Electronic Supplementary Material (ESI) for Environmental Science: Water Research & Technology. This journal is © The Royal Society of Chemistry 2015

1 Nanostructured polyaniline incorporated ultrafiltration membrane

2 for desalination of brackish water

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1 S.1 Membrane preparation

2 Membranes were prepared by two step processes involving preparation of casting 3 solution followed by spreading over non-woven fabric and subsequent phase inversion process as 4 described below:

5 Preparation of casting solution

6 Solutions containing 18 wt% PSF, 2 wt% PEG-200 and 2 wt% zinc chloride (ZnCl₂) and 7 different concentrations of PANI viz., 0.5, 1.0, 2.0 and 3 wt% were prepared for membrane 8 casting. In a typical process, after mixing PSF with DMF, PEG-200 was added, followed by 9 addition of measured quantity of ZnCl₂ and the components were thoroughly mixed.

10 Casting of the membranes

The membranes were prepared by phase-inversion method. In the typical process, non-11 woven polyester fabric (product number: TNW006013, supplied by Hollytex Inc., New York, 12 USA) was used as a mechanical support for the membrane. The casting solution was drawn 13 manually at a speed of 20 mm/s using a casting knife leaving a gap of 200 micron over the 14 fabric. The produced membranes were immersed in water bath containing distilled water, at 27°C 15 for 12 hours to complete the phase inversion. The membranes were labeled as PANIO, PANIO.5, 16 PANI1, PANI2 and PANI3, corresponding to weight percent of PANI in casting solution as 0%, 17 0.5%, 1%, 2%, and 3%, respectively. 18

19 S.2 Experimental procedure

Stirred batch filtration cell was used to measure the MWCO of the membranes. For other characterizations and experiments involving salt solutions, continuous cross-flow filtration set up was used. Detailed description of cross flow filtration unit is available¹, and is shown in Fig. S1.



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2 Fig. S1: Image of experimental set-up

A pump was used for circulation of liquid through the chamber carrying clamped membrane. The flow was regulated by valve and measured using rotameter. The permeate was collected for further analysis. The trans-membrane pressure was measured using pressure gauge fitted on the top of the membrane carrying chamber.

7 S.3 Experiments with salt solution

8 The cross flow filtration experiments were carried out using solutions of 1000 mg/l 9 concentration of NaCl, Na₂SO₄ and MgSO₄. The TMP was varied in the range of 276 to 690 kPa 10 and cross flow rate (CFR) was varied from 20 to 80 l/h.

11 S.4 Measurement of cloud point: method

PSF, ZnCl₂ and PEG-200 were dissolved in DMF to form a homogeneous solution at predetermined concentration. For PANI/ PSF/ZnCl₂/PEG system, first PANI was added to the solvent then, the other components were added. The solution was titrated with de-ionized water (non-solvent) using a 100 μ l micropipette. The turbidity of the solution was analyzed by measuring the absorbance value at 680 nm². During the titration method, the solution was severely agitated using magnetic stirrer.

1 S.5 Measurement of porosity

Porosity of each membrane was determined gravimetrically³. The piece of
membrane was dried, and peeled off from the fabric before noting down the dry weight. Porosity
was calculated as:

$$5 \quad \varepsilon = \frac{w_0 - w_i}{\rho_w A l} \times 100\% \tag{1}$$

6 where, ε is the membrane porosity, w₀ and w_i are the weight of wet and dry membrane, ρ_w is
7 water density, l is the membrane thickness, and A is the average area of the membrane samples.
8 Porosity was estimated five times for each sample and the average value was reported.

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10 S.6 Measurement of permeability

Permeabiltiy of the membranes was determined using cross-flow filtration setup [2]. The membrane was thoroughly washed and cut into rectangular dimension (14.5 cm X 5.5 cm) to be fitted in the filtration unit. Then, the feed tank was filled up by distilled water and the membrane was compacted at 827 kPa for 3 hours. Permeate flux was measured at 276, 414, 552 and 690 kPa. It was calculated using the following equation:

$$16 \quad J_w = \frac{Q}{\Delta t \times A} \tag{2}$$

17 where, J_w is the pure water flux and Q is the amount of permeate collected; Δt is the time interval 18 of permeate collection and A is the membrane area. The slope of the linear graph, obtained by 19 plotting the flux against the TMP is designated as permeability of the membrane.

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21 S.7 Measurement of MWCO

MWCO refers to the molecular weight of solute (in daltons) that shows 90% rejection by the membrane. To determine the MWCO, the membranes were cut in circular disc of 7.6 cm diameter, to be fitted in the batch cell and were compacted at 690 kPa for three hours. Feed solution was prepared using neutral solutes of various molecular weights, i.e., polyethylene glycol (PEG) (35, 20, 10, 6, 4 and 0.4 kDa). The experiments were conducted using concentration 10 kg/m³, transmembrane pressure drop 207 kPa and stirring speed 2000 rpm. The rejection of solutes was determined using the following equation:

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$$R = (1 - \frac{C_p}{C_f}) \times 100\%$$
 (3)

2 where, R is the percentage rejection, C_p is the permeate concentration and C_f is the feed 3 concentration. C_p and C_f were measured using a digital refractometer (Model no 300034, 4 manufacturer: SPER scientific, supplied by Cole-Parmer, Kolkata, India), against the calibration 5 with known solute concentration.

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7 S.8 SEM investigations

SEM images of the top surface of the membranes are presented in Fig. S2. It 8 can be observed (Fig. S2a) that the membrane without PANI (PANI0) has denser morphology, 9 i.e., small sized pores and low pore density. However, incorporation of PANI leads to pore 10 opening, suggesting that it acts as pore forming material. Further, pore size and number density 11 12 are increased with PANI concentration (Fig S2b to S2e). This can be ascribed to the interaction of PANI with ZnCl₂ leading to reduction in cross-link density and less denser packing of PSF 13 chains, ultimately resulting in increase of porosity and pore size. Presence of bright spots on the 14 top surface of the membrane, suggest that during phase inversion, hydrophilic PANI comes to 15 the top surface of membrane due to better affinity towards water⁴. Moreover, the insolubility of 16 PANI in water and its ability of forming strong bond with PSF/ZnCl₂ prevent its leaching out 17 from the membrane surface. 18



2 Fig. S2: SEM images of top surfaces of PANI/PSF membranes (a) PANI0, (b) PANI0.5,
3 (c) PANI1, (d) PANI2 and (e) PANI3. (f-i) shows the SEM of bottom surfaces of membranes
4 (f) PANI0, (g) PANI0.5, (h) PANI2 and (i) PANI3

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6 In Figs. S2(f) to S2(i), the bottom surface images of different membranes are presented. In none 7 of these figures, significant presence of PANI (bright regions) is not noticeable. This part is less 8 exposed to water, compared to the top surface and hence, hydrophilic PANI accumulates only on 9 the top surface of the membrane during phase inversion, making it more available for surface 10 interaction with solutes. On the bottom surface, $ZnCl_2$ has stronger effect to make the membrane 11 denser due to unavailability of pore-forming PANI. The increased PANI concentration also 12 increases the affinity of membrane top surface towards water making it more water permeable. 1 2 3 4

5 S.9 AFM measurements and surface roughness

(a) (b) -75 (C) (d) 150 125 100 75 50 Membrane **Average surface** (e) roughness (nm) (a) PANI0 5 (b) PANI0.5 6 (c) PANI1 10 (d) PANI2 24 (e) PANI3 26

8 Fig. S3: Atomic force microscopy (AFM) images of membranes (a) PANI0, (b) PANI0.5, (c)
9 PANI1, (d) PANI2, (e) PANI3.

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Being hydrophilic in nature, PANI attracts more water inside the membrane matrix, forming the pores that grow in number and size with PANI concentration. Average skin thickness of the membranes decreases from 31.7 to 25.5 μ m with PANI concentration and this effect in combination with enhanced porosity makes the membrane more permeable. The visual observation of accumulation of PANI over membrane and increase in roughness with PANI is
 verified and quantified via AFM images (Fig. S3). The results show that the average surface
 roughness increases from 5 to 26 nm with increase in PANI loading.

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5 S.10 Water contact angle trend

6 To analyze hydrophilic behavior of the membranes, surface static contact angle of the 7 membranes with water is measured. The results (Fig. S4) revealed that the contact angle 8 decreases steadily with concentration of PANI. For PANI0, the value of the contact angle is 82° 9 and it decreases to 75°, for PANI0.5. This value further goes down to 66° for PANI3. 10 Accumulation of hydrophilic PANI leads to higher hydrophilicity of the membrane surface, 11 which in turn results in higher permeability.





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15 S.11 Mechanical property measurement

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2 Fig. S5: Variation of mechanical properties of the membranes with concentration of PANI

Fig. S5 shows the variation of breaking stress and elongation of membranes as a function of PANI concentration. It can be seen that both breaking strength and elongation decrease with PANI loading and that can be attributed to increase in porosity and associated stress concentration effects. Nevertheless, in spite of decrease in load bearing ability, the strength of even PANI3 membrane is enough to withstand the exerted trans-membrane pressure (TMP). This is particularly important from the viewpoint of the commercial applicability of these composite membranes.

10 S.12 PANI structure, oxidation state and protonation/deprotonation process:

Depending on the redox level, PANI can exist in three different states, namely, the fully reduced (leucoemeraldine or LB), the half oxidized (emeraldine or EB), and the fully oxidized (pernigraniline or PB) state ⁴. Chemically, PANI is composed of reduced (-B-NH-B-NH–) and oxidized (-B-N=Q=N-) repeated units where symbols 'B' and 'Q' denote benzenoid and quinoid forms of $-C_6H_4$ - ring. These units are distributed along the backbone and PANI can be represented by general structure [(-NH-B-NH-B-)_y–(-N=Q=N-B-)_(1-y)]_n, as shown in Fig. S6



(1-y)=0.5, Emeraldine Base (EB), half oxidized, half reduced form (1-y)=0, Leucoemeraldine Base (LB), fully reduced form

2 Fig. S6: General structure of the neutral (undoped) form of polyaniline

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where 'y' and 'n' are oxidation state (OS) and degree of polymerization (DP) respectively. 4 Therefore, depending on the oxidation state, different forms of polyaniline can be realized, viz., 5 leucoemeraldine (LB, fully reduced, y=1), pernigraniline (PB, fully oxidized, y=0) and 6 emeraldine base (EB, 50 % oxidized and 50 % reduced, y=0.5). The above-mentioned different 7 forms of PANI can be readily converted to one another by simple redox methods as shown in 8 Fig. S7. Only the amine nitrogen atoms constitute the reduced units whereas the oxidized units 9 are made up of imine nitrogen atoms. The imine nitrogen atoms, have high affinity to be 10 protonated in low pH as these groups do not have hydrogen bonds. 11



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5 S.13 FTIR investigations





1 The comparison of FTIR spectra among PANIO, PANI2, both for before and after filtration is presented in Fig. S8. From the gross spectral details, it can be clearly seen that the 2 stretch in the region between 3250-3400 cm⁻¹ is present in PANI2 (i.e. PANI/PSF composite 3 having 2 wt% PANI loading) but not well developed in PANIO (i.e. pure PSF matrix based 4 membrane). This band is due to free-charge carrier absorption in the doped PANI⁵. The stretch in 5 this region appears in presence of 1° or 2° amine. As PANI molecules have amine groups present 6 in the polymer chain, this stretch is reflected in the FTIR spectrum of PANI2 membrane. This 7 observation confirms successful incorporation of PANI in the membrane matrix. Further, the 8 peak at 1640 cm⁻¹ is present only in PANI2 due to presence of N-H bend, in 1° amine. It is 9 important to point out that there is no significant difference in peak positions in the spectra of 10 PANI2 before and after salt filtration, indicating no adsorption of salt molecules on the 11 membrane. Even after control experiment (with PANI0), no difference in any peak position is 12 observed, conforming absence of any strong bond, contributed by any phenomenon, like 13 adsorption. This is important from the view point of membrane fouling confirming charge-14 charge repulsion in the dominating salt-rejecting mechanism. 15

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