

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

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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  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Cu}^{2+}$  were 60, 90, and 180 min, respectively. The maximum adsorption capacities of  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Cd}^{2+}$  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

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## 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; Lalhrualtuanga *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

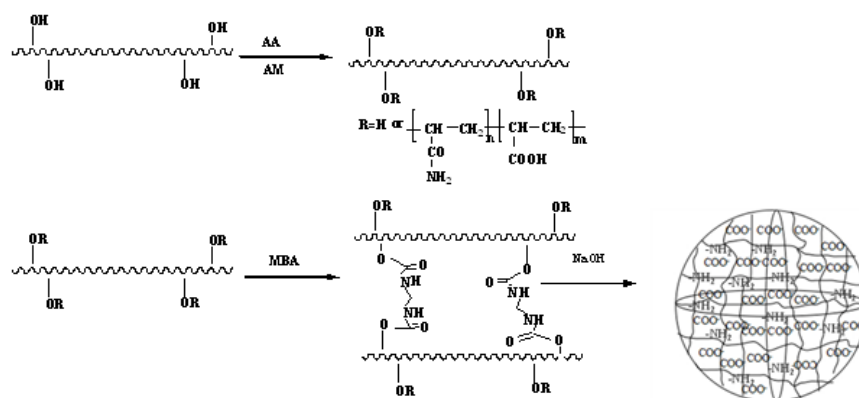
Sugarcane bagasse (SB) was obtained from Guangzhou Sugarcane Industry Research Institute, and after a ball-milling pretreatment, the SB powder was sized between 0.15 mm and 0.074 mm.

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  $\text{cm}^{-1}$  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  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ , or  $\text{Cu}^{2+}$ . 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<sup>-1</sup> 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<sup>-1</sup> to study the effect of the initial heavy metal ion concentration on the adsorption capacity of hydrogel and adsorption isotherm. The solutions containing Pb<sup>2+</sup>, Cd<sup>2+</sup>, and Cu<sup>2+</sup>, 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<sup>-1</sup> 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<sup>-1</sup> solution containing Pb<sup>2+</sup>, Cd<sup>2+</sup>, and Cu<sup>2+</sup>, 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.

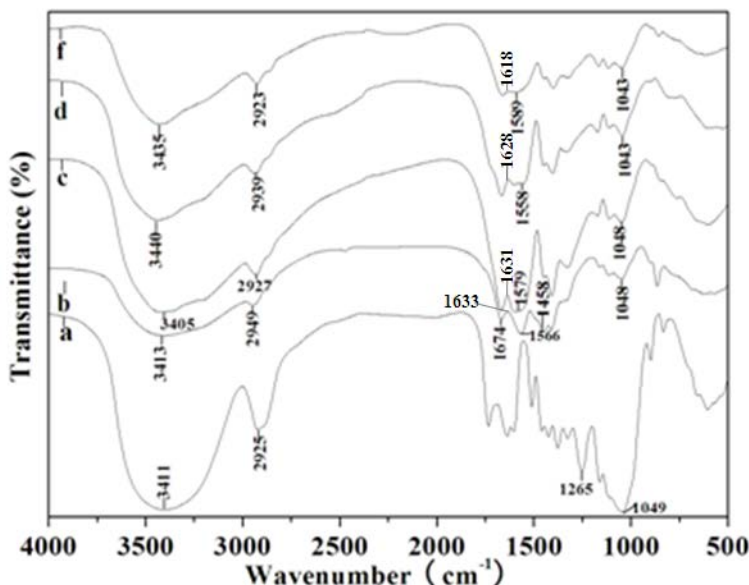
## RESULTS AND DISCUSSION

### 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  $3411\text{ cm}^{-1}$  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  $1566\text{ cm}^{-1}$  (asymmetric  $-\text{COO}^-$  stretching) and  $1674\text{ cm}^{-1}$  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  $\text{COO}^-$  (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  $1458\text{ cm}^{-1}$  is assigned to the skeletal  $\text{C}=\text{C}$  stretching vibrations in the aromatic rings. The absorption at  $1049\text{ cm}^{-1}$  is due to the  $\beta$ -1, 4-glycosidic bond and the band at  $1633\text{ cm}^{-1}$  is due to the  $-\text{C}=\text{O}$  and  $-\text{NH}_2$  of AM (Jin *et al.* 2006). The region from  $3100$  to  $3500\text{ cm}^{-1}$  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  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$  ions on the hydrogels, FTIR spectra were obtained for hydrogels after the adsorption of  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Cu}^{2+}$  ions in Fig. 2. The asymmetric stretching vibrations of  $-\text{COO}^-$  groups at  $1566\text{ cm}^{-1}$  before adsorption shifted to  $1589$ ,  $1558$ , and  $1579\text{ cm}^{-1}$  upon the adsorption of  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Cu}^{2+}$  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  $1633\text{ cm}^{-1}$  before adsorption shifted to  $1618$ ,  $1628$ ,  $1631\text{ cm}^{-1}$  upon the adsorption of  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Cu}^{2+}$  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.

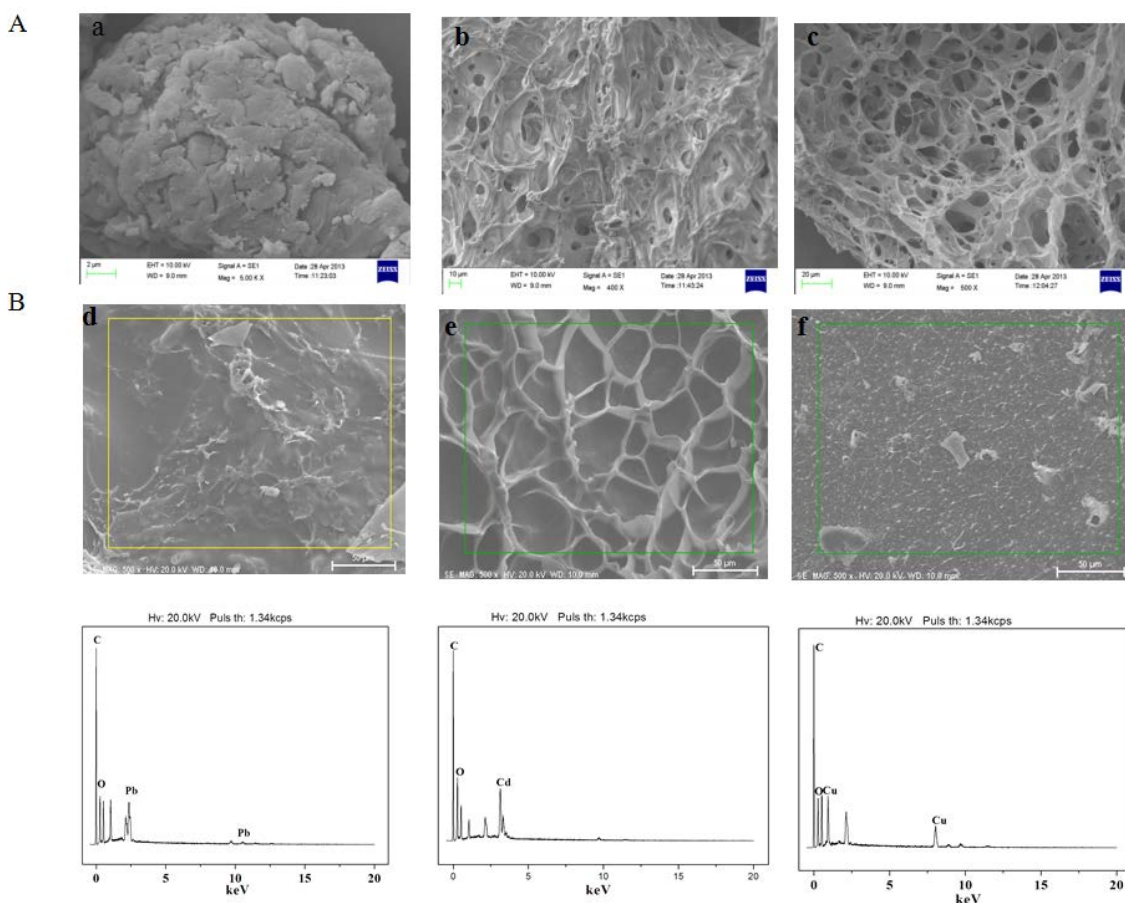


**Fig. 2.** FT-IR spectra of SB (a), hydrogels before adsorption (b) and after adsorbing  $\text{Pb}^{2+}$  (f),  $\text{Cd}^{2+}$  (d) and  $\text{Cu}^{2+}$  (c)

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



**Fig. 3.** A: SEM images of SB (bar 2  $\mu\text{m}$ , 5000 $\times$ ) (a), SB/P(AA-co-AM)(bar 10 $\mu\text{m}$ , 400 $\times$ ) (b), SB/P(AA-co-AM) hydrogels swelled in water (bar 10 $\mu\text{m}$ , 400 $\times$ ) (c); B: SEM (bar 50  $\mu\text{m}$ , 500 $\times$ ) (d, e, f) and EDX spectra of hydrogels loaded  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ , 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  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Pb}^{2+}$ , which increased from 19 to 213 mg/g for  $\text{Cu}^{2+}$ , from 1 to 232 mg/g for  $\text{Cd}^{2+}$ , and from 36 to 246 mg/g for  $\text{Pb}^{2+}$ , 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  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Cd}^{2+}$  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  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Cd}^{2+}$  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  $\text{COO}^-$  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.

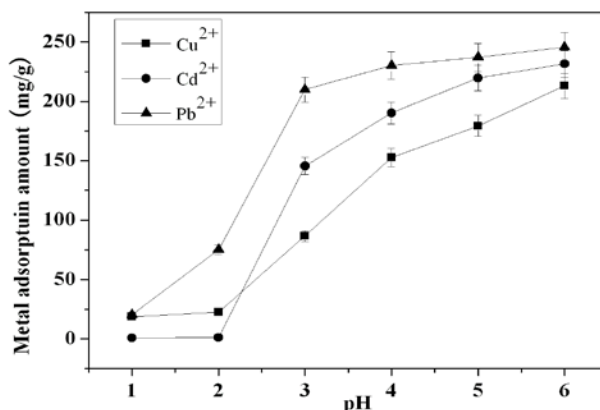
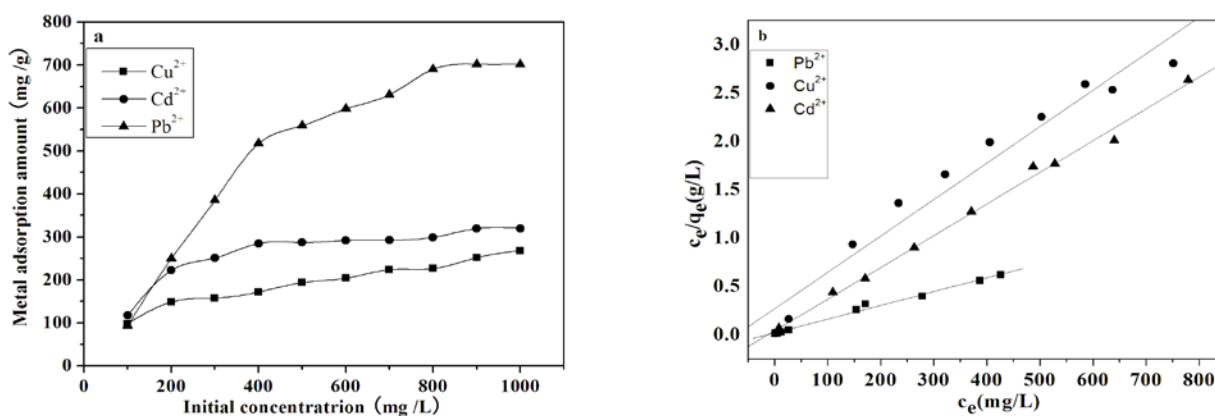


Fig. 4. The effect of initial pH on the heavy metal ion adsorption

## 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  $\text{mg L}^{-1}$ , 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  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Cu}^{2+}$  increased with increasing initial metal ion concentration from 100 to 1000  $\text{mg L}^{-1}$ , 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  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Cu}^{2+}$  at the initial concentration of 1000  $\text{mg L}^{-1}$ .



**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



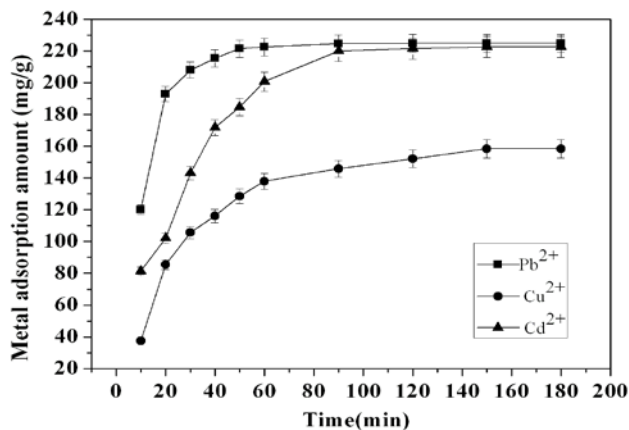
sites on the adsorbent (Abdel-Halim and Al-Deyab 2011). The  $q_m$  in the Langmuir adsorption isotherm (Eq. 2) model indicated that the adsorption capacity of hydrogels was high. By contrast, the maximum adsorption capacity of  $Pb^{2+}$  was two to five times higher than for many similar adsorbents (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	$7.289 \times 10^{-2}$
$Cd^{2+}$	0.878	2.257	1.764	0.995	320	304.878	$8.185 \times 10^{-2}$
$Cu^{2+}$	0.982	1.973	1.748	0.989	268	265.252	$1.408 \times 10^{-2}$

## 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 ( $\text{min}^{-1}$ ), 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)	$k_1$ ( $\text{min}^{-1}$ )	$q_e$ (cal) (mg/g)	$R^2$	$k_2$ (g/mg/min)	$q_e$ (cal) (mg/g)	$R^2$
Pb <sup>2+</sup>	225	0.068	143.741	0.985	$7.545 \times 10^{-4}$	238.663	0.997
Cd <sup>2+</sup>	222	0.037	90.288	0.981	$1.304 \times 10^{-4}$	281.690	0.996
Cu <sup>2+</sup>	158	0.026	121.540	0.974	$1.750 \times 10^{-4}$	194.932	0.975

### Desorption and Reusability Behaviors

Table 3 shows that after five adsorption-desorption cycles, the adsorption capacities of Pb<sup>2+</sup>, Cd<sup>2+</sup>, and Cu<sup>2+</sup> were still high at 227, 179, 98 mg/g, respectively. After the first cycle, the recovery rate of Pb<sup>2+</sup>, Cd<sup>2+</sup>, and Cu<sup>2+</sup> were 97%, 99%, and 98%, respectively.

After five cycles, the recovery rates of Pb<sup>2+</sup>, Cd<sup>2+</sup>, and Cu<sup>2+</sup> 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 Pb<sup>2+</sup>, Cd<sup>2+</sup>, and Cu<sup>2+</sup> adsorption on

hydrogels was caused mainly by chemical adsorption. The release of adsorbed  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Cu}^{2+}$  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 (%)
$\text{Pb}^{2+}$	235	97	233	97	233	95	230	96	227	95
$\text{Cd}^{2+}$	186	99	185	99	184	99	180	97	179	96
$\text{Cu}^{2+}$	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  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Cu}^{2+}$  was pH-dependent, and the maximum adsorption capacities for  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Cu}^{2+}$  were achieved at pH 6.0.
2. The adsorption equilibrium time for  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Cu}^{2+}$  was 60, 90, and 180 min, respectively. The maximum adsorption capacities were 268 mg/g for  $\text{Cu}^{2+}$ , 700 mg/g for  $\text{Pb}^{2+}$ , and 320 mg/g for  $\text{Cd}^{2+}$ .
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.

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