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Synthesis and desalination performance of Ar^{+}–N^{+} irradiated polysulfone based new NF membrane

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ABSTRACT

In the last few years, membrane technology has gained more attention from polymer chemists throughout the globe. Nowadays, surface modification of membrane is very useful in biotechnology and food science. In the present investigation, we have synthesized polysulfone based composite nanofiltration (NF) membranes, and characterized these membranes by FT-IR, SEM and membrane performance studies. Surface plasma treatment was carried out by irradiation with argon and nitrogen beams in suitable conditions. It was observed that nitrogen beam caused surface roughness that was more severe than the Ar beam. After irradiation, water contact angle was slightly increased. For pure water permeability, flux increased linearly with the operating pressure. However, for the salt solution, the flux was decreased marginally and salt rejection increased after irradiation due to surface modification. The modification effect was characterized in terms of contact angle, AFM employed roughness measurement and dielectric property. It revealed that irradiated NF membranes showed higher salt rejection and lower flux as compared to the nonmodified membranes. Accordingly, the roughness of the membrane surface intensively affected the performance of RO membrane.

1. Introduction

The need for drinking water with good microbiological and chemical quality is clearly increasing around the world. Simultaneously, membrane processes have met a large expansion in desalting of brackish and seawater in the two last decades. In the 20th century, membrane technologies have made great progress, and commercial markets have been spreading very rapidly. Porous membranes are a major tool in water treatment. The transfer mechanism of RO membranes involves both pore flow and solution diffusion. Categorically, four types of membranes are distinguished, namely reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF) and microfiltration (MF) [1]. At present, reverse osmosis (RO) is the best possible membrane process in liquid/liquid separation. Because of vastly expanding populations, increasing water demand, and the deterioration of water resource quality and quantity, water is going to be the most precious resource in the world. Therefore, RO membranes play very crucial roles in obtaining fresh water from nonconventional water resources such as seawater and wastewater [2]. Not only in water treatment, but by tailoring appropriate [3] pore size, pore structure and pore distribution, membranes can be used for fuel cell and other filtration applications too.

According to Zhou et al. [4], in RO and NF membranes, water molecules (0.27 nm) permeate while hydrated salt ions (e.g. Na^{+1} 0.72 nm diameter) are rejected. The efficiency of the membrane can be improved by two methods, the phase inversion method and surface modification by interfacial polymerization for thin film composite membranes. The pore size of the membrane can be controlled by phase inversion techniques but getting symmetric pores is still a big challenge. Usually, composite RO and NF membranes are prepared by phase inversion technique [5]. Recently, surface modification [6] has been used to increase the efficiency of RO membranes, thin film composites [5] and charged surface membranes [7].

Recently, the transport parameters of the RO composite membranes have been tested by performing electron radiation and gamma radiation on RO composite membranes, so that these membranes can be used in the treatment of radioactive liquid effluents with an activity that involves an absorbed dose in the membrane within the studied range [8].

Cold plasma treatment to the polymers changes their properties such as biocompatibility permeability, adhesion, and hydrophilicity. The surface reactions on polymers are etching, cleaning, cross-linking,

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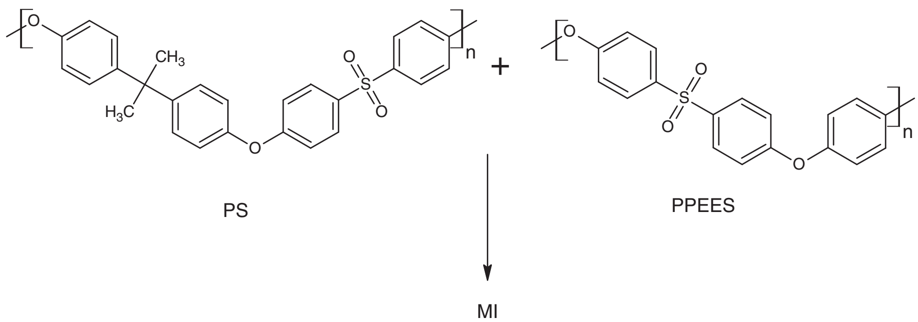

Fig. 1. Schematic representation of formation of composite membrane (M1).

grafting, addition, substitution, and formation of functional groups depending on the presence of active species in plasma [9]. Cold plasma is a mixture of electrons, ionized gas and molecular fragments of the gas. Its contents and effect on the material surface depend on the composition of the gas in the discharge, the composition of the sample treated and all the process parameters. This type of surface modification is effective for water purification [10].

A very popular technique is surface grafting—a technology that can provide polymers with a new, stable and monofunctional surface. The most versatile technique seems to be cold plasma and its applications for treatment of polymer surfaces have grown rapidly in the last decade. A great contribution to this is the fact that plasma techniques are fast, clean and environmentally friendly [11].

In the present investigation, we have synthesized polysulfone based nanofiltration (NF) membranes, and characterized these membranes by FT-IR, SEM and membrane performance studies. Surface modification was done by bombarding with argon and nitrogen under suitable conditions. The modified polymer was characterized by the contact angle, AFM and dielectric property. The desalination properties of surface-modified membranes were compared with the original membrane [12].

2. Experimental

2.1. Materials and methods

Polysulfone (PS) with a molecular weight of 35,000 Da and poly (1,4-phenylene-ether-ether sulfone) (PPEES) were obtained from Sigma-Aldrich, Co., Germany. 1-Methyl-2-pyrrolidone (NMP) and analytical grade NaCl were procured from Merck India, Ltd. These were used without any further purification.

Solutions containing 80 wt.% of PS (0.8 g) and 20 wt.% of PPEES (0.4 g) in 4.5 ml of 1-methyl-2-pyrrolidone (NMP) were prepared by mild stirring for 24 h at a constant temperature of 65 °C. The so obtained viscous solution was cast over a glass plate using K-Control coater. Further the cast membrane was kept for slow solvent evaporation and finally the membrane (M1) (Fig. 1) was separated by spraying water at the sides and stored in double distilled water [13–15].

2.2. Plasma treatment

Irradiation with N^+ and Ar^+ beams was carried out in a vacuum chamber [13]. Since the mass of Ar^+ is larger, the energy used for beam bombardment was chosen to be double of that used for N^+ beams and the two energy levels used were 30 and 60 kV, respectively. Membranes were then characterized for water contact angle (contact angle meter, model OCA 15 EC, Data Physics Company), surface roughness using atomic force microscopy (Nanosurf®, easyScan2), and dielectric constant using LCR meter (Agilent Technologies) [16].

2.3. Flux-retention measurement

Flux-retention measurements were carried out with a 3.5% sodium chloride solution (35,000 ppm) at different pressures ranging from 2 to 14 bar pressure. Pure water was prepared using Milli-Q-Plus demineralising unit and pure water permeability was measured. The flux-rejection measurements were carried out in a stirred dead-end filtration set-up containing membranes with an area of 12.5 cm^2. The stirred permeation cell was pressurized by nitrogen. The obtained data was recorded as a function of pressure by means of a computer. The concentrations were determined by conductivity measurements [17–19].

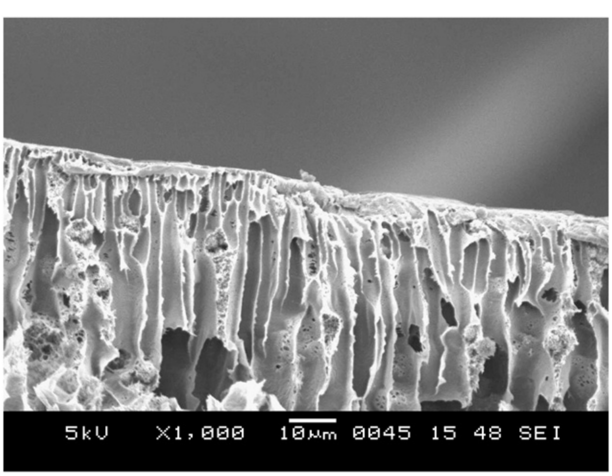

Fig. 2. Cross-section of membrane M1.

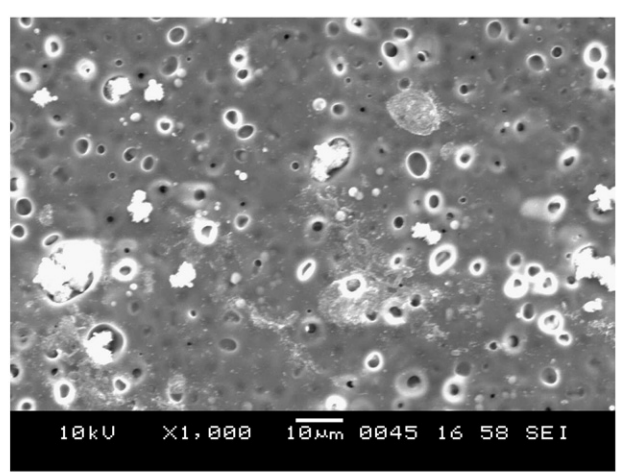

Fig. 3. Surface picture of M1.