Desalination 351 (2014) 220–227

Contents lists available at ScienceDirect

Desalination

journal homepage: www.elsevier.com/locate/desal

Preparation and antifouling properties of PVDF ultrafiltration membranes with polyaniline (PANI) nanofibers and hydrolysed PSMA (H-PSMA) as additives

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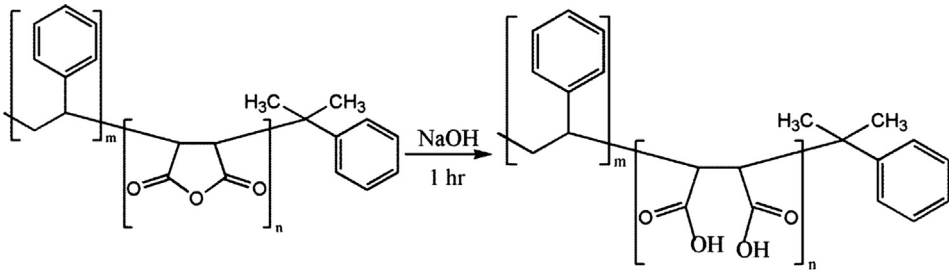
HIGHLIGHTS

- PANI nanofibers were used as hydrophilic agent for PVDF UF membranes
- Hydrolysed PSMA was used as an additive
- Membrane properties enhanced with PANI nanofiber content
- 1.0 wt.% of PANI nanofibers was the threshold content for the prepared membranes
- Membranes showed high rejection for heavy metal ions Pb^{2+} and Cd^{2+}

GRAPHICAL ABSTRACT

PVDF ultrafiltration membranes were prepared by phase inversion method with hydrolyzed polystyrene-co-maleic anhydride (H-PSMA) and PANI nanofibers as additives. Membranes showed better permeability, antifouling properties and high rejection of 98.52% and 97.38% for heavy metal ions Pb^{2+} and Cd^{2+} respectively.



PSMA **Hydrolyzed PSMA (H-PSMA)**

ARTICLE INFO

Article history:
Received 5 April 2014
Received in revised form 1 August 2014
Accepted 2 August 2014
Available online xxxx

Keywords:
PANI nanofibers
PVDF
H-PSMA
Ultrafiltration membrane

ABSTRACT

Polyaniline (PANI) nanofibers were used as hydrophilic additives to study their effect on the performance of polyvinylidene fluoride (PVDF) ultrafiltration (UF) membranes. PVDF UF membranes were prepared by the phase inversion method with hydrolyzed polystyrene-co-maleic anhydride (H-PSMA) and PANI nanofibers as additives. PANI nanofibers were synthesized by rapid mixing reaction and were used as a hydrophilic modifying agent with varying concentrations (0–1.5 wt.%) in the membranes. The synthesized PANI nanofibers were characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), scanning electron microscope (SEM) and transmission electron microscope (TEM) analysis. Hydrolyzed PSMA was prepared by the hydrolysis of PSMA and was used as a novel pore forming additive. The addition of PANI nanofibers into the membranes increased the membrane hydrophilicity, porosity, water uptake and permeability. The membranes also showed good antifouling nature during BSA (bovine serum albumin) filtration when compared to the pristine membrane without PANI nanofibers. Membrane with 1.0 wt.% PANI content showed highest permeability among the synthesized membranes. The membrane having highest permeability was subjected to heavy metal ion rejection which showed high rejection of 98.52% and 97.38% for heavy metal ions Pb^{2+} and Cd^{2+} respectively.

1. Introduction

Membrane filtration is one among the most promising technologies for water treatment application [1]. Ultrafiltration membranes have

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http://dx.doi.org/10.1016/j.desal.2014.08.002
0011-9164/

been widely used in various separation processes, generally in water treatment [2]. The properties of a membrane such as its hydrophilicity, porous structure, and antifouling nature have great influence on membrane performance [3]. Achieving high permeability, high surface porosity and good pore structure of membranes is very crucial [4]. These properties are usually observed in asymmetric membranes. Among the various polymer materials, polyvinylidene fluoride (PVDF) is one of the outstanding materials that can form asymmetric membranes [2,5].

PVDF is considered as one of the excellent polymer materials in membrane science [5,6]. This homopolymer contains alternating CH_2 and CF_2 groups along the polymer chain making it a distinctive polymer. It provides high mechanical strength, good chemical resistance, and thermal stability and also exhibits good membrane forming abilities [6]. Most of the polymeric materials applied to water treatment like PVDF are hydrophobic in nature. When a hydrophobic polymer membrane comes in contact with the protein solutions, fouling takes place on the membrane surface. Therefore, the hydrophobic nature of PVDF often results in intense membrane fouling and tremendous decline of water flux which limits its use in water treatment [7].

Many studies have been performed to improve the hydrophilicity of PVDF membranes such as physical blending, plasma treatment, chemical grafting, surface modifications, and blending with hydrophilic additives [8]. Polystyrene-co-maleic anhydride (PSMA) is a hydrophobic, alternating copolymer having alternating styrene and maleic anhydride units. PSMA can behave as a dispersant in soluble form because of its alternating structure, and is also used as an additive in blends or composites [9]. On hydrolysis in alkaline conditions, the anhydride ring of PSMA opens up and gives two carboxylic groups making it hydrophilic and hence can be used as an hydrophilic additive [10].

In the recent years, modifications on PVDF blends have been devoted to the blending of polymers with inorganic materials [4]. Nanoparticles which have been used to modify the PVDF membranes include alumina Al_2O_3 [2], silica (SiO_2) [11], ZnO [12], and TiO_2 [13] nanoparticles. These nanoparticles when used as additives enhance the pore formation and the interconnectivity of pores in the membrane and also improve the membrane hydrophilicity [14].

Polyaniline (PANI) is a well-known polymer which has gained importance due to its ease of preparation, high conductivity, chemical stability, and low cost and also exhibits great separation characteristics [15]. PANI nanofibers possess high surface energy and hydrophilic property because of which they are used to achieve super hydrophilic surfaces [16]. PANI has been used to prepare membranes for gas separation, pervaporation and electrodialysis [15].

Zhao et al. [17] reported that polysulfone (PSf) UF membranes with poly(vinylpyrrolidone) (PVP) and PANI nanofibers as additives exhibited higher protein rejection, higher antifouling property, better additive stability than PSf/PVP membranes. Fan et al. [18] prepared nanocomposite UF membranes with PANI nanofiber layer on the polysulfone substrate layer. The nanocomposite membrane showed better permeability and good hydrophilicity than the polysulfone substrate layer. Zhao et al. [19] prepared PSf/PANI nanocomposite membranes with *N*-methyl-2-pyrrolidone (NMP) as solvent. The nanocomposite membranes exhibited hydrophilic surface, higher porosity, wider pores beneath the skin layer, and less macrovoids than the neat PSf membrane. Fan et al. [16] studied the effect of PANI nanofibers on the structure and performance of the polysulfone membrane. PANI-polysulfone membranes showed better permeability, less fouling and better pore interconnection than the polysulfone membrane. However the effect of PANI nanofibers on PVDF membranes has not yet been studied. As PVDF membranes are hydrophobic, an attempt has been made to improve its hydrophilicity by the addition of PANI nanofibers.

In the present work, polyaniline (PANI) nanofibers and H-PSMA were used as hydrophilic additives to improve the hydrophilicity of PVDF. Polyaniline nanofibers were added in increasing concentrations into the PVDF–HPSMA membranes and their effect on membrane performance was studied. To the best of our knowledge it is the first time polyaniline (PANI) nanofibers and H-PSMA were being used as additives in PVDF membranes.

2. Experimental section

2.1. Materials

PVDF (M_w ~ 1,80,000), poly(styrene-co-maleic anhydride), cumene terminated (PSMA) (M_n ~ 1600) and aniline (99.5%) were purchased from Sigma-Aldrich Co., Bangalore, India. Ammonium peroxydisulfate (APS) and bovine serum albumin (BSA) (M_w ~ 69 kDa) were purchased from Central Drug House (CDH), New Delhi, India. Hydrochloric acid (HCl) and *N*-methyl-2-pyrrolidone (NMP) were purchased from Merck India, Ltd. Polyethyleneimine (PEI) (M_n ~ 60,000), 50 wt.% aq. solution (branched), was purchased from Acros Organics, USA. Cadmium nitrate tetrahydrate and lead (II) nitrate were purchased from Sigma-Aldrich Co., Bangalore, India.

2.2. Preparation of PANI nanofibers

PANI nanofibers were prepared by rapidly mixing reactions, a facile one step method using APS as oxidant, following the procedure reported in the literature [20]. First an aqueous solution of aniline (3.2 mmol) in 1 M HCl and solution of APS (0.8 mmol) in 1 M HCl were prepared. In the typical reaction, the two solutions were rapidly mixed under stirring to ensure sufficient mixing before the polymerization. Polymerization was observed when the aqueous dispersion turned to characteristic green color of polyaniline. The product formed was isolated from the dispersion by centrifugation, purified using HCl and water until the suspension reached a neutral pH and then dried in oven at 40 °C for 24 h.

2.2.1. Characterization of PANI nanofibers

FTIR spectrum and X-ray diffraction (XRD) pattern were obtained to confirm the formation of PANI nanofibers. An ATR-FTIR spectrophotometer (JASCO 4200) was used to obtain the IR spectrum. XRD pattern was obtained from Rigaku Miniflex 600 with Cu Kα radiation. Scanning electron microscope (JEOL JSM-6380LA) and transmission electron microscope (JEOL JEM-2100) were used to observe the morphology of the PANI nanofibers.

2.3. Hydrolysis of polystyrene-co-maleic anhydride (PSMA)

PSMA was subjected to hydrolysis in aqueous solution under alkaline conditions (Scheme 1). PSMA (2 g) was added to 100 mL of 1 N NaOH solution and stirred for 1 h until complete dissolution took place. The hydrolyzed-PSMA (H-PSMA) was precipitated using 1 N HCl adding drop wise until white precipitate was obtained. The hydrolyzed product was washed with minimum amount of water to neutralize the acid and kept for drying in oven for 24 h.

2.4. Preparation of PVDF–H-PSMA–PANI membrane

PVDF–H-PSMA–PANI membranes were prepared by immersion precipitation method [21] as follows. First 2 wt.% of H-PSMA was dissolved in NMP under stirring. Then the synthesized PANI nanofibers were added to the solution. The solution containing PANI nanofibers was sonicated for 30 min for their uniform dispersion and then kept under stirring. Then 20 wt.% PVDF was added to the same dispersion and stirred for 15 h at 70 °C. After the complete dissolution of PVDF, the casting solution was sonicated for 15 min and left still for 30 min to remove any trapped air bubbles. The solution was then casted on to the glass plate and dipped in the water coagulation bath for 24 h for the phase inversion to occur. The PVDF and H-PSMA concentration in the casting solution was fixed at 20 and 2 wt.% respectively for all the membranes, whereas the concentration of PANI nanofibers was varied as 0, 0.1, 0.5, 1.0, and 1.5 wt.% and accordingly the membranes were