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PREPARATION OF POLYSULFONE NANO-STRUCTURED MEMBRANE FOR SULPHATE IONS REMOVAL FROM WATER

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ABSTRACT

Polysulfone nanofiltration (NF) membranes with higher pore size and higher charge density are capable of removing metal ions from water. In the present study the graft-modification of ultrafiltration (UF) membranes by UV irradiation was considered. UF membranes were prepared via phase inversion method using polysulfone (17% wt) as polymer and N-methyl-2-pyrrolidone (75% wt) as solvent in which polyethylene glycol with molecular weight of 3000 g/mol (8% wt) was used comparatively as big sized pore former. Prepared UF membrane was modified by polymerization of acrylic acid as monomer in the presence of UV irradiation on the membrane surface. Effect of grafting conditions including acrylic acid concentration and irradiation time on membrane performance properties as pure water flux and sulphate rejection were studied. FTIR-ATR and AFM were employed to characterize the chemical and structural changes on the modified membrane surface. The results showed pure water flux significantly declined and sulphate rejection improved with increase in both graft irradiation time and monomer concentration. At 25 °C, pure water flux of this prepared NF membrane was 13.26 L/m^2.h at 300 kPa. The rejection of 96.3% and 58.8 % to Na_2SO_4 and $MgSO_4$ solutions were obtained respectively. The RMS roughness of this membrane was 1.65 nm which is in the range of NF membrane properties.

Key words: Sulphate ion; Nanofiltration Membrane; Polyethylene glycol; Polysulfone; UV graft

INTRODUCTION

A large amount of metal ions are released by human activities in the environment: air, water and ground. Water pollution is one of the most significant environmental problems in the world. The main techniques currently used for the treatment of water polluted by metallic species are the traditional physicochemical methods such as the precipitation by chemical agents, the adsorption on activated carbon, the ion-exchange on resins and the membrane processes (ultra- and nanofiltration, reverse osmosis, electro-membrane processes) among which the filtration techniques can easily and cheaply separate the metal ions in their colloidal forms or in the particle state. On the other hand, for metal ions in a dissolved state, more complex techniques like ion-exchange, nanofiltration and reverse osmosis should be used to remove the ions.

Nanofiltration membrane is a kind of pressure-driven membrane between reverse osmosis (RO) and ultrafiltration membrane (Schafer *et al*., 2005). It has advantages such as low operation pressure, high permeate flux, high rejection of multivalent anion, relatively low investment, low operation and maintenance cost and environmental friendliness. Modified polysulfone (PSf) NF membranes may be prepared from an UF membrane through UV-graft modification in order to remove metal ion pollutions from water. Modification of UF membrane can be performed through either membrane material modification (Liu and Bai 2005; Chakrabarty *et al*., 2008; Rahimpour *et al*., 2008;) or membrane surface modification (Bequet *et al*., 2002; Qiu *et al*., 2005; Akbari *et al*., 2006).

In the present work, both of these modifications

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were applied. PSf nanofiltration membranes were prepared from origin UF membrane during a modification step in order to remove metal ions from water. Origin PSf UF membrane was prepared via phase inversion process (Scott, 1990). Polyethylene glycol (PEG) was used in MW of 3000 Da as pore former agent as far as a membrane with no PEG, had no pore and no pure water flux (PWF) (Bowen *et al*., 2001). Then, in the modification step, UV photografting process was applied in the presence of acrylic acid (AA) for membrane surface modification. This method may impart not only the hydrophilicity, but also the new functions such as decreasing in pore size, giving negative charge to membrane surface and finally causing formation of nanofiltration membrane. The goal of our research was to conduct a detailed investigation on graft condition on membrane morphology and performance.

MATERIALS AND METHODS

Materials

Polysulfone (PSf, MW: 75000 Da) was supplied by Acros Organics and used as membrane material. N-methylene-2-pyrrolidone (NMP) from Merck Co., Germany, as a solvent for PSf was used without further purification. Polyethylene glycolwith average molecular weights (200, 400, 600, 2000, 6000, 10000 and 20000 Da.) were purchased from Merck Co. Acrylic acid was purchased from Merck and used as received. Other chemicals were supplied from Merck Co.

Methods

Original membrane preparation

Original PSf membranes were prepared through phase inversion process using a homogenous polymeric solution containing PSf (17% wt), PEG (8% wt) and N-methyl-2-pyrrolidone (NMP) (75% wt). After achieving a homogenous and transparent solution, dope solution was cast using an adjustable casting knife on a glass plate. Then the glass plate bearing PSf solution film was immersed into water coagulation. After about 1 minute of phase inversion progress (solvent exchange between polymer and non-solvent), membrane was formed. During phase inversion process, dissolving PEG in water causes formation of porous PSf membrane. The obtained membrane belongs to UF category of membranes.

Membrane modification

After fabrication of PSf UF membrane via phase separation method, membrane modification by UV- assisted grafting polymerization in the presence of AA, was performed. UV-induced grafting process, increases membrane wettability and shifts membrane pore size distribution to a smaller size and makes NF membrane. A schematic drawing of UV irradiation chamber is shown in Fig. 1.

RESULTS

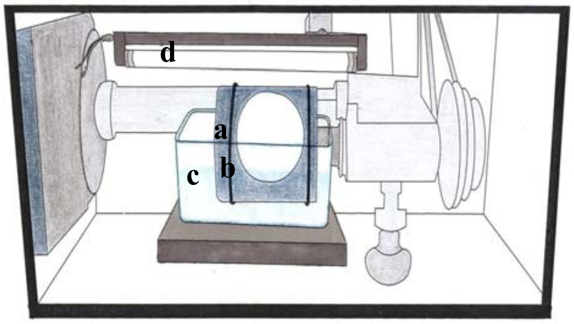


Fig. 1: UV-Irradiation chamber including:
(a) membrane sample, (b) rotating cylinder,
(c) monomer solution, (d) UV-lamp

FT-IR spectroscopy

The efficiency of UV-graft reaction was checked by FT-IR measurement before and after UV-irradiation treatment (Fig. 2). In b, c and d spectra, there were two bands, one at 3396 1/cm assigned for (OH) and another large band at 1732 1/cm due to (C=O). With increase in irradiation time (t_{irr}), transmission peak intensity decreased that can be contributed to increase in AA deposition on surface. Whilst in spectra of original membrane (a), no band at 3396 and 1733 1/cm was observed.

AFM analysis

From 3-dimensional photographs of one original and modified membranes, it can be seen that with increasing in irradiation time, roughness decreased from 7.8 to 1.65 nm. On the basis of information existent in references, asymmetric reverse osmosis and nanofiltration membranes

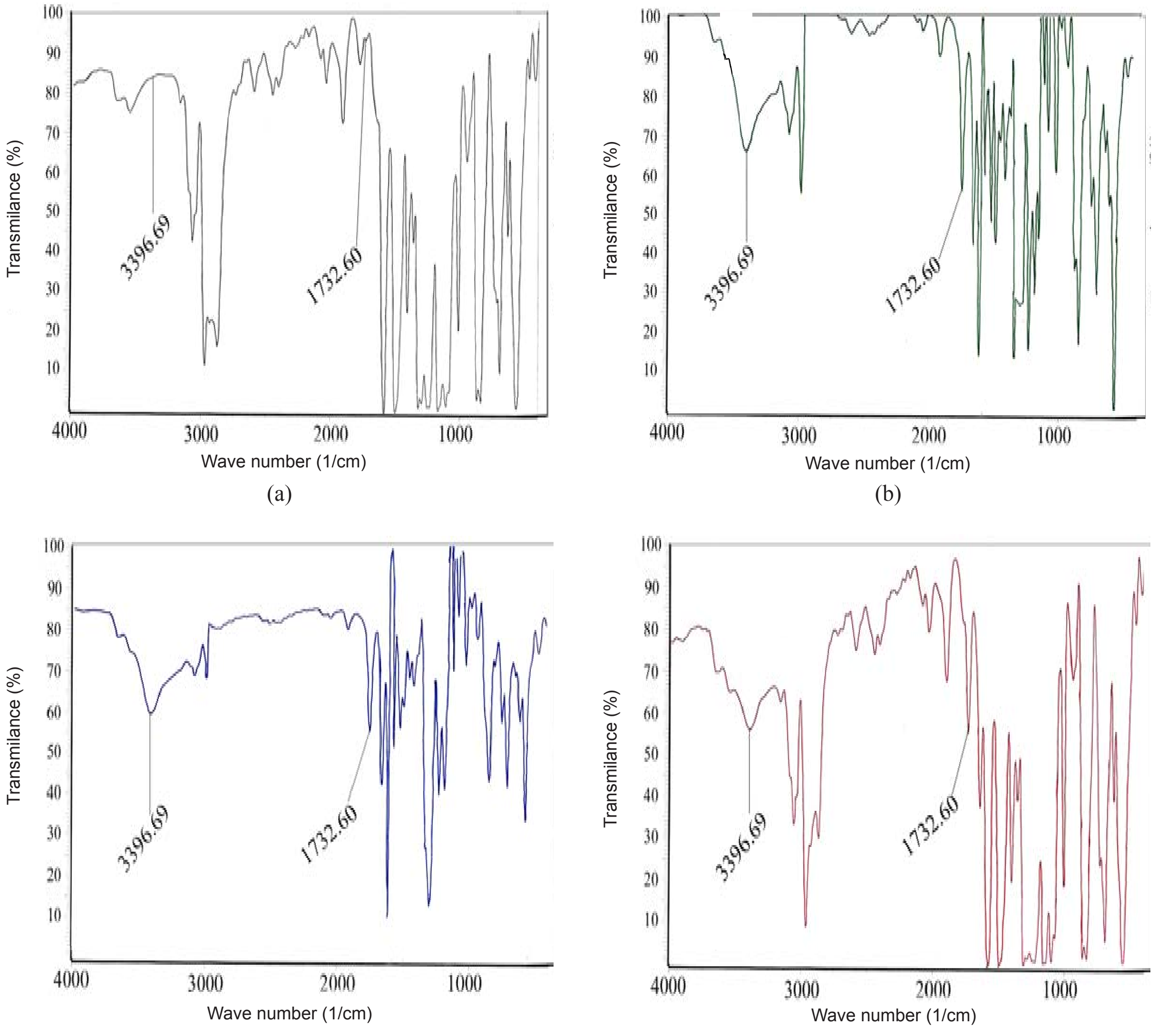


Fig. 2: FT-IR spectroscopy of membranes: (a) origin membrane; (b) photografted membrane for 1h; (c) for 2h and (d) for 3h ([AA]=6%)

feature small roughness parameters, ranging from 0.84 to 5.14 nm (Khulbe *et al*., 2007); so this roughness range confirmed that membranes were in NF membrane category. The decrease in surface roughness is an evidence of pore size decrease (Khulbe *et al*., 2007).

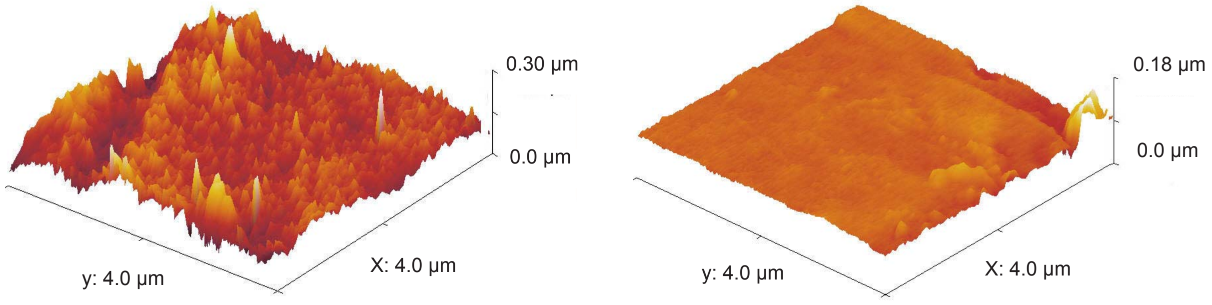
Filtration experiments

Effect of graft condition

Effect of graft condition (AA concentration and irradiation time) on membrane performance was investigated (Figs. 4 and 5). It was found that increase in graft parameters leaded to decrease in pore size from 9.01 to 3.42 nm (from MWCO calculations (Causserand *et al*., 2004)), increase in charge density around pores and finally induced decrease in PWF, increase in MWCO and rejection of 0.001 M sulphate solutions. It is worth noticing that the rejection related to each sulphate was different from others. Generally rejection decreased in the following order:

$Na_2SO_4 > MgSO_4$

Induced negatively charged NF membrane rejected



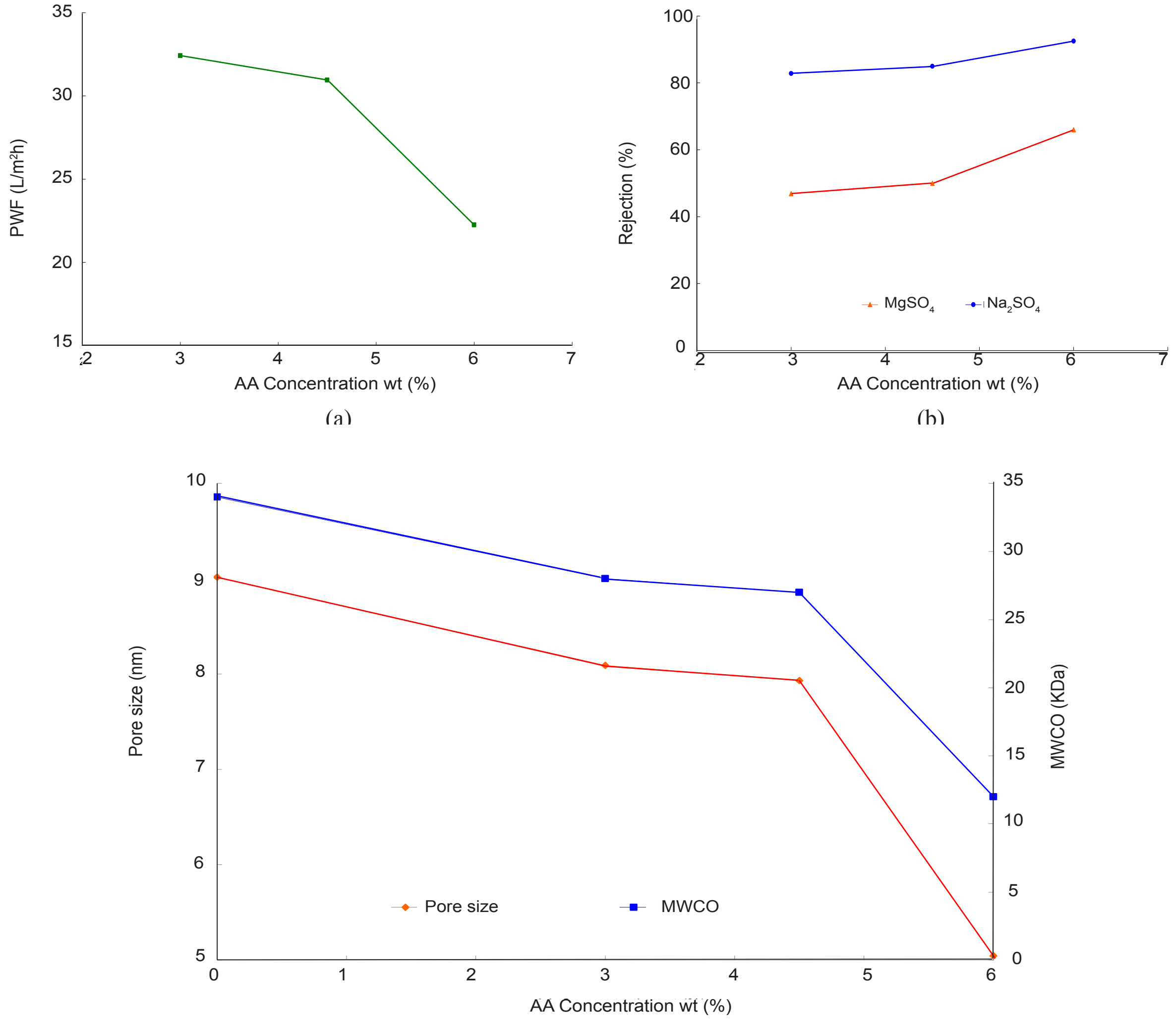
(a) (b)

Fig. 3: Three dimensional AFM images: (a) origin membrane; (b) photografted membrane ([AA]=6% for 3h)

electrolyte solutes with lower cationic charge density ($Na^+ > Mg^{2+}$). This order is according to Donnan effect (Schafer *et al*., 2005).

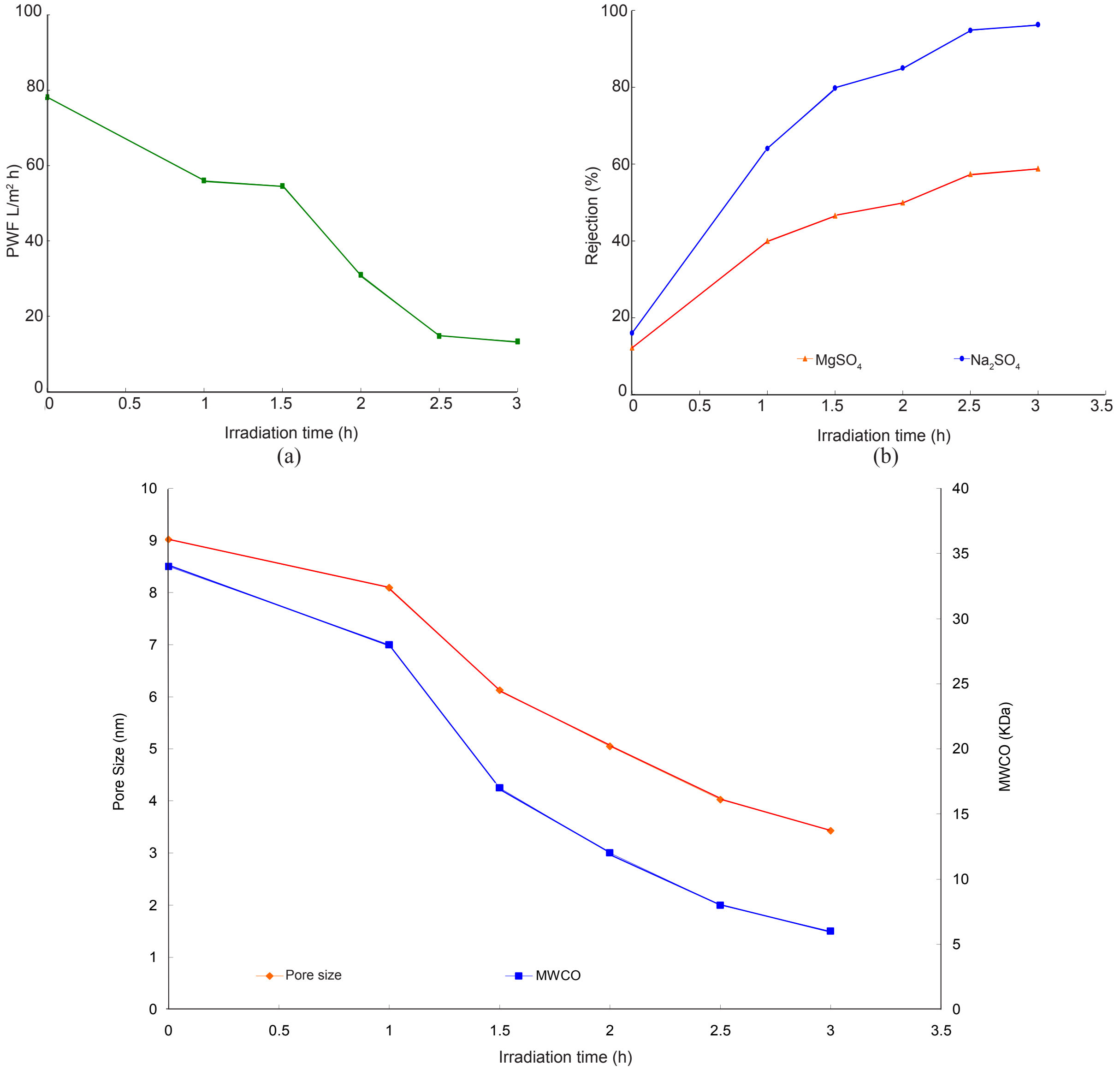
DISCUSSION

Prepared PSf NF membranes succeeded in removal of sulphate ions such as Na2SO4 (up to 96%) and MgSO4 (50%) from water in a low operating pressure (300kPa). Generally,



(c)

Fig. 4: Effect of AA concentration on PWF (a), sulphate rejection (b) and pore size (c) (t_{irr}= 2h)



(a)

(b)

(c)

Fig. 5: Effect of irradiation time on PWF (a), sulphate rejection (b) and pore size (c) ([AA]= 4.5%)

modification processes make the NF membrane a possible candidate for water softening (Rahimpour *et al.*, 2008; Anim-Mensah *et al.*, 2008; Ghizellaoui *et al.*, 2005; Bodzek *et al.*, 2002; Bequet *et al.*, 2000). Rejection of MgSO4 and NaCl has been shown 90% and 67%, respectively (Rahimpour *et al.*, 2010). PSf NF membranes were prepared from an UF membrane in a two steps procedure. In the first step an appropriate UF membrane with desirable pore size was prepared from phase inversion process. In the second step, the pore size declined by an UV-induced polymerization. NF performance improved by using PEG (in the first step) and graft condition (in the second step). As a result from the experiments, increase in graft intensity (monomer concentration and irradiation time) lead to decrease in pore size from 9.01 to 3.42 nm which is accompanied by PWF decrease, sulphate rejection increase and MWCO decrease. Effect of irradiation time on PWF was more intensive rather than monomer concentration. These negatively charged NF membranes rejected electrolyte solutes with higher anionic charge density and with lower cationic charge density more effectively. Occurrence and intensity of AA polymerization onto the membrane surface were confirmed by FT-IR spectroscopy. Polymerizing AA onto pore surface and pore walls lead to decrease in surface roughness from 7.8 to 1.65nm.

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