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## A novel hybrid PES nanofiltration membrane: Preparation, characterization and separation performance

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**Abstract:** The amine functionalized silica nanoparticles were synthesized using the sol-gel method and characterized by using FT-IR, XRD. A novel poly ether sulfone (PES)/ amine functionalized silica nanoparticles mixed matrix nanocomposite membranes were prepared via the phase inversion induced by immersion precipitation technique. The effect of co-solvent such as 1,4-dioxane, acetone, tetrahydrofuran (THF) were studied by using scanning electron microscopy (SEM), pure water flux(PWF), Molecular weight cut off (MWCO) and contact angle (CA).The prepared membranes were tested their performances for removal of humic acid (natural organic matter).

**Keywords:** Nanofiltration, Phase inversion method, humic acid.

### Introduction

Recently, nanofiltration (NF) membranes are widely used in various industries such as dye industries, pharmaindustries, water treatment etc <sup>1-2</sup>. In general, nanofiltration is a pressure driven process that has pore size in the range of 1-5 nm. The main advantages of NF membrane is higher rejection for divalent ions such as  $\text{Ca}^{2+}, \text{Mg}^{2+}$  ion, removal of humic acid, lower energy process than reverse osmosis <sup>3-4</sup>. Humic acids account for about 50–90% of the total fresh water organic matter and present a yellowish or brown color in water. HA exists in the aquatic environment and is considered as a degradation product of lignin, carbohydrates, proteins, etc <sup>5</sup>. The removal of humic acid is major challenge in membrane separation process. This is due to the following reasons that (i) pore plugging effect (ii) reacts with chlorine during water treatment leads to the production of harmful chlorinated organic compounds <sup>6</sup>. There are various polymers are used to prepare the membranes. Especially, the PES based membranes are received much attention. This is due to the high glass transition temperature 225 °C, higher mechanical strength and amorphous nature <sup>7</sup> . In general, integrally skinned asymmetric NF membranes are receiving much attention among the researchers. This can be due to the presence of surface active skin layer, which can provide better rejection performances for membrane <sup>8</sup>. Specifically, the phase inversion technique is being used to prepare the asymmetric membranes <sup>9</sup>. Recently, various nanoparticles are incorporated into the membranes by using phase inversion method. So, it is necessary to study about the effect of solvent in nanocomposite membrane preparation. Generally, the volatile solvents are used to prepare the NF membranes. So, the present research work is mainly focused the effect of volatile solvents such as acetone, dioxane, tetrahydrofuran (THF) in the preparation of aminated silica composite PES membranes. The characteristics of the membranes were discussed mainly in terms of membrane morphology, surface hydrophilicity and permeation and rejection of humic acid solution.

## Experimental

### Materials and Methods

Commercial grade polyethersulfone Udel P-3500 ( $T_g$ -195°C) was supplied by Amoco Polymers Inc., USA. Analar grade N-methyl-2-pyrrolidone(NMP) and Tetrahydrofuran from SRL Chemicals Ltd., India, were sieved through molecular sieves (type 5Å) to remove moisture and stored in dry condition prior to use. 1,4dioxane(>99%) was obtained from RFCL Ltd, DELHI. Acetone (>99.5%) was supplied by memba chem industries pvt ltd. Sodium lauryl sulfate (SLS) of analar grade was obtained from Qualigens Fine Chemicals Ltd., India, and was used as a surfactant in the coagulation bath. TetraethylorthoSilicate which is used as silica precursor for amine functionalized silica nanoparticle was supplied by Merck Schuchardt, Germany . Cetyltrimethylammoniumbromide (CTAB), HCl, ammonia solution were purchased from SRL Chemicals Ltd., India, . absolute ethyl alcohol was purchased from hayman ltd ,U.K. Distilled water was employed for the NF experiments and for the preparation of the gelation bath Polyethylene glycols of different molecular weights varying from 200 Da to 10000 Da were procured from Merck (I) Ltd., and were used as supplied, for the determination of molecular weight cut-off of the membranes. Humic acid was obtained from Hi-media Laboratories Pvt. Ltd., and used as the model compound for natural organic matter in drinking water was purchased from SRL Chemicals Ltd., India, 3-Aminopropyltriethoxysilane (APTES, 99%) was purchased from Aldrich.

### Synthesis of Amine functionalized Silica nanoparticles

Monodispersed amine-functionalized silica nanoparticles with a controlled size were prepared by the Stober's precipitation method. 1.5 g of CTAB (hexa cetadecyl tetra ammonium bromide) and 50 ml of ethanol were mixed together and stirred for 0.5h at room temperature. Consequently silica precursors TEOS (tetraethyl orthosilicate) and ammonium propyl trimethoxy silane was added drop wise to the mixture and stirred continuously for with the addition of distilled water. Ammonia solution was added slowly to maintain the pH of the mixture around 10. The obtained solid product was centrifuged, washed in 10%v/v of HCl/ alcohol solution to remove the template and the particles were washed with deionized water and centrifuged several times to clean out the remained surfactants <sup>10</sup>. Then dried at 80°C for 12h. The obtained nanoparticles was characterized by using FT-IR,XRD.

### Membrane preparation method

The wet phase inversion technique was used to prepare all membranes <sup>11</sup>. The prepared silica nanoparticle was dispersed in corresponding volume of solvent co-solvent mixture as mentioned in the composition table (**Table 1**) and ultrasonificated for 30 mins for the proper distribution. The PES polymer of 17% was simultaneously added to the round bottom flask and allowed for constant mechanical stirring for 12 h at room temperature. The casting solution is allowed to stand still for 4 h to rid out of the air bubbles . The casting conditions were maintained as relative humidity (15±2%) and temperature (45±1 °C), for the preparation of membranes. In order to avoid the precipitation of polymer solution by the atmospheric moisture relative humidity value was always kept less than 15%. The thickness of the membranes was maintained at 0.22±0.02mm. After casting, the membranes were allowed for the partial evaporation of 20 Seconds and along with the cast film the glass plate was immersed in a non-solvent water coagulation bath which is maintained at 15±3° C. The thickness of the membranes maintained in the present study was 0.22 ±.03 mm. It was measured by using Vernier Caliper at various parts of the membrane. Finally, the resulted membranes were kept in deionized water, and the deionized water was replaced every day.

**Table 1 Composition of casting solution**

Membrane	SiO <sub>2</sub> Np. (wt.%)	Solvent NMP (wt.%)	Co-Solvent (wt.%)
M1	0	81	-
M2	0.5	80.5	-
M3	0.5	64.4	Acetone (16.1)
M4	0.5	64.4	Dioxane (16.1)
M5	0.5	64.4	T.H.F (16.1)

## Characterization of amine functionalized nanocomposite membranes

### X-ray Diffraction (XRD) analysis

Wide angle X-ray diffraction (WAXD) patterns of Amine functionalized silica nanoparticle was recorded by Bruker AXS D8 Advance X-ray diffractometer. The diffractograms were measured at diffraction angle  $2\theta$  in the range of  $10\text{--}70^\circ$  using  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). tube voltage of 40 kV and tube current of 30mA were kept constant throughout the experiment.

### FT-IR analysis

FTIR spectra of synthesized nanoparticle was recorded using an attenuated total reflectance (ATR) technique with a spectrometer (Thermo Nicolet, Avatar 370) in the range of  $4000\text{--}500\text{cm}^{-1}$ . The IR spectrum for the amine functionalized silica powder was obtained by the KBr pellet method.

### Scanning Electron Microscopy (SEM) analysis

The cross sectional images of the PES and blend membranes were taken by scanning electron microscope (SEM, Cam Scan MV2300). The membranes were cut into small pieces and cleaned with blotting paper. The pieces were immersed in liquid nitrogen for 60–90 s and were frozen. The dried samples were gold sputtered for producing electric conductivity and photographs were taken in very high vacuum conditions operating at 5 kV.

### Pure water flux (PWF) analysis

Membranes after 30 min compaction were subjected to a trans membrane pressure of 1025 kPa to measure the pure water flux. The permeability was measured under steady state conditions and the pure water flux was calculated by the Eq. (1). The pure water flux was measured three times and average of it was reported for accuracy. The pure water flux ( $J_w$ ) was determined by following Eq (1).

$$J_w = \frac{Q}{A\Delta T} \quad (1)$$

Where,

$J_w$  is the water flux ( $\text{lm}^{-2}\text{h}^{-1}$ );  
 $Q$  is the quantity of water permeated (l);  
 $\Delta T$  is the sampling time (h);  
 $A$  is the membrane area ( $\text{m}^2$ ).

### Contact angle Measurement

Contact angle measurements of water on the wet membrane surfaces were carried out by sessile drop method at ambient temperature using goniometer (GBX Instruments, Germany). Membrane samples size of  $3 \times 3 \text{ cm}^2$  were washed thoroughly with water and mopped with blotting paper to remove the moisture content prior to the experiment. Then they were put on a sintered glass plate with active layer on the upside to study the polar interactions between the membrane-water interfaces. The sessile drop was formed on the membrane surface by depositing  $5 \mu\text{L}$  of milli-Q water slowly and steadily on the membrane surface with a micro syringe. The contact angle was measured at membrane–water–air interphase at room temperature within 30 s of the addition of water drop. For each sample, measurements were performed at six different locations and average was considered for accuracy.

### Humic acid rejection studies

The characterized membranes were mounted in the nanofiltration cell. The feed was filled with humic acid solution and pressurized to 1025KPa. The humic acid used in the present study were dissolved in water at a concentration of 1(g/l) was used as a natural organic matter (NOM) standard solution for the rejection studies. The feed solution pH was adjusted to 6 by adding small amount of either 0.1M HCl or 0.1M NaOH. The permeate was collected over measured time intervals in graduated tubes and the contents were analyzed for the solute concentration using total organic carbon analyzer (Shimadzu, TOC-V CPH). The percentage solute

rejection (%SR) was calculated from the concentration of the feed ( $C_f$ ) and the concentrate of the permeate ( $C_p$ ) by the following Eqn. 3.

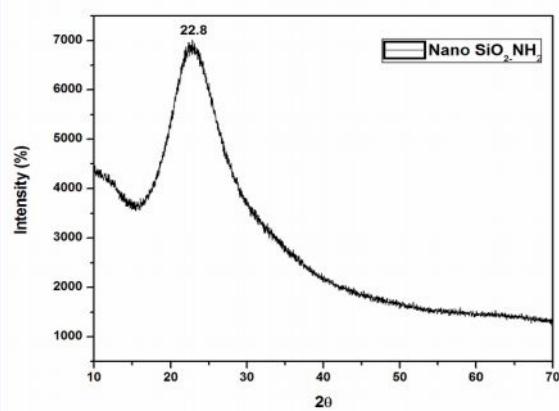
$$SR(\%) = [1 - C_p/C_f] \times 100 \quad (3)$$

$C_p$  and  $C_f$  are the concentration of permeate and feed respectively.

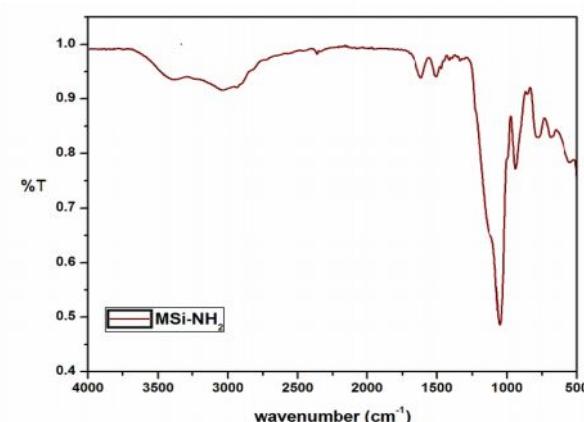
## Results and Discussion

### Characterization of $\text{SiO}_2\text{-NH}_2$ nanoparticles

The X-ray Diffraction result of prepared amine functionalized silica nanoparticle was shown in **Fig.1**. A broad reflection peak centered at  $2\theta$  value of  $22.8^\circ$  confirms the amorphous silica phase<sup>8</sup>. The FT-IR results of amine modified silica nanoparticles are displayed in **Fig.2**. The obtained characteristic bands are shown in **Table 2**. The bands at  $1100 \text{ cm}^{-1}$  (Si-O-Si) The band at around  $3394 \text{ cm}^{-1}$  is assigned to vibration of primary amine groups (-NH<sub>2</sub>)<sup>12</sup>. From the IR result, the presence of amine functional group was confirmed on the nano silica.



**Fig.1.** X-ray diffraction patterns of nano  $\text{SiO}_2\text{-NH}_2$



**Fig.2.** FT-IR results of nano  $\text{SiO}_2\text{-NH}_2$

**Fig.2.** FT-IR results of nano  $\text{SiO}_2\text{-NH}_2$  **Table 2:** IR-stretching frequencies of functional groups of aminated- $\text{SiO}_2$

Functional groups of $\text{SiO}_2\text{-NH}_2$	Stretching frequencies (cm <sup>-1</sup> )
N-H primary amine	3394
N-H secondary amine	3047
Carbonyl group	1606
N-H bending	1506
Si-O-Si	1053

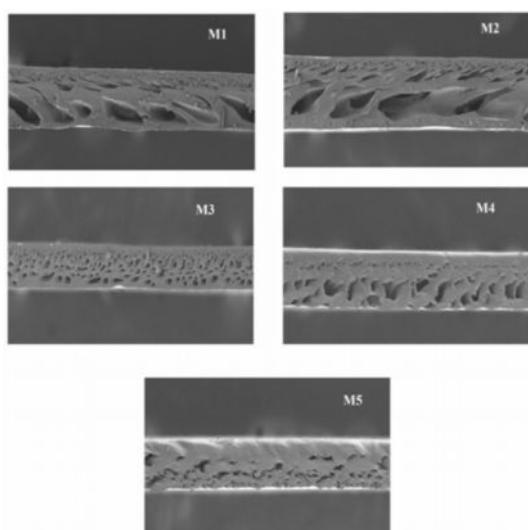
### Membrane morphology study

The cross sectional images are shown in **Fig. 3**. The thickness and the integrity of skin layer are intimately related to solvent evaporation, the ratio of the less volatile solvent to the more volatile solvent<sup>12</sup>. The thickness of skin layer increases from M3 to M5. The M5 has a high denser membrane structure due to loss of highly volatile T.H.F. solvent during casting. Among the membranes, the membrane M3 shows reliable skin layer thickness with number of small pores in the cross sectional area.

### Effect of co-solvent on Pure water flux and Contact angle

The pure water flux of M1 and M2 is high due to the larger macro void growth (shown in **Table 3**). The membranes M3, M4, M5 has a reliable pure water flux within the range of nanofiltration. This can be following

reason that the addition of volatile co-solvent increases the viscosity of PES. membrane casting solution, and suppressed the growth of macro void formation due to fast evaporation of volatile solvents during membrane preparation.



**Fig.3. cross sectional SEM images of membranes**

**Table 3: Pure water flux, Porosity, Contact Angle, MWCO of PES Membranes**

Membrane	Pure water flux (l/m <sup>2</sup> h)	Contact angle (θ)	MWCO (Da)
M1	181.1	72	8000
M2	195.9	62	8000
M3	165.9	63	1500
M4	159.2	63	1500
M5	134.3	65	1500

The contact angle values were decreased for composite membranes than pure membrane. The M3 has lower contact angle value among the co-solvent added membranes. This is due to the less skin layer thickness. This is due to the presence of more nanoparticle concentration at the membrane interface or surface. The contact angle value of M4 is slightly high due to the inhomogeneous distribution of nanoparticles. The similar results were reported by Rajesh *et.al*<sup>13</sup>.

#### Humic acid rejection by NF membranes

The co solvent added nanocomposite membranes (M3-M5) showed better rejection profile than membrane (M1 & M2). This is mainly due to highly compacted pore structure provides better rejection properties. Further, the presence of nanoparticles on the membranes surfaces provides good surface wetting properties. So, all co solvent added membranes shows 98% of rejection against humic acid.

**Table 4: humic acid rejection of membranes**

Membrane code	Rejection (%) of HA
M1	87.66
M2	85.45
M3	98.19
M4	98.01
M5	98.25

## Conclusion

In this study polyethersulfone polymer based membranes were prepared with incorporating amine functionalized silica nanoparticles by using different co-solvents. The amine functionalization on silica nanoparticles has been confirmed by FT-IR studies. The incorporation of nanoparticles improved the hydrophilic character of the PES membranes, which is confirmed by contact angle. The morphological analysis (SEM) confirmed that addition of co-solvent improves the smaller pore size with dense membrane skin layer. Among the co solvents, the addition of acetone as a co-solvent in to the PES nanocomposite membrane improves the higher selectivity for humic acid (natural organic matter) with better permeation properties.

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