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Micro-nano structure poly(ether sulfones)/poly(ethyleneimine) nanofibrous affinity membranes for adsorption of anionic dyes and heavy metal ions in aqueous solution

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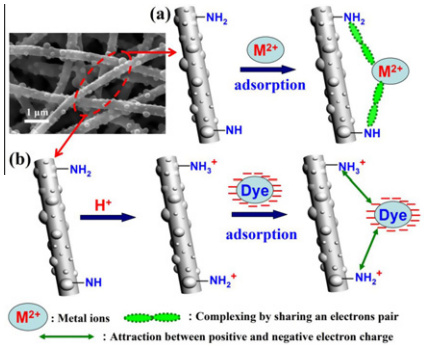
HIGHLIGHTS

- A novel micro-nano structured PES/PEI nanofibrous membrane was fabricated.
- The adsorption of PES/PEI nanofibrous membranes for metal ions and anionic dyes was tested.
- Isotherms, kinetic model and thermodynamic parameters were investigated.
- Two different kinds of adsorption mechanism were proposed for adsorption of anionic and cationic compounds.
- The regeneration efficiency of PES/PEI nanofibrous membranes was studied.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, a novel micro-nano structure poly(ether sulfones)/poly(ethyleneimine) (PES/PEI) nanofibrous membrane was fabricated and utilized as an adsorbent for anionic dyes or heavy metal ions from aqueous solutions. A series of adsorption experiments were carried out to investigate the influence of membrane dosage, initial solution pH value, contact time, initial solution concentration and adsorption temperature on the adsorption performance. The experimental results showed that the removal of the anionic dyes and metal ions on this PES/PEI nanofibrous membrane was a pH-dependent process with the maximum adsorption capacity at the initial solution pH of 1 for anionic dyes and 5–7 for metal ions, respectively, and the PES/PEI nanofibrous membranes could be regenerated successfully. The adsorption equilibrium data were all fitted well to the Langmuir isotherm equation, with a maximum adsorption capacity values of 1000.00 mg/g, 344.83 mg/g, 454.44 mg/g, 94.34 mg/g, 161.29 mg/g and 357.14 mg/g for Sunset Yellow FCF, Fast Green FCF, Amaranth, Pb(II), Cu(II) and Cd(II), respectively. The kinetic study indicated that the adsorption of metal ions and anionic dyes could be well fitted by the pseudo-second-order equation, suggesting the intra-particle diffusion process as the rate-limiting step of the adsorption process. Thermodynamic parameters such as free energy, enthalpy and entropy of adsorption of anionic dyes and metal ions were also evaluated and the results showed that the adsorption was a spontaneous physical adsorption process. In addition, two different kinds of adsorption mechanism were proposed to explain the adsorption of anionic and cationic compounds on the PES/PEI nanofibrous membrane.

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1. Introduction

The removal of heavy metal pollutants and dyes from wastewater has become a critical issue because of their adverse effects on human health and the environment [1,2]. Adsorption has been proved to be a well-established and economical method for the treatment of wastewater contaminated by metal ions and dyes. Nowadays, almost all the adsorbents developed for the removal of heavy metal ions and dyes rely on the interaction of the target compounds with the functional groups that are present on the surfaces of the adsorbents [1]. Therefore, a large surface area and many adsorption sites of the matrix are essential for adsorption affinity membranes to remove the contaminants from wastewater, and the specific surface area was one of the most important factors to affect the adsorption capacity of the adsorbents [3–5]. Electrospinning technology for the preparation of nanofibers or nanostructure materials is one of the most important objects in the recent research topics. In addition, the nanofibers or nanostructure materials fabricated by electrospinning have been widely used as affinity nanofibrous membranes [6–9], because of their superior properties such as fine diameters, large specific surface area, high porosity, small inter-fibrous pore size and stability in liquid media [10,11].

In the adsorption process, the functional groups such as amino and carboxyl groups on the surface of the adsorbents played an important role in determining the effectiveness, capacity, selectivity, and reusability of the adsorbent materials [12–14]. Further more, adsorbents with amino groups showed bifunctional properties which enable them to adsorb cationic and anionic target compounds at different pH values in aqueous solutions [1]. Neutral nitrogen of amine group with a lone pair electrons have been found to be one of the most efficient functional groups for the removal of heavy metal ions [15,16], and protonic amino groups with a cationic charge can adsorb anionic pollutants by means of electrostatic attraction [1,17].

Polyethyleneimine (PEI), with a large amount of amino and imino groups in its polymer chain, has been widely investigated not only as an immobilization material for sensors [18–21], but also as a chelating agent for heavy metal ions removal [22–25]. Based on our preliminary work [26], a novel micro-nano structure nanofibrous affinity membranes of poly(ether sulfones) (PES) blended with PEI were fabricated by electrospinning technique followed by solvent etching in crosslinking solution. Primary investigation for the removal of copper ion was performed, indicating that this micro-nano structure nanofibrous affinity membrane owned potential application in affinity membranes.

The aim of this work is to investigate the adsorption capabilities and mechanism of the micro-nano structure PES/PEI nanofibrous membrane for the removal of heavy metal ions (that is Pb(II), Cu(II) and Cd(II), respectively) and three anionic dyes, namely Sunset Yellow FCF (SY FCF), Fast Green FCF (FG FCF) and Amaranth (AM), from aqueous solutions. The effects of various operating parameters including membrane dosage, initial solution pH value, contact time, initial solution concentration, solution temperature, and recycling efficiency of this micro-nano structure PES/PEI nanofibrous affinity membrane were thoroughly investigated. Various kinetic and equilibrium models for the adsorption of these target ions and molecules on the micro-nano structure PES/PEI nanofibrous membrane were also discussed.

2. Materials and methods

2.1. Materials

Branched polyethyleneimine (PEI) (M_w = 60,000 g/mol) in 50% (w/v) aqueous solution was purchased from Sigma–Aldrich and concentrated under vacuum at 40 °C to obtain 80% (w/v) PEI aqueous solution for further application. Poly (ether sulfones) (PES) (M_w = 64,000 g/mol) was kindly supplied by Shanghai Solvay Co., Ltd., China. The preparation process of the micro-nano structure PES/PEI nanofibrous membrane could be found in our previous work [26]. N,N-dimethylacetamide (DMAc), glutaraldehyde (GA) (25% aqueous solution), acetone, sodium hydroxide (NaOH), ethylenediaminetetraacetic acid (EDTA), $Pb(NO_3)_2$ (M_w = 331.21 g/mol), $Cu(NO_3)_2{\cdot}3H_2O$ (M_w = 241.60 g/mol), $Cd(NO_3)_2{\cdot}4H_2O$ (M_w = 308.48 g/mol), Sunset Yellow FCF (SY FCF), Fast Green FCF (FG FCF) and Amaranth (AM) were purchased from Shanghai Chemical Reagent Plant and used as received. The characteristics and structures of the dyes are summarized in Table 1.

2.2. Preparation of micro-nano structure PES/PEI nanofibrous membranes

The detailed preparation procedure of micro-nano structure PES/PEI nanofibrous membranes was shown in our previous work [26]. Firstly, PEI was concentrated under vacuum at 40 °C to obtain 80% (w/v) PEI aqueous solution. Secondly, PES was dissolved in DMAc at 50 °C for 8 h until it became a homogeneous solution. And then, PES solution and PEI solution were mixed together at 30 wt.% total polymer concentration, and a solution with PEI/PES blend ratio of 1:1.4 was used for the electrospinning experiment. Typical parameters for electrospinning experiments were as follows [26]: the applied electric voltage was 18 kV, the solution feed rate was 2.2 μl/min, and the distance between the spinneret and the collector (a grounded metallic drum) was 15 cm. The grounded rotating metallic drum with diameter of 10 cm and length of 30 cm was used to collect the deposited nanofibers at a rotating speed of 180 rpm. Finally, the electrospun PES/PEI nanofiber scaffold was immersed in GA/water/acetone solution for 2 h. In this solution, PEI was not only solvent etched by solvent water but also simultaneously crosslinked by GA. The GA crosslinking solutions were prepared by mixing water and acetone at weight ratio of 70/30, and a given amount of GA was then added into the water/acetone mixture and 0.5 M HCl solution was used to adjust the pH value of the solution to 4.0.

2.3. Measurements of micro-nano structure PES/PEI nanofibrous membranes

The morphology of the electrospun PES/PEI nanofibrous membrane was examined by scanning electron microscopy (SEM) (JSM-5600LV, Japan). The average diameter of the nanofibers in the experiment was measured from the SEM image using image analysis software. The Brunauer–Emmett–Teller (BET) surface area, pore volume and pore width of the micro-nano structure PES/PEI nanofibrous membrane were characterized by using N_2 adsorption–desorption isotherms with a surface area analyzer (ASAP 2010, micromeritics Co., USA). FT-IR spectrum was obtained in attenuated total reflectance (ATR) mode using a Nicolet 8700 FT-IR spectrometer (USA) with a resolution of 4 cm^{-1}, in the range of 4000–750 cm^{-1}. Thermal analysis was performed with a NETZSCH TG 209 F1 (Germany). The test was conducted under air purge (20 mL/min) with sample weights of about 5 mg over a temperature range of 30–900 °C at heating rate of 10 °C/min. The X-ray photoelectron spectroscopy (XPS) measurements were made on a Kratos Axis Ultra^{DLD} spectrometer (Kratos Analytical-A Shimadzu Group Company) with monochromatic Al Kα radiation as the excitation and an X-ray power of 75 W. Survey scans were taken from 0 to 1200 eV binding energies, using both electrostatic and magnetic lenses, with a 40 eV pass energy, a step size of 0.5 eV, and dwell time of 100 ms. Elemental peaks were fit using CasaXPS software