

ADSORPTION BEHAVIOR OF Cd²⁺, Pb²⁺, AND Ni²⁺ FROM AQUEOUS SOLUTIONS ON CELLULOSE-BASED HYDROGELS

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Removal of Cd²⁺, Pb²⁺, and Ni²⁺ from aqueous solutions using cellulose-graft-acrylic acid (C-g-AA) hydrogels was investigated. Various factors affecting the adsorption capacity, such as pH, time, initial ions concentration, and competitive ions, were tested. The results showed that the adsorption of hydrogels was very pH dependent, and maximum adsorption was obtained at a pH of 5.0. The adsorption capacities of hydrogels for the heavy metal ions were 562.7 mg/g (Cd²⁺), 825.7 mg/g (Pb²⁺), and 380.1 mg/g (Ni²⁺), respectively. The adsorption behavior can be very well described by the pseudo-second-order kinetic model and the Langmuir isotherm model. The observed affinity order of competitive ions adsorption is Pb²⁺>Ni²⁺>Cd²⁺ in mmol/g. The hydrogels can be regenerated after releasing heavy metal ions and reused three times with 15% loss of adsorption capacity. Scanning electron microscope (SEM) images and Fourier transform infrared spectroscopy (FTIR) spectra before and after ion adsorption on the hydrogels revealed that the complexation between heavy metal ions and carboxyl groups on hydrogels was the main adsorption mechanism.

Keywords: Heavy metal ions; Adsorption behavior; Hydrogels; Cellulose

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INTRODUCTION

Heavy metal pollution can cause a serious environmental problem due to its toxic and carcinogenic effects on the natural environment and its accumulation in living organisms (Mance 1987; Nriagu and Pacyna 1988; Liu *et al.* 2008). The toxicity of heavy metals might be caused by blocking essential functional groups of biomolecules and by disrupting the integrity of biomembranes (Bayramoglu *et al.* 2007). Heavy metals are generally discharged to the environment via mining activities, fossil fuels, battery manufacture, automobile emissions (Ozay *et al.* 2009), metal plating, and electric device fabrication (Denizli *et al.* 2005) with diverse routes. In order to remove dissolved heavy metal ions from various environments, conventional techniques including chemical precipitation, ion exchange, reverse osmosis, membrane separation, electrochemical treatments, and solvent extraction processes are widely used (Akkaya and Ulusoy 2008; Jang *et al.* 2008; Zhao and Mitomo 2008). In general, these techniques are often costly or ineffective, especially in removing heavy metal ions at low concentrations (Laus and de Fávère 2011).

In recent years, one of the new developments for heavy metal removal has been the biosorption method, which is considered to be effective and economic due to the fact that the raw materials for bio-adsorbents manufacture, such as cellulose (Chen *et al.* 2008; Tripathy *et al.* 2009; Liu *et al.* 2010; Wang *et al.* 2011), starch (Güçlü *et al.* 2010; Zheng *et al.* 2010), or chitosan (Li *et al.* 2009; Xu *et al.* 2011) are very abundant, low-cost, biodegradable, and environmentally friendly (Irani *et al.* 2011; Miretzky and Muñoz 2011). Cellulose, the most abundant natural polymer with excellent biocompatibility, is recognized as the most likely candidate. However, the poor solubility and limited reactivity of cellulose in common solvents limits its modification to some extent for expected materials. Some efficient solvents have been also developed for the production of cellulose-based adsorbents; examples include lithium chloride/ N,N-dimethylacetamide (LiCl/DMAc) (Zhou *et al.* 2004), N-methylmorpholine-N-oxide (NMMO) (Cai *et al.* 2004, 2006), and ionic liquid (Zhu *et al.* 2006). However, most of these solvents are often difficult to recover or require harsh reaction conditions (long reaction time or high temperature). It has been reported that cellulose can dissolve in pre-cooled 85% phosphoric acid in a few minutes with very limited hydrolysis (Boerstoel *et al.* 2001; Keshk 2008). Also reported (Zhou *et al.* 2011) was the synthesis of cellulose-graft-acrylic acid (C-g-AA) hydrogels by free radical polymerization in phosphoric acid solution. The hydrogels were proven to be excellent dye adsorbents with extremely high amounts of MB adsorption. In the present work, the adsorption behavior of C-g-AA hydrogels to Cd^{2+} , Pb^{2+} , and Ni^{2+} from aqueous solutions was investigated to demonstrate the potential application of new materials for the removal of heavy metals in wastewater.

EXPERIMENTAL

Materials

Cellulose-graft-acrylic acid (C-g-AA) hydrogels were prepared in phosphoric acid according to our previous work (Zhou *et al.* 2011). The structures of the hydrogels (SEM morphology and FT-IR spectra) and grafting reaction mechanism were also reported. $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and $\text{Pb}(\text{NO}_3)_2$ (analytical grade) were purchased from Aladdin-Reagent Inc. (Shanghai, China) to be used as heavy metal ions sources for the adsorption experiments. The other reagents used were all chemically pure and all solutions were prepared using distilled water.

Adsorption Experiment

Batch adsorption tests were carried out to study the effect of various parameters on the adsorption behaviour of Ni^{2+} , Cd^{2+} , and Pb^{2+} on C-g-AA hydrogels. A thermostated shaker bath at 30°C with a constant speed of 100 rpm was used for the adsorption process. The amount of adsorbed heavy metal ions at adsorption equilibrium, q_e (mg/g), was calculated using the following equation,

$$q_e = (C_0 - C_e)V / m \quad (1)$$

where C_0 and C_e (mg/L) are the initial and equilibrium ions concentration, respectively, V (mL) is the solution volume, and m (g) is the mass of dried hydrogels. All tests were carried out in triplicate, and the average was used in the analysis.

The effect of medium pH values on heavy metal ion adsorption was examined. A series of Ni^{2+} , Cd^{2+} , and Pb^{2+} solutions (100 mL, 600 mg/L) with different pH values (2.0 to 6.0) adjusted with 0.01 mol/L HNO_3 or 0.01 mol/L NaOH solutions were mixed, each with 50 mg hydrogels for 6 h. The adsorption isotherm experiments were conducted at a solution pH of 5.0 with initial Ni^{2+} , Cd^{2+} , or Pb^{2+} concentrations in the range of 200 to 2000 mg/L. 50 mg hydrogels were added into each of the 100 mL ion solutions for 6 h. The kinetic adsorption experiments were conducted at a solution pH of 5.0, and 500 mg hydrogels were added to 1 L of 1000 mg/L Ni^{2+} , Cd^{2+} , and Pb^{2+} solutions. At predetermined time intervals (5 to 500 min), samples were taken with a syringe and analyzed for residual ion concentration.

Competitive heavy metal ion adsorption from aqueous solutions containing Ni^{2+} , Cd^{2+} , and Pb^{2+} was performed at a solution pH of 5.0. The concentration of Ni^{2+} , Cd^{2+} , and Pb^{2+} was 5 mmol/L or 10 mmol/L for each metal ion.

At the end of the adsorption period, instead of filtration, centrifugation at 5000 rpm for 10 min was carried out to purify the solution, by reason that the use of any filter papers in filtration will bring substantial systematical errors on the analyzed solution (Engin *et al.* 2010).

The initial and final concentrations of Ni^{2+} , Cd^{2+} , or Pb^{2+} in the solutions were measured by an atomic absorption spectrometer (AAS) (ZEEnit 700, German).

Desorption and Regeneration

Desorption measurements were achieved using 0.1 mol/L HNO_3 as a desorbing agent. The hydrogels at adsorption equilibrium, once loaded with Ni^{2+} , Cd^{2+} , or Pb^{2+} (separated from 1000 mg/L ions solution), were placed in the desorption medium and shaken at 100 rpm for 120 min. The final ion concentration was determined by AAS, as described earlier. To determine their reusability, the desorbed hydrogels were regenerated with 0.1 mol/L NaOH for 30 min and then used for another adsorption. Three consecutive absorption-desorption cycles were conducted using the same hydrogels.

Characterization

Fourier transform infrared spectroscopy (FTIR)

The chemical structures of dried hydrogel samples with or without heavy metal ion adsorption were characterized using a Bruker Vector 33 Fourier transform infrared spectrophotometer in the region of 500 to 4000 cm^{-1} with a KBr disc technique. Prior to the measurement, dried hydrogel samples were prepared using a freeze-drying method.

Scanning electron microscopy (SEM)

The hydrogel samples in the equilibrium swelling state with or without heavy metal ions adsorption were freeze-dried under a vacuum until all water was sublimed. The samples were subsequently fractured carefully into pieces, and then coated with gold before observation. Images showing the morphology of hydrogel samples were observed by SEM (Quanta 200, Fei Company) with an accelerating voltage of 15 kV.

RESULTS AND DISCUSSION

Effect of pH on Ions Adsorption

The solution pH is known to be an important variable affecting the amount of ion adsorption by an adsorbent. It can influence the protonation of the functional groups on the adsorbents as well as the solution chemistry of the heavy metal ions. Figure 1 shows the effects of solution pH (2.0 to 6.0) on the adsorption capacity of Cd^{2+} , Pb^{2+} , and Ni^{2+} for C-g-AA hydrogels. It was evident that the amount of heavy metal ion adsorption depended on pH values of the adsorption medium.

The uptake of Cd^{2+} , Pb^{2+} , and Ni^{2+} was found to increase sharply when the pH value was increased from 2.0 to 3.0, beyond which values a gradual increase in the adsorption capacity was obtained. The carboxyl groups of AA monomers in the hydrogels structure are primarily responsible for the specific binding of metal ions. At low pH values, on the one hand, more H^+ competed with metal ions for adsorption sites, which made it more difficult for the metal ions to bind to activated sites. On the other hand, carboxyl groups existed in the form of $-\text{COOH}$ rather than $-\text{COO}^-$, which can hinder the interaction between hydrogels and metal ions. For both of these reasons, the result was very low ion uptake. Conversely, at higher pH values, more ionized carboxylic groups were available, thereby increasing the interaction between the carboxylic groups and the metal ions and causing an increase in Ni^{2+} , Cd^{2+} , and Pb^{2+} adsorption. Nevertheless, little changes in the adsorption capacities were observed when the pH values lie between 3.0 and 6.0. To avoid the significant formation of precipitation at approximately $\text{pH} > 7.0$ for all metal ions, the pH of 5.0 was selected as the initial solution pH value for the subsequent adsorption experiments.

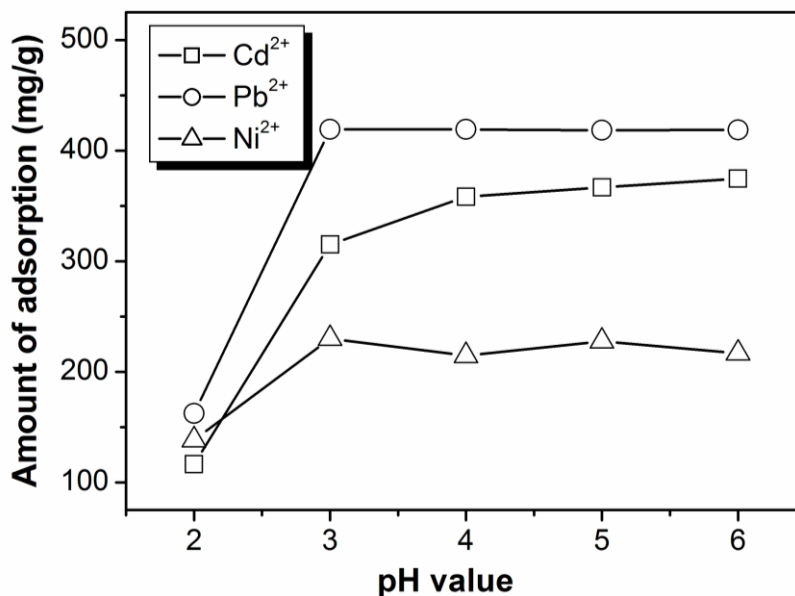


Fig. 1. Effect of the pH values on the adsorption amount of heavy metal ions on C-g-AA hydrogels (Ion concentration 600 mg/L; adsorbent dose 50 mg/100 mL; time 6 h)

Effect of Initial Ion Concentration and Adsorption Isotherms

Initial ion concentration plays an important role in determining the amount of heavy metal ion adsorption by an adsorbent. In this study the adsorption amounts of heavy metal ions on hydrogels were measured at different ion concentrations (200 to 2000 mg/L). The result (Fig. 2) shows that the adsorption amount increased almost linearly with the initial ion concentration from 200 to 1200 mg/L. When the C_0 was 2000 mg/L, the q_m reached 562.7 mg/g (Cd^{2+}), 825.7 mg/g (Pb^{2+}), and 380.1 mg/g (Ni^{2+}), respectively, much higher than the literature-reported q_m of heavy metal ions on other adsorbents (Table 1). This demonstrates that the C-g-AA hydrogels have an excellent capacity for removing Cd^{2+} , Pb^{2+} , and Ni^{2+} from wastewater.

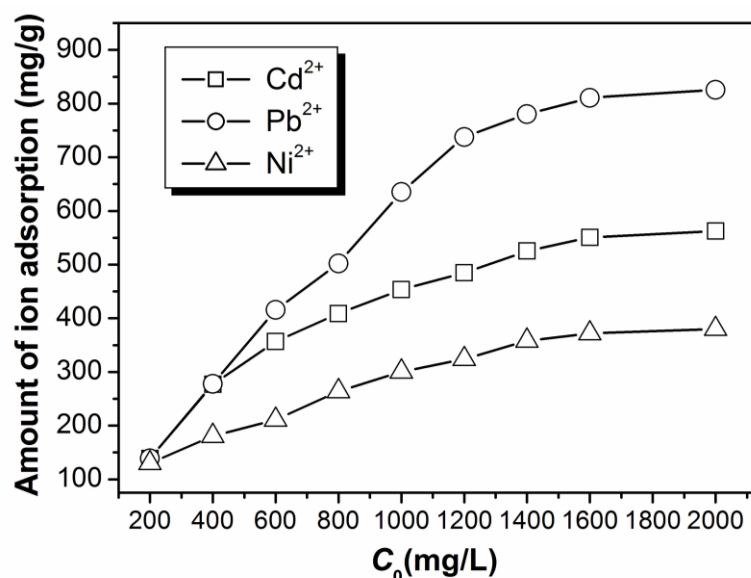


Fig. 2. Effect of the initial ion concentration on the adsorption amount of heavy metal ions on C-g-AA hydrogels (Adsorbent dose 50 mg/100 mL; pH 5.0; time 6 h)

The equilibrium adsorption isotherm is fundamental in describing the amount of adsorbate adsorbed on the adsorbent and the concentration of dissolved adsorbate at equilibrium. The present adsorption isotherm data were evaluated by means of the Langmuir and Freundlich adsorption models. The two models are expressed by the following equations, respectively (Shukla *et al.* 2006; Chairat *et al.* 2008).

$$C_e/q_e = 1/bq_m + C_e/q_m \quad (2)$$

$$q_e = k_f C_e^{1/n} \quad (3)$$

In these equations q_m (mg/g) represents the monolayer maximum uptake of metal ions, and b (L/mg) is the Langmuir adsorption constant and is related to the free energy of adsorption. k_f ((mg/g)(L/mg)^{1/n}) and n are the Freundlich adsorption constants, indicative of the adsorption extent and adsorption intensity, respectively. The slopes and intercepts of plots of C_e/q_e versus C_e were used to determine q_m and b , and in the same way k_f and n can be obtained from the plot of $\ln q_e$ against $\ln C_e$.

Table 1. The q_m for Heavy Metal Ions Adsorption on Different Adsorbents

Adsorbents	Adsorption Capacity for Metal Ions (mg/g)	References
C-g-AA hydrogels	Cd ²⁺ : 562.7. Pb ²⁺ : 825.7. Ni ²⁺ : 380.1.	In this work
Polyacrylate/polyethyleneglycol interpenetrating network hydrogel	Ni ²⁺ : 102.4. Cr ³⁺ : 49.4. Cd ²⁺ : 33.4.	Nriagu and Pacyna 1988
Magnetic p(AMPS) hydrogels	Cd ²⁺ : 140.9. Pb ²⁺ : 140.8. Ni ²⁺ : 114.9.	Miretzky and Muñoz 2011
P(AMPSG/AAc/NVP/HEMA) hydrogels	Cd ²⁺ : 7.08. Pb ²⁺ : 37.09. Hg ²⁺ : 39.52.	Irani <i>et al.</i> 2011
CTS-DMTD hydrogels	Au ³⁺ : 198.5. Pb ²⁺ : 16.2. Pt ²⁺ : 13.8.	Liu <i>et al.</i> 2010
Starch-graft-acrylic acid/montmorillonite Nanocomposite hydrogels	Cu ²⁺ : 135.0. Pb ²⁺ : 360.5.	Mance 1987
P(AMPSG/AAc/NVP/HEMA) hydrogels	Pb ²⁺ : 27.0. Cd ²⁺ : 23.0.	Wang <i>et al.</i> 2011
Chitosan(chitin)/cellulose composite biosorbents	Pb ²⁺ : 26.3. Ni ²⁺ : 13.2.	Zhou <i>et al.</i> 2004

The values of the Langmuir and Freundlich constants and the correlation coefficients are listed in Table 2. Based on the coefficients of determination obtained, it can be concluded that the Langmuir equation gave a better fit ($R^2 > 0.999$) to the experimental data than the Freundlich equation. The q_m values calculated from the Langmuir model (Cd²⁺: 571.4 mg/g, Pb²⁺: 840.3 mg/g, Ni²⁺: 423.7 mg/g) were very close to the experimental results (Cd²⁺: 562.7 mg/g, Pb²⁺: 825.7 mg/g, Ni²⁺: 380.1 mg/g). The Langmuir equation assumes that the surface of adsorbents is homogeneous, and thus it can be assumed that the carboxyl groups in C-g-AA hydrogels are equivalent to each other. Owing to phosphoric acid solution, which provides a homogeneous system for synthesis of C-g-AA hydrogels, all cellulose chains were equally accessible by AA molecules, and hydrogels with uniform substitution were obtained.

Table 2. Isotherm Parameters for Ions Adsorption on C-g-AA Hydrogels

Metal ions	$q_{m,exp}^*$	Langmuir model			Freundlich model		
		b	q_m	R_2	k_f	n	R^2
Cd ²⁺	562.7	0.0203	571.4	0.9962	156.0	5.417	0.9523
Pb ²⁺	825.7	0.0477	840.3	0.9984	182.1	3.968	0.9283
Ni ²⁺	380.1	0.0053	423.7	0.9864	59.50	3.969	0.9640

* Experimental data

Effect of Contact Time and Adsorption Kinetics

The kinetics of adsorption for the prepared adsorbent is desirable to determine whether the behavior of heavy metal ion adsorption on the adsorbents can be described by a theoretical model that is predictive. Figure 3 shows the results of the time-dependent Cd^{2+} , Pb^{2+} , and Ni^{2+} adsorption performances of the C-g-AA hydrogels. The adsorption amount of all the three tested metal ions increased rapidly at the beginning of adsorption: more than 90% of the adsorption amount of Ni^{2+} , Cd^{2+} , and Pb^{2+} occurred within 20 min. This is because adsorption sites on the hydrogels were unfilled, and ions easily interacted with these sites. After 60 min, ion uptake remained almost constant, and even after prolonged time, the adsorption capacity hardly increased.

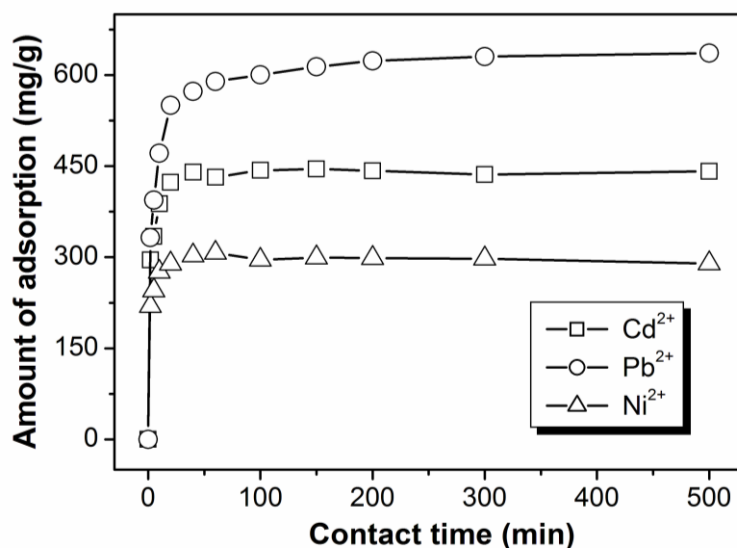


Fig. 3. Effect of the contact time on the adsorption amount of heavy metal ions on C-g-AA hydrogels (Ion concentration 1000 mg/L; adsorbent dose 50 mg/100 mL; pH 5.0; time 6 h)

Kinetic studies can be beneficial to the understanding of the adsorption mechanism of the metal adsorption process and to the evaluation of the performance of the adsorbents used for metal adsorbed. Lagergren pseudo-first-order and Ho's pseudo-second-order kinetic models are two widely used models that are applied for solid-liquid adsorption. The two models are given by the following equations, respectively (Chiou and Li 2002; Li *et al.* 2007).

$$\ln[(q_{e1} - q_t)/q_{e1}] = -k_1 t \quad (4)$$

$$t/q_t = 1/k_2 q_{e2}^2 + t/q_{e2} \quad (5)$$

In these equations q_{1e} , q_{2e} and q_t (mg/g) are the amounts of ions adsorbed onto hydrogels at equilibrium and at time t (min), respectively. k_1 (min^{-1}) and k_2 ($\text{g}/(\text{mg}\cdot\text{min})$) are the kinetic rate constants of the pseudo-first-order and pseudo-second-order models. The slopes and intercepts of plots of $\log(q_e - q_t)$ versus t were used to determine k_1 and q_{e1} , and in the same way q_{e2} and k_2 can be obtained from the plot of t/q_t against t .

All the parameters were calculated, and results are summarized in Table 1. It can be shown that the correlation coefficients for the pseudo-first-order kinetic model were much lower, and that the calculated q_{e1} deviated considerably from the experimental data, which suggests that this adsorption system is not a pseudo-first-order kinetic adsorption process. This is because in many cases, the pseudo-first-order equation does not fit well to the whole range of contact time and is generally applicable only over the initial stage of the adsorption processes (Ho and McKay 1999). The coefficients of determination for the pseudo-second-order kinetic model obtained were above 0.999. The calculated q_e (Cd^{2+} : 442.5 mg/g, Pb^{2+} : 641.0 mg/g, Ni^{2+} : 289.9 mg/g) also agree very well with the experimental data (Cd^{2+} : 450.2 mg/g, Pb^{2+} : 645.4 mg/g, Ni^{2+} : 310.3 mg/g). The results show that the adsorption process of Ni^{2+} , Cd^{2+} , and Pb^{2+} onto C-g-AA hydrogels followed the pseudo-second-order model and that the adsorption is probably controlled by the chemical process (Wu *et al.* 2009).

Adsorption of Competitive Ions

In the next series of experiments the removal of coexisting competitive ion of Ni^{2+} , Cd^{2+} , and Pb^{2+} was considered, since the natural and industrial effluents rarely contain a single heavy metal ion, and some of the ions in the effluent may reduce the adsorption of others or may coadsorb along with another ions. The concentration of each ion in aqueous solution was fixed at 5 mmol/L or 10 mmol/L, and the results are shown in Fig. 4. As compared with the adsorption amount under non-competitive conditions (data not shown), the binding capacities of metal ions under competitive conditions were decreased, and the maximum adsorption amounts of each ion were 1.037 mmol/g (Cd^{2+}), 2.848 mmol/g (Pb^{2+}), and 1.446 mmol/g (Ni^{2+}), vs. 1.640 mmol/g (Cd^{2+}), 3.687 mmol/g (Pb^{2+}), and 2.920 mmol/g (Ni^{2+}) under mixture solutions of 5 mmol/L and 10 mmol/L, respectively. The affinity order of the three metal ions adsorption was $\text{Pb}^{2+} > \text{Ni}^{2+} > \text{Cd}^{2+}$. The ion selectivity observed for Pb^{2+} was higher, which might be attributed to the bigger ionic radius of Pb^{2+} ions (1.19 Å).

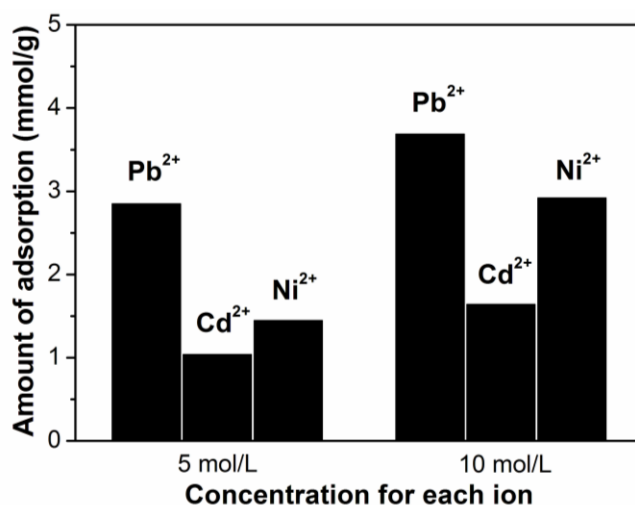


Fig. 4. The competitive removal of Cd^{2+} , Pb^{2+} , and Ni^{2+} from mixed ions solution (concentration of each ion was all fixed to 5 mmol/L or 10 mmol/L; adsorbent dose 50 mg/100 mL; pH 5.0)

For carboxylate anions the stability constants of divalent metal ions follow the order $\text{Pb} > \text{Cu} > \text{Cd} > \text{Zn} > \text{Ni} \sim \text{Co} > \text{Ca} \sim \text{Mg}$ (Bunting and Thong 1970), which proves that the large Pb^{2+} metal ions form preferably π bonds rather than electrostatic bonds. As to Cd^{2+} and Ni^{2+} ions, it seems that the C-g-AA hydrogels prefer electrostatic bonds with Ni^{2+} but π bonds with Cd^{2+} . An explanation for this behavior could be the influence of steric hindrance effects of the crosslinking chains on the bonds formation, but this hypothesis must be verified by further investigations.

Adsorption Mechanism

One challenge for the adsorption field is to clearly identify the adsorption mechanism, in particular the interactions occurring at the adsorbent/adsorbate interface. In present study, the Cd^{2+} , Pb^{2+} , and Ni^{2+} adsorption onto the surface of C-g-AA hydrogels is assumed to occur through ion-exchange and chelation between positively charged Cd^{2+} , Pb^{2+} , and Ni^{2+} and nonionized or ionized carboxylic groups within the hydrogels. FTIR (Fig. 5) spectra and SEM images (Fig. 6) of the C-g-AA hydrogels before and after Cd^{2+} , Pb^{2+} , and Ni^{2+} adsorption were investigated to confirm the above adsorption mechanism.

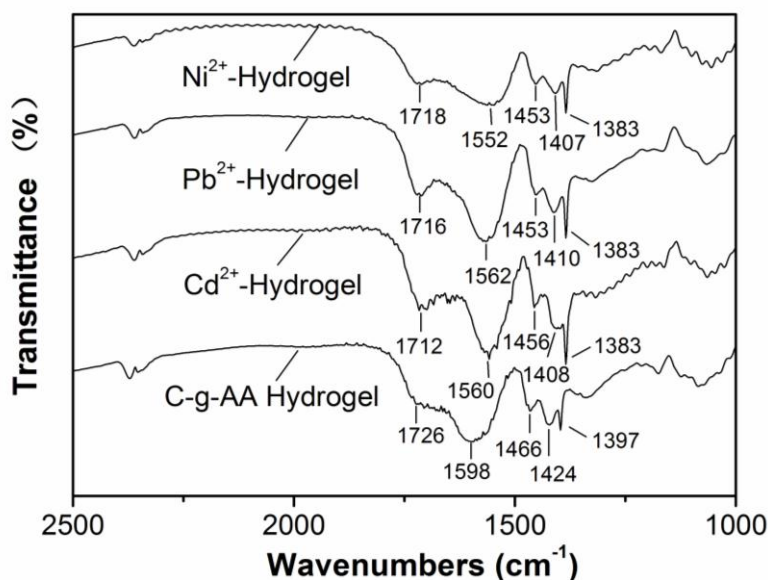


Fig. 5. FTIR spectra of C-g-AA hydrogels before and after Cd^{2+} , Pb^{2+} , or Ni^{2+} adsorption

For FTIR analysis, significant changes in the FTIR spectra were found after Cd^{2+} , Pb^{2+} , and Ni^{2+} adsorption. The presence of a broad and weak absorption band at 1726 cm^{-1} , corresponding to the stretching vibration of $-\text{COOH}$ of C-g-AA hydrogels, was sharpened and shifted to lower wave numbers of 1712 , 1716 , and 1718 cm^{-1} for Cd^{2+} , Pb^{2+} , and Ni^{2+} adsorbed hydrogels, respectively. The absorption band at 1598 cm^{-1} , assigned to asymmetric stretching vibration of $-\text{C}=\text{O}$ in the carboxylate, was shifted to 1560 , 1562 , and 1552 cm^{-1} after Cd^{2+} , Pb^{2+} , and Ni^{2+} adsorption, respectively. Meanwhile, the bands at 1466 cm^{-1} and 1424 cm^{-1} , related to the symmetric stretching vibrations of $-\text{C}=\text{O}$ in the carboxylate, were shifted to 1456 and 1408 cm^{-1} , to 1453 and

1410 cm^{-1} , and to 1453 and 1407 cm^{-1} for Cd^{2+} , Pb^{2+} , and Ni^{2+} adsorbed hydrogels, respectively. All the information suggests that, along with the shift of some characteristic groups, the complexation may be the predominant adsorption mechanism between the adsorbent and adsorbate, and that $-\text{COO}^-$ groups may be the main adsorption sites for Cd^{2+} , Pb^{2+} , and Ni^{2+} adsorption onto the C-g-AA hydrogels. In general, it is observed that the major changes in the FTIR spectra after adsorption are quite similar for all the three tested metal ions, indicating that the mechanisms of Cd^{2+} , Pb^{2+} , and Ni^{2+} adsorption onto C-g-AA hydrogels are essentially the same.

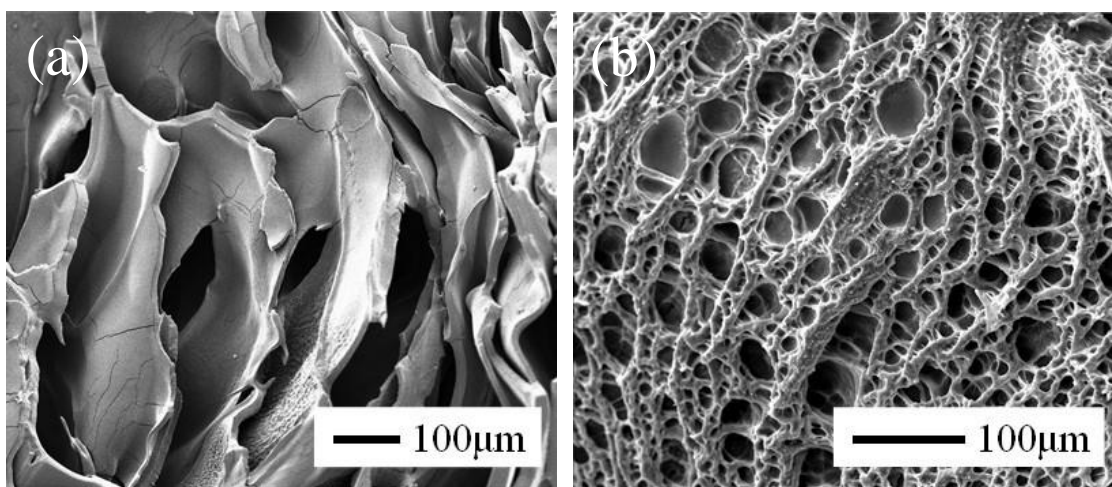


Fig. 6. SEM micrograph of C-g-AA hydrogels before (a) and after (b) competitive adsorption

SEM images (Fig. 6) show that the hydrogels with or without ion adsorption exhibited regular netlike structures. No phase separation was observed, which implies the formation of a complete three-dimensional porous inner structure consisting of crosslinking cellulose-graft-acrylic acid chains. The pure hydrogels exhibited a very loose structure (Fig. 6a). The reason is that there are numerous carboxylate anions ($-\text{COO}^-$) in hydrogels surface and inner structures. The electrostatic repulsions among the carboxylate anions can result in the expansion of the hydrogels network and the increase in the size of pores. Therefore, metal ions can easily diffuse in and adhere to the hydrogels network. By contrast, the network of ion-loaded hydrogels (after competitive adsorption) was much narrower and the pores in hydrogels became smaller (about 10 to 50 μm wide) (Fig. 6b).

The effect of the absorbed ions might work in the following way: the cationic metal ions can adhere to the surface of the anion hydrogels and incorporate into the inner structure, which results in the weaker electrostatic repulsions of the hydrogels network. In addition, the presence of abundant inorganic electrolytes (5 mmol/L or 10 mmol/L for each metal ion, namely, 15 mmol/L or 30 mmol/L for the total metal ions) in the liquid phases tends to reduce the osmotic pressure difference between hydrogel networks and the external solution. These two reasons can lead to an intense shrinkage of the porous hydrogels.

Desorption and Regeneration Evaluation

The above results show that the C-g-AA hydrogels possess excellent adsorption capabilities for metal ions. But in practice, it is also necessary that such adsorbent materials are able to be used repeatedly, as motivated by economic and environmental factors. Therefore, the desorption and regeneration ability of the ion-loaded hydrogels have been investigated. 0.1 mol/L HNO₃ and 0.1 mol/L NaOH were used as the desorbing agent and the regenerating agent, respectively.

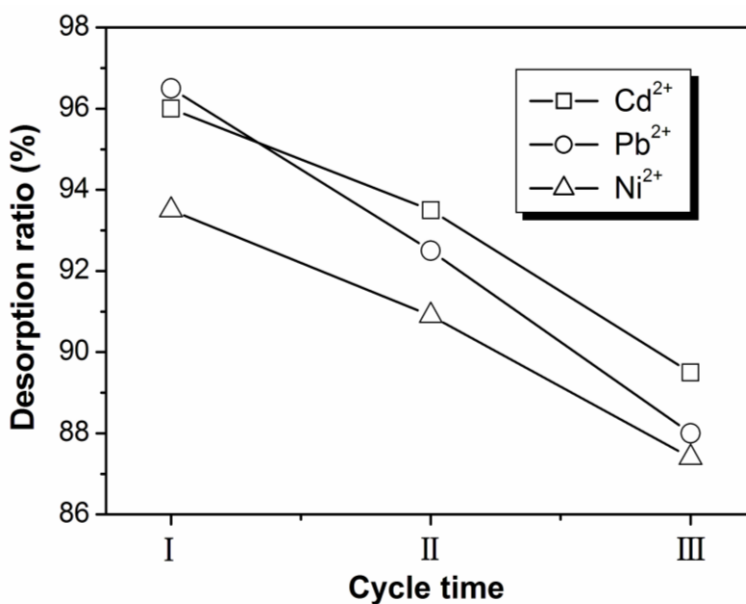


Fig. 7. The desorption ratio of absorbed C-g-AA hydrogels in three consecutive absorption-desorption cycles (Release medium is 0.1 mol/L HNO₃)

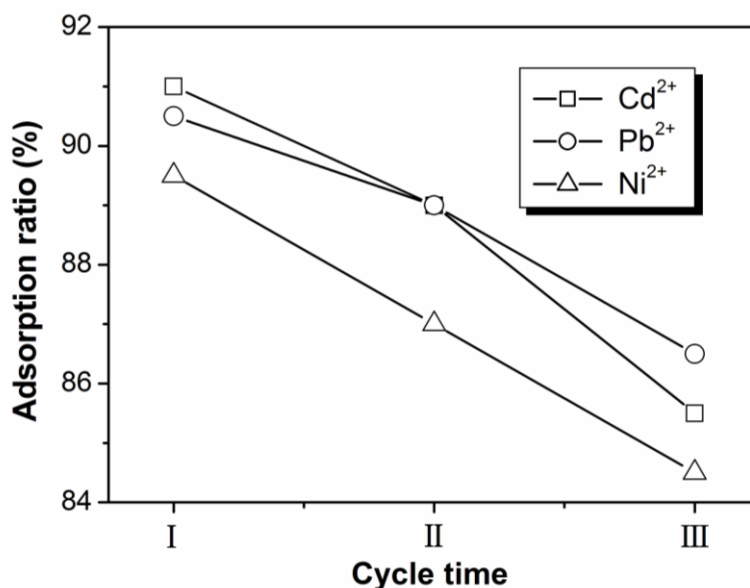


Fig. 8. The adsorption ratio of reused C-g-AA hydrogels in consecutive three absorption-desorption cycles (Release medium is 0.1 mol/L HNO₃)

From the desorption ratio as shown in Fig. 7, it can be seen that all the metal ions showed over 95% desorption ratio in their first absorption-desorption cycle, and that even with the increased absorption-desorption cycles, over 87% desorption ratio was obtained. From the regeneration ratio shown in Fig. 8, it can be seen that the amount of ion adsorption decreased after regeneration. Nevertheless, they maintained nearly 85% of their original adsorption capacity after three cycles of adsorption-desorption, which indicates that the C-g-AA hydrogels were well suited for the design of a continuous sorption process.

CONCLUSIONS

Cellulose-graft-acrylic acid (C-g-AA) hydrogels were quite efficient for the adsorption of heavy metal ions from an aqueous solution at pH 5.0. The required time to achieve the adsorption equilibrium was no more than 60 min. The experimental isotherm data agreed well with Langmuir model, and the maximum adsorption capacity of Cd^{2+} , Pb^{2+} , and Ni^{2+} were found to be 562.7 mg/g, 825.7 mg/g, and 380.1 mg/g, respectively. The adsorption process could be best described by the pseudo-second-order kinetic model. The desorption study showed that ion-loaded hydrogels can be effectively desorbed and that the regenerated adsorbent can be reused three times with 15% loss of adsorption amount. The present study provides relatively comprehensive data for the C-g-AA hydrogels application to the removal of metal ions in wastewater.

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