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Electrospinning of Nafion and polyvinyl alcohol into nanofiber membranes: A facile approach to fabricate functional adsorbent for heavy metals

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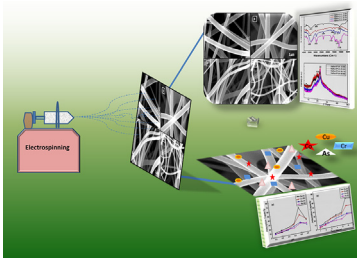
HIGHLIGHTS

- Novel approach to fabricate Nafion with PVA into nanofiber mats by electrospinning.
- Membrane possessed metal ion adsorption properties and strong mechanical properties.
- Adsorption capacity for metal ions (mg g^{-1}) Cu^{2+} 59.1, Cr^{3+} 42.5, Co^{2+} 24.7, As^{3+} 22.7.
- Scope for other applications by engineering surface area and exposing ionic properties.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel approach to fabricate Nafion PFSA resin with polymer polyvinyl alcohol (PVA) into nanofiber membrane, as a functional adsorbent for heavy metal ions had been achieved. Nafion PFSA in N,N-dimethylacetamide (DMAc) was blended with aqueous solution of PVA by sol gel method and fabricated by electrospinning. Electrospun Nafion-PVA mats had exhibited more stability, better mechanical and adsorption properties. These nanofiber membranes possessed adsorption properties based on observed adsorption capacity for Cu (II) 59.1 mg g^{-1}, Cr (III) 42.5 mg g^{-1}, Co (II) 24.7 mg g^{-1}, and As (III) 22.7 mg g^{-1} metal ions in an aqueous solution. These nanofiber membranes were characterized by Scanning Electron Microscopy (SEM), High-Resolution Transmission Electron Microscopy (HRTEM) images, Fourier-transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD) and X-ray Photoelectron Spectroscopy (XPS) for their morphological, structural and adsorption properties.

1. Introduction

Nano composite membranes had opened a great scope for chemical engineering as engineered materials can be synthesized by constituting two or more compounds with unique properties for various applications. Also electrospinning appeared to be the best tool of innovation for nano and micro fibrous membrane synthesis. Fabrication of resins, polymers into nanofiber membranes by electrospinning had been achieved successfully and widely applied in environmental chemistry for waste water treatment by adsorption

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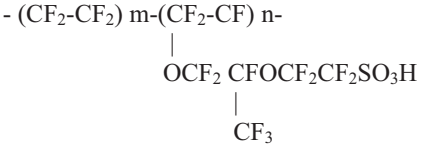
reactions, photo catalysis and others. Among them, Nafion PFSA (Perfluoro sulphonic acid) resin widely known as good membrane material due to its excellent thermal, chemical, and mechanical properties [1]. It had been extensively used for fuel cells [2–7], metal ion recovery [8,9], catalyst [10,11] and other applications.

Typically, Nafion is commercially available in several forms, including extruded and solution cast films of various thicknesses and equivalent weights (i.e., ion exchange capacities), dispersions in water/alcohol solutions, and as pellets. Nafion NR 40 is a superacid resin in a bead-form, strongly acidic resin developed for heterogeneous acid catalysis of a wide variety of organic reactions. It is a copolymer of tetrafluoroethylene and perfluoro-3, 6-dioxa-4-methyl-7-octenesulfonyl fluoride.



Electrospun nanofiber membranes of Nafion PFSA with carrier polymers polyvinyl pyrrolidone (PVP) [6–8] polyethylene oxide (PEO) [12–14], polyvinyl alcohol (PVA) [15–17], polyacrylic acid (PAA) [18], had been reported.

PFSA membranes had been extensively used in fuel cells, chlor-alkali industry, electrochemical devices, water electrolysis, batteries, sensors, and super acid catalysts and other applications [1,18]. They are widely used because of their excellent oxidative and chemical stability as well as high-proton conductivity [4], whereas only few investigations were found for PFSA membranes used as metal ion adsorbent material [8,9].

Although fabrication and electrospinning of PFSA into nanofiber membranes had been reported through improve performance, however, under mild conditions it is poorly soluble in most common solvents. PFSA chains can be dissolved in special solvent mixtures under high pressure and elevated temperature but aggregate into micelles structures when cooled to room temperature. Such aggregation results in insufficient polymer chain entanglement in PFSA solutions, rendering them unsuitable for electrospinning [8].

As a polymer PVA also possess mechanical and chemical adequacy, though PVA itself does not have fixed charges, several organic groups like hydroxyl, amine, carboxylate, sulfonate, and quaternary ammonium can be incorporated to impart hydrophilicity and/or ionic properties [2]. Several methodologies are known for cross linking/blending of compounds to obtain 3D networks in PVA for different applications.

In our study we have investigated the blending of Nafion with polyvinyl alcohol (PVA) which can be fabricated by electrospinning into nanofiber membrane. Nafion resin cannot be individually electrospun due to low shear viscosity and was electrosprayed. The affinity of Nafion with PVA for nanofiber formation had been reported in previous studies, but not yet known for metal ion removal. Therefore polyvinyl alcohol was selected as a copolymer to blend with Nafion NR40 resin to synthesize nanofiber membrane. The synthesized nanofiber mats had been characterized for their morphology, physiochemical structure and adsorption properties.

2. Experimental

2.1. Materials and Method

Nafion®40 Pellets were imported from DuPont Co. Inc., USA. Polyvinyl alcohol (PVA), N,N-dimethylacetamide (DMAc), metal salts: copper nitrate, chromium nitrate, cobalt nitrate and arsenic trioxide were purchased from Sinopharm Chemical Reagent Co. Ltd. All the chemicals and reagents used were of analytical grade.

2.2. Fabrication of Nafion and PVA and electrospinning

For fabrication of Nafion, 5% stock solution was prepared by adding 2.5 g Nafion®40 pellets into 47.5 ml DMAc solvent charged into a 250 ml three-necked flask equipped with Graham condenser attached, and provided by N_2 inlet. Nitrogen gas was supplied for 1 h to deoxygenate the solution, thereafter it was vigorously vortexed for 24 h and temperature 120 °C was maintained throughout the process.

10% PVA aqueous solution was prepared by rotation at 80 °C for 5 h. This solution is mixed with previously prepared 5% Nafion solution to blend these into a composite. For this PVA and Nafion were blended in different ratio as 90:10, 80:20, 70:30, and 60:40, thereafter rotated for 2 h to get a homogeneous solution. The solution was desonicated to remove bubble prior to use for electrospinning.

For electrospinning a 10 ml disposable syringe was used to stock each of the prepared solutions. A syringe pump was used to feed the solution through an extension tube ended in a blunted 22 gauge needle. To collect the nanofibers, an aluminum foil fixed over a glass sheet as collector was located in 18–20 cm distance from the needle. High voltage potential (15 kV) was also applied between the needle and the collector [19]. The polymer solution was forced to leave the needle and collected as nanofibers over collector. The nanofiber membranes were separated from the collector surface, dried to remove moisture and used for further analysis and application.

2.3. Characterization and instrumentation

The micrographs of nanofiber mats were analyzed by XL30 Philips SEM (Scanning Electron Microscopy, Netherland) and JEM-2011 (JEOL Transmission Electron microscopy 200 kV, Japan). X-ray diffraction patterns of the membranes were recorded using an X-ray Diffractometer (D/MAX-rB, Rigaku, Japan). Also Fourier-transform infrared spectra (FT-IR Spectroscopy) of fiber samples was recorded on a Bruker Vector 22 spectrometer (USA). For adsorption detection the metal ion solutions concentrations were determined by an Inductively Coupled Plasma spectrometer (ICP, Optima 2100 DV, USA), also chemical bonding and adsorption of metal ions on surface of nanofiber mats was confirmed by X-ray Photoelectron Spectra (XPS, Axis Ultra DLD, Kratos).

2.4. Adsorption of metal ions on Nafion/PVA membranes

2.4.1. Adsorption behavior of membrane and effect of contact time

The adsorption of Cu^{2+}, Cr^{3+}, Co^{2+} and As^{3+} metal ions from aqueous solution was investigated by batch method. All metal ion solutions were prepared containing 100 mg l^{-1} concentration of each metal and solution pH 5.9 was maintained, this was adjusted with HNO_3 or NaOH solutions at the beginning of each experiment (not controlled afterwards). Dried membranes samples 0.05 g were equilibrated in aqueous solutions (100 ml) which were agitated at a constant speed of 150 rpm at 30 °C. The effect of contact time on the adsorption by the membranes was studied for every 60 mins. until 10 h to get 5 consecutive values. Membranes were removed and the solution was filtered using a 0.45 mm Uniflo filter. The concentrations of the metal ions in the solution were determined using an ICP/OES spectroscopy.

All experimental samples were run in triplet to ensure accuracy. Adsorption capacity of membranes for amount of metal ions adsorbed per unit mass of the membrane (mg metal ions/