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## Introduction

Population growth, industrialization, and contamination (personal care products, agricultural pesticides, heavy metals, micro-pollutants, drugs, chemicals, and microbes) are serious problems for providing safe and clean drinking water.<sup>1-4</sup> Membrane technologies for water desalination/purification have a wide range of advantages and attract wide attention for developing new types of stable and sustainable membranes.<sup>4</sup> Nanofiltration (NF) membranes show many advantages such as low energy consumption, and high permeation flux performance over reverse osmosis (RO).<sup>5,6</sup> The surface charge of NF membranes plays an important role due to Donnan exclusion and is responsible for high flux, salt rejection and fouling resistivity.<sup>7,8</sup>

Generally, NF membranes have been derived from polyamide,<sup>9</sup> sulphonated polysulfone,<sup>10</sup> and sulphonated polyphenylene oxide.<sup>11</sup> At present, NF membranes are prepared by different techniques such as phase inversion,<sup>12</sup> chemical cross-linking,<sup>13</sup> photo-radiation plasma,<sup>14</sup> low-temperature plasma,<sup>15</sup> and layer-by-layer deposition technique.<sup>16</sup> Polyamide membranes are chemically unstable in the presence of sanitizing agents, especially chlorine.<sup>17</sup> Furthermore, the membrane is itself susceptible to fouling (organic fouling, inorganic fouling, colloidal fouling, and biofouling).

# Self-assembled silica nanocrystal-based anti-biofouling nanofilter membranes<sup>†</sup>

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Herein, we report synthesis of organosiloxane 3-(2-((3-aminopropyl)diethoxysilyl)ethylthio)-5-(4-((3-aminopropyl)diethoxy silyl)phenyl)-4*H*-1,2,4-triazol-4-amine (TS) by Barbiar–Grignard reaction. Hybrid nanofiltration (NF) membranes were prepared from TS and poly(vinyl alcohol) (PVA) *via* sol–gel process followed by cross-linking and grafting of phosphonic acid groups. Physicochemical properties of these membranes revealed their stable (thermal, mechanical, and chemical) and chlorine tolerant nature. HRTEM analysis reveals homogenous silica distribution in the membrane matrix. The cross-link density of the membrane and the preparation conditions were studied in terms of NF performance. An *Escherichia coli* bacterium was used to study antibacterial activity and anti-biofouling properties of the hybrid membrane. The short-term bacterial stability test showed that membrane TS-60a has good anti-fouling properties. Moreover TS-60a membrane showed excellent stability and anti-biofouling capability in long-time operation.

Examination of fouled NF membranes exhibited more than 50% (w/w) of dry fouling layer, which was of biological origin.18 To avoid biofouling, generally anti-adhesion and antimicrobial strategies for NF/RO membranes have been adopted.<sup>19</sup> In antimicrobial strategies generally silver nanoparticles have been used, which does not comply with the regulations of the United States Environmental Protection Agency (USEPA) for water quality (silver content should be less than 3.4 ppb). Leaching of silver nanoparticles may pose a regulatory risk for applications in water treatment.<sup>19</sup> Charged or hydrophilic modified NF membranes with a smooth surface are less sensitive to biofouling.19 Anti-biofouling NF membranes are challenging because of their architecture (pore size, surface roughness and charged nature), hydraulic resistance, separation performance, mechanical stability, chemical stability, cost and flexibility of assembly.

Attempts were made to develop organic/inorganic hybrid NF membranes due to their rigidity, stability (cross-linking), and ease of tailoring the pore architecture and processability.<sup>20</sup> Thus, there is great opportunity for development of organic/inorganic hybrid membranes using polysiloxanes and poly(vinyl alcohol) (PVA). Polysiloxanes are used for biomedical applications,<sup>21–25</sup> while PVA forms chlorine-tolerant stable ether-type linkages due to acetalisation with formaldehyde.<sup>26</sup> We reported 3-((4-(5-(2-((3-aminopropyl)diethoxysilyl)ethylthio)-1,3,4-oxadiazol-2-yl)phenyl)diethoxysilyl)propan-1-amine (APDSMO)based quaternary ammonium-grafted hybrid NF membranes with antimicrobial activity.<sup>27</sup> But, the 1,2,4-triazole ring also showed antibacterial and antifungal activity.<sup>28</sup> Thus, the hybrid NF membrane with 1,2,4-triazole ring is also expected to exhibit antimicrobial activity, good performance and stabilities.

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Herein, we report phosphonic acid-grafted hybrid NF membranes, containing 4-amino-1,2,4-triazole. Membrane preparation was achieved in aqueous media by acid-catalyzed sol-gel followed by cross-linking. Grafting of the phosphonic acid group, tailoring of pore texture and incorporation of antimicrobial active compounds, were responsible for antibiofouling and high membrane performance.

## **Experimental section**

#### Materials

Aminopropyltriethoxysilane (APTEOS) (99%) and polyethylene glycol (PEG; different molecular weights) were obtained from Sigma-Aldrich chemicals. Poly(vinyl alcohol) (Mw: 125 000), formaldehyde (37% in water), phosphorous acid, hydrochloric acid, sulphuric acid, *p*-chlorobenzoic acid, hydrazine hydrate, carbon disulphide, sodium hydroxide, sodium chloride, sucrose, magnesium chloride, sodium hypochlorite, *N*-methylpyrrolidone, dimethylformamide, hexane, iodine crystals, magnesium turnings, tetrahydrofuran (THF), streptomycin, fluconazole, acetone and methanol were obtained from SD. Fine Chemicals, India. Solvents were used after proper distillation and double-distilled water was used for experiments.

#### Synthesis of organosiloxane (TS)

Synthesis of 3-(2-chloroethylthio)-5-(4-chlorophenyl)-4H-1,2,4triazole-4-amine (TC) was achieved through multistep synthesis (Scheme 1; details of TC synthesis are included in section S1, ESI<sup>†</sup>). Synthesis of organosiloxane (TS) has been reported earlier.<sup>20,27,29</sup> In a general preparation method, to a threenecked round-bottom flask (250 ml, equipped with a magnetic stirrer, nitrogen inlet, drying tube, condenser, and addition funnel), a mixture of Mg turnings (1.5 g) and APTEOS (44.4 ml; 0.2 mol) in THF (30 ml) and iodine crystals were added under constant stirring conditions. After 30 min, 20 mL solution of 3-(2-chloroethylthio)-5-(4-chlorophenyl)-4H-1,2,4-triazol-4-amine (TC) (2 mmol) in THF was added dropwise over 30 min, then further refluxed at 10 h. After 10 h the clear solution turned to a greenish yellow liquid. The reaction mixture was cooled at room temperature and THF was removed by vacuum rotary evaporator. Viscous liquid was washed with 30 ml hexane and dried under vacuum.

Yield: 80% (yellow coloured transparent semisolid). IR (KBr) cm<sup>-1</sup>: 3395 (-NH), 2981 (-Ar-H), 1590 (C=N triazole), 1528 (NH), 1317 (N–N), 1013 (Si–O–C), 760 (Si–Ph), 681(C–Si); <sup>1</sup>H NMR (D<sub>2</sub>O):  $\delta$  7.67 (Ph–Si), 7.28 (Ph–triazole), 3.47, 1.02 (–O–CH<sub>2</sub>–CH<sub>3</sub>), 3.43 (–OCH<sub>2</sub>CH<sub>3</sub>), 2.63, 1.47 (–SCH<sub>2</sub>CH<sub>2</sub>), 2.57, (–CH<sub>2</sub>–CH<sub>2</sub>–Si–) 0.99(–CH<sub>2</sub>Si–Ph), 0.43,0.45 (–CH<sub>2</sub>Si); <sup>13</sup>C NMR (DMSO-d<sub>6</sub>):  $\delta$  174.68, 173.55, 136.3, 130.54, 128.18, 17.66, 57.23, 42.49, 30.25, 23.07, 16.91, 10.27. Anal. calcd for [C<sub>24</sub>H<sub>46</sub>N<sub>6</sub>O<sub>4</sub>SSi<sub>2</sub>] (570.91): C, 50.45; H, 8.15; N, 14.76; S, 5.64, Si, 9.87%. Found: C, 50.5; H, 8.13; N, 14.71; S, 5.61; Si, 9.84%.

#### Preparation of hybrid NF membrane

PVA was dissolved in distilled water (10 wt%) under stirring conditions for 24 h. Further, TS (desired amount) was added to PVA solution under constant stirring (300 rpm) for 6 h.



Scheme 1 Schematic reaction steps involved in preparation of organosiloxane (TS).

Obtained solutions were transformed into a gel by adding 1 M HCl and pH was maintained according to Table 1. The resultant white viscous gels were cast on a PVC sheet and the desired thickness was maintained with a doctor blade. After partial drying (10 min), thin films were gelated (precipitated) in hexane at 10 °C for 20 min. The membrane was further dried at room temperature for 24 h (slow evaporation of solvent) followed by in a vacuum oven at 80 °C for 24 h. The obtained membrane was cross-linked by formal reaction under varied cross-linking conditions (Table 1). Cross-linked membranes were subjected to phosphorylation using 1:1 (w/w) formaldehyde and phosphorus acid, for 3 h at 70 °C. Different prepared membranes were designated as TS-*X*(*y*), where *X* is the weight percentage of TS, and *y* denotes different cross-linking conditions, as described in Table 1.

#### Instrumental characterization of the membranes

FTIR spectra of dried membrane samples were obtained Spectrum GX series 49 387 spectrometer in the range of 4000– $450 \text{ cm}^{-1}$ . The IR spectrum for a synthesized intermediate was

Membrane	Membrane preparation conditions				
	Formaldehyde concentration (wt%)	Time (h)	pН	$T/^{\circ}\mathbf{C}$	Cross-linking density (mol $g^{-1}$ )
TS-30	2.5	3	2	60	0.009
TS-40	2.5	3	2	60	0.0302
TS-50	2.5	3	2	60	0.061
TS-60a	2.5	3	2	60	0.0808
TS-60b	2.0	3	2	60	0.0696
TS-60c	1.5	3	2	60	0.0454
TS-60d	1.0	3	2	60	0.0062
TS-60e	2.5	4	2	60	0.0542
TS-60f	2.5	2	2	60	0.0122
TS-60g	2.5	1	2	60	0.0818
TS-60h	2.5	3	3	60	0.0622
TS-60i	2.5	3	4	60	0.0316
TS-60j	2.5	3	5	60	0.0102
TS-60k	2.5	3	6	60	0.0002
TS-60l	2.5	3	2	70	0.082
TS-60m	2.5	3	2	50	0.011
TS-60n	2.5	3	2	40	0.0068
Error limiter E	ormaldehyde concentration $(\pm 0.1 \text{ wt}\%)$ tim	$p_{\rm e}(\pm 0.05  \rm h)  \rm pH$	$(\pm 0.05)$ to	mperature (	$(\pm 2 ^{\circ}\text{C})$ and cross-linking density ( $\pm 0.0002$ )

Error limits: Formaldehyde concentration ( $\pm 0.1$  wt%), time ( $\pm 0.05$  h), pH ( $\pm 0.05$ ), temperature ( $\pm 2$  °C), and cross-linking density ( $\pm 0.0002$ ).

obtained by the KBr pellet method. Wide-angle X-ray diffractograms of the nanocomposite membranes were recorded using Philips Xpert X-ray diffractometer with Cu-K $\alpha$  (1.54056) radiation. <sup>1</sup>H and <sup>13</sup>C were used to characterize the synthesized material recorded by an NMR spectrometer (Bruker 500 MHz) in a D<sub>2</sub>O and d<sub>6</sub>-DMSO solvents.

The thermal degradation processes and stabilities of the membranes were investigated using a thermo gravimetric analyzer (Mettler Toledo TGA/SDTA851 with *Star* software) under a nitrogen atmosphere with a heating rate of 10 °C min<sup>-1</sup> from 30 to 450 °C. Differential scanning calorimetry (DSC) measurements were carried out in a temperature range of 30–450 °C with a heating rate of 5 °C min<sup>-1</sup>. The dynamic mechanical stabilities of the composite membranes were evaluated by using a Mettler Toledo dynamic mechanical analyzer 861 instruments with Star software under nitrogen with a heating rate of 10 °C min<sup>-1</sup> from 30 to 320 °C to verify the effect of the silica content in the form of a polymeric membrane.

The surface morphology of thoroughly dried membranes was studied by a JEOL 1200EX transmission electron microscope (TEM). The JEOL 1200EX transmission electron microscope with tungsten electron source was operated at an accelerating voltage of up to 120 kV. Atomic force microscopy (AFM) images of dried membranes were recorded using an NTEGRA AURA (NTMDT). Semi-contact mode SPM NSG 01 tip was used to determine the surface roughness. The tip used had a radius of curvature of approximately 10 nm and the natural frequency for the cantilever was 300 kHz. In this measurement mode, the cantilever where the tip is located oscillates with its natural frequency and the sample topography is obtained from the subsequent changes in the oscillation amplitude. Differences in viscoelastic properties can be detected from the changes in the oscillation phase. For scanning electron microscopy (SEM), gold sputter coatings were carried out on desired membrane samples at pressures ranging between 1 and 0.1 Pa. The sample was loaded in the machine, which was operated at  $10^{-2}$  to  $10^{-3}$  Pa with EHT 15.00 kV with 300 V collector bias using Leo microscope to record SEMs. The optical densities of microbial solutions were evaluated by using a VARIAN 50 bio UV-Vis spectrophotometer instruments. The Total Organic Count (TOC) content in the feed and permeate solutions was obtained by employing a customized acid digestion method, followed by analysis with a liquid TOC elementar.

#### Membrane permeation measurements

Water flux across hybrid membranes was measured in a twocompartment cell separated by circular membrane disk (4.0 cm<sup>2</sup>) placed at the bottom of the cell with top active layer towards the feed solution. Feed compartment was well stirred by a mechanical stirrer (300 rpm). Electrolyte concentration in the feed and permeate was determined by conductivity measurements (Toshniwal TCM 15).<sup>30,31</sup> For the neutral organic molecule solutions, a customized total organic carbon (TOC) digestion method was used to quantitatively measure the concentration of neutral organic solutes in the permeate and in the retentate. Calibration plots for all three types of analyses were run with standard feed solutions prior to the studies to ensure accuracy of the measurements. Water flux and solute rejection were estimated by following equations:

Flux 
$$(l m^{-2} h^{-1}) = \frac{\text{permeate } (l)}{\text{membrane area } (m^2) \times \text{time } (h)}$$
 (1)

$$Rejection = \left[1 - \frac{\text{permeate concentration}}{\text{feed concentration}}\right]$$
(2)

The chlorine-tolerant nature of the membranes was assessed in terms of flux and rejection performance, after membrane treatment in sodium hypochlorite (pH 5–6) aqueous solution (5000 ppm) solution for 24 h.

### Antibacterial activity

Antibacterial properties of hybrid (TS-X) NF membranes were tested against *Escherichia coli* bacteria by using reported methods.<sup>20,27</sup> Standard testing protocol for water-insoluble antimicrobials was used.<sup>32,33</sup> Antibacterial tests were performed in triplicate to insure reproducibility.

# **Results and discussion**

### Membrane structure

The monomer precursor (TS) was synthesized by Barbier-Grignard reaction using TC and APTEOS (Scheme 1). <sup>1</sup>H NMR spectra for TS showed two peaks at 7.26 and 7.67 ppm due to phenyl ring protons (Fig. S1, ESI<sup>†</sup>). The presence of triazole and phenyl rings were confirmed by <sup>13</sup>C NMR signals at  $\delta$  value 174.6, 173.5 and 136.3, 130.5, 128.1, 117.6 ppm (Fig. S2, ESI<sup>†</sup>).

A carbon peak for  $-OCH_2-(57.23 \text{ ppm})$  confirmed the presence of a  $-OCH_2CH_3$  group in TS.

Guide peaks in FT-IR spectra of TC (Fig. S3, ESI<sup>†</sup>) confirmed reaction between 5-(4-chlorophenyl)-1,2,4-triazole-4-amine-2thiol and 1,2-dichloroethane in the presence of weak base. TC showed two medium intensity bands at ca. 745 and 661  $cm^{-1}$  (v(Ph-Cl) and v(C-Cl)). After Barbiar-Grignard reaction these two bands disappeared and new bands appeared at ca. 776 and 691 cm<sup>-1</sup> (v(Si–Ph) and v(Si–C) vibration band). Presence of triazole ring in TC and TS was confirmed by the strong intensity band at ca. 1080 and 1095 cm<sup>-1</sup> (C-N-C stretching vibration) (Fig. 1). TS showed medium intensity bands at 3433 cm<sup>-1</sup> and 1552 cm<sup>-1</sup> (v(N-H), while the band at ca. 1596 cm<sup>-1</sup> (v(C=N) was assigned to the triazole ring.<sup>33</sup> In the case of TS-60a membrane, a broad band at ca. 1400-1445  $cm^{-1}$  and a strong band at *ca.* 1649  $cm^{-1}$  confirmed phosphorylation of the -NH group. The absorption band at around 1260 cm<sup>-1</sup> was a characteristic band of the -Si-O-Si-



Fig. 1 FT-ATR spectra of TS-60a and TS-30 membrane.

asymmetrical stretching vibration. This confirmed molecular level hybridisation between organic and inorganic segments.<sup>34</sup> The band at *ca.* 1021 cm<sup>-1</sup> (-C-O-C- stretching vibration for acyclic ether ring of PVA) showed formal cross-linking with formaldehyde. These results confirmed formation of a phosphonic acid-functionalized cross-linked hybrid membrane. On the basis of spectral and elemental analysis, structures for TS and hybrid NF membranes were proposed (Scheme 1 and Scheme S1 (ESI)).

#### Surface morphologies of hybrid NFM

TEM images (TS-60a membrane as representative case) (Fig. 2) revealed homogeneous silica distribution in the membrane matrix. HRTEM (Fig. 2a&b) analysis confirmed 2–5 nm particle size of silica and inter-planar distance was below 0.24 nm confirming the crystalline silica in the membrane matrix.<sup>35</sup> WXRD analysis showed an increase in the amorphous region with TS content (reduced PVA content), which is a favourable condition for formation of Si–*O*–C bonds (availability of more silica) (Fig. S4, ESI†). The absence of evident peaks in TS showed its amorphous nature.

Scanning electron microscopy results are systematized in Fig. 3 and Fig. S5, (ESI<sup>†</sup>). Surface analysis of membrane TS-60a & TS-30 showed the upper surface is dense (Fig. 3a&c), while the bottom surface in the membrane has a porous nature (Fig. 3b&d). The bottom surface of the TS-60a membrane looks like a honeycomb structure (Fig. 3b). Membrane cross-section SEM images showed that the membranes are arranged with a layer morphology and the upper surface in dense in nature while lower surface is porous in nature (Fig. 3c&f). The surface morphology of the synthesised organosiloxane looks like a crushed stone (Fig. S5a, ESI<sup>†</sup>) and the elemental mapping data support their elemental analysis (Fig. S5b, ESI<sup>†</sup>). The successful grafting of the membrane surface by phosphonic acid was confirmed by the phosphorous mapping (green dot) in TS-60a and TS-30 membrane (Fig. S5c&d, ESI<sup>†</sup>). The synthesized organosiloxane (TS) elemental analysis is further supported by the EDX analysis (Fig. S5e, ESI<sup>†</sup>).

Membrane fouling is controlled by interaction between the membrane surface and solute such as protein, carbohydrates and bacteria. Thus surface roughness of the membrane is important in determining the susceptibility to membrane fouling. Previously, a number of studies suggested that surface roughness may be the most important factor to avoid membrane fouling.<sup>19</sup> Membrane surface images were obtained in semi-contact mode of AFM study and the pictures are systematized in Fig. 4. For the surface roughness analysis, measurement of a small portion of the membrane (1.4 × 1.4  $\mu$ m) were selected and NOVA P9 INTEGRA software was used for analysis. Obtained data concluded that membrane roughness decreased with increasing organosiloxane (TS) content. TS-60a membrane has the lowest surface roughness 55 nm.

#### Thermal, mechanical, and chemical stability

Thermal stabilities of pristine and hybrid membranes were analysed by thermogravimetric analysis (TGA) (Fig. S6, ESI<sup>†</sup>). The NF membranes showed two-steps of weight loss. The first step (50-170 °C) occurred due to dehydration, while the second step (280-450 °C) occurred due to degradation of the organic segment. After 450 °C, no significant weight loss was observed. TS-60a membrane showed higher weight loss (60%) in 300-400 °C, indicating that more phosphoric acid is contained in this membrane. At 500 °C, the remaining weight indicates that membrane TS-60a was thermally stable in comparison to other synthesized membranes. DSC thermograms (Fig. S7, ESI<sup> $\dagger$ </sup>) revealed dependence of  $T_{g}$  on organosiloxane (TS) content. The increase in glass transition temperature  $(T_g)$  (85–114 °C) from TS-30 to TS-60a membrane indicates that cross-linking and ionic interactions between respectively organic and inorganic segments increased. The  $T_{\rm g}$ value of pristine PVA membrane was 78 °C.36

Mechanical stability is another problem for NF membranes. We determined Young's modulus with DMA analysis. With the help of the Young's modulus, membranes' cross-linking densities were determined by following equation.<sup>37</sup>



Fig. 2 TEM images of NF membrane (TS-60a): (a) low resolution and (b) high resolution (linear inter-planar lines were separated by 0.24 nm).

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Fig. 3 SEM images of (a) TS-60a, (b) TS-60a (bottom portion), (c) cross-section of TS-60a, (d) TS-30, (e) TS-30 (bottom portion), (f) cross-section of TS-30 membrane.

$$\rho = \frac{E'}{3d\varphi RT} \tag{3}$$

where, the Young's modulus, E', was determined from the measurements with a dynamic mechanical analyser under 10 Hz frequency at varying temperature (30–320 °C) (Fig. S8, ESI†), d is the membrane density,  $\varphi$  is the front factor (=1), R is universal gas constant, and T is absolute temperature.

Cross-linking densities for different membranes are depicted in Table 1. Cross-linking data revealed that with increasing silica content (TS) in the membrane matrix, Young's modulus increased due to (Si–O–C) bonds formed in organic PVA and organosiloxane (TS). Membrane preparation conditions (temperature, pH, concentration of cross-linking agent (formaldehyde), and cross-linking time) also play an important role in mechanical stability. Thus it is necessary to optimize the TS content in the membrane matrix, crosslinking density and Young's modulus to achieve mechanically stable hybrid membranes.

The chlorine-tolerant nature of the hybrid membrane was assessed in terms of weight loss after treatment of the membrane in 5% NaClO(aq) solution for different time intervals (0–72 h) (Fig. S9, ESI<sup>†</sup>). Weight loss for the hybrid membrane increased with silica content. Moreover, no appreciable weight loss was observed after 25 h treatment. The acid stability of the membrane was also investigated by weight loss of the membrane in equilibrium with  $H_2SO_4$  (1–8 M) for 30 days (Fig. S10a, ESI<sup>†</sup>). The membrane showed about 0–6% weight loss in equilibrium with 5 M  $H_2SO_4$ . Solvent resistivity of the hybrid membranes was evaluated by their weight loss under different environments for 30 days (Fig. S10b, ESI†). About 2.9–5.0% weight loss in 30 days under different environments (NMP, DMSO, DMF and THF) confirmed solvent resistivity. The chemical stability test indicates that the triazole moiety was stable in the membrane matrix. Oraganosiloxane is chemically bonded with plasticizer (PVA) and cross-linked with formaldehyde; thus there is no chance of its leaching out from the membrane matrix.

#### Inter-chain spacing in the membrane matrix

Hybrid NF membranes were scanned in reflection mode at  $2\theta$  angle (Fig. S4, ESI<sup>†</sup>) and maximum peak intensity and interplanar distance values are given in Table S1 (ESI). The interplanar distance decreased with silica content in the membrane phase, which may be due to the enhanced membrane compactness. Diffraction patterns of hybrid NF membranes confirmed reduction in the crystalline region with silica content. Thus, incorporation of silica in the membrane phase enhanced the amorphous region. Inter-planar distance of less than 0.35 nm (value to ensure moderate amount of bonds Si-O-C) also indicated condensation reaction (removal of a water molecule) and hybridization of organic and inorganic segments by covalent bond (Si-O-C).<sup>35</sup>

#### Membrane filtration performance

Membrane flux for different solvents (water, methanol, ethanol, THF, DMF, DMSO, acetic acid and hexane; selected due to varied dielectric constant) varied in a similar fashion to their dielectric constant: water > methanol > ethanol >



Fig. 4 AFM 3D images of membrane upper surface for (a) TS-30a and (b) TS-60a.

 $\rm DMSO > \rm DMF > \rm THF >$  acetic acid (Fig. 11, ESI†). Also, membrane flux was dependent on silica content in the membrane matrix.

#### Effect of TS content on membrane performance

Fig. 5 shows the improvement in membrane performance with TS content, and TS-60a membrane exhibited best separation performance. At high organosiloxane content (>60%), membranes turned unstable and brittle in nature. With increase in silica content, membrane flux decreased (from 60.73 to 54.09 l  $m^{-2} h^{-1}$ ), while salt rejection increased (from 0.63 to 0.28). According to the "Space Charge" model,<sup>38</sup> the surface charge density and the pore radius are two important parameters for NF membranes. The amount of phosphoric acid groups increases with increasing TS concentration, which increase the effective membrane surface charge density. On the other hand, degree of cross-linking has been directly related to TS content. Thus, salt rejection increases with increasing TS concentration and *vice versa* for water flux.

# Effect of formaldehyde concentration on nanofiltration performance

The effect of cross-linking agent (formaldehyde) concentration (1.0–2.5 wt%) on membrane performance was investigated for TS-60 membrane (Fig. S12, ESI<sup>†</sup>). Flux decreased (from 62.05 to 54.09 l m<sup>-2</sup> h<sup>-1</sup>) while rejection increased (from 0.63 to 0.37) with formaldehyde concentration. Above 2.5 wt% concentration of formaldehyde, no significant effect was observed on membrane filtration performance.

#### Effect of cross-linking temperature and time

Membrane flux reduced (from 61.52 to 53.3 l m<sup>-2</sup> h<sup>-1</sup>), while rejection increased (from 0.63 to 0.38) with increase in cross-linking temperature (Fig. S13a, ESI<sup>†</sup>), which may be due to enhanced cross-linking density. Fig. S13b (ESI<sup>†</sup>) shows a

similar variation trend with increasing cross-linking time. Thus the observation indicates that both higher curing temperature and longer curing time results in a higher degree of cross-linking density and a dense membrane. Curing time and temperature data revealed that 3 h cross-linking time and 60  $^{\circ}$ C temperatures to give a satisfactory NF membrane.

# Effect of membrane-forming solution pH and membrane thickness on their performance

Previous analysis in our lab concluded that acid-catalyzed solgel of siloxane results a linear structure while base catalysis forms a cluster-like structure.<sup>39</sup> Here, we the investigated effect of pH (membrane-casting solution) in the acidic region (2.0–6.0) on membrane performance. The obtained results indicate that flux reduced (64.7–52.08 l m<sup>-2</sup> h<sup>-1</sup>) with lowered



Fig. 5 Performance of NF membranes at different TC content. Feed solution: 1.0 g L<sup>-1</sup> NaCl; applied pressure: 1.2 MPa; temperature: 25 °C.

pH, while rejection was enhanced (0.35–0.63). Beyond pH 3.0, filtration performance was unaffected (Fig. S14, ESI†), because of complete hydrolysis of siloxane.

The membrane thickness showed a significant effect on its performance (Fig. S15, ESI†). With increasing membrane thickness membrane flux decreased (54.03–12.96 l m<sup>-2</sup> h<sup>-1</sup>) with minor alteration in rejection (from 0.66 to 0.63). Membrane thickness analysis showed that 100  $\mu$ m thick membranes were suitable for NF processes.

#### Effect of feed concentration on nanofiltration performance

Membrane filtration experiments were performed at 25 °C and 1.2 MPa operating pressure with varied concentration of NaCl solution  $(1-4 \text{ g L}^{-1})$  (Fig. 6). Increase in feed concentration resulted in a decrease in membrane flux and rejection.<sup>40</sup> This observation was generally addressed by charged NF membrane. Decrease in flux (Fig. 6) may be attributed to an increase in osmotic pressure with NaCl concentration, which further reduced the real NF driving force of TS-60a membrane. A negatively charged membrane surface (phosphoric acid functionalization) exchanges H<sup>+</sup> with Na<sup>+</sup> and forms an electrical double layer at the membrane/solution interfacial zone. The resulting Donnan potential increased with NaCl feed concentration and thus deteriorates the salt rejection of TS-60a membrane.

#### Separation performance of different substances

Different probe molecules (inorganic electrolytes and organic molecules) were used to study the membrane rejection performance (Fig. S16, ESI<sup>†</sup>) and followed the trend: NaCl < MgSO<sub>4</sub> < Na<sub>2</sub>SO<sub>4</sub> < sucrose < PEG 2000. The same trend was also observed for a commercial NF membrane grafted with carboxylic acid groups (NTR 7450).<sup>41</sup> TS-60 membrane showed significantly higher rejection for divalent anions (SO<sub>4</sub><sup>-2</sup>) in comparison with monovalent anions (Cl<sup>-</sup>). This observation is in accordance with Donnan exclusion theory,<sup>42</sup> with strong electrostatic repulsion between SO<sub>4</sub><sup>-2</sup> and -PO<sub>3</sub><sup>-2</sup> groups (fixed to the membrane matrix). The charge and size of the molecule/ion is also an important factor to control membrane



Fig. 6 Performance of TS-60a membrane for NaCl solutions with different concentrations (other experimental conditions similar to Fig. 5).



Fig. 7 Performance evaluation of TS-60a membrane for prolonged period (other experimental conditions similar to Fig. 5).

performance. Organic probe molecules (sucrose and PEG) showed relatively high rejection because of large molecule size and absence of any interaction with membrane matrix.

#### Membrane anti-fouling behaviour

Filtration performance of TS-60a membrane was studied for feed NaCl solution  $(1.0 \text{ gL}^{-1})$  at constant pressure (1.2 MPa)(Fig. 7), and negligible alteration (less than 1%) was observed after 300 h operation. The chlorine tolerant nature of the membrane was assessed by deterioration in membrane performance after 24 h treatment in NaOCl solution (5000 ppm) at 30 °C. Membrane performance was unaffected, maybe due to acetylated PVA and chemically inert silica. A short-term stability test for the prepared hybrid membranes was performed at 1.2 MPa operating pressure with *E. coli* broth solution, as reported earlier.<sup>43</sup> The membrane maintained performance after 50 h operation (Fig. 8a). 1 cm<sup>2</sup> pieces of



**Fig. 8** Anti-biofouling performance of different NF membranes. (a) Variation of membrane flux for TC-60a and TC-30 with time in bacterial environment (LB media; feed solution  $1.000 \pm 0.001$  OD at 600 nm) (other experimental conditions similar to Fig. 5). (b) Optical image for 50 h used TC-60a membrane; (c) optical image for 50 h used TC-30 membrane.

Table 2 Comparative performance of NF membranes

Membrane	$R_{ m NaCl}$	$J_{\rm NaCl} ({\rm l} \ {\rm m}^{-2} \ {\rm h}^{-1})$	Testing conditions	Ref.
NF-7	0.37	21.3	1 g $L^{-1}$ NaCl; 25 °C; 6.0 bar	44
PPO	0.36	63	1 g L <sup>-1</sup> NaCl; 25 °C; 3.5 bar	45
QAPPESK	0.31	52	1 g L <sup>-1</sup> NaCl; 25 °C; 4.0 bar	6
MO-6	0.55	52.13	1 g L <sup>-1</sup> NaCl; 25 °C; 9.0 bar	20
OA-6	0.68	14.88	2 g L <sup>-1</sup> NaCl; 25 °C; 11.0 bar	27
TS-60a <sup>a</sup>	0.63	54.09	1 g L <sup>-1</sup> NaCl; 25 °C; 12.0 bar	This work
<sup><i>a</i></sup> Maximum error is	$5 \pm 0.01\%$ .		-	

used membrane (50 h) was immersed in 100 ml distilled water at 300 rpm for 3 h, then 1 µl solution was dispersed in LB Media (nutritionally enriched media for bacterial growth) and the obtained pictures are presented in Fig. 8(b&c). Antibacterial properties of hybrid NF membranes were tested against Escherichia coli. MIC value for TS-60 hybrid membrane showed 7000 µg ml<sup>-1</sup> MIC value (lower than for poly(vinyl pyridine)).32 To explore bacteriostatic or bactericidal nature of hybrid membranes, different weighted amounts of samples (10–10 000  $\mu$ g ml<sup>-1</sup>) were incubated with *E. coli* in aqueous LB broth for 24 h. 100 µL aliquots were placed on nutrient soft agar plates followed by incubation at 37 °C for 24 h, and bacterial colonies were counted. Hybrid membranes showed bacteriostatic properties. For drinking water purposes, we analysed the filtered water with the TOC analyzer and found no measurable carbon, indicating that organosiloxane (TS) does not leach out from membrane matrix. TS-60a membrane showed minimum bacterial fouling because of small surface roughness and high amount of TS content. TS-60a membrane separation performance compared with previously reported membranes (Table 2), confirming that this membrane is suitable for NF filtration.

# Conclusions

Herein, we report preparation methodology of organosiloxane (TS) monomer and anti-fouling stable NF membranes via solgel reaction followed by formal cross-linking. The resultant phosphonic acid-grafted NF membranes were uniform, transparent, and flexible. It was possible to tailor the thermal, chemical, and mechanical stabilities of these hybrid NF membranes by incorporating organosiloxane (TS) in the organic segment. The biofouling nature of these membranes was confirmed by their unaffected filtration performance (TS-60a) under a bacterial environment. The representative membrane (TS-60a) showed 54.09 l m<sup>-2</sup> h<sup>-1</sup> flux and 0.64 rejections for NaCl (1 g l<sup>-1</sup>) feed solution. Prepared membranes (TS-60a) exhibited good thermal, mechanical, and chemical (solvent and chlorine) stability. Membrane charge density and cross-linking density controlled the membrane performance. We believe the prepared NF membranes will have an impact as solvent-resistant membranes for the petroleum industry. The reported method is also extendable to develop other hybrid anti-biofouling NF membranes with desired properties without silver nanoparticles. In addition,

membranes retained their permeability after 30 days operation in *E. coli* broth solution, which confirmed their effective antibiofilm forming activity.

Water-soluble TS constitutes a new family of materials that are applicable to preparing charged NF membranes with good anti-biofouling and stable nanofiltration performances.

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