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Self-assembled nanofiltration membrane containing antimicrobial organosilica prepared by sol–gel process

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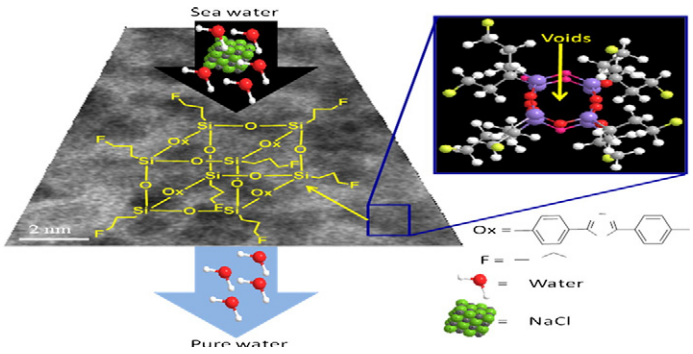
HIGHLIGHTS

- Synthesis of organosilaxane (APDSPO) by Barbiar–Grignard reaction
- Antimicrobial membrane to avoid biofouling
- Stable nanofiltration membranes
- Anti-biofouling NF membrane for water desalination/purification

GRAPHICAL ABSTRACT



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ABSTRACT

A new silica monomer precursor, bis(4′-aminopropyldiethoxysilylphenyl) 1,3,4-oxadiazole (APDSPO), was synthesized by Barbiar–Grignard reaction. Nanofiltration membranes containing APDSPO (biocide active) and polyvinyl alcohol (PVA), were prepared by acid catalyzed sol–gel followed by formal cross-linking. These membranes were designed with good stabilities (hydraulic, mechanical and chemical), separation performance, and low surface roughness. These membranes showed microbial growth inhibiting properties and thus anti-biofilm/fouling nature. About 35.2 L m^{-2} h^{-1} flux and 54.5% salt rejection for feed NaCl solution (1 g/L) at 0.62 MPa applied pressure, indicate the suitability of membrane (PO-6) for water purification. Membrane performance data also ruled out anti-biofouling nature of PO-6 membrane.

1. Introduction

Pollution of surface or ground water by excess salt, infatuated water-borne bacteria, virus and pathogens, etc. is a serious problem for providing drinking water [1]. Membrane based water purification technologies, such as nanofiltration (NF), has wide range of advantages like low energy consumption, easy integration and scaling up in comparison with traditional separation methods [2,3]. Generally, NF membranes are derived from poly amide and the chemical is unstable in the presence of sanitizing agents, especially chlorine, which is generally used for preventing bacteriological contamination of potable water [4,5]. Growth of microorganisms on the membrane surface (biofouling) is the most serious problem for these membranes, which severely affects the membrane performance [6,7]. Autopsy studies of fouled membranes (NF used during water desalination/treatment) confirmed more than 50% (w/w) of dry fouling layers of biological origin [8,9]. Unlike organic–inorganic fouling, biofouling cannot be reduced by pretreatment, because of

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the self-replicating nature of microbes [8]. Therefore, absence of anti-biofouling properties of the membranes jeopardizes their long durability [10–12].

Generally, three strategies: biocide dosing (continuous or intermittent), chemical or physical cleaning procedures, and developing a membrane resistant to biofouling, are used to avoid biofouling. Biofouling membrane for water treatment poses particular challenges because of its architecture (pore size, surface roughness and charged nature), and chemical, mechanical and hydraulic stabilities. Polysiloxane based polymers are generally used for health care [13], and biomedical products [14–16], because of their low cytotoxicity and desirable physical properties [17]. In general charged membranes exhibited better salt rejection, separation and anti-fouling characteristics in comparison with uncharged NF membranes [18–20].

On hydrophobic membrane surfaces, water born microbes (*Escherichia coli*) easily grow and deteriorate their throughput. To reduce the membrane biofouling, silver and TiO_2 nanoparticles were previously used [21–23]. Compounds bearing 1,3,4-oxadiazole ring possess significant biological properties including antifungal, antibacterial and antiviral [24]. PVA cross-linking was employed to obtain highly functionalized membranes with reasonable swelling and without impairing other properties [25]. We adopted both approaches to architect a stable membrane with high separation performance.

In this work, we are reporting phosphonic acid functionalized 1,3,4-oxadiazole based antimicrobial organic–inorganic nanocomposite membrane derived by acid catalyzed sol–gel in aqueous media. Cross-linked membranes exhibited high stabilities (thermal, mechanical, dimensional and chemical), and antimicrobial activities under saline conditions. Furthermore, high membrane flux and about 54.5% salt rejection indicate the suitability of prepared membrane for water purification.

2. Materials and methods

2.1. Materials

Aminopropyltriethoxysilane (APTEOS) (99%) was obtained from Sigma-Aldrich chemicals. PVA (Mw: 125,000), formaldehyde (37% in water), phosphorous acid, hydrochloric acid (HCl), sulfuric acid (H_2SO_4), *p*-chloro benzoic acid, hydrazine hydrate, sodium hydroxide (NaOH), sodium chloride (NaCl)l, sodium hypochlorite, *N*-methyl pyrrolidone (NMP), dimethylformamide (DMAc), hexane, iodine crystal, magnesium turnings, tetrahydrofuran (THF), acetone and methanol, etc. were obtained from s d fine-chem ltd, Mumbai, India. Luria Agar base (Miller's modification), Luria Bertani HiVeg™ Broth, Miller were purchased from HiMedia Laboratories Pvt. Ltd. Mumbai, India. Solvents were used after proper distillation, while double distilled water was used for experiments.

2.2. Synthesis of APDSPO monomer

APDSPO organosiloxane was synthesized by Barbier–Grignard reaction (Fig. 1). To a three-necked round-bottom flask (250 mL) (equipped with a magnetic stirrer, nitrogen inlet, drying tube, condenser, and funnel) mixture of Mg turning (1.5) and APTEOS (44.4 mL; 0.2 mol) in THF (30 mL) and crystal of iodine were added under refluxed and stirred conditions. After 30 min, 20 mL solution of bis(4-chlorophenyl)-1,3,4-oxadiazole (2 mmol) in THF was slowly added in drop wise manner. A greenish yellow colored viscous liquid was obtained after 10 h refluxing, and mixture was cooled at room temperature followed by removal of THF using vacuum rotary evaporator. To the obtained viscous liquid, 30 mL hexane was added and filtered for removal of impurities.

Yield: 63% (yellow colored); analytically calculated for [$C_{28}H_{44}N_4O_5Si_2$] (572.84): C, 58.70; H, 7.74; N, 9.76; Si, 9.81; experimentally found: C, 58.68; H, 7.72; N, 9.71; Si, 9.80.

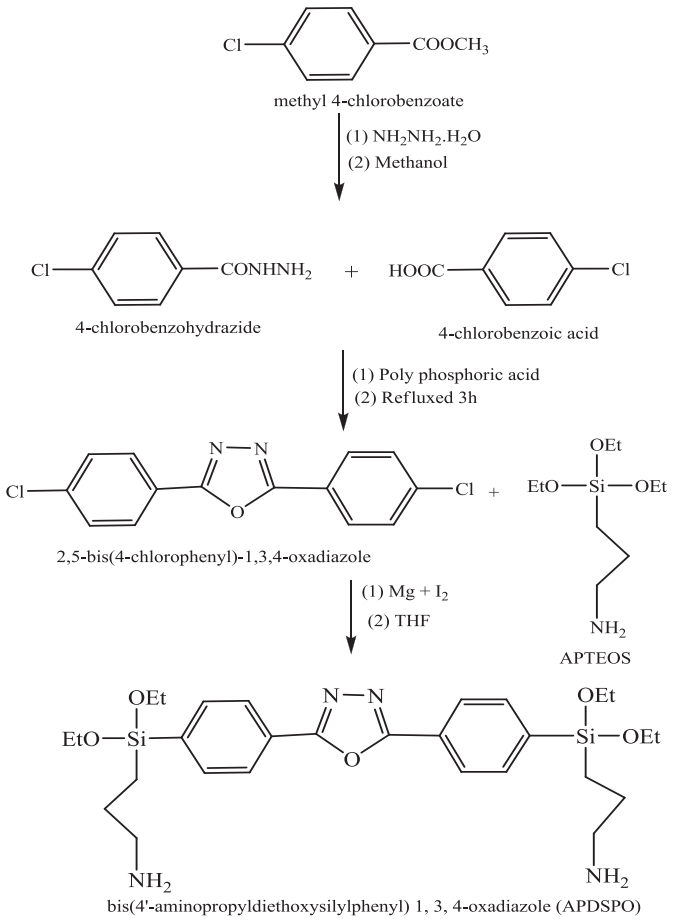

Fig. 1. Synthesis route for bis(4′-aminopropyldiethoxysilylphenyl) 1,3,4-oxadiazole (APDSPO).

2.3. Preparation of nanocomposite membranes

Preparation procedure of nanocomposite membranes has been depicted in Fig. S1 (Electronic Supporting Information, ESI). Desired amount of APDSPO was added to 10 wt.% PVA solutions (aq) and mixture was kept under constant stirring for 6 h. Solution was transformed into gel form by adding 1 M HCl (2 mL) under constant stirring for 6 h. Resultant viscous yellowish sol was transformed into thin film with help of doctor blade on a clean PVC plate (glass plates covered by PVC sheet). The cast solution was dried for 10 min, gelated in hexane at 10 °C, and further dried under IR lamps at ambient temperature for 24 h and under vacuum at 60 °C (24 h). Obtained films were subjected to effective cross-linking using formaldehyde solution (2.5% w/v $HCHO + H_2SO_4$) for 3 h at 60 °C. Residual formaldehyde solution was removed by washing with methanol. Obtained membranes were subjected to phosphorylation using 1:1 (w/w) formaldehyde and phosphorus acid, for 3 h at 70 °C. The prepared nanocomposite membrane was named PO-X, where X is the (weight percentage of APDSPO)/10 in the membrane phase. Optimized PO-6 membrane contained APDSPO (60 wt.%) and PVA (40 wt.%).

2.4. Instrumental characterization of the membranes

FTIR spectra of samples were obtained with a Spectrum GX series 49387 spectrometer in the range of 4000–400 cm^{-1}. To confirm the functional group in membrane, attenuated total reflection (ATR) infrared spectroscopy was employed (with a Perkin Elmer Spectrum GX with resolution ± 4 cm^{-1}, incident angle 45°). Wide angle X-ray diffractograms of the nanocomposite membranes were recorded using