Preparation of submicron ion-exchange fibers and application in copper ions removal from aqueous solutions

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(Received: 18 October, 2009; published: 21 February, 2010)

Abstract: The submicron ion-exchange fibers (IEF) of polystyrene (PS) and styrene-isoprene-styrene block copolymer (SIS) blends (80/20, w/w) obtained by electrospinning technology were further sulfonated with sulfuric acid to produce strong acidic cation ion exchange fibers. Scanning electron microscopy (SEM) images showed that there were obvious increase in the diameters, scratches, cracks, and micro-pores on the rough IEF surface. Fourier transform infrared (FT-IR) spectroscopy analysis showed there were many sulfonated acid groups introduced onto the benzene wreath of styrene. The maximum adsorption capacity and the adsorption rate of copper ions were carried out and their removal rate determined by spectrophotometry. The results of the adsorption for copper ions showed that submicron IEF from PS/SIS blends with a high porosity (85%) and a high specific surface (760 m²/g) possess a rapid adsorption rate and a high ion adsorption amount (305.9 mmg/g). This high adsorption capacity suggests that the IEF can be efficiently applied to filter out toxic metal ions, and has excellent efficiency to remove copper ions from aqueous solution.

Introduction

Heavy metals are toxic and their presence in streams leads to the accumulation in living organisms, causing health problems in human beings, plants and animals [1]. Copper ion (Cu²⁺) is a typical environmental heavy metal pollutant. The source of wastewater containing Cu²⁺ includes mining, smelting, electrolyzing, painting, alloying, electroplating, textile processing and printing. Due to the toxic nature of most Cu²⁺ to aquatic life, wastewater cannot be discharged without adequate treatment [2].

Ion exchange fiber (IEF) is the most employed adsorbent for heavy metals removal from aqueous solution because of its advantages such as good handling characteristics, flexibility to be processed in diverse forms, and physical requirements of strength and dimension stability [3]. Besides its physical characteristics, the adsorption capacity is excellent. Especially, the introduction of ionic functional groups to nano-microscaled fibrous fabrics obtained by electrospinning technology is a promising option to provide novel ion exchangers with a high adsorption capacity, rapid kinetics and a high catalytic activity. Zhang and co-workers [4] prepared nanofibers, the available surface area of which was greatly increased, up to as much as two orders of magnitude. The porous nature of the nanofibers resulted in elevated permeability compared to the commercial fibers, and provided the highest dynamic...
adsorption capacity. The potential application of this material can be in the separating technology as novel nanofibrous membranes for fine filtration and neutralization of toxic metals, and in the biomedical field as scaffolding materials in tissue engineering and drug delivery system, etc [5].

Laforgue et al. [6] prepared mats from electrospun Nafion/poly (vinyl alcohol) blends and compared their proton conductivity to that of homogeneous Nafion films. Haider and Park [7] reported that their chitosan nanofiber were effective in adsorbing Cu$^{2+}$ and Pb($^{2+}$) ions with a high mechanical strength in the swollen state and their equilibrium adsorption capacities for Cu$^{2+}$ and Pb($^{2+}$) were 6 and 11 times higher than the reported highest values of the chitosan microsphere and the plain chitosan. Among all absorbents, PS based materials are noticeable due to its cheap and easily induction of ion exchange groups. Matsumoto et al. [8] prepared the nanometer IEF of PS via electrospinning, the nano-microfiber fabrics provides novel functional materials with a large adsorption capacity and a high catalytic activity. However, the adsorbing applications such as heavy metals removal from aqueous solution are not reported in their work. Particularly, PS with poor mechanical and brittle properties limited their applications in filter areas, so it is suitable to blend it with tough materials, such as SIS.

In the present work, the new IEF, which were durable, low in cost and high in ion exchange capacity, were prepared. For this purpose, PS was first blended with SIS which imparts good thermal and chemical stability, then electrospun and sulfonated into the IEF. The remarkable characteristics of the PS/SIS IEF has higher value of IEC and more rapid adsorption rate for Cu$^{2+}$ than that of the submicron IEF of pure PS and the conventional IEF due to more exposure of the IEF functional groups to the metal ions.

Results and discussion

Morphologies of PS/SIS blend fibers

The morphological images of these PS/SIS fiber mats were observed under SEM (JSM-6360LV instrument with a voltage of 15KV). Fig.1 shows the SEM micrographs of the as-spun nanofiber (EF) and the IEF of PS/SIS blends.

![Fig. 1. SEM images of PS/SIS fibers: (a) EF, (b) IEF.](image)

Via comparison of Fig.1, the morphology of the IEF was significantly different from that of EF. The diameter of the EF was ~386 nm, and without any serious cracks on
the smoothing fiber surface, while, the diameter of the IEF was in the order of 1008 nm. The result showed that there was an increase in the diameters of IEF. This is due to the fact that two styrene groups were linked by formaldehyde, the sulfuric acid groups attacked and were attached to the benzene wreath of styrene, which may, in turn, result in the change of the structures. It was observed that there were obvious deep scratches, cracks, and micro-pores on the rough surfaces, which may play a vital role in the adsorption/sorption of metal ions.

**FT-IR spectra analysis**

To justify the introduction of functional groups onto the PS/SIS fabric, FT-IR spectra analysis was carried out on a Nexus 670 spectrometer. Fig. 2(a) showed the features of PS/SIS blends: C=C bands (1690 cm\(^{-1}\)), C–H of benzene wreath (2924 cm\(^{-1}\)), monosubstituted peaks of the benzene wreath (759 cm\(^{-1}\) and 697 cm\(^{-1}\)). As shown in Fig. 2(b), the broad and strong peak in the range of 1200 cm\(^{-1}\) was the absorption peak of the sulfuric acid groups, and a stronger and broader absorption peak appeared at 3400 cm\(^{-1}\), which was –OH stretching vibration absorption peak. The disappearance of the benzene wreath stretching vibration (from 1400 to 1600 cm\(^{-1}\)) replaced by O–H bending vibration (1440 cm\(^{-1}\)) indicated that most sulfuric acid groups were covalently attached to the benzene wreath of styrene in the sulfonation reaction. The absorption peak of styrene at 1040 cm\(^{-1}\) was replaced by the peak at 1003 cm\(^{-1}\) of the symmetrical stretching vibration of the sulfuric acid. Furthermore, the vibration peaks at 887 cm\(^{-1}\) characterizes the para–substituted structure of the benzene wreath [9]. These demonstrated that the sulfuric acid groups were attached to the benzene wreath of styrene in the sulfonation reaction.

**Fig. 2.** FT-IR spectra of the fibers: (a) EF, (b) IEF.

*IEC and Cu\(^{2+}\) ions adsorption*

The sulfonated group amounts of the IEF from 80/20 PS/SIS blends were tested. The maximum IEC of the IEF sulfonated PS/SIS blends for 4 hours was 4.78 mmol/g (the adsorption amount, 305.9 mg/g). The cation-exchange adsorbents from electrospun fibers according to the above approach had higher sulfonation group densities than that of sulfonated polymer membranes and textiles which were obtained by radiation-induced graft polymerization of styrene with the subsequent sulfonation of polystyrene chains (0.5-3 mg/g) [10], and the IEF ranged from 0.78 to 1.34 mmol/g from pure nanofibers of PS reported by Matsumoto et al. [8]. This showed that the
IEF of PS/SIS blends with smaller pore diameter and larger surface area were enhanced in IEC.

In order to determine the contribution of sulfuric acid groups to the total IEC, a set of batch experiments towards Cu$^{2+}$ ions adsorption from the aqueous solutions of CuCl$_2$ (pH=5.3) were performed. Thus sulfonated group density was calculated on the base of the gram-equivalent value of Cu$^{2+}$ ions.

![Fig. 3. Kinetic curve of the IEF of PS/SIS adsorption for Cu$^{2+}$ at different times.](image)

Figure 3 shows the adsorption of Cu$^{2+}$ ions onto the IEF mat from PS/SIS blends in a 20 mg/L solution as a function of contact time within 1 h. The adsorption rate which represents the ratio of the amount of the adsorption and the initial of Cu$^{2+}$ ions increased sharply within 10 min, increased to 90%, and reached equilibrium within 30 min. It can be concluded that at the initial stage the adsorption sites are more, and the metal ions can exchange easily with the sulfonated acid groups, and the slow adsorption rate in later stage is due to the slow diffusion of solute into the interior of the adsorbent. Maximum adsorption occurred after 30 min and there was almost no adsorption beyond this time with the maximum adsorption rate up to 99.4% for Cu$^{2+}$. This is due to submicroscale IEF with a high specific surface area (760m$^2$/g), high porosity (85%) and the introduction of sulfonated acid groups. The shape of the curve indicated that the adsorbent binding Cu$^{2+}$ capacity increased sharply up to 10min and was homogeneously saturated after 30 min. These characteristics are desirable for the treatment of industrial wastewater, e.g. metal ions pollution in ground water, which need a rapid adsorption rate and a high adsorption capacity.

**Conclusions**

In this work, the novel IEF were produced by sulfonating the nanofibers from PS/SIS blends. SEM images showed that the structure of IEF had changed greatly and the FT-IR spectra analysis showed that the IEF were connected with sulfuric acid groups. The maximum IEC and the adsorption amount of the submicron IEF from PS/SIS blend fibers were 4.78 mmol/g and 305.9 mg/g. In addition, the amount of sorption of metal ions on submicron IEF increased with increasing adsorption time. The sorption rate of the IEF was rapid during the first 10 min and the equilibrium was attained within 30 min. The submicron IEF from PS/SIS blends have distinct advantages over current technologies due to the high surface area per unit mass resulting from the
very fine diameter, the rapid adsorption rate, and the high IEC. Therefore, this system is promising as an adsorbent which can screen toxic metal ions.

**Experimental**

**Materials**

The triblock copolymer SIS used in this paper was obtained from Shell Chemical Co. (Kraton D1107), supplied in the form of rubbery pellets containing 14% polystyrene by weight with molecular weight (Mₙ) of 2.2 x 10⁴. PS was supplied by Propilven C.A, with a melt flow index of 18.68 g/10 min (230 °C, 5000 g). Tetrahydrofuran (THF) and dimethylformamide (DMF) were offered from Peking Chemical, China. Concentrated sulfuric acid (98%), glacial acetic acid and polyformaldehyde were provided by Vas Chemicals of China.

**Electrospinning nanofibers**

The 12 wt% PS/SIS blend solutions (80/20, w/w) dissolved in the mixture of THF and DMF (80/20, v/v) were added to a 10 mL glass syringe with a needle tip (0.7 mm diameter). The feeding rate of the polymer solution was 1.5 mL/h, which was controlled by a syringe pump. A used voltage was 20 kV and the distance between the needle tip to the collector was 15 cm. After the electrospinning, all the fibrous non-woven mats were collected from the aluminum foils, and dried at 100 °C in a vacuum oven for two days.

**Sulfonation and IEC tests**

The Electrospun nanofibers of PS/SIS blends must be chemically activated to make them perform as an ion exchange material. IEF were obtained under the following conditions: 2 g of original fibrous membranes were first put into a 100 mL bottle containing 30 mL of sulfuric acid (98%), 3 g of polyformaldehyde, and 10 mL of glacial acetic acid for crosslinking at 50 °C for 6 h. Then 50 mL of sulfuric acid (98 %) were added to sulfonate for 4 h at 80 °C. Finally the sulfonated products were diluted by different concentrations (70 %, 50 %, 25 % and 5 %) of 98 % sulfuric acid, and followed by washing with deionized water until the flushing water was neutral, and dried in a vacuum oven for 24 h at 100 °C to obtain the strongly acidic cation-exchange fibers. The details of the process have been reported in an earlier publication [11] and the schematic chemistry/chemical structures illustrating the functional modification is presented following reaction equation (1).

\[
\begin{align*}
\text{[CH-CH₂]ₙ} + \text{HCHO} & \longrightarrow \text{CH₂CH₃CH₂CH₂CH₂CH₂CH₂CH₂CH₂SO₃H} \\
\text{H₂SO₄} & \longrightarrow \text{CH₂CH₃CH₂CH₂CH₂CH₂CH₂CH₂CH₂SO₃H}
\end{align*}
\]

The IEC representing the number of replaceable H⁺ ions per unit mass of the exchange material was determined by backward titration experiments. The samples
of sulfonated fibrous membranes (0.2 g) were first put into 0.1 M HCl for 12 h at 25 °C to be converted to the H⁺ form. Then these samples were washed with deionized water and dried in oven at 100 °C. Finally these samples were put into a flask with 20 ml of 0.5 M standard NaOH solution, and shaken for 12 h. Then the value of IEC was calculated by using the mass balance equation for the adsorbent.

\[
Q_w = (V_0 - V_1) \times C / W
\]

where \( Q_w \) is the adsorption capacity (mmol/g), \( C \) is the concentration of hydrochloric acid solution (mmol/L), \( V_0 \) is titration volume of hydrochloric acid used in blank solution (L), \( V_1 \) is titration volume of hydrochloric acid used in metal ion solution (L) and \( W \) is the weight of the adsorbent (g).

The adsorption of Cu²⁺ ions from an aqueous solution (pH=5.3) and the kinetics experiments were investigated at 25 °C. 0.2 g of IEF samples were mixed well with 50 ml solution containing of CuCl₂ (20 mg/L) in 100 mL conical flasks. The pHs of the suspensions were adjusted to around 5.3 by the addition of 0.01 mol/L HCl solution. The bottles with samples were shaken at 25 °C and then centrifuged at 3000 rpm for 30 min. At the end of predetermined time interval the mL solution was collected at appropriate time intervals for trace metal ion determination by using an atomic absorption spectrophotometer (Optical Instrument Co. Shanghai, China, Model 721W). The amount of metal ions adsorbed per gram of dried weight of IEF (mg/g) was calculated according to the equation (3) [12], and the adsorption rate was calculated according the equation (4):

\[
Q = (C_0 - C_i) \times V / W
\]

\[
R = (C_0 - C_i) / C_0 \times 100
\]

where \( Q \) is the adsorption amount (mg/g), \( C_0 \) is the initial concentration of metal in solution (mg/L), \( C_i \) is the millilitre solution concentration of metal in solution (mg/L), \( V \) is the volume of metal ion solution (L) and \( W \) is the weight of the adsorbent (g), \( R \) is adsorption rate (%)

Acknowledgements

This work was supported by the Program of Introducing Talents of Discipline to Universities (No111-2-04).

References