetylation: 95%) were purchased from Aladdin Chemistry Co, Ltd. Acrylamide (AM) and urea were purchased from Sinopharm Chemical Reagent Co., Ltd. Ammonium persulfate (APS, AR) and N, N-methylenebisacrylamide (MBA, AR) were provided by Shanghai Xitang Biotechnology Co., Ltd., China. Without special instructions, the chemicals were used as received. All aqueous solutions were prepared with deionized water.

2.2. Preparation of RH-CTS/PAM gel

Initially, air-dried RH was washed with deionized water to remove impurities, and then pulverized by a pulverizer and passed through the 80 mesh sieve. The resulted RH powder was dispersed in 1 mol/L HCl with a solid-liquid ratio of 25 mg/mL and stirred for 24 h to remove metal elements. After that, the RH powder was washed with deionized water until neutral and dried for further use. 12.0 g RH powder after pickling was dispersed in 48 g 14 wt% NaOH aqueous solution precooled to 0 °C and stirred for 1 min. Then, 48 g 24 wt% urea aqueous solution pre-cooled to 0 °C was added immediately and stirred vigorously for 2 min, and the supernatant was separated, which referred to RH solution. 1.0 g CTS powder was dispersed in 50 g alkaline aqueous solvent containing LiOH/KOH/urea/H₂O in the ratio of 4.5:7:8:80.5 by weight and stirred for 5 min, and then stored under frozen (-65 °C) for 4 h. The frozen solid was fully thawed and stirred extensively at room temperature, resulting a transparent CTS solution. The RH and CTS solution were mixed at a volume ratio of 2:1 and stirred until the mixed solution was homogeneous. Then, the mixed solution was added to an aqueous solution containing AM (0.5 g/mL), APS (0.6 mol%, initiator for AM), and MBA (2 mol%, crosslinker for AM) in a volume ratio of 3:2. The obtained sol was bubbled and sealed in a centrifuge tube, and kept in a forced convection oven for 3 h at 60 °C to complete the gelation process. Then, the obtained RH-CTS/PAM gel was washed with deionized water to remove unreacted reagents, and then dried to constant weight at 60 °C. The preparation process of RH-CTS/PAM gel is shown in the Supporting Information (SI).

2.3. Characterizations

The functional groups of samples were detected using a Fourier transform infrared Nicolet 5700 spectrophotometer (FTIR, American). The surface morphologies of freeze-dried RH-CTS/PAM gel was examined by field emission scanning electron microscopy (SEM, Hitachi S-4800). Swelling ratio (SR) of RH-CTS/PAM gel was calculated according to $SR = (W_s - W_d)/W_d$, moisture content of the raw and swollen samples was calculated according to $(W_r - W_d)/W_r \times 100\%$ and

 $(W_{\rm s} - W_{\rm d})/W_{\rm s} \times 100\%$, respectively, where $W_{\rm r}$, $W_{\rm d}$ and $W_{\rm s}$ was the weight of raw, dried and swollen samples, respectively. The stability of RH-CTS/PAM gel in solutions was tested by immersing the material in the solution at various pH values for 12 h. The pH value at the point of zero charge (pH_{PZC}) of RH-CTS/PAM gel was measured by Δ pH drift method in a series of 0.01 mol/L NaCl aqueous with different initial pH. The surface chemistry of the adsorbent was determined by X-ray photoelectron spectroscopy (XPS, K-Alpha 1063, Thermo Fisher Scientific, England).

2.4. Batch sorption of heavy metals

Heavy metal nitrates (i.e., Cu(NO₃)₂, Cd(NO₃)₂ and Pb(NO₃)₂) were employed to prepare the stock solutions of individual (i.e., Pb(II), Cu(II) and Cd(II)) and multicomponent systems (i.e., Pb(II)/Cu(II), Pb(II)/Cd (II), Cd(II)/Cu(II) and Pb(II)/Cd(II)/Cu(II)). In multicomponent systems, the concentration of each component was the same. The pH values of the solution were adjusted by 0.1 mol/L HCl or NaOH solutions. Adsorption experiments were performed in 10 mL centrifuge tube, and the adsorbent was swollen with deionized water before adsorption and dosage was 1 mg dried gel/mL. The centrifuge tubes were placed in an incubator shaker (QYC2112, Fuma, Shanghai, China) with fixed oscillation frequency of 160 rpm/min. After being shaken for a definite time, the adsorbent was separated by decantation and the supernatant was monitored on an atomic absorption spectrophotometer (Z-2000, Hitachi, Japan). The adsorption kinetics experiment lasted for 2 h, and each data point was conducted separately to reduce errors. The adsorption isotherm experiment in individual and multicomponent systems was followed by different concentrations of Pb(II), Cu(II) and Cd (II) range from 20 to 500 mg/L. Differently charged cations (i.e., Na(I), K(I), NH₄(I), Ca(II) and Mg(II)) with concentrations ranged from 1 to 5 mmol/L were used as interfering ions to investigate the effect of ionic species and strength on adsorption performance. For regeneration, the spent adsorbent was eluted with 0.1 mol/L HCl solution for 3 h, and further washed with deionized water till neutral condition. Adsorption amount at every cycle in the recyclability tests was determined. All the experiments were performed twice under identical condition.

3. Results and discussion

3.1. Characterization of RH-CTS/PAM gel

The FTIR spectrum of RH powder was agree with previous studies, which contained functional groups of the standard polymers α -cellulose and coirpith-lignin (Chen et al., 2014; Ye et al., 2010). The FTIR spectrum of the residue showed that peaks at 1730 and 827 cm⁻¹ were disappeared, peaks at 1649, 1513 and 1456 cm^{-1} were weakened, and peaks at 1268, 1163, 1059 and 900 cm^{-1} were strengthened as compared to the pristine spectrum of RH powder, which was similar to the changes of RS before and after NaOH/urea treatment (Dong et al., 2018). This result indicates that the main component in the RH solution is lignin. Typical peaks of CTS (Ma et al., 2017b; Nair et al., 2014) could be observed, such as amide I (1657 cm^{-1}) and amide II (1598 cm^{-1}) vibrations, antisymmetric stretch C-O-C (1090 cm^{-1}) and C-N stretch (1160 cm^{-1}) , and skeletal vibration of C-O stretching (1030 cm^{-1}) . For PAM (Hu et al., 2016; Liu et al., 2012), the typical peaks at 1698, 1593 and 1408 cm^{-1} could be observed, which was assigned to amide C = O stretching vibration, N-H bending vibration and C-N stretching vibration, respectively. For RH-CTS/PAM gel, the main signals of lignin could not be observed, which could mainly due to the overlap with other peaks of CTS and PAM. The peaks of CTS weakened (1160 and 1030 cm^{-1}) and peak at 1598 cm^{-1} had red shift to 1557 cm^{-1} , and the typical peaks of PAM remained unchanged. This result indicates the formation of weak hydrogen bonds between CTS and lignin in RH solution (Nair et al., 2014) as well as the separate hydrogel network of PAM, confirming the successful preparation of RH-CTS/PAM double

network hydrogel.

The freeze-dried RH-CTS/PAM gel exhibited a macroporous network structure, indicating a high buried water content of the raw RH-CTS/PAM gel. The moisture content of the raw and swollen gel was calculated, and which was 75.1 and 96.8%, respectively. The high moisture content of the swollen RH-CTS/PAM gel is mainly due to the hydrophilic functional groups inside the material. Significantly, the high moisture content of swollen gel at equilibrium state is conducive to the rapid adsorption of heavy metal ions, since high water content enhances permeability and thus provides transport channels for the diffusion of heavy metal ions (Ma et al., 2017a). The RH-CTS/PAM gel showed good water retention and repeat drving and swelling ability. and the swelling equilibrium of the dried gel reached in 90 min with a SR value of 30. Moreover, the RH-CTS/PAM gel was stable in solutions with pH values ranging from 1.00 to 13.00. The gel could withstand high-level deformations without any observable damage and return to its original shape when the applied pressure was released, which is another key factor that considered to be applied in water treatment (Xu et al., 2016).

3.2. Selective adsorption

Fig. 1 shows the removal efficiency of each metal ion in a mixed solution of Pb(II), Cu(II), Cd(II), Ni(II), Mn(II) and Zn(II) with the initial concentration ranging from 50 to 300 mg/L by RH-CTS/PAM gel. The RH-CTS/PAM gel exhibited better removal efficiency on Pb(II), Cu(II) and Cd(II) in the mixed solution from a low concentration (50 mg/L) to a high concentration (300 mg/L). However, the order of removal efficiency of Ni(II), Mn(II) and Zn(II) varied due to the changes in concentration. Generally, there are many factors that affect the interaction between the adsorbent and target ions in the mixed solution, such as (i) the concentration and electronegativity of ions. (ii) the size of ionic radius, and (iii) the stability constants of associated metal hydroxides (Hadi et al., 2013). The relative selectivity coefficients ($\beta_{Pb/M}$, Section S1 of the SI) were greater than 1, in which the values of $\beta_{Pb/Cu}$ and $\beta_{Pb/Cu}$ _{Cd} were smaller than the other three, suggesting that the RH-CTS/PAM gel could preferentially adsorb Pb(II) in multicomponent systems, followed by Cu(II) and Cd(II). Therefore, Pb(II), Cu(II) and Cd(II) were selected as the target metal ions in this study, and the adsorption performance of the RH-CTS/PAM gel on Pb(II), Cu(II) and Cd(II) in individual and multicomponent systems was systematically studied.



Fig. 1. Selective removal of heavy metal ions on RH-CTS/PAM gel, $C_0 = 50/100/200/300$ mg/L, T = 298 K, pH = 5.00 \pm 0.01, m/V = 1 g/L.



Fig. 2. Time-dependent adsorption of Pb(II) in the system of (a) Pb(II), (b) Pb(II)/Cd(II), (c) Pb(II)/Cu(II) and (d) Pb(II)/Cd(II), Cu(II) in the system of (e) Cu (II), (f) Cu(II)/Pb(II), (g) Cu(II)/Cd(II) and (h) Cu(II)/Pb(II)/Cd(II), Cd(II) in the system of (i) Cd(II), (j) Cd(II)/Pb(II), (k) Cd(II)/Cu(II) and (l) Cd(II)/Pb(II)/Cu(II), $C_0 = 20/100/200 \text{ mg/L}, T = 298 \text{ K}, \text{ pH} = 5.00 \pm 0.01, m/V = 1 \text{ g/L}.$

3.3. Adsorption kinetics

Adsorption kinetic curves of Pb(II), Cu(II) and Cd(II) in individual and multicomponent systems are shown in Fig. 2. In individual system, the equilibrium time of Pb(II) at the concentration of 20, 100 and 200 mg/L was reached in 3, 5 and 10 min, respectively, and the same equilibrium time occurred in the adsorption of Cu(II) and Cd(II) as well. At the concentration of 20 mg/L, the equilibrium time of Pb(II), Cu(II) and Cd(II) remained unchanged in binary and ternary systems as compared to the individual system. However, at a concentration of 100 or 200 mg/L, the equilibrium time of Pb(II), Cu(II) and Cd(II) in binary and ternary systems was longer than that in individual system. Specifically, the equilibrium time of Pb(II) in Pb(II)/Cd(II), Pb(II)/Cu(II) and Pb(II)/Cd(II)/Cu(II) at 100 mg/L was 10, 20 and 20 min, respectively. The equilibrium time of Cu(II) in Cu(II)/Pb(II), Cu(II)/Cd(II) and Cu (II)/Pb(II)/Cd(II) at 100 mg/L was 30, 30 and 20 min, respectively. The equilibrium time of Cd(II) in Cd(II)/Pb(II), Cd(II)/Cu(II) and Cd(II)/Pb (II)/Cu(II) at 100 mg/L was 10, 10 and 20 min, respectively. It was worth noting that as the concentration increased to 200 mg/L, the equilibrium time of Pb(II) and Cd(II) in each system became longer, except for Pb(II) in the ternary system (20 min). Simultaneously, the equilibrium time of Cu(II) in the binary (i.e., Cu(II)/Pb(II) and Cu(II)/ Cd(II)) and ternary (Cu(II)/Pb(II)/Cd(II)) systems remained unchanged as the concentration increased from 100 mg/L to 200 mg/L, while which was extended by 5 min in the individual system (Cu(II)). Moreover, the coexistence of Pb(II), Cu(II) and Cd(II) could significantly accelerate the adsorption rate of Pb(II) and Cu(II), which was 10 min faster in ternary system (Pb(II)/Cd(II)/Cu(II)) compared with that in binary systems. Overall, as compared to the individual system, the adsorption rate of Pb(II) and Cu(II) in the binary system (Pb(II)/Cu(II)) was most affected, while that of Cd(II) (Cd(II)/Pb(II), Cd(II)/Cu(II)) was the least affected. This result can be due to the similar electronegativity (2.33 of Pb(II), 1.90 of Cu(II) and 1.69 of Cd(II)) and stability constant value (7.82 of Pb(II), 7.00 of Cu(II) and 4.17 of Cd(II)) of Pb(II) and Cu (II), suggesting that electronegativity and stability constant value may be the main factors affecting the adsorption rate of ions.

The pseudo-first order and pseudo-second order models (Section S2 of the SI) were employed to describe the adsorption kinetic process of Pb (II), Cu(II) and Cd(II) in individual and multicomponent systems. The pseudo-second order model gave a better fitting of kinetic data in most cases according to the correlation coefficient (R²), suggesting that chemical interaction involved in the adsorption process (Wei et al., 2019). Several of these exceptions might be due to the low concentration of Cu (II) (20 mg/L) and effects of ion coexistence (Cu(II)/Pb(II), Cu(II)/Cd(II)) (Zhou et al., 2017a). The intraparticle diffusion model (Section S2 of the SI) was also used to describe the whole process of kinetic adsorption. The liner fitting curves of Pb(II), Cu(II) and Cd(II) in individual and multicomponent systems with concentration of 20 mg/L contained two main steps over the whole time range. At concentration of 100 and 200 mg/L, there were three different linear zones for Pb(II), Cu(II) and Cd(II) adsorption in multicomponent systems, except for Cd(II) adsorption in binary systems (Cd(II)/Pb(II), Cd(II)/Cu(II)). This result indicates that certain competition between heavy metal ions exist when the coexistence of multiple heavy metal ions in high concentration.

3.4. Adsorption modeling and thermodynamics

Temperature-dependent adsorption data of Pb(II), Cu(II) and Cd(II) in different systems are shown in Fig. 3. In the individual system, the 100 mg/L of Pb(II), Cu(II) and Cd(II) that could be substantially removed by RH-CTS/PAM gel. Whereas, the concentration of completely removable Pb(II), Cu(II) and Cd(II) was reduced in the multicomponent systems, except for Pb(II) and Cd(II) in the binary system of Pb(II)/Cd(II). The reason for the decrease in concentration should be the competition between the heavy metal ions for the adsorption sites. Langmuir, Freundlich and Langmuir-Freundlich models (Section S3 of the SI) were used to further describe the interactive behavior between RH-CTS/PAM gel and heavy metal ion. The isotherm data of Pb(II), Cu(II) and Cd(II) were better fitted with the Freundlich and Langmuir-Freundlich isotherm models according to the correlation coefficient (R^2), suggesting that the adsorption occurs as the heavy metal ions adsorbs onto the heterogeneous hydrogel surfaces (Ma et al., 2018b). The theoretical maximum



Fig. 3. The nonlinear fitting curves from Langmuir-Freundlich isotherm model for the temperature-dependent adsorption data of Pb(II) in the system of (a) Pb(II), (b) Pb(II)/Cd(II), (c) Pb(II)/Cu(II) and (d) Pb(II)/Cd(II), (cu(II), cu(II), f) Cu(II)/Pb(II), (g) Cu(II)/Cd(II) and (h) Cu(II)/Pb(II)/Cd(II), and Cd (II) in the system of (i) Cd(II), (j) Cd(II)/Pb(II), (k) Cd(II)/Cu(II) and (l) Cd(II)/Pb(II), cu(II), t_{contact} = 6 h, pH = 5.00 \pm 0.01, *m*/V = 1 g/L.

adsorption capacity calculated from Langmuir model (298 K) was used to compare the removal effect of RH-CTS/PAM gel on Pb(II), Cu(II) and Cd (II) in different systems. The theoretical maximum adsorption capacity of Pb(II), Cu(II) and Cd(II) by RH-CTS/PAM gel in individual system were 374.32, 196.68 and 268.98 mg/g, respectively. The theoretical maximum adsorption capacity of Pb(II) in the system of Pb(II)/Cd(II), Pb(II)/ Cu(II) and Pb(II)/Cd(II)/Cu(II) were 254.78, 297.00 and 245.16 mg/g, respectively. The theoretical maximum adsorption capacity of Cu(II) in the system of Cu(II)/Pb(II), Cu(II)/Cd(II) and Cu(II)/Pb(II)/Cd(II) were 143.80, 147.72 and 120.08 mg/g, respectively. The theoretical maximum adsorption capacity of Cd(II) in the system of Cd(II)/Pb(II), Cd(II)/ Cu(II) and Cd(II)/Pb(II)/Cu(II) were 198.34, 225.39 and 105.99 mg/g, respectively. Apparently, the theoretical maximum adsorption capacity of Pb(II), Cu(II) and Cd(II) in multicomponent systems was lower than that of individual systems, which was mainly due to the restricted functional groups on the surface of RH-CTS/PAM gel. The adsorption capacity of Pb(II) and Cd(II) in the binary system (Pb(II)/Cd(II)) was most affected as compared to the other systems (i.e., Pb(II)/Cu(II) and Cd (II)/Cu(II)), which could be due to the similar ionic radius (120 of Pb(II), 72 of Cu(II) and 97 of Cd(II)) of Pb(II) and Cd(II). This result indicates that ionic radius may be the main factors affecting the adsorption capacity of Pb(II), Cu(II) and Cd(II). It is noteworthy that the R_L values (Section S3 of the SI) calculated from Langmuir model parameters was between 0 and 1, and the Freundlich constant n was greater than 1, which illustrates the favorable adsorption of Pb(II), Cu(II) and Cd(II) by RH-CTS/PAM gel in individual as well as multicomponent systems (Foo and Hameed, 2010). The theoretical adsorption capacity of the RH-CTS/ PAM gel was much higher than that of other reported chitosan and lignin based adsorbents, revealing the great potential of the RH-CTS/PAM gel in heavy metal removal.

Thermodynamic parameters such as the standard free energy change (ΔG^0), standard enthalpy change (ΔH^0) and standard entropy changes (ΔS^0) were calculated according to the van't Hoff equation ((Section S3 of the SI)). The ΔG^0 values were found to be negative and decreased with increasing temperature, and the ΔH^0 as well as the ΔS^0 values were positive for the adsorption of Pb(II), Cu(II) and Cd(II) in individual and multicomponent systems. This result indicates that the

adsorption of Pb(II), Cu(II) and Cd(II) by RH-CTS/PAM gel is spontaneous and higher temperature is more favorable for the adsorption process. The free energy (E) calculated from the Dubinin-Radushkevish (D-R) isotherm model (Section S3 of the SI) for Pb(II), Cu(II) and Cd(II) adsorption ranged from 12.55 to 17.14, 12.35 to 15.91 and 12.31 to 19.05 kJ/mol, respectively, which was in the energy range of a chemisorption process (8–16 kJ/mol) (Helfferich, 1962.) for Cu(II) and beyond the energy range for Pb(II) (i.e., Pb(II), Pb(II)/Cd(II)) and Cd(II) (i.e., Cd(II)/Pb(II), Cd(II)/Pb(II)/Cu(II)). Therefore, it can infer that the adsorption process of Cu(II) in these systems is mainly dominated by chemisorption, while both physisorption and chemisorption are involved in the adsorption process of Pb(II) and Cd(II) in some systems.

3.5. Effect of environmental conditions

The effects of pH and interfering ions (i.e., Na(I), K(I), NH₄(I), Ca(II) and Mg(II)) on the adsorption of Pb(II), Cu(II) and Cd(II) in individual and multicomponent systems were tested. The RH-CTS/PAM gel showed negligible adsorption of Pb(II), Cu(II) and Cd(II) at pH below 1.50, and the removal efficiency increased quickly when the pH value ranged from 1.50 to 2.50 and remained unchanged at pH above 3.00. The pH of bulk solution precipitation (pH_{BSP}) of Pb(II), Cu(II) and Cd(II) with an initial concentration of 50 mg/L was 5.87, 5.86 and 8.53, respectively, and no precipitation occurred at pH below pH_{BSP}. The pH_{PZC} of RH-CTS/PAM gel measured by Δ pH drift method was about 6.43, suggesting that the charges on the RH-CTS/PAM gel surface were positive at pH below 6.43 and negative at pH above 6.43. The result suggests that electrostatic interaction plays a role in the adsorption of Pb(II), Cu(II) and Cd(II).

The concentrations of interfering ions ranged from 1 to 5 mmol/L and the concentration of Pb(II), Cu(II) and Cd(II) was set as 100 mg/L (0.48 mmol/L of Pb(II), 1.57 mmol/L of Cu(II) and 0.89 mmol/L of Cd (II)). Na(I), K(I) and NH₄(I) had a negligible effect on Pb(II), Cu(II) and Cd(II) removal even at high concentration level (5 mmol/L). Ca(II) and Mg(II) showed the greatest effect on the adsorption efficiency. At the concentration of 5 mmol/L, amount of reduction in adsorption efficiency of Pb(II), Cu(II) and Cd(II) followed the order of Cu(II) (17.3%) > Cd(II) (3.5%) > Pb(II) (1.2%) in individual system, while

followed the order of Cd(II) (14.4%) > Cu(II) (6.9%) > Pb(II) (5.6%)in ternary system. In binary system, amount of reduction in adsorption efficiency of Pb(II), Cu(II) and Cd(II) followed the order of Pb(II) (4.8%) > Cd(II) (0.9%), Cu(II) (9.7%) > Pb(II) (5.4%) and Cd(II) (11.5%) > Cu(II) (8.7%) in the system of Pb(II)/Cd(II), Pb(II)/Cu(II) and Cd(II)/Cu(II), respectively. It can be found that the adsorption efficiency reduction of Pb(II), Cu(II) and Cd(II) in different systems followed the sequence of Pb(II)/Cd(II)/Cu(II) > Pb(II)/Cu(II) > Pb(II)/ Cd(II) > Pb(II), Cu(II) > Cu(II)/Pb(II) > Cu(II)/Pb(II)/Cd(II) > Cu(II)/Cd(II), and Cd(II)/Pb(II)/Cu(II) > Cd(II)/Cu(II) > Cd(II) > Cd (II)/Pb(II), respectively. From this point of view, the inhibitory effect of interfering ions on the uptake of Pb(II), Cu(II) and Cd(II) in different systems was random. In fact, many factors are suspected of having an effect on the adsorption of heavy metal ions, such as electronegativity, ionic radius, the stability constants of associated metal hydroxides, the lowered activity coefficient of ions at high ionic strength, competition and electrostatic repulsion among metal ions, and so on (Hanzlik et al., 2004).

3.6. Recyclability tests

The minimum required eluant (HCl) to adsorbent ratio (L/g) for complete elution of Pb(II), Cu(II) and Cd(II) in different systems were tested. The minimum required HCl to adsorbent ratio for complete elution of Pb(II), Cu(II) and Cd(II) in individual system was in the following order: Pb(II) (0.4) > Cu(II) (0.2) = Cd(II) (0.2). Meanwhile, the minimum ratio required for complete elution of heavy metal ions in the binary system of Pb(II)/Cd(II), Pb(II)/Cu(II) and Cd(II)/Cu(II) was 0.2, 0.2 and 0.3, respectively, and it was 0.3 in the ternary systems. Therefore, the ratio of 0.4 L/g was used in the experiment of elution rate and regeneration performance of RH-CTS/PAM gel. The time required for elution of Pb(II), Cu(II) and Cd(II) in individual system was 20, 5 and 10 min, respectively, which was the same as the time required in multicomponent systems except for Pb(II) in the system of Pb(II)/Cd (II) (10 min). This is probably because of the reduced adsorption amount of Pb(II), Cu(II) and Cd(II), as well as the interaction between Pb(II), Cu(II) and Cd(II) in multicomponent systems. After five consecutive adsorption-desorption processes, the adsorption ratio of the RH-CTS/PAM gel only dropped by 2.3%, 1.8% and 3.1% toward Pb(II), Cu(II) and Cd(II), respectively. This result confirms that the RH-CTS/ PAM gel has good regeneration performance.

3.7. Adsorption mechanism

According to the discussion of adsorption kinetic, modeling and thermodynamics results, it can infer that the adsorption process of Pb (II), Cu(II) and Cd(II) involves both physisorption and chemisorption. The FTIR and XPS studies of RH-CTS/PAM gel before and after adsorption of Pb(II), Cu(II) and Cd(II) were performed to further understand the interaction mechanism.

As can be seen from the FTIR spectra, the peak of O–H stretching vibration at about 3500 cm^{-1} had red shift and strengthened after the adsorption of Pb(II), Cu(II) and Cd(II) in individual and multicomponent systems. Moreover, the peak at 1557 cm^{-1} also had red shift and new peaks at 1602 cm^{-1} was appeared. It was worth noting that the red shift displacement was larger and the intensity of the newly added peak in RH-CTS/PAM gel-Cu(II) was stronger than that of RH-CTS/PAM gel-Pb(II) and RH-CTS/PAM gel-Cd(II). The results suggest that CTS and lignin in RH solution play a role in the adsorption process, and the interaction between functional groups and heavy metal ions is different, which is consistent with the results of adsorption modeling and thermodynamics.

The survey spectrum is shown in Fig. 4a, new peaks of Pb 4f, Cu 2p and Cd 3d appeared after adsorbing Pb(II), Cu(II) and Cd(II). The highresolution O 1s XPS spectrum (Fig. 4b) of RH-CTS/PAM gel presented three different peaks at binding energy (BE) of 532.5, 531.4 and 530.6 eV, corresponding to the C–O–H, C–O–C and C=O groups, respectively. After the adsorption of heavy metal ions, the BE of O 1s increased, in which the BE of C=O group increased the most, and the integral area ratio of C-O-C decreased. This result demonstrates that the C-O-C and C=O groups in RH-CTS/PAM gel participate in the adsorption of heavy metal ions, but their interaction with heavy metal ions is different. Fig. 4c showed the high-resolution XPS spectra of N 1s spectrum, after the adsorption of heavy metal ions, the BE of N 1s increased slightly and the integral area ratio of -NHCO- decreased, demonstrating the participation of -NHCO- group in the adsorption process. But the peak indexed to $-NH_2$ group at BE of 399.5 eV remained unchanged after adsorbing heavy metal ions, which could be due to the lone pair of electrons of nitrogen atom in amide group of PAM were occupied (Ma et al., 2018a). The shift of the BE of O 1s and N 1s can be attributed to the interaction of metal with O and N atoms, in which O and N atoms donate electrons to metal ions and the electron density toward O and N atoms in these groups decreased and the BE increased (Luo et al., 2014). In the high-resolution XPS spectra of C 1s spectra (Fig. 4d), the change in BE and integral area of the assigned peaks were ignorable after the adsorption of heavy metal ions, except for the BE of C-N group, which shifted from 285.7 to 285.3 eV after adsorbing Cd(II). The shift of BE can be attributed to the decreased electron density of the adjacent N atoms and thus the BE of the C atoms reduced. The XPS spectra of Pb 4f7/2, Cu 2p3/2 and Cd 3d5/2 could be assigned to two peaks, and the BE were differed from that of Pb(II) (138.3 eV), Cu(II) (932.6 eV) and Cd(II) (405.0 eV). Combined with the XPS spectra of O 1s and N 1s, the peaks at BE of 138.5, 136.6, 933.8, 932.8, 406.1 and 405.2 eV corresponded to the bond of Pb-O, Pb-N, Cu-



Fig. 4. (a) Wide-scan XPS spectra, high-resolution XPS spectra of (b) O 1s, (c) N 1s and (d) C 1s of RH-CTS/PAM gel before and after adsorption of Pb(II), Cu(II) and Cd(II).

O, Cu-N, Cd-O and Cd-N, respectively. These results suggest the existence of chelation or coordination interaction between the functional groups (i.e., O and N-containing groups) and heavy metal ions (Pb(II), Cu(II) and Cd(II)), as well as physical interaction (Deng et al., 2003; Peng et al., 2016; Zhou et al., 2017b).

4. Conclusions

The RH-CTS/PAM gel consisting of lignin, CTS and PAM was synthesized by one-step radical polymerization. The macroporous structure, high buried water content and large number of functional groups of RH-CTS/PAM gel gave rise to the exceptional removal rate of heavy metal ions. Ultrafast adsorption kinetic rate (i.e., 10 min) was determined on Pb(II), Cu(II) and Cd(II) removal with initial concentration of 200 mg/L. Moreover, the utilization of lignin derived from RH in the preparation of adsorbent is very useful for the recycle of RH, which is expected to guide an effective way to recycle the crop by-product.

5. Notes

The authors declare no competing financial interest.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (51672077, 51872089), Hunan Provincial Natural Science Foundation of China (2017JJ2026), Key Laboratory of Jiangxi Province for Persistent Pollutants Control and Resources Recycle (Nanchang Hangkong University) (ES201880051).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.biortech.2019.121793.

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