Journal of Colloid and Interface Science 420 (2014) 145–151

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis

# Adsorption of silver ions on polypyrrole embedded electrospun nanofibrous polyethersulfone membranes

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ARTICLE INFO

*Article history:*
Received 31 October 2013
Accepted 9 January 2014
Available online 16 January 2014

*Keywords:*
Electrospinning
Nanofibrous membranes
Polypyrrole
Polyethersulfone
Silver ion removal

ABSTRACT

In this study we developed polypyrrole embedded electrospun nanofibrous polyethersulfone nanofibrous membranes for the removal of silver ions. Polypyrrole and polyethersulfone dissolved in *N*-methyl-2-pyrrolidone (NMP) were electrospun into nanofibrous membranes via an electrospinning process. The morphology of as-spun polypyrrole/polyethersulfone nanofibers was examined by scanning electron microscopy. The average diameter of electrospun nanofibers ranged from 410 nm to 540 nm. The adsorption capability of nanofibrous polypyrrole/polyethersulfone membranes was measured and compared with that of bulk polypyrrole. The influence of various process conditions on adsorption efficiency was also examined. The experimental results suggested that the electrospun nanofibrous membranes exhibited good silver ion uptake capabilities. The metal uptake of nanofibrous membranes increased with the initial metal ion concentrations and the pH value, while decreased with the temperature and the filtering rate of the solutions. Furthermore, the electrospun membrane could be reused after the recovery process.


## 1. Introduction

Water pollution has become an issue of global concern, since the pollution could hardly be reformed. Ground, surface, and processing water frequently contain dissolved metals that are resulted from operations of mines, factories, and other industries. These metals are toxic to people, difficult or expensive to remove, and also cause damage to the environment. Metal contaminated water may include ions of copper, zinc, nickel, lead, cadmium, mercury, chromium, uranium, etc. All of these are toxic to animals, plants, or other organisms, and may deleteriously influence sensitive environments. Furthermore, metal ions are dangerous because they tend to bioaccumulate, i.e., the concentration of a chemical increases in a biological organism over time, compared to the chemical's concentration in the environment. The removal of metal ions has thus become one of the imminent issues for the ecosystem. Among various water purification technologies, membrane filtration [1–7] is very promising, mainly due to the fact that the process is pressure driven and operates without heating. It is thus energetically lower than conventional thermal separation processes and is cost competitive.

In this study, we developed polypyrrole (PPy) loaded nanofibrous polyethersulfone (PES) membranes via electrospinning for the removal of silver ions. Polypyrrole is a type of organic polymer by polymerization of pyrrole. Due to its conducting properties, PPy and related polymers have found applications in electronic devices and chemical sensors [8]. Furthermore, the metal binding capability of PPy has made it a candidate for the removal of metal ions [9,10]. Wang et al. [11] developed polypyrrole-coated electrospun nanofiber mats to recover gold (Au) from aqueous solutions, and found that the polypyrrole-coated electrospun nanofibers are good candidate membrane materials for the recovery of Au. Choi and Jang [12] proposed that polypyrrole-impregnated porous carbon could be readily synthesized using vapor infiltration polymerization of pyrrole monomers. Their results showed that the modified porous carbon exhibited an improved complexation affinity for heavy metal ions such as mercury, lead, and silver ions due to the amine group of polypyrrole. Bhaumik et al. [13] prepared polypyrrole–polyaniline (PPy-PANI) nanofibers as adsorbent of Cr (VI) via coupling propagating $PPy^{+}$ and $PANI^{+}$ free radicals by simultaneous polymerization of Py and ANI monomers in the presence of $FeCl_3$ oxidant. Recently, Wang et al. [14] developed polyacrylonitrile/polypyrrole core/shell nanofiber mat via the electrospinning method followed by in situ polymerization for the removal of hexavalent chromium from aqueous solution. Despite these developed mats exhibiting good metal ion removal capabilities, they required complex processes for manufacturing.

We prepared the PPy loaded polyethersulfone (PES) [15] membranes via a simple one-step electrospinning process. For

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0021-9797/$ - see front matter 
http://dx.doi.org/10.1016/j.jcis.2014.01.011

the electrospinning of polypyrrole (PPy) loaded nanofibrous polyethersulfone (PES) membranes, PPy and PES were first dissolved in *N*-methyl-2-pyrrolidone (NMP). They were then electrospun into nanofiber-structured membranes. After electrospinning, the morphology of the electrospun membranes was characterized. Parameters affecting the adsorption property of silver ions on the nanofibrous membranes were investigated. The recovery of the fabricated membrane for metal ion removal was also examined.

## 2. Materials and method

### 2.1. Materials

Polypyrrole and *N*-methyl-2-pyrrolidone (NMP) were purchased from Sigma-Aldrich (Saint Louis, MO, U.S.A.). The polyethersulfone (PES) used was provided commercially by Trump Chemical Corp. of Taiwan, and had a melt flow index of 30 g/10 mins. For silver ion removal test, silver nitrate ($AgNO_3$) and nitric acid were also purchased from Sigma–Aldrich (Saint Louis, MO, U.S.A.).

### 2.2. Electrospinning

The electrospinning setup utilized in this study consists of a syringe and needle (the internal diameter is 0.42 mm), a ground electrode, an aluminum sheet, and a high voltage supply. The needle was connected to the high voltage supply, which could generate positive DC voltages and current up to 35 kV and 4.16 mA/125 W respectively. For the electrospinning of nanofibrous membranes, a predetermined ratio of PES was first dissolved in NMP at four different concentrations of 30%, 32%, 35% and 38% by weight, and was then delivered by a syringe pump with a volumetric flow rate of 0.72 mL/h. The distance between the needle tip and the ground electrode was 12, 14 or 16 cm, and the positive voltage applied to polymer solutions was set to 15 kV. Table 1 lists the test trials and the processing parameters. The processing condition that produced the most uniform fiber diameter distribution was identified. Nanofibers with the addition of polypyrrole, 2%, 5%, 8%, and 10% by weight percentages respectively (Table 2), were then electrospun by employing the optimal processing condition. In addition, nanofibrous membrane of virgin PES was also prepared as a control. All electrospinning experiments were carried out at room temperature.

### 2.3. Characterization of nanofibers

The morphology of electrospun PES/PPy nanofibrous membranes was observed on a scanning electron microscope (FESEM; Jeol Model JSM-7500F, Japan) after gold coating. The average diameter of the nanofibers was obtained by averaging the diameters of ten randomly selected fibers. The porosity of the nanofibrous membranes was obtained by calculating the following expression:

$$\text{Pore}(\%) = \left\{1 - \frac{\rho_{\text{membrane}}}{\rho_{\text{polymer}}}\right\} \quad (1)$$

where $\rho_{\text{membrane}}$ and $\rho_{\text{polymer}}$ are the densities of the nanofibrous membrane and the polymer respectively.

A Fourier Transform Infrared (FTIR) spectrometry was employed to examine the spectra of electrospun PES/PPy membranes. The FTIR analysis was conducted on a Bruker Tensor 27 spectrometer in the absorption modes at resolution of 4 $cm^{-1}$ and 32 scans. Membrane samples were pressed as KBr disks, and spectra were recorded over the 400–4000 $cm^{-1}$ range.

### 2.4. Metal removal capability of PES/PPy nanofibrous membranes

The metal removal capability of the nanofibrous PES/PPy membranes was studied using the vacuum filtration assembly shown schematically in Fig. 1. The as-spun membrane was cut into a round disk that has a diameter of 43 mm and a thickness of 1.3 mm for the tests. A predetermined amount of solutions (100 mL) containing different concentrations of silver ions was placed at the top of the setup. With the application of vacuum pressure, the solutions were drawn to pass through the nanofibrous membranes. The filtering rates through the membranes could be adjusted by the throttle value ranging from 0.6 to 72 L/

**Table 1**
Processing parameters used for the electrospinning of virgin PES nanofibers.

| Test | Weight of PES (mg) | Weight of NMP (mg) | Distance (cm) | Concentration of PPy (wt%) | Porosity (%) | Fiber diameter (nm) |
|---|---|---|---|---|---|---|
| A | 3000 | 7000 | 12 | 30 | 85.4 | 1680 |
| B | 3200 | 6800 | 14 | 32 | 88.8 | 1160 |
| C | 3500 | 6500 | 16 | 35 | 88.4 | 540 |
| D | 3800 | 6200 | 12 | 38 | 87.8 | 910 |
| E | 3000 | 7000 | 14 | 30 | 87.5 | 490 |
| F | 3200 | 6800 | 16 | 32 | 89.2 | 400 |
| G | 3500 | 6500 | 12 | 35 | 89.5 | 740 |
| H | 3800 | 6200 | 14 | 38 | 88.4 | 830 |
| **I** | **3000** | **7000** | **16** | **30** | **87.4** | **650** |
| J | 3200 | 6800 | 12 | 32 | 84.9 | 1540 |
| K | 3500 | 6500 | 14 | 35 | 86.6 | 440 |
| L | 3800 | 6200 | 16 | 38 | 87.4 | 560 |

* Voltage: 15 kV, Flow rate (mL/h): 0.72 mL/h.

**Table 2**
Processing parameters used for the electrospinning of PPy loaded PES nanofibers.

| Test | Weight of PES (mg) | Weight of PPy (mg) | Weight of NMP (mg) | Concentration of PPy (wt%) | Porosity (%) | Fiber diameter (nm) |
|---|---|---|---|---|---|---|
| A | 2940 | 60 | 7000 | 2 | 85.4 | 540 |
| B | 2850 | 150 | 7000 | 5 | 88.8 | 490 |
| C | 2760 | 240 | 7000 | 8 | 88.4 | 560 |
| D | 2700 | 300 | 7000 | 10 | 87.8 | 410 |

* Voltage: 15 kV; flow rate (mL/h): 1.08 mL/h; distance: 16 cm.