

PMMA MODIFIED CELLULOSE ACETATE NANOFIBERS FOR HEAVY METAL IONS ADSORPTION IN WATER

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Introduction

In the environmental pollutants, heavy metals, which are non-biodegradable and tend to accumulate in living organisms, have gained increasing significance.^[1,2] The removal of heavy metals from water has become one of the major topics in water treatment. Various methods have been reported for removal of heavy metal ions from water, such as reverse osmosis,^[3] ion exchange,^[4] electro-chemical precipitation,^[5] filtration,^[6] advanced oxidation,^[7] biological treatment and adsorption.^[8] Among all them, adsorption is generally preferred for heavy metal ion removal due to availability of different adsorbents, high efficiency, easy of handling, reversibility, and low cost possibility. Electrospinning is a simple and versatile method for preparing continuous fibers with diameters ranging from micrometers down to several nanometers,^[9,] and the resultant nanomaterials may be used in water treatment.^[10] We will report cellulose acetate (CA) nanofibers prepared by electrospinning and modified by grafting poly(methacrylic acid) (PMAA) and the adsorption of Cu^{2+} , Hg^{2+} and Cd^{2+} on the modified CA nanofibers.

Experimental

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. All chemical reagents in this work were used as received.

CA nanofibers were prepared by electrospinning in which the electric potential and distance from syringe-tip to the collector was fixed at 20 kV and 15 cm, respectively. The CA nanofibers was immersed in a MAA aqueous solution (10 vol.%) with H_2SO_4 (0.4 M) and ammonium cerium(IV) nitrate (0.073M) and then, transferred to an oil bath at 80°C for 3 h with continuous stirring. The resultant PMAA modified CA nanofibers was rinsed in deionized water for several times to remove free PMAA and dried in vacuum at 30°C.

The adsorption experiments were carried out by suspending the PMAA modified CA nanofiber into the solutions with Cu^{2+} , Cd^{2+} , and Hg^{2+} ions at room

temperature (25°C) with stirring. The amount of the adsorbed metal ions was determined by measuring the concentration of the metal ion in the solution. The adsorption capacity Q (mg/g) was calculated by

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

where C_i and C_f (mg/L) are the initial and final ion concentrations of the solution, respectively. V (ml) and m (mg) are the solution volume and adsorbent mass, respectively. The recovery of the CA nanofiber was achieved by desorption of metal ions in saturated ethylenedinitrilo tetraacetic acid (EDTA) solution.

field emission scanning electron microscopy, an Surface Area and Porosity Analyzer, Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy, UV-vis spectroscopy and X-ray photoelectron spectroscopy (XPS) were used to characterize the CA nanofiber and its adsorption to metal ions.

Results and Discussion

Figure 1 shows the SEM micrographs of the CA and PMAA modified CA fibers. The surface of the 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. The specific surface of the CA fiber is 3.94 m^2/g , the CA fiber modified by PMAA remains its nano- or micro-fibril morphology. XPS survey spectra and the ATR-IR spectra for the CA and PMAA modified CA fiber confirm the success of grafting PMAA on the surface of CA fiber. Figure 3a and 3b show of the CA and PMAA modified CA fibers, respectively.

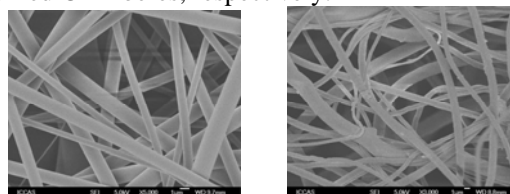


Figure 1. SEM images of the (a) CA and (b) PMAA modified CA fibers

Cu^{2+} has frequently been chosen as a model ion due to its characterized blue color. Figure 3c shows the ATR-

IR spectra of the PMAA modified CA membranes after Cu^{2+} adsorption. The absorption peak of C=O stretching at 1734 cm^{-1} before adsorption shifts a little to 1730 cm^{-1} , which indicates the reaction between $-\text{COO}^-$ group with low electronegativity and Cu^{2+} . So it is suggested that the chelating of $-\text{COO}^-$ and metal ions occur in the adsorption. Figure 4a and 4b show the color change of the adsorbents before and after adsorption of Cu^{2+} , which confirms the effective adsorption of Cu^{2+} on to the PMAA modified CA fiber. Meanwhile, the desorption of Cu^{2+} by EDTA saturated solution can also be confirmed by the discolor of the adsorbents (Figure 4c).

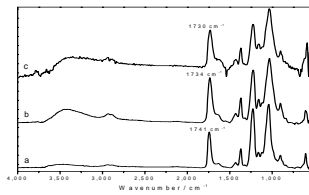


Figure 3. ATR-FTIR spectra of (a) CA as-electrospun membrane, (b) surface PMAA modified CA membrane and (c) surface PMAA modified CA membrane after Cu^{2+} adsorption

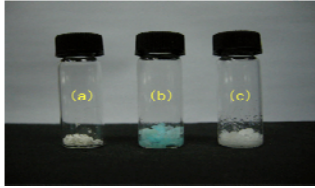


Figure 4. The CA-g-PMAA adsorbents: (a) before adsorption of Cu^{2+} ; (b) after adsorption of Cu^{2+} ; and (c) after desorption of Cu^{2+} using EDTA saturated solution

The Cu^{2+} adsorption kinetic is strongly depended on the pH. The high pH value leads to a much faster adsorption and a higher adsorption capacity. But when $\text{pH}=3.40$, almost no Cu^{2+} ion can be adsorbed onto the PMAA modified CA fiber. The adsorption of Cu^{2+} onto the PMAA modified electrospun membrane obeys the intraparticle diffusion equations as^[46]

$$Q_t = kt^{1/2} + I \quad (2)$$

where k is the intraparticle diffusion rate constant. It is suggested that initial adsorption with fast kinetics may result from the outer-surface adsorption and a relatively slow adsorption following may be determined by particle diffusion. The adsorption capacity of the metal ions increases with increasing pH.

The adsorption properties of the recovered PMAA modified CA fiber indicate that the adsorption capacity Q for Cu^{2+} and Cd^{2+} is decreased slowly with reusing cycles but for Hg^{2+} is almost unchanged

Conclusions

Cellulose acetate (CA) non-woven membrane was prepared by electrospinning and was surface modified with poly(methacrylic acid) using Ce(IV) ion initiated radical graft copolymerization. The resultant PMAA modified CA membrane can be used for the adsorption of heavy metal ions in waster water. Adsorption experimental results indicate that a higher initial ion concentration or initial pH value corresponds to a higher adsorption capacity. Moreover, the resultant membrane has a high adsorption capacity for Hg^{2+} . The membrane can be easily recovered by de-adsorbed the metal ions using saturated ethylenedinitrilo tetraacetic acid solution and be re-used for the adsorption of metal ions.

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