

Removal of Heavy Metals from Aqueous Solutions Using Acrylic-modified Sugarcane Bagasse-based Adsorbents: Equilibrium and Kinetic Studies

Weiying Kong, Junli Ren,* Shuaiyang Wang, and Qifeng Chen*

Recently, more and more attention has been centered on developing cheaper, highly efficient, environmentally friendly adsorbents for the removal of metal ions from industrial effluents. The present work deals with the removal of metal ions from an aqueous solution using a highly efficient, biodegradable adsorbent from hydrogel prepared by the free radical graft polymerization of sugarcane bagasse with acrylic acid and acrylamide using *N, N*-methylene-bis-acrylamide as a crosslinker. FTIR and SEM/EDX spectroscopies were used to characterize the structure and the morphology of adsorbent before and after the metal ions adsorption. The effects of pH, contact time, and initial concentration of metal ion on the adsorption capacity were studied. The adsorption equilibrium time of Pb^{2+} , Cd^{2+} , and Cu^{2+} were 60, 90, and 180 min, respectively. The maximum adsorption capacities of Cu^{2+} , Pb^{2+} , and Cd^{2+} were 268, 700, and 320 mg/g, respectively. The adsorption data were fit to often-used models for adsorption kinetics and isotherms. It was determined that the experimental results were well fitted to the pseudo-second-order equation and Langmuir adsorption isotherms.

Keywords: Sugarcane bagasse; Adsorbent; Metal ions; Adsorption kinetics

Contact information: State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou, 510640, China;

* *Corresponding authors:* renjunli@scut.edu.cn; qfchen@scut.edu.cn

INTRODUCTION

Heavy metal ions such as cadmium, copper, lead, nickel, and zinc poses a serious threat to the environment and is of great concern worldwide. Industrial effluents are the major source of contamination containing heavy metal ions. Heavy metals are generally poisonous and cannot be degraded. In addition, toxic metals can be accumulated in living tissues, causing various diseases and disorders (Dabrowski *et al.* 2004; Fu and Wang 2011). Thus, the safe and effective waste water treatment containing heavy metal ions is always a challenge to industrialists and environmentalists, and there is a need for more cost-effective and safer treatments (Alyüz and Veli 2009). Conventional treatments for the removal of metal ions from aqueous solutions include chemical precipitation (Ku and Jung 2001), ion exchange (Alyüz and Veli 2009), membrane filtration (Bessbousse *et al.* 2008), carbon adsorption (Nadeem *et al.* 2006), cementation (Makhloufi *et al.* 2000), and electro dialysis (Smara *et al.* 2007). However, they are limited by technical or economic issues (Miretzky *et al.* 2006; Santos *et al.* 2011). In comparison with the other processes, adsorption is a potential alternative treatment to conventional technologies for the removal of toxic metals (Fu and Wang 2011; Guan *et al.* 2011; Li *et al.* 2013). The sorption process possesses some advantages, especially in water treatment, such as

flexibility in design and operation and producing superior effluent suitable for reuse without other pollutants (Fu and Wang 2011; Li *et al.* 2013). Until now, many conventional sorbents have been prepared, and their disadvantages include their expense and lower adsorption capacity. In addition, these sorbents are not reusable or biodegradable, which limits their application due to the growing public issues on energy sources, resources, and the environment (Peñaranda and Sabino 2010).

Recently a great deal of attention has been directed toward the production of bio-adsorbents from renewable resources such as starch (Huang *et al.* 2011), cellulose (O'Connell *et al.* 2008), lignin (Guo *et al.* 2008; O'Connell *et al.* 2008), chitin/chitosan (Kannamba *et al.* 2010), agricultural wastes (Sud *et al.* 2008), bamboo charcoal (Huang *et al.* 2012; Lalhruitluanga *et al.* 2010; 2011; Ma *et al.* 2010; Wang *et al.* 2011), and other polysaccharides (Liu *et al.* 2009). Agricultural wastes are currently receiving wide attention as raw materials to prepare bio-adsorbents because of their abundant availability, low cost, renewability, biodegradability, high efficiency, and good reusability (Li and Bai 2006). Furthermore, they have relatively high hydroxyl functional groups and present a porous structure. Therefore, it is necessary to develop biomass-based adsorbents to replace conventional materials. Among the various agro-wastes, sugarcane bagasse is a residue that results from the crushing of sugarcane and is chemically composed of cellulose, hemicelluloses, and lignin. There are many binding sites available to take up metallic ions, so it is a potential material for preparing low-cost natural bio-adsorbents. However, bio-adsorbents based on sugarcane bagasse for removing metal ions in aqueous solutions have seldom been reported.

In this work, we developed a highly efficient and environmentally friendly adsorbent prepared by the free radical graft polymerization of sugarcane bagasse with acrylic acid and acrylamide using *N, N*-methylene-bis-acrylamide as a crosslinker. The structure and the surface morphology of adsorbent before and after the metal ions adsorption were characterized by Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) together with energy-dispersive spectroscopy (EDS) (SEM/EDX). The effects of pH, contact time, and initial concentration of the metal ion on the adsorption capacity were investigated and kinetic and isotherm studies were conducted.

EXPERIMENTAL

Materials

Sugarcane bagasse (SB) was obtained from Guangzhou Sugarcane Industry Research Institute, and after a ball-milling pretreatment, the SB powder was sized between 0.15 mm and 0.074 mm.

Analytical-reagent grade acrylic acid (AA), acrylamide (AM), and *N, N*-methylene-bis-acrylamide (MBA) were purchased from Guangzhou Chemical Reagent Factory (Guangzhou, China). Ammonium persulfate (APS) was purchased from Shanghai Chemical Reagent Corp. (Shanghai, China).

The metal ions Pb^{2+} , Cd^{2+} , and Cu^{2+} were provided as $Pb(NO_3)_2$, $CdCl_2 \cdot 2.5H_2O$, and $Cu(NO_3)_3 \cdot 3H_2O$, which were purchased from Guangzhou Chemical Reagent Factory (Guangzhou, China). These reagents were of analytical grade and prepared with deionized water.

Preparation of Sugarcane Bagasse-based Adsorbent

The SB-based adsorbent was prepared by free radical graft copolymerization of AA, AM, and SB by using MBA as a crosslinker and APS as the initiator. First, 1.0 g of sugarcane bagasse was dispersed in 20 mL of deionized water, and the solution was placed in a 250-mL three-necked flask equipped with a magnetic stirrer, reflux condenser, and nitrogen line. The reactor was immersed in a water bath at 70 °C. Simultaneously, oxygen-free nitrogen gas was bubbled into the solution for 30 min, and a deionized water solution containing 0.1 g of APS was added. After 15 min of stirring, 1.0 g of AA solution (with 70% neutralization by ammonium bicarbonate), 1.0 g of AM, and 0.025 g of MBA were added sequentially to the reaction mixture. The entire volume of solution in the reactor was maintained at 40 mL. After a 2-h reaction, the hydrogel (SB/P(AA-co-AM)) was washed with deionized water and ethyl alcohol several times and soaked in a 1 M NaOH solution. Finally, the adsorbent hydrogel was cut into small pieces with 5×5×5 mm dimension and dried at 60 °C until reaching a constant weight. The proposed crosslinking reaction mechanism is shown in Fig. 1.

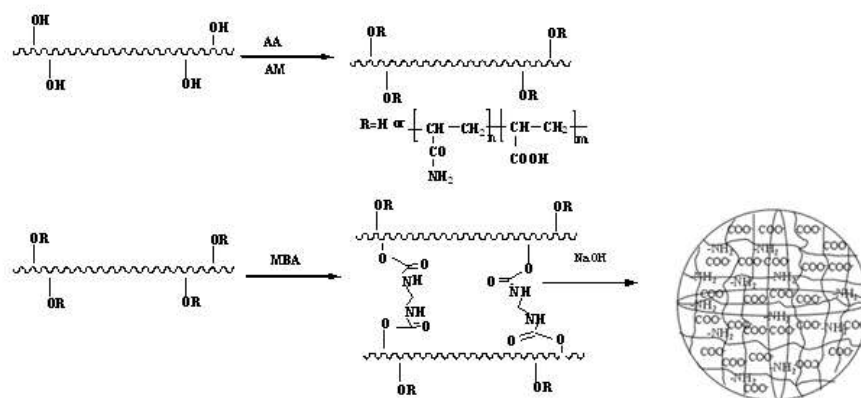


Fig. 1. Proposed free-radical scheme for a crosslinking reaction involving cellulose-based material and acrylics

FTIR Spectra

FTIR spectra of SB and SB-g-P(AA to AM) adsorbent hydrogels were performed by a Nicolet 750 spectrophotometer within the frequency range of 400 to 4000 cm^{-1} by the method of transmission. The 1% finely ground samples were mixed with KBr to press a plate for measurement.

Morphology of Adsorbent Hydrogels

SEM/EDX analysis was used to investigate the morphology of the prepared hydrogels before and after the adsorption of water or metal ions. The surface morphology of hydrogels was investigated using SEM (Hitachi S3700). Specimens were coated with gold for 30 s in a sputter coater.

Heavy Metal Ion Adsorption of Sugarcane Bagasse-based Adsorbent

The adsorption capacity of SB/P(AA-co-AM) adsorbent hydrogel for heavy metal ions was investigated in batch experiments. In each experiment, 0.1 g of the dried adsorbent was added to a 25-mL solution of the metal ions Pb^{2+} , Cd^{2+} , or Cu^{2+} . The flasks

were stirred with a magnetic bar at 120 rpm, and the pH was adjusted with 1 M nitric acid.

After equilibrium was reached, the filtrate was measured for metal ion concentration by atomic absorption spectroscopy (AAS) (Hitachi Z-2000, Japan). Every value reported was the mean of at least three separate measurements, and standard deviation was less than 5%. The amount of metal ion adsorbed on the adsorbent was calculated according to Eq. 1,

$$Q = \frac{(C_0 - C) \times V}{m} \quad (1)$$

where Q is the amount of heavy metal ion adsorbed (mg/g), C_0 and C are the concentrations of the metal ions in the aqueous phase before and after the treatment, respectively (mg/L), V (L) is the volume of the aqueous phase, and m (g) is the amount of dry hydrogel.

Effects of pH

Dry adsorbent was immersed in a series of 200 mg L⁻¹ single heavy metal ion solutions at pH 1, 2, 3, 4, 5, and 6 at 25 °C for 3 h to determine the optimum pH for the maximum adsorption. The amount of metal ion adsorbed onto hydrogels was calculated according to Eq. 1.

Isotherm Study

Dry hydrogels were equilibrated at room temperature for 3 h in a single heavy metal ion solution at concentrations of 100, 200, 300, 400, 500, 600, 700, 800, 900, 1,000, and 1,100 mg L⁻¹ to study the effect of the initial heavy metal ion concentration on the adsorption capacity of hydrogel and adsorption isotherm. The solutions containing Pb²⁺, Cd²⁺, and Cu²⁺, respectively, were prepared at pH 6. The amount of metal ion adsorbed by adsorbents was determined by Eq. 1.

Kinetics Study

The studies on adsorption kinetics were conducted with an initial feed concentration of 200 mg L⁻¹ at pH 6 and at 25 °C. The concentration of heavy metal ions in the solutions were analyzed at a series of time points (0, 10, 20, 30, 40, 50, 60, 90, 120, 150 and 180 min). The amount of adsorbed metal ions was calculated according to Eq. 1.

Desorption and Reusability Behaviors

A desorption study was conducted to explore the potential reusability of the hydrogels and recovery of metal ions. The metal ions were released from sugarcane bagasse-based adsorbents by treating with 1 M hydrochloric acid (HCl) for 2 h in a total volume of 25 mL. The acid-treated adsorbents were soaked in a 1 M sodium hydroxide (NaOH) solution to neutralize the acid, filtered, and washed with distilled water. Then the adsorption process was conducted again according to the section on heavy metal ion adsorption by SB-based adsorbents described above.

The dried adsorbent was added to a 200 mg L⁻¹ solution containing Pb²⁺, Cd²⁺, and Cu²⁺, respectively, at pH 6 in a total volume of 25 mL. After equilibrium was reached, the metal ion concentration of the filtrate was measured. The adsorption-desorption process was repeated five times, and the amount of adsorbed and desorbed metal ions were calculated according to Eq. 1.

RESULTS AND DISCUSSION

FTIR Spectral Analysis

Figure 2 shows FTIR spectra of SB (spectrum a) and adsorbent SB/P(AA-co-AM) (spectrum b). The absorption band at 3411 cm^{-1} is attributed to the stretching vibration of the hydroxyl groups on SB in spectrum a. Clearly, this band intensity became weak after the reaction. New absorption bands appeared at 1566 cm^{-1} (asymmetric $-\text{COO}^-$ stretching) and 1674 cm^{-1} which is a shift of $\text{C}=\text{O}$ stretching vibration caused by the superposition of $\text{C}=\text{O}$ in the amide I and $\text{C}=\text{O}$ in COO^- (Wu *et al.* 2012) in spectrum b. These peaks were indicative of the occurrence of graft copolymerization, demonstrating that AA and AM were grafted on the backbone of SB. The band at 1458 cm^{-1} is assigned to the skeletal $\text{C}=\text{C}$ stretching vibrations in the aromatic rings. The absorption at 1049 cm^{-1} is due to the β -1, 4-glycosidic bond and the band at 1633 cm^{-1} is due to the $-\text{C}=\text{O}$ and $-\text{NH}_2$ of AM (Jin *et al.* 2006). The region from 3100 to 3500 cm^{-1} corresponds to the absorption bands of hydrogen bonds caused by $-\text{OH}$ and $-\text{NH}_2$. Thus it was confirmed that P (AA-co-AM) chains were successfully grafted onto the macromolecular chains of SB.

In order to confirm the presence of Pb^{2+} , Cd^{2+} , Cu^{2+} ions on the hydrogels, FTIR spectra were obtained for hydrogels after the adsorption of Pb^{2+} , Cd^{2+} and Cu^{2+} ions in Fig. 2. The asymmetric stretching vibrations of $-\text{COO}^-$ groups at 1566 cm^{-1} before adsorption shifted to 1589 , 1558 , and 1579 cm^{-1} upon the adsorption of Pb^{2+} , Cd^{2+} and Cu^{2+} ions, respectively, indicating that $-\text{COO}^-$ groups were connected with the metal ions (Wang *et al.* 2013).

In addition, the stretching vibrations of $-\text{NH}_2$ groups at 1633 cm^{-1} before adsorption shifted to 1618 , 1628 , 1631 cm^{-1} upon the adsorption of Pb^{2+} , Cd^{2+} and Cu^{2+} ions, respectively, indicating that the $-\text{NH}_2$ groups were possibly involved in the sorption. The complexation interactions were the main driving force for adsorption, and represented the chemical adsorption mechanism.

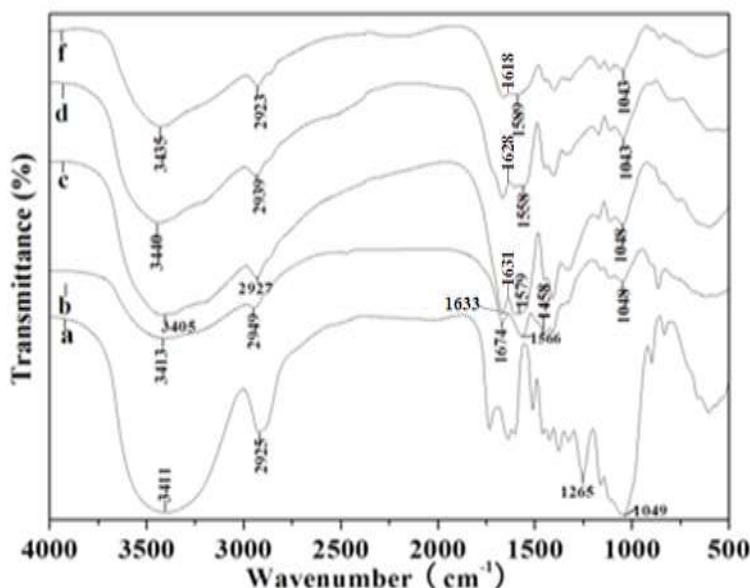


Fig. 2. FT-IR spectra of SB (a), hydrogels before adsorption (b) and after adsorbing Pb^{2+} (f), Cd^{2+} (d) and Cu^{2+} (c)

Morphological Analysis

Figure 3 displays the SEM images of SB and SB-g-P(AA-co-AM) adsorbent hydrogels before and after the adsorption of metal ions. The image of SB in Fig. 3a shows a dense surface whereas dried hydrogels display a macroporous structure. Many small and interconnected pores can be observed in Fig. 3b. The average diameter of the observed particles in SEM images could be estimated about 10 μm . After the adsorption of water, the pores change much in size (Fig. 3c) and they are the regions of water permeation and interaction sites of external stimuli with the hydrophilic groups of the graft copolymers. The porous structure of hydrogels favors the diffusion of metal ions from the exterior to the interior of the material and provides a higher specific surface area and more ligands for metal ion loading.

In order to confirm the presence of Pb^{2+} , Cd^{2+} , Cu^{2+} ions on adsorbent hydrogels, EDX spectra of hydrogels loaded Pb^{2+} , Cd^{2+} , Cu^{2+} , respectively, are illustrated in Fig. 2B. The EDX spectra show lead, copper and cadmium peaks, which was indicative of the existence of Pb^{2+} , Cd^{2+} , Cu^{2+} ions on the SB-g-P(AA-co-AM) adsorbent hydrogels.

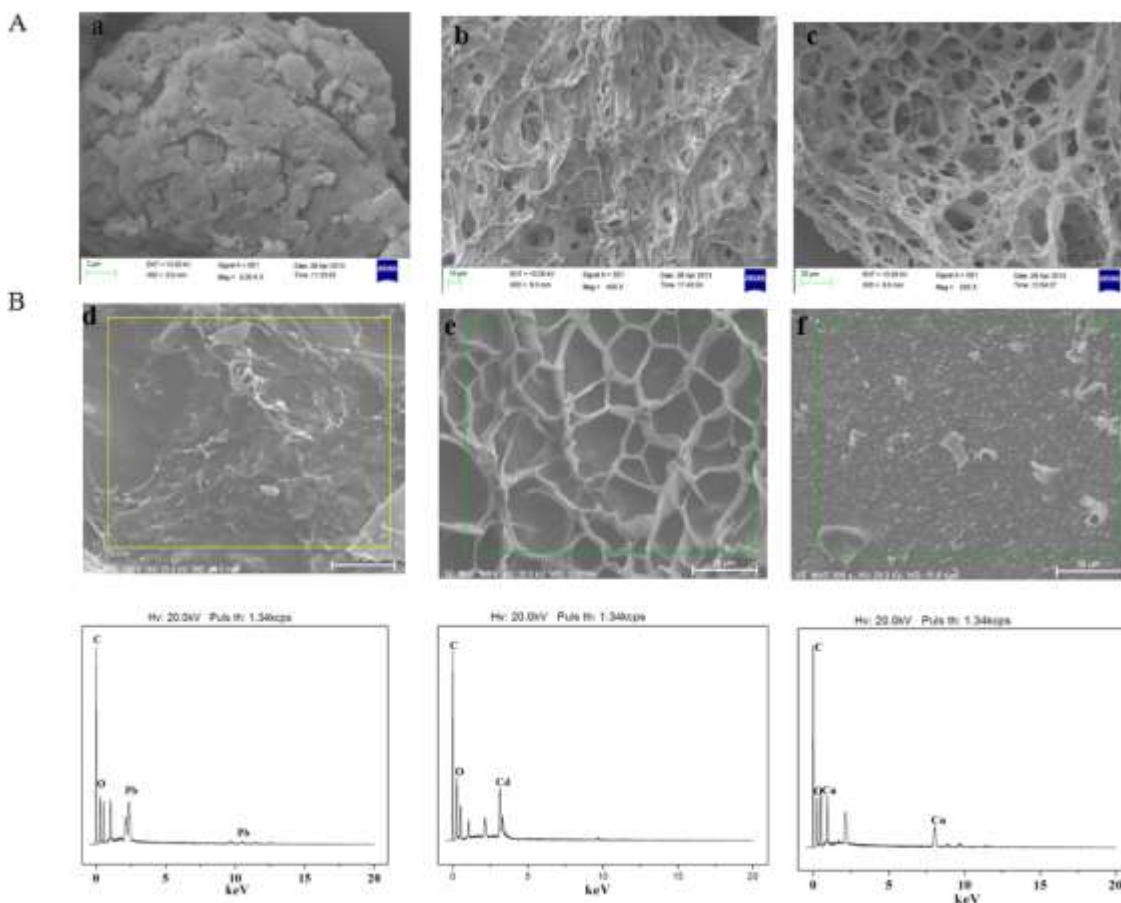


Fig. 3. A: SEM images of SB (bar 2 μm , 5000 \times) (a), SB/P(AA-co-AM)(bar 10 μm , 400 \times) (b), SB/P(AA-co-AM) hydrogels swelled in water (bar 10 μm , 400 \times) (c); B: SEM (bar 50 μm , 500 \times) (d, e, f) and EDX spectra of hydrogels loaded Pb^{2+} , Cd^{2+} , Cu^{2+} , respectively

Effect of pH

The pH is an important parameter for hydrogels in the adsorption of metal ions. It affects the electronic status of the pendant functional groups, such as protonation/deprotonation of the basic groups, as well as dissociation/association of the acidic groups. In addition, it may also modify the oxidation form of the metal ions present in the medium. The effect of initial pH on the adsorption capacity of sugarcane bagasse-based hydrogels is shown in Fig. 4.

Figure 4 shows that increasing the pH from 1 to 6 led to an increase in the adsorption levels of hydrogels for Cu^{2+} , Cd^{2+} , and Pb^{2+} , which increased from 19 to 213 mg/g for Cu^{2+} , from 1 to 232 mg/g for Cd^{2+} , and from 36 to 246 mg/g for Pb^{2+} , which meant that the adsorption capacities of prepared hydrogels were highly dependent on the pH value of solution. This same phenomenon was also reported by Li *et al.* (2013). The Pb^{2+} , Cu^{2+} , and Cd^{2+} adsorption amounts increased minimally in the pH range from 1 to 2, and then increased markedly from pH from 2 to 4. Subsequently, with pH rising from 4 to 6, the adsorption amounts of Pb^{2+} , Cu^{2+} , and Cd^{2+} slowly increased. This phenomenon could be explained by the theory that the reactive functional groups within the network of hydrogels were protonated at lower pH values. Metal ions had to compete with protons for adsorbency, and the protonated functional groups hindered the interaction between the adsorbent and heavy metal cations (Ijagbemi *et al.* 2010). Furthermore, the hydrogels soaked in NaOH solution contained many ionic groups ($-\text{COONa}$) that were almost completely ionized, and a large number of hydrophilic COO^- groups existed. However, in an acidic medium, those groups became $-\text{COOH}$ groups, which also prevent sorption of heavy ions into the hydrogel. Meanwhile, the $-\text{NH}_2$ groups were present in the form of $-\text{NH}_3^+$ at the low pH, which led to the decrease of the complexing ability of the nitrogen atom, thereby, made them difficult to chelate with heavy metal ions (Shafaei *et al.* 2007). Hence, to avoid the precipitation of heavy ions as well as lower adsorption, follow-up experiments should be carried out at a pH value of 6.0.

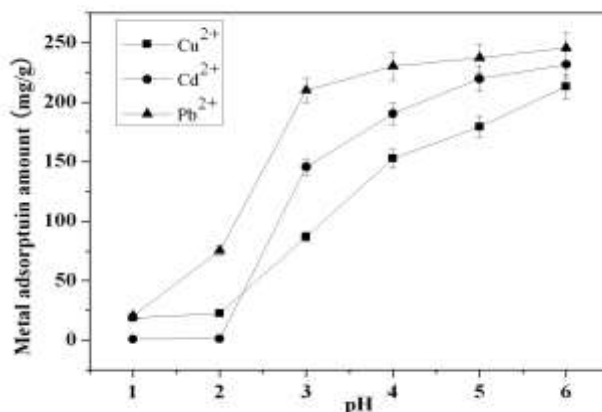


Fig. 4. The effect of initial pH on the heavy metal ion adsorption

Isotherm Study

Studies were carried out using sugarcane bagasse-based adsorbent hydrogels to determine the effect of the initial metal ion concentration, which varied from 100 to 1100 mg L^{-1} , on the adsorption capability at a pH of 6.0 and 25 °C. The effects of the initial heavy metal ion concentrations on the adsorption capacity are displayed in Fig. 5.

Figure 5a shows that the adsorption amounts of Pb^{2+} , Cd^{2+} , and Cu^{2+} increased with increasing initial metal ion concentration from 100 to 1000 mg L^{-1} , after which the adsorption amounts remained constant. This phenomenon was due to the increase in metal ion concentration accelerated the diffusion of the metal ion into the polymeric network because of the enhanced driving force of the concentration gradient. In addition, the equilibrium level demonstrated that the maximum adsorption amounts were achieved for Pb^{2+} , Cd^{2+} , and Cu^{2+} at the initial concentration of 1000 mg L^{-1} .

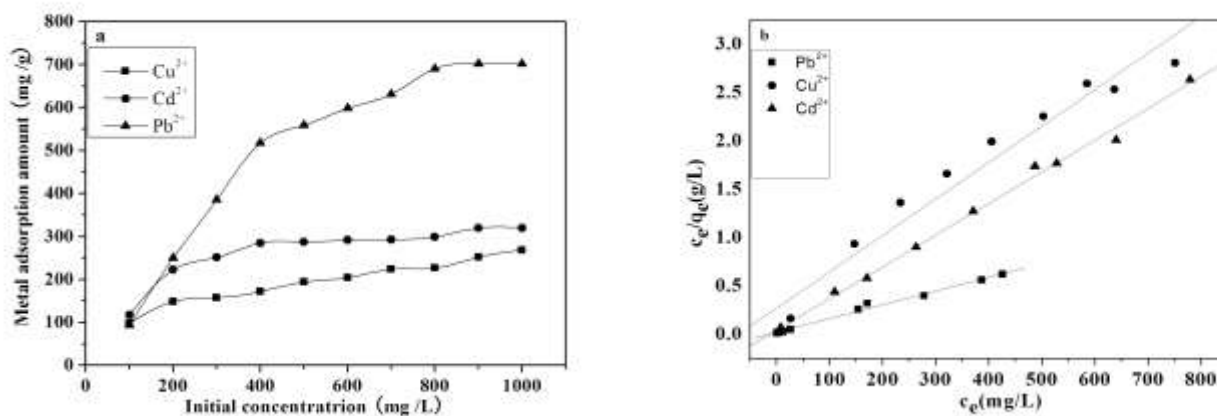


Fig. 5. Effect of initial heavy metal ion concentration on adsorption of heavy metal ions (a) and plots of C_e/q_e versus C_e for the Langmuir isotherm model (b)

Data for the sugarcane bagasse-based hydrogels adsorbing metal ions were then fitted to the Langmuir and Freundlich isotherm equation in the linearized form to analyze the adsorption capacity of the sugarcane bagasse-based hydrogels, which were expressed as,

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \quad (2)$$

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \quad (3)$$

where C_e is the equilibrium concentration of adsorbate (mg/L), q_e is the amount of the heavy metal ion adsorbed by the hydrogel at equilibrium (mg/g), b is the Langmuir adsorption affinity constant (L/mg), q_m is the amount of adsorbate required to occupy all of the available sites (mg/g), k_f is the Freundlich equilibrium constant (L/mg), and n is the Freundlich equilibrium constant.

The parameters obtained by fitting the data to Eqs. 2 and 3 of the adsorption isotherm models are summarized in Table 1. From the table, the R^2 values for all heavy metal ions in the Langmuir adsorption isotherm were consistently higher than that for the Freundlich adsorption isotherm, and the plots of C_e/q_e vs. C_e showed perfect straight lines (Fig. 4b). In addition, the theoretical q_m values obtained from the Langmuir adsorption isotherm were in good agreement with the experimental values. As a result, the Langmuir adsorption isotherm was a better mathematical fit to equilibrium data than the Freundlich adsorption isotherm. Therefore, the adsorption process of hydrogels for heavy metal ions acted like a monolayer adsorption process, which took place at specific homogeneous

sites on the adsorbent (Abdel-Halim and Al-Deyab 2011). The q_m in the Langmuir adsorption isotherm (Eq. 2) model indicated that the adsorption capacity of hydrogels was high. By contrast, the maximum adsorption capacity of Pb^{2+} was two to five times higher than for many similar adsorbents (Li *et al.* 2013; Jiang *et al.* 2006). The maximum adsorption capacity for Cu^{2+} was one to three times as high as many similar adsorbents (Wang *et al.* 2013; Li *et al.* 2013; Jiang *et al.* 2006), and the maximum adsorption capacity for Cd^{2+} was one to seven times higher than many similar adsorbents (Wang *et al.* 2013; Li *et al.* 2013; Jiang *et al.* 2006). Thus, these results indicated that SB-g-P (AA to AM) adsorbent was an effective adsorbent for the removal of heavy metal ions from the aqueous solution.

Table 1. Parameters of the Adsorption Isotherm Models

Ion	Freundlich			Langmuir			
	R^2	n	k_f	R^2	$q_{m(exp)}(mg/g)$	$q_{m(cal)}(mg/g)$	b
Pb^{2+}	0.956	1.105	1.092	0.992	700	704.225	7.289×10^{-2}
Cd^{2+}	0.878	2.257	1.764	0.995	320	304.878	8.185×10^{-2}
Cu^{2+}	0.982	1.973	1.748	0.989	268	265.252	1.408×10^{-2}

Kinetics

To achieve the proper design of an adsorbent, the adsorption equilibrium needs to be supplemented with adsorption kinetics, which offers information on the rate of metal adsorption. The time required to achieve adsorption equilibrium for Pb^{2+} , Cd^{2+} , and Cu^{2+} from aqueous solutions was determined for the sugarcane bagasse-based adsorbent hydrogels. The relationship between adsorption capacity and adsorption time is illustrated in Fig. 6.

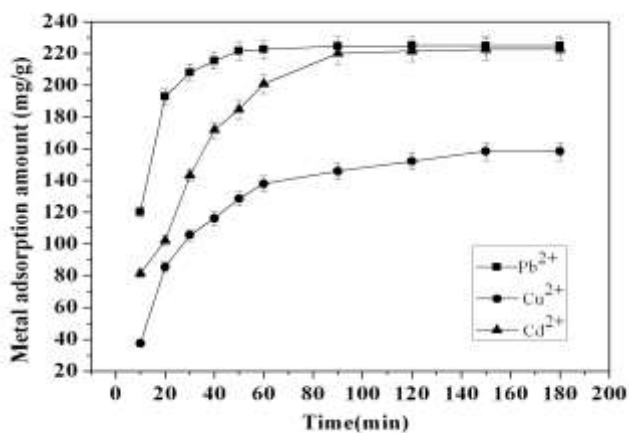


Fig. 6. The effect of contact time on adsorption of heavy metal ions

Figure 6 shows that the metal adsorption amounts of Pb^{2+} , Cd^{2+} , and Cu^{2+} were enhanced quickly with prolonged contact time from 10 to 60 min, after which the amounts of Pb^{2+} , Cd^{2+} , and Cu^{2+} leveled off. The adsorption equilibrium was achieved in 60 min for Pb^{2+} , 90 min for Cd^{2+} , and 180 min for Cu^{2+} , respectively (Fig. 5). The Pb^{2+} adsorption rate was much higher than that of the other heavy metal ions. This finding indicated that the adsorption process was very fast, and that it may be dominated by chelation. (Shafaei *et al.* 2007). These phenomena were due to the polymeric

superhydrophilic network and an abundance of $-\text{COO}^-$ and $-\text{NH}_2$ groups in the sugarcane bagasse-based hydrogels. The sugarcane bagasse-based hydrogels were shown to be good adsorbents for the heavy metal ions, with a high adsorption capacity and fast adsorption rate.

To examine the controlling mechanism of an adsorption process such as mass transfer and chemical reaction, the kinetic data were fitted by the pseudo-first-order and pseudo-second-order kinetic models, which were respectively expressed as,

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (4)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} = \frac{t}{q_e} \quad (5)$$

where q_t (mg/g) is the adsorption amount at time t (min), q_e (mg/g) is the adsorption capacity at adsorption equilibrium, k_1 is the kinetics rate constant for the pseudo-first-order equation (min^{-1}), and k_2 is the kinetics rate constant for the pseudo-second-order equation (g/mg/min).

The pseudo-first-order equation (Eq. 4) and the pseudo-second-order equation (Eq. 5) were utilized to characterize the adsorption experiment. The parameters of the equations are listed in Table 2.

Table 2 shows that the R^2 for all heavy metal ions in the pseudo-second-order equation was larger than that for the pseudo-first order equation. In addition, the theoretical q_e values obtained from the pseudo-second order kinetic model agreed better with the experimental values than the pseudo-first-order kinetic model. This indicated that the pseudo-second-order kinetic model more accurately reflected the adsorption kinetics than the pseudo-first-order kinetic model did.

Table 2. Parameters of Adsorption Kinetics Models

Ion	Pseudo-first-order model				Pseudo-second-order model		
	q_e (exp)	k_1 (min^{-1})	q_e (cal) (mg/g)	R^2	k_2 (g /mg/min)	q_e (cal) (mg/g)	R^2
Pb ²⁺	225	0.068	143.741	0.985	7.545×10^{-4}	238.663	0.997
Cd ²⁺	222	0.037	90.288	0.981	1.304×10^{-4}	281.690	0.996
Cu ²⁺	158	0.026	121.540	0.974	1.750×10^{-4}	194.932	0.975

Desorption and Reusability Behaviors

Table 3 shows that after five adsorption-desorption cycles, the adsorption capacities of Pb²⁺, Cd²⁺, and Cu²⁺ were still high at 227, 179, 98 mg/g, respectively. After the first cycle, the recovery rate of Pb²⁺, Cd²⁺, and Cu²⁺ were 97%, 99%, and 98%, respectively.

After five cycles, the recovery rates of Pb²⁺, Cd²⁺, and Cu²⁺ only dropped to 95%, 96%, and 92%, respectively. This phenomenon showed that prepared adsorbent hydrogels had a good cycle performance. The metal ion adsorption capacity and recovery rate were very high. In addition, the adsorbent hydrogels could release the metal ions in HCl solution, indicating that HCl was a quite effective desorption agent. Moreover, desorption with HCl once again suggested that the Pb²⁺, Cd²⁺, and Cu²⁺ adsorption on

hydrogels was caused mainly by chemical adsorption. The release of adsorbed Pb^{2+} , Cd^{2+} , and Cu^{2+} could be ascribed to the relatively weak energy of interaction between ions and hydrogels.

Table 3. Cycle Adsorption Capacity and Recovery Rate of Metal Ions

Ion	Cycle 1		Cycle 2		Cycle 3		Cycle 4		Cycle 5	
	A (mg/g)	R (%)	A (mg/g)	R (%)	A (mg/g)	R (%)	A (mg/g)	R (%)	A (mg/g)	R (%)
Pb^{2+}	235	97	233	97	233	95	230	96	227	95
Cd^{2+}	186	99	185	99	184	99	180	97	179	96
Cu^{2+}	154	98	125	97	118	96	107	94	98	92

Note: A is the adsorption capacity of metal ions; R is the recovery rate of metal ions.

CONCLUSIONS

1. The present study demonstrates that the adsorption of sugarcane bagasse-based hydrogels for Pb^{2+} , Cd^{2+} , and Cu^{2+} was pH-dependent, and the maximum adsorption capacities for Pb^{2+} , Cd^{2+} , and Cu^{2+} were achieved at pH 6.0.
2. The adsorption equilibrium time for Pb^{2+} , Cd^{2+} , and Cu^{2+} was 60, 90, and 180 min, respectively. The maximum adsorption capacities were 268 mg/g for Cu^{2+} , 700 mg/g for Pb^{2+} , and 320 mg/g for Cd^{2+} .
3. The adsorption process of sugarcane bagasse-based hydrogels for heavy metal ions was fitted to the pseudo-second-order equation and the Langmuir adsorption isotherm very well.
4. Sugarcane bagasse-based hydrogels were confirmed to be an effective adsorbent of heavy metal ions and had highly efficient recovery and regeneration performance. These prepared adsorbent hydrogels could have great potential applications in waste water treatment.

ACKNOWLEDGMENTS

The authors want to express their gratitude for grants from the Author of National Excellent Doctoral Dissertation of China (201169), the National Natural Science Foundation of China (No. 31070530), and the Fundamental Research Funds for the Central Universities (2014ZG0003), South China University of Technology (SCUT). Moreover, the authors are grateful to the kind support from the Committee of the 4th Conference on Biorefinery towards Bioenergy (ICBB2013) in Xiamen, China.

REFERENCES CITED

- Abdel-Halim, E. S., and Al-Deyab, S. S. (2011). "Hydrogel from crosslinked polyacrylamide/guar gum graft copolymer for sorption of hexavalent chromium ion," *Carbohydr. Polym.* 86(3), 1306-1312.

- Alyüz, B., and Veli, S. (2009). "Kinetics and equilibrium studies for the removal of nickel and zinc from aqueous solutions by ion exchange resins," *J. Hazard. Mater.* 167(1-3), 482-488.
- Bessbousse, H., Rhallou, T., Verchère, J. F., and Lebrun, L. (2008). "Removal of heavy metal ions from aqueous solutions by filtration with a novel complexing membrane containing poly(ethyleneimine) in a poly(vinyl alcohol) matrix," *J. Mater. Sci.* 307(2), 249-259.
- Dabrowski, A., Hubicki, Z., Podkościelny, P., and Robens, E. (2004). "Selective removal of the heavy metal ions from waters and industrial wastewaters by ion-exchange method," *Chemosphere* 56(2), 91-106.
- Fu, F., and Wang, Q. (2011). "Removal of heavy metal ions from wastewaters: A review," *J. Environ. Manage.* 92(3), 407-418.
- Guan, W., Pan, J., Ou, H., Wang, X., Zou, X., Hu, W., Li, C., and Wu, X. (2011). "Removal of strontium(II) ions by potassium tetratitanate whisker and sodium trititanate whisker from aqueous solution: Equilibrium, kinetics and thermodynamics," *Chem. Eng. J.* 167(1), 215-222.
- Guo, X., Zhang, S., and Shan, X-Q. (2008). "Adsorption of metal ions on lignin," *J. Hazard. Mater.* 151(1), 134-142.
- Huang, L., Xiao, C., and Chen, B. (2011). "A novel starch-based adsorbent for removing toxic Hg(II) and Pb(II) ions from aqueous solution," *J. Hazard. Mater.* 192(2), 832-836.
- Huang, Z.-H., Zhang, F., Wang, M.-X., L. V., R., and Kang, F. (2012). "Growth of carbon nanotubes on low-cost bamboo charcoal for Pb(II) removal from aqueous solution," *Chem. Eng. J.* 184, 193-197.
- Jin, S. P., Liu, M. Z., Zhang, F., Chen, S. L., and Niu, A. Z. (2006). "Synthesis and characterization of pH-sensitivity semi-IPN hydrogel based on hydrogen bond between poly (N-vinylpyrrolidone) and poly (acrylic acid)," *Polym.* 47, 1526-1532.
- Kannamba, B., Reddy, K. L., and AppaRao, B. V. (2010). "Removal of Cu(II) from aqueous solutions using chemically modified chitosan," *J. Hazard. Mater.* 175(1-3), 939-948.
- Ku, Y., and Jung, I.-L. (2001). "Photocatalytic reduction of Cr(VI) in aqueous solutions by UV irradiation with the presence of titanium dioxide," *Water Res.* 35(1), 135-142.
- Lalhruitluanga, H., Jayaram, K., Prasad, M. N. V., and Kumar, K. K. (2010). "Lead(II) adsorption from aqueous solutions by raw and activated charcoals of *Melocanna baccifera* Roxburgh (bamboo)-A comparative study," *J. Hazard. Mater.* 175(1-3), 311-318.
- Lalhruitluanga, H., Prasad, M. N. V., and Radha, K. (2011). "Potential of chemically activated and raw charcoals of *Melocanna baccifera* for removal of Ni(II) and Zn(II) from aqueous solutions," *Desalination* 271 (s 1-3), 301-308.
- Li, N., and Bai, R. (2006). "Highly enhanced adsorption of lead ions on chitosan granules functionalized with poly(acrylic acid)," *Ind. Eng. Chem.* 45(23), 7897-7904.
- Li, Z., Wang, Y., Wu, N., Chen, Q., and Wu, K. (2013). "Removal of heavy metal ions from wastewater by a novel HEA/AMPS copolymer hydrogel: Preparation, characterization, and mechanism," *Environ. Sci. Pollut. Res.* 20(3), 1511-1525.
- Liu, F., Luo, X., Lin, X., Liang, L., and Chen, Y. (2009). "Removal of copper and lead from aqueous solution by carboxylic acid functionalized deacetylated konjac glucomannan," *J. Hazard. Mater.* 171(1-3), 802-808.

- Jiang, K., Sun, T. H., Sun, Li. N., and Li, H. B. (2006). "Adsorption characteristics of copper, lead, zinc and cadmium ions by tourmaline," *J. Environ. Sci.* 18(6), 1221-1225.
- Ma, J. W., Wang, F. Y., Huang, Z. H., and Wang, H. (2010). "Simultaneous removal of 2,4-dichlorophenol and Cd from soils by electrokinetic remediation combined with activated bamboo charcoal," *J. Hazard. Mater.* 176(1-3), 715-720.
- Makhloufi, L., Saidani, B., and Hammache, H. (2000). "Removal of lead ions from acidic aqueous solutions by cementation on iron," *Water Res.* 34(9), 2517-2524.
- Miretzky, P., Saralegui, A., and Cirelli, A. F. (2006). "Simultaneous heavy metal removal mechanism by dead macrophytes," *Chemosphere* 62(2), 247-254.
- Nadeem, M., Mahmood, A., Shahid, S. A., Shah, S. S., Khalid, A. M., and McKay, G. (2006). "Sorption of lead from aqueous solution by chemically modified carbon adsorbents," *J. Hazard. Mater.* 138(3), 604-613.
- O'Connell, D. W., Birkinshaw, C., and O'Dwyer, T. F. (2008). "Heavy metal adsorbents prepared from the modification of cellulose: A review," *Bioresour. Technol.* 99, 6709-6724.
- Peñaranda, A. J., and Sabino, M. (2010). "Effect of the presence of lignin or peat in IPN hydrogels on the sorption of heavy metals," *Polym Bull.* 65(5), 495-508.
- Santos, V. C. G. D., De Souza, J. V. T. M., Tarley, C. R. T., Caetano, J., and Dragunski, D. C. (2011). "Copper ions adsorption from aqueous medium using the biosorbent sugarcane bagasse *in natura* and chemically modified," *Water Air Soil Poll.* 216(1), 351-359.
- Smara, A., Delimi, R., Chainet, E., and Sandeaux, J. (2007). "Removal of heavy metals from diluted mixtures by a hybrid ion-exchange/electrodialysis process," *Sep. Purif. Technol.* 57(1), 103-110.
- Shafaei, A., Ashtlani, F. Z., and Kanghazchi, T. (2007). "Equilibrium studies of the sorption of Hg(II) ions onto chitosan," *Chem. Eng. J.* 133(1-3), 311-316.
- Sud, D., Mahajan, G., and Kaur, M. P. (2008). "Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions – A review," *Bioresour. Technol.* 99(14), 6017-6027.
- Wang, X. J., Wang, Y., Wang, X., Liu, M., Xia, S. Q., Yin, D. Q., Zhang, Y. L., and Zhao, J. F. (2011). "Microwave-assisted preparation of bamboo charcoal-based iron-containing adsorbents for Cr(VI) removal," *Chem. Eng. J.* 174(1), 326-332.
- Wang, W. B., Kang, Y. R., and Wang, A. Q. (2013). "One-step fabrication in aqueous solution of a granular alginate-based hydrogel for fast and efficient removal of heavy metal ions," *J. Polym. Res.* 101(10), 1-10.
- Wu, F., Zhang, Y., Liu, L., and Yao, J. M. (2012). "Synthesis and characterization of a novel cellulose-g-poly(acrylic acid-co-acrylamide) superabsorbent composite based on flax yarn waste," *Carbohydr. Polym.* 87(4), 2519-2525.

Article submitted: January 17, 2014; Peer review completed: March 16, 2014; Revised version received and accepted: April 9, 2014; Published: April 15, 2014.