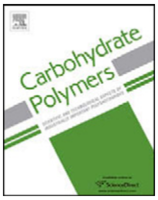
Carbohydrate Polymers 83 (2011) 743–748

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol



Electrospun membrane of cellulose acetate for heavy metal ion adsorption in water treatment

Ye Tian[a,c], Min Wu[b,*], Ruigang Liu[a], Yanxiang Li[a,c], Deqian Wang[a,c], Junjun Tan[a,c], Rongcheng Wu[e], Yong Huang[a,b,d,*]

[a] State Key Laboratory of Polymer Physics and Chemistry, Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China
[b] State Engineering Research Center of Engineering Plastics, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, China
[c] Graduate School, Chinese Academy of Sciences, Beijing 100039, China
[d] Laboratory of Cellulose and Lignocellulosics Chemistry, Guangzhou Institute of Chemistry, Chinese Academy of Sciences, Guangzhou 510650, China
[e] Beijing China Sciences Environment Protection Co. Ltd., Beijing 100080, China

ARTICLE INFO

Article history:
Received 23 May 2010
Received in revised form 19 August 2010
Accepted 22 August 2010
Available online 20 September 2010

Keywords:
Electrospinning
Metal ions
Cellulose acetate
Water treatment

ABSTRACT

Cellulose acetate (CA) nonwoven membrane for heavy metal ion adsorption was prepared by electrospinning and surface modification with poly(methacrylic acid) (PMAA). The morphology and graft modification of the membrane were characterized by SEM and ATR-FTIR. The adsorption of heavy metal ions Cu^{2+}, Hg^{2+} and Cd^{2+} on this membrane was investigated. The adsorption capacity increased with the increasing of initial pH value in the system. This membrane has quite high adsorption selectivity for Hg^{2+}. The adsorbed metal ions can be easily de-adsorbed from the membrane surface by using saturated ethylenedinitrilo tetraacetic acid solution, and can be re-used for the metal ion adsorption.

1. Introduction

Water pollution due to toxic heavy metals caused by industries and agricultural sources is one of the most serious environmental and public problems. Although many of the heavy metals are needed at the micronutrient level for the human beings, animals and plants, excessive metals may produce a range of toxic effects (Sud, Mahajan, & Kaur, 2008; Ngah & Hanafiah, 2008; O'Connell, Birkinshaw & O'Dwyer, 2008). For example, excessive copper ions can lead to weakness, lethargy and anorexia (Theophanides & Anastassopoulou, 2002). Mercury with high concentration can result in neurobehavioral disorders, attention deficit hyperactivity disorders, and intellectual retardation (Weiss & Landrigan, 2000). Excessive cadmium is associated with nephrotoxic effects and bone damage (Friberg, 1985). Therefore the removal of toxic heavy metals from water has become one of the major topics in water treatment.

Various methods, both physical and chemical ones, have been reported for removal of heavy metal ions from water, such as reverse osmosis (Li, Dong, & Nenoff, 2007), ion exchange (Aderhold, Williams, & Edyvean, 1996), electro-chemical precipitation (Kongsricharoern & Polprasert, 1993, 1996), filtration (Madaeni & Mansourpanah, 2003), advanced oxidation (Kurbus, Slokar, Le Marechal, & Voncina, 2003), biological treatment and adsorption (Ki, Gang, Um, &, Park, 2007). Among all methods mentioned above, adsorption is generally preferred for heavy metal ion removal due to its availability of different adsorbents, high efficiency, easily handling, reversibility, and possible low cost. The main requirement for adsorbents is a low cost/benefit ratio. Cellulose, which constitutes the most abundant polymer resource, is an inexpensive material. Among the cellulose derivatives, cellulose acetate (CA) is an important cellulose ester in industry out of its desirable physical properties. CA fiber has comparatively high modulus, adequate flexural and tensile strength (Aoki, Teramoto, & Nishio, 2007). So it is usually used as a film base in photography (Fujf, 2003) and as a component in adhesives (Ilicheva, Feldman, & Nikolskii, 1997). Furthermore, it can also be used as reverse osmosis (Bodalo, Gomez, Gomez, Leon, & Tejera, 2005; Khokhlova et al., 2005) and nanofiltration membranes (Choi, Fukushi, & Yamamoto, 2007). Grafted with functional groups such as $-COOH$, $-SO_3H$ and $-NH_2$ groups, CA can bond with heavy metal ions through surface complexation mechanisms (Liu & Bai, 2006).

Electrospinning is a simple and versatile method for fabricating continuous fibers with diameters ranging from micrometers to several nanometers (Dzenis, 2004; Li & Xia, 2004). High specific surface area with excellent adsorption capacity can be obtained

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[*] Corresponding author. Tel.: +86 10 82543772.
E-mail address: wumin@mail.ipc.ac.cn (M. Wu).

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doi:10.1016/j.carbpol.2010.08.054

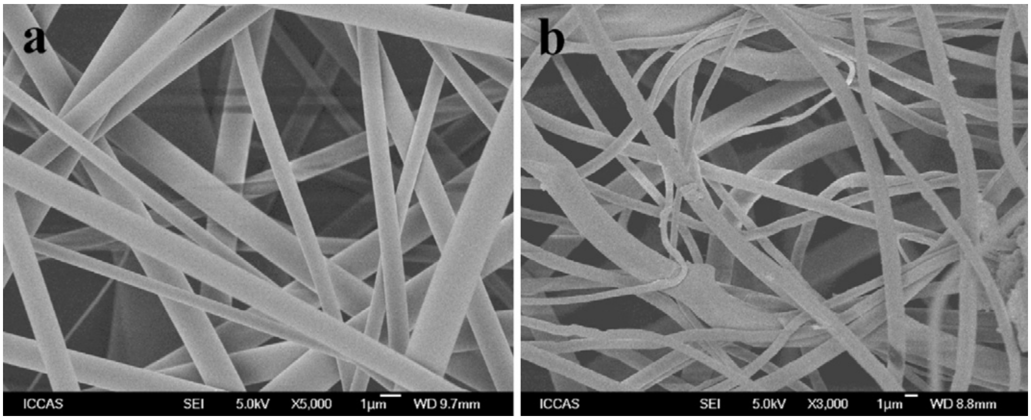

Fig. 1. SEM images of the (a) non-modified and (b) PMAA-modified electrospun CA membrane.

by electrospinning. So in this work, cellulose acetate (CA) nonwoven membrane has been fabricated by electrospinning. And the surface of electrospun CA micro-fibers was modified by grafting poly(methacrylic acid) (PMAA) using Ce^{4+} initiated polymerization (Gupta & Khandekar, 2003; Gupta & Sahoo, 2001). Then the PMAA chain can provide adsorptive –COOH groups on the CA micro-fibers. The adsorption and desorption of Cu^{2+}, Hg^{2+} and Cd^{2+} of the modified electrospun CA nonwoven membrane were investigated and the recycling of the electrospun CA nonwoven membrane was discussed. This work may provide some helpful information for fabrication of the low cost, high efficiency adsorbents for heavy metal ion removal using biomass.

2. Experimental part

2.1. Materials

Cellulose acetate (CA, M_w = 61,000 g/mol, acetyl content of 40%, Fluka) was dried in vacuum at 50 °C before use. Methacrylic acid (MAA, Sigma) was purified by vacuum distillation. Ammonium cerium(IV) nitrate ($(NH_4)_2Ce(NO_3)_6$, Alfa Aesar) was used as received. *N*,*N*-dimethylacetamide (DMAc), acetone and sulphuric acid (H_2SO_4, 95–98%) were all analytical grade supplied by local chemical agent suppliers and were used as received. Anhydrous copper(II) sulphate ($CuSO_4$), mercuric(II) acetate ($Hg(CH_3COO)_2$), cadmium(II) chloride ($CdCl_2 \cdot 1.5H_2O$), chromium(II) chloride ($CrCl_2$) and lead(II) nitrate ($Pb(NO_3)_2$) were analytical grade from local chemical agent works and were used to prepare the heavy metal ion solutions for adsorption experiments. All the metal ion solutions and standards were prepared using deionized water. Rhodamine B (Sigma), polyvinyl alcohol (PVA) with the average degree of polymerization 1750 ± 50, potassium iodide (KI) and Vitamin C were all used as received. Ethylenedinitrilo tetraacetic acid (EDTA, Acros) was used as received for desorption.

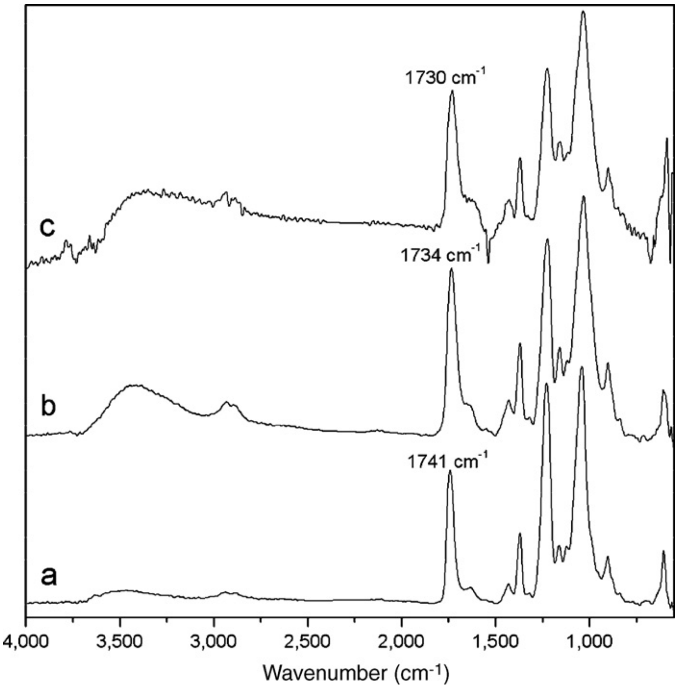

Fig. 2. ATR-FTIR spectra of (a) non-modified electrospun CA membrane, (b) PMAA surface modified CA membrane and (c) PMAA surface modified CA membrane after Cu^{2+} adsorption.

2.2. Preparation of CA nonwoven membrane

Homogeneous CA solution (20 wt.%) in acetone/DMAc (2:1, w:w) mixed solvent was pumped through a syringe with an 8 gauge stainless steel needle at a constant flow rate of 4 mL/h. A grounded Al-foil served as the collector. In this work, the electric potential and distance from syringe-tip to the collector were fixed at 20 kV and 15 cm, respectively. The collected CA nonwoven membrane with grammage of 12.8 g/m^2 was used for further modification and characterization.

2.3. Modification of CA nonwoven membrane with PMAA

The resultant CA nonwoven membrane was modified through Ce^{4+} initiated polymerization (Gupta & Khandekar, 2003; Gupta & Sahoo, 2001). The membrane was first immersed in MAA aqueous solution (10 vol.%) with H_2SO_4 (0.4 mol/L) and ammonium cerium(IV) nitrate (0.073 mol/L). The reaction mixture was then purged with nitrogen and then transferred to an oil bath at 80 °C for 3 h with continuous stirring. The resultant PMAA-modified CA nonwoven membrane was rinsed with deionized water for several times to remove free PMAA and dried in vacuum at 30 °C.

2.4. Adsorption and desorption of heavy metal ions

The solutions containing desired concentration of Cu^{2+}, Cd^{2+}, and Hg^{2+} were prepared by directly dissolving anhydrous copper sulphate ($CuSO_4$), mercuric acetate ($Hg(Ac)_2$), and cadmium chloride ($CdCl_2 \cdot 1.5H_2O$) in deionized water, respectively. The pH of the solutions was adjusted by dilute NaOH and HCl aqueous solutions. The adsorption experiments were carried out by suspending 0.1 g

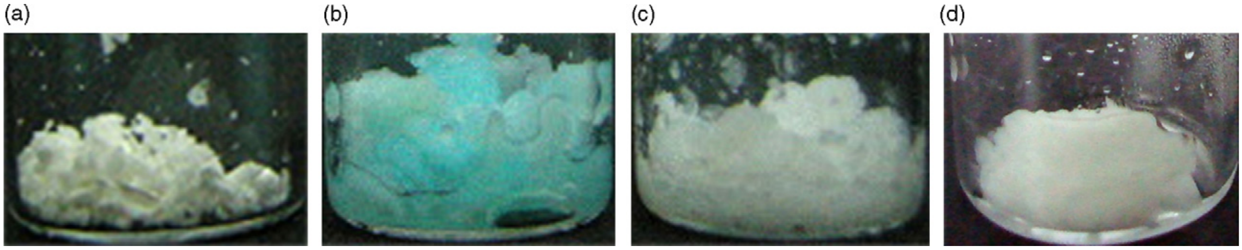

Fig. 3. The photographs of CA-g-PMAA adsorbents before adsorption of Cu^{2+} (a); after adsorption of Cu^{2+} (b); and after desorption of Cu^{2+} using EDTA saturated solution (c). And the photograph of non-modified electrospun CA membrane after adsorption of Cu^{2+} (d) is for comparison.

of the PMAA-modified electrospun CA nonwoven membrane in 50 mL solutions with metal ions at room temperature (about 25 °C) under continuous magnetic stirring. The amount of the adsorbed metal ions was determined by measuring the concentration of the metal ions in the solution. The adsorption capacity Q (mg/g) was calculated by

$$Q = \frac{(C_i - C_f) \cdot V}{m} \tag{1}$$

where C_i and C_f (mg/L) are the initial and final concentrations of the metal ion solution, respectively. V (mL) and m (mg) are the solution volume and adsorbent mass, respectively. The recovery of the PMAA-modified electrospun CA nonwoven membrane was achieved by desorption of metal ions in 25 mL saturated ethylenedinitrilo tetraacetic acid (EDTA) solution (the saturated concentration is 0.2 g/L).

2.5. Concentration measurement of heavy metal ions

The concentrations of metal ions were measured through a ternary-complex method (Haddad, 1977; Oshima & Nagasawa, 1970). The metal ions, Rhodamine B, and KI (stabled with Vitamin C) could form negative complex ions, which had the special absorption wavelength around 590 nm. And the intensity of this absorption peak can be used to represent the concentration of the corresponding metal ions. The UV–vis absorption peaks for the negative complex ions of Cu^{2+}, Hg^{2+} and Cd^{2+} were at 592, 589 and 595 nm, respectively. So a standard curve was firstly drawn by measuring the intensity of the absorption peaks of the negative complex ions with known ion concentrations for each kind of metal ions. And when the absorption peak intensities of the negative complex ions were measured, the metal ion concentrations of the aqueous solutions can be calculated through comparison with the corresponding standard curves.

2.6. Characterization

The morphology of the electospun micro-fibers was observed by using a JEOL JSM-6700F field emission scanning electron microscopy (FE-SEM). Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy (Bruker TENSOR 27) was used to determine the vibration frequency changes in the adsorbents. The concentrations of heavy metal ions were measured by ultraviolet–visible (UV–vis) spectroscope (Shimadzu 1601-PC).

3. Results and discussions

3.1. Electrospinning and surface modification of CA nonwoven membrane

In this work, acetone/DMAc mixed solvent is used for electrospinning of CA, and then the electrospun CA membrane is modified with PMAA. Fig. 1 shows the SEM micrographs of the electrospun CA fibers with and without PMAA surface modification. Fig. 1a shows that the nano- or micro-fibers are randomly deposited to form a nonwoven mat. The surface of the non-modified electrospun CA fibers is smooth and the cross-section is round. The diameter of the fibers is in the range from 500 nm to 1.5 μm and the average diameter is 750 nm. After grafting, the morphology and diameter of the fibers shows no big difference (Fig. 1b) from the original fibers. That is resulted from the heterogeneousness of this reaction, and the perfect thermal and chemical stability of CA fibers.

Fig. 2a and b show the ATR-IR spectra of CA membranes with and without PMAA modification. The peak around 1740 cm^{-1} is due to the carbonyl vibration in the –COOR groups of CA or in the –COOH groups of PMAA. After grafting, this peak shifts a little from 1741 cm^{-1} to 1734 cm^{-1}. That means the state of carbonyl groups has changed from all –COOR to partly –COOH that is in PMAA. The broad adsorption around 3400 cm^{-1} is due to the –OH groups. This peak becomes obviously stronger after grafting because more –OH groups are on the fiber surface. And these –OH groups are from the –COOH groups of grafted PMAA polymer chains. So the two differences in ATR-IR show the success of grafting PMAA onto the surface of the electrospun CA fibers. The graft content can be calculated by weighting estimation as follows: graft content = $[(W_g - W_0)/W_0] \times 100\%$, where W_g and W_0 are the weights of the modified and non-modified CA fibers, respectively. And by this way, the content of the PMAA chains in the resultant membrane is around 3.68 wt.%.

3.2. Adsorption mechanism

In the study of metal ion adsorption, Cu^{2+} has often been chosen as a model ion due to its characterized blue color. Fig. 3a and b show the adsorbents change its color from white to blue after adsorption of Cu^{2+}. Meanwhile, after the EDTA saturated solution treatment, the adsorbents discolored from blue back to white (Fig. 3c). The color changes prove that the PMAA-modified CA membrane can effectively adsorb Cu^{2+}, and can release Cu^{2+} using EDTA saturated solution. On the other hand, the electrospun CA membrane without surface modification is incapable of adsorbing Cu^{2+} (Fig. 3d). Fig. 2c shows the ATR-IR spectra of the PMAA-modified CA membranes after Cu^{2+} adsorption. The absorption peak of $-COO^-$ stretching at 1734 cm^{-1} shifts to 1730 cm^{-1} after adsorption, and it is indicated that the electronegativity turns lower for $-COO^-$ groups which attract electropositive ions such as Cu^{2+}. So the mechanism of adsorption is the chelating of $-COO^-$ groups with metal ions.

3.3. Effect of pH values on adsorption behaviors

Due to the ionization and deionization of the –COOH groups on the surface of the modified CA membrane, its adsorption behavior for metal ions could be influenced by the initial pH value. Fig. 4a shows the adsorption kinetics of Cu^{2+} at different pH values. Q_t represents the mass of metal adsorbed at time t. The results show that the Cu^{2+} adsorption kinetics is strongly dependent on the pH val-

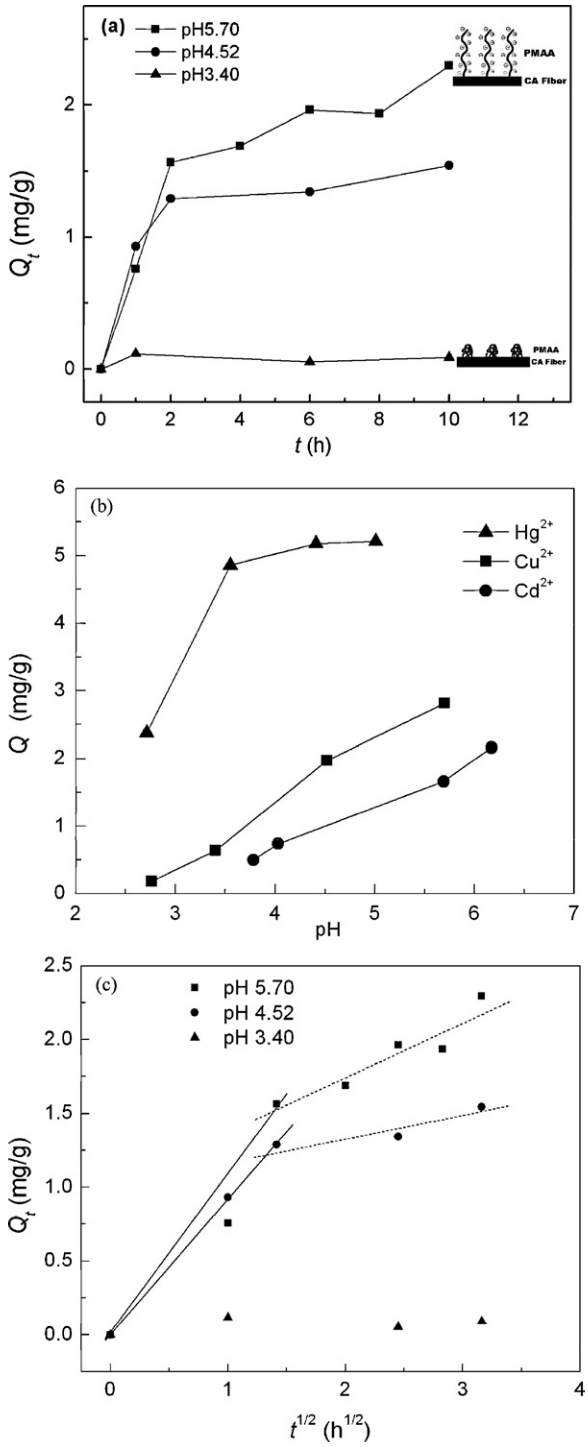

Fig. 4. (a) Q_t (adsorbed metal mass at time t) as a function of time t of the PMAA-modified electrospun CA membrane at different pH; (b) effect of pH value on the adsorption capacity Q (mg/g) of Cd^{2+}, Cu^{2+}, and Hg^{2+} on the PMAA-modified electrospun CA membrane; (c) Q_t as a function of $t^{1/2}$ of the PMAA-modified electrospun CA membrane at different pH; the initial concentrations of metal ions being 12 mg/L.

ues. The increase of pH value leads to a much faster adsorption and a higher adsorption capacity. At low pH value, e.g. pH = 3.40, almost no Cu^{2+} can be adsorbed onto the PMAA-modified membrane. In Fig. 4b, the dependence of the adsorption capacity Q as a function of pH value for Cd^{2+}, Cu^{2+}, Hg^{2+} is shown. The pH value of all the experiments is below 7, because the metal ions will be precipitated in basic media. It is shown the adsorption capacity for Cd^{2+}, Cu^{2+}, Hg^{2+} increases with increasing pH value. On this adsorbent surface, it is the ionized carboxyl group (–COO$^-$) on the PMAA chains that is responsible for the binding of metal ions. The behavior of PMAA chains is pH-responsive (Li, Liu, Kang, Neoh, & Yang, 2008; Qian, Li, & Nie, 2009). At higher pH, the carboxyl group –COOH can be ionized to –COO$^-$, and the electric repulsion between –COO$^-$ can overcome the tendency of the grafted PMAA chains to aggregate in water. So the grafted PMAA chains which have –COO$^-$ on it was dissolved in water. (See the upper inset in Fig. 4a) While at lower pH, the carboxyl group is deionized to –COOH and the uncharged chains will aggregate on the surface (see the under inset in Fig. 4a) and the grafted PMAA will loss the ability to bind the metal ions. So the adsorption capacity will increase at higher pH value.

The mechanisms controlling the adsorption kinetics include external diffusion, boundary layer diffusion and intraparticle (meso- and micropores) diffusion. The mathematical expression for the intraparticle diffusion model can be expressed as (Weber & Morris, 1963)

$$Q_t = kt^{1/2} + I \tag{2}$$

where k is the intraparticle diffusion rate constant and the intercept I is constant (mg/g) that gives information about the thickness of boundary layer. If we draw the plots Q_t of Cu^{2+} vs. $t^{1/2}$ at different pH (Fig. 4c), two linear regions can be observed. In the first, sharper region, the linear plot passes through the origin, and that means the intraparticle diffusion is the rate-limiting step. In the second region, the intraparticle diffusion starts to slow down due to low ion concentration left in the solution. And the value of intercept I is not zero, that shows there exists the boundary layer diffusion effect.

3.4. *Effect of initial ion concentrations on adsorption behaviors*

The initial metal ion concentration is another important factor to influence the adsorption behaviors of the adsorbent. Fig. 5 shows the adsorption capacity Q (mg/g) as a function of the initial ion concentration (c_0). It can be seen that Q value is linearly increasing with c_0 in the range of our investigation. To be specific, for the adsorption of Hg^{2+}, the resultant membrane can remove a majority of the Hg^{2+} in the water when the initial concentration of Hg^{2+} is lower than 50 mg/L. Meanwhile, the adsorption capacity for Hg^{2+} is much higher than that of Cu^{2+} and Cd^{2+} at the same initial ion concentration. It is suggested that the –COO$^-$ groups on the adsorbent have particular strong tendency to form complexes with Hg^{2+}. To measure the selectivity of adsorption, we use the parameter of distribution coefficient K_D, which describes the binding ability of adsorbent surface to an element. K_D is a ratio of the element concentration in solid state (C_s, mg/g) and in water state (C_w, mg/L), as Eq. (4):

$$K_D = \frac{C_s}{C_w} \tag{4}$$

Fig. 6 shows the K_D values of the surface modified electrospun CA membrane for Hg^{2+}, Cu^{2+}, Cd^{2+} and another two metal ions Pb^{2+}, Cr^{2+}. The K_D value of Hg^{2+} is far higher than the others. This means the surface modified electrospun CA membrane has quite high selectivity for Hg^{2+}. This feature is useful while trace Hg^{2+} need to be removed from a mixed metal ion solution.

3.5. *Desorption of metal ions and reuse of the membrane*

In application, it is important to reduce costs by re-using the adsorbents. Saturated EDTA solution could help de-adsorbing metal ions from the membrane. The adsorption properties of the recovered PMAA-modified CA membrane are shown in Fig. 7. The adsorption capacity Q for Cu^{2+} and Cd^{2+} is slowly decreasing with re-using cycles, which may be attributed to the loss of some

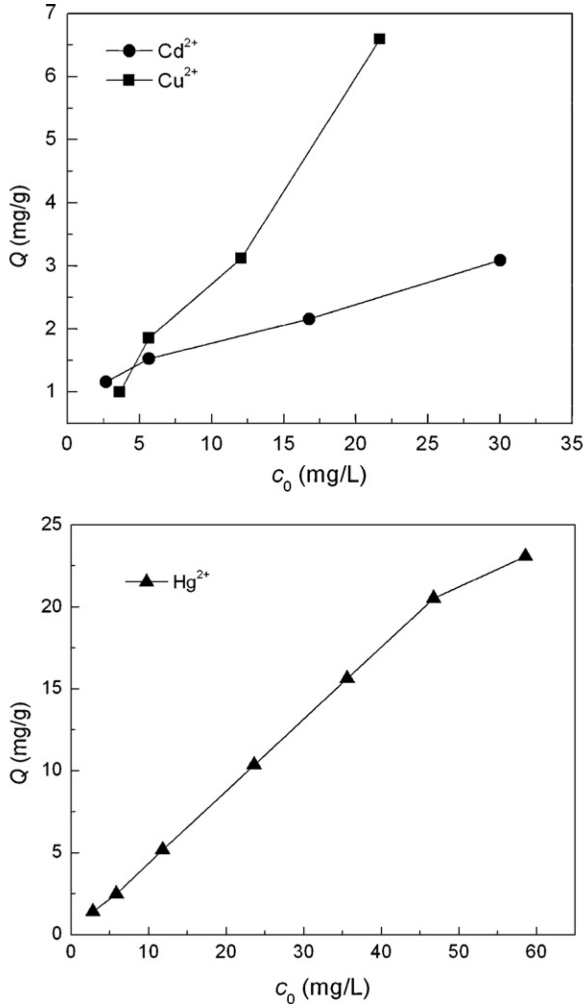

Fig. 5. Effect of initial metal ion concentration (c_0) on the adsorption capacity Q (mg/g) of Cd^{2+}, Cu^{2+}, and Hg^{2+} on the surface modified electrospun CA membrane.

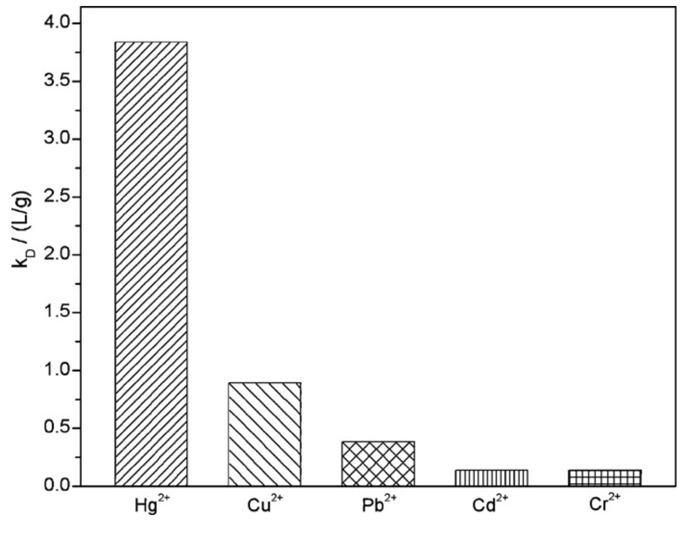

Fig. 6. K_D values of the surface modified electrospun CA membrane for different heavy metal ions.

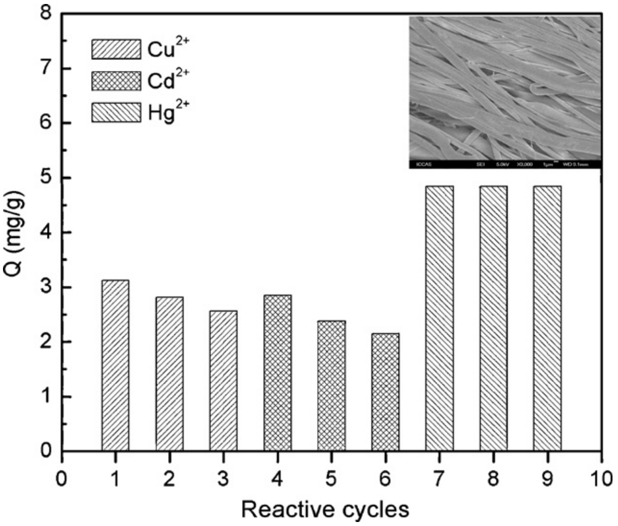

Fig. 7. Recycling efficiency of the surface modified electrospun CA membrane, the initial ion concentration being around 10 mg/L; Inset: SEM images of the PMAA-modified elctrospun CA membrane recovered by de-adsorbing Cu^{2+} with saturated EDTA solution.

adsorption active sites during the desorption process. However, the adsorption capacity for Hg^{2+} steadily remains at a high value (4.8 mg/g). This is because that this adsorption material has efficient adsorption ability for Hg^{2+}, and the residual adsorptive sites are more than enough for removing all of the Hg^{2+}. The inset shows the SEM images of the PMAA-modified CA elctrospun membrane recovered by de-adsorbing Cu^{2+} with saturated EDTA solution, which indicates that the fibril morphology of the membrane is kept during the recycling procedure.

4. Conclusions

Cellulose acetate (CA) nonwoven membrane was prepared by electrospinning and was surface modified with poly(methacrylic acid) (PMAA) using Ce^{4+} initiated radical graft copolymerization. The resultant PMAA-modified CA membrane could be used for the adsorption of heavy metal ions in water. Adsorption experimental results indicate that higher initial pH value corresponds to higher adsorption capacity. Moreover, this membrane has high adsorption selectivity for Hg^{2+}. The membrane can be easily recovered by de-adsorbing the metal ions using saturated ethylenedinitrilo tetraacetic acid solution and be re-used for the adsorption of metal ions. This work may provide some helpful information for fabricating low cost, high efficiency adsorbents for heavy metal ion removal using plant-residues.

Acknowledgement

This work was supported by National Natural Scientific Foundation of China (Nos. 50773086 and 50821062) and National Program on Key Basic Research Project (973 Program, No. 2011CB933700).

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