**Electronic Supplementary Information**

# Introducing deep eutectic solvents as flux boosting and surface cleaning agents for thin film composite polyamide membrane

Nidhi Maalige R.,[a] Sweedal A. Dsouza,[a] Matheus M. Pereira,[b] Veerababu Polisetti,[c] Dibyendu Mondal,[a]* and Sanna Kotrappanavar Nataraj *[a,d]

[a]Centre for Nano & Material Sciences, JAIN (Deemed to be University), Jain Global Campus, Bangalore- 562112, India.

[b]CICECO – Aveiro Institute of Materials, Chemistry Department, University of Aveiro, 3810-193 Aveiro, Portugal.

[d] CSIR-Central Salt and Marine Chemicals Research Institute (CSIR-CSMCRI), G. B. Marg, Bhavnagar 364 002, India

[d]IMDEA Water Institute, Avenida Punto Com, 2. Parque Científico Tecnológico de la Universidad de Alcalá. Alcalá de Henares. 28805 MADRID.

*Corresponding authors: dmtapu@gmail.com; m.dibyendu@jainuniversity.ac.in; sk.nataraj@jainuniversity.ac.in; sknata@gmail.com

## Experimental section

### Materials

Standard thin film composite polyamide (TFC-PA) membrane were collected from CSIR-CSMCRI lab Bhavnagar Gujarat.[1] Choline chloride- 99.9%, Ethylene glycol-99.0%, urea-99%, glycerol-99.5%, MgSO4-99.0%, and NaCl-99.50% purchased from SDFCL, India. Humic acid - 90% purchased from Nice chemical, India. Deionized (DI) water was used in all the experimental processes.

### Preparation of deep eutectic solvent

The DES were prepared in following manner.[2] In typical experiment, 1:2 molar ratio of choline chloride: ethylene glycol, choline chloride: urea and choline chloride: glycerol has taken in 100 mL glass containers and keep it for stirring at 80 °C until a clear homogenous liquid was formed.

### DES treatment on standard polyamide membrane

The standard polyamide membrane has taken and cut it to into four pieces. Further the membranes kept for solvent (DES) treatment for 24 h by varying temperature. The membranes were first treated with ChoCl-EG at 30°C, 40°C and 50°C about 24 h followed by ChoCl:U and ChoCl: Gly. The results which provided in the main manuscript are the average of the data obtained from three times repetition with three different TFC-PA membranes.The TFC-PA membrane modified with the respective DESs at different temperatures, which further used for the water purification studies for three times repeatedly. After the DES treatment membranes were washed with DI water and used for the performance studies using different feed solutions. Pristine TFC-PA and DES treated PA membranes codes are shown in table S1.

**Table S1**: Detailed solvent treated condition for polyamide membranes and sample codes

| Sl.No | Membrane code | Solvent treated membranes |
|---|---|---|
| 1 | TFC-PA | Pristine polyamide membrane without DES treatment |
| 2 | $TFC_{ChoCl\text{-}EG}$-30 | TFC-PA membrane treated with ChoCl:EG @ 30 °C for 24h |
| 3 | $TFC_{ChoCl\text{-}EG}$-40 | TFC-PA membrane treated with ChoCl:EG @ 40 °C for 24h |
| 4 | $TFC_{ChoCl\text{-}EG}$-50 | TFC-PA membrane treated with ChoCl:EG @ 50 °C for 24h |
| 5 | $TFC_{ChoCl\text{-}U}$-30 | TFC-PA membrane treated with ChoCl:Urea @ 30 °C for 24h |
| 6 | $TFC_{ChoCl\text{-}U}$-40 | TFC-PA membrane treated with ChoCl:Urea @ 40 °C for 24h |
| 7 | $TFC_{ChoCl\text{-}U}$-50 | TFC-PA membrane treated with ChoCl:Urea @ 50 °C for 24h |
| 8 | $TFC_{ChoCl\text{-}Gl}$ -30 | TFC-PA membrane treated with ChoCl:Glycerol @ 30 °C for 24h |
| 9 | $TFC_{ChoCl\text{-}Gly}$ -40 | TFC-PA membrane treated with ChoCl:Glycerol @ 40 °C for 24h |

| | | |
|---|---|---|
| 10 | $TFC_{ChoCl\text{-}Gly}$-50 | TFC-PA membrane treated with ChoCl:Glycerol @ 50 °C for 24h |

**Membrane filtration**

In a cross flow nanofiltration (NF) set up all experiments were carried out in lab scale NF cell with an effective area 0.001952 $m^2$. The active layer of membrane faced towards the feed side. All the experiments were carried out about 12 hours with three times repetition. An optimized range of inlet operating pressure of 1 to 4 bars was applied using booster pumps (KEMFLO) capable of maintaining a pressure between 0-14 bars. All the flux and rejection of contaminants were measured at every 60 min interval. The permeate flux and % rejection of contaminant was calculated using the formula.

$$J_W = \frac{\Delta v}{A.\Delta t} \quad \text{..... (1)}$$

Where, *J*w is the steady state permeate flux, through a film area (A), was calculated as the volume of permeate (Δv) collected during time period (Δt).

$$\%R = 1 - \frac{C_p}{C_f} \times 100 \quad \text{..... ..... (2)}$$

Where %R is the rejection efficiency, $C_f$ and $C_p$ are the concentration of the feed and permeate respectively.

**Antifouling studies:** To check the antifouling properties of the resultant membrane surfaces, long-term experiments were conducted for about 250 hours using humic acid as feed at 4 bar pressure as showed in main manuscript. The flux rate was measured for the first run ($J_{w1}$) and at the end of the experiment the fouled membrane was taken out, washed with distilled water for 2 minutes and reused in under similar experimental condition. Further,

the fouled membrane was taken out, washed with ChoCl-EG at 40 °C and reused in under similar condition. The flux rate for the second run of humic acid feed ($J_{w2}$) was measured In order to evaluate the fouling propensity of the membranes, the flux recovery ratio ($R_{FR}$) and the flux decline rate ($R_{FD}$) were calculated as follows (Equation 3 and 4).

$$R_{FR} = \frac{J_{W2}}{J_{W1}} \times 100 \quad \text{..... (3)}$$

$$R_{FR} = 1 - \frac{J_{W2}}{J_{W1}} \times 100 \quad \text{..... (4)}$$

**Recovery of solvents:** Since, the membranes were soaked in the deep eutectic solvents, there is no wastage of solvents after membrane treatment. The solvents were utilised up to 6 cycles without losing its performance.

**Surface cleaning property:** we have further carried out the experiments for long term studies until the flux rate reduces 50% compare to initial about 250h each cycle. Firstly we run the 10,000 ppm of humic acid for pristine PA membrane at 4 bar pressure followed by 24 h water wash then experiments were carried out repeatedly 3 times until the flux rate decreases. Later the membranes was treated with ChoCl-EG DES at 40°C to check the flux recovery.

**Characterization technique:**

**ATR-IR analysis:** Attenuated total reflection infrared spectroscopy ATR-IR (Perkin Elmer spectrum GX series 59387 ATR-IR spectrophotometer) was used to identify the functional group of pristine TFC and DES treated TFC membranes. The data was recorded over the range of 500-4000 $cm^{-1}$.

**FESEM morphology:** The morphology of the pristine PA and DES treated PA membrane was observed using field emission scanning electron microscopy (FESEM JSM- 7100F). Before

analysis by SEM, all samples were sputter-coated with a thin gold film to improve the imaging resolution during the SEM observation.

**AFM morphology:** For analyzing the surface morphology and roughness of the membranes, atomic force microscopy was employed using the atomic force microscope (AFM), Ntegra Aura, Model: nt-mdt (Russia).

**Contact angle:** The static contact angle of water is defined as the angle between the membrane surfaces and the tangent line at the contact point of the water droplet on the membrane surface.to check the hydrophilicity of PA and DES treated PA membrane were measured using contact angle analyzer (KRUSS), Germany. A water droplet of 5 µL was placed on the top- or bottom-side surface of the membrane sample. The measurements were repeated thrice for each membrane, and the average value was reported.

**NMR spectroscopy:** To analyze the leaching of DES on PA membranes nuclear magnetic resonance (NMR) spectroscopy analysis was done using for pristine ChoCl: EG before and after PA treated ChoCl: EG DES solution. $d_6$-DMSO was used as solvent.

**Conductivity meter:** To analyze the conductance of $MgSO_4$ feed and permeates were measured using conductivity meter (*HANNA* instrument USA).

**UV-Visible Spectroscopy:**To analyze the feed and permeates concentration of humic was measured using UV-Visible spectroscopy. The absorbance studies were performed in (Shimadzu) UV-Visible spectrophotometer with standard 1 cm quartz cuvette.

**Zeta Potential**: For analyzing the surface charge of the membranes, streaming the potential analysis was employed using the streaming the potential instrument, Anton-Par (Austria).

**Molecular docking studies:** The interaction sites of TFC-PA membranes with the DES were identified using the Auto-dock vina 1.1.2 program.[3] The structure of TFC-PA membranes were prepared using Discovery Studio,v 16 (Accelrys, San Diego, CA, USA) and used in the molecular docking. Auto DockTools (ADT)[2] was used to prepare the membranes input files. Ligand (hydrogen bond *donor* (HBD) and hydrogen bond *acceptor* (HBA)) 3D atomic coordinates was computed by Discovery Studio, v 16(Accelrys, San Diego, CA, USA) and

ligand rigid root was generated using AutoDockTools (ADT), setting all possible rotatable bonds defined as active by torsions. The grid center at the center of mass (x-, y-, and z-axes, respectively) to cover the whole interaction surface of TFC-PA was 72 Å × 40 Å × 40 Å. The binding model that has the lowest binding free energy was searched out from 10 different conformers for each ligand (HBD and HBA).

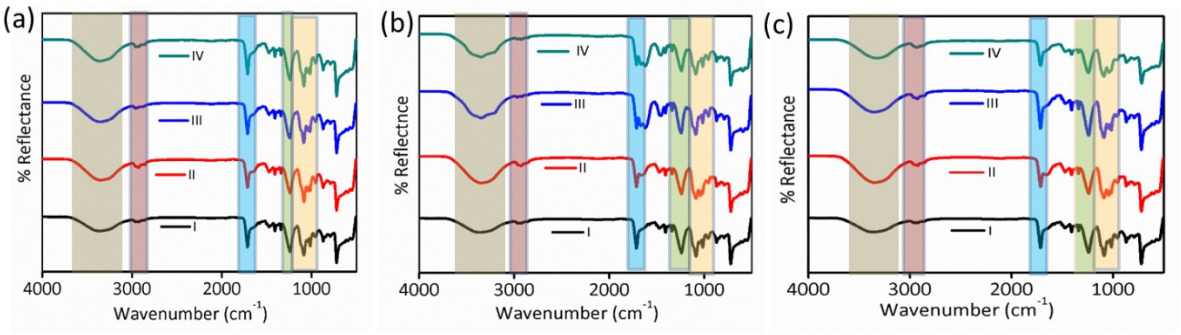


Fig S1**:** ATR-IR spectra for (a) $TFC_{ChoCl}$-EG-30, 40 &50 (b) $TFC_{ChoCl\text{-}U}$-30, 40 &50 & (c) $TFC_{ChoCl\text{-}Gly}$-30, 40 & 50. S1-(a): I represents the TFC-PA membrane, II represents $TFC_{ChoCl\text{-}EG}$-30 membrane, III represents $TFC_{ChoCl\text{-}EG}$-40 membrane & IV represents $TFC_{ChoCl\text{-}EG}$-40. S1-(b): I represents the TFC-PA membrane, II represents $TFC_{ChoCl\text{-}U}$-30 membrane, III represents $TFC_{ChoCl\text{-}U}$-40 membrane & IV represents $TFC_{ChoCl\text{-}U}$-40. S1-(c): I represents the TFC-PA membrane, II represents $TFC_{ChoCl\text{-}Gly}$-30 membrane, III represents $TFC_{ChoCl\text{-}Gly}$-40 membrane & IV represents $TFC_{ChoCl\text{-}Gly}$-40. The same has been included in the revised manuscript.

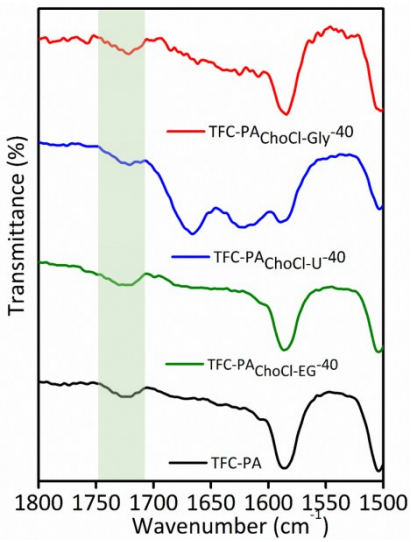


Fig S2: ATR-IR spectra for TFC-PA, $TFC_{ChoCl\text{-}EG}$-40, $TFC_{ChoCl\text{-}U}$-40, and $TFC_{ChoCl\text{-}Gly}$-40

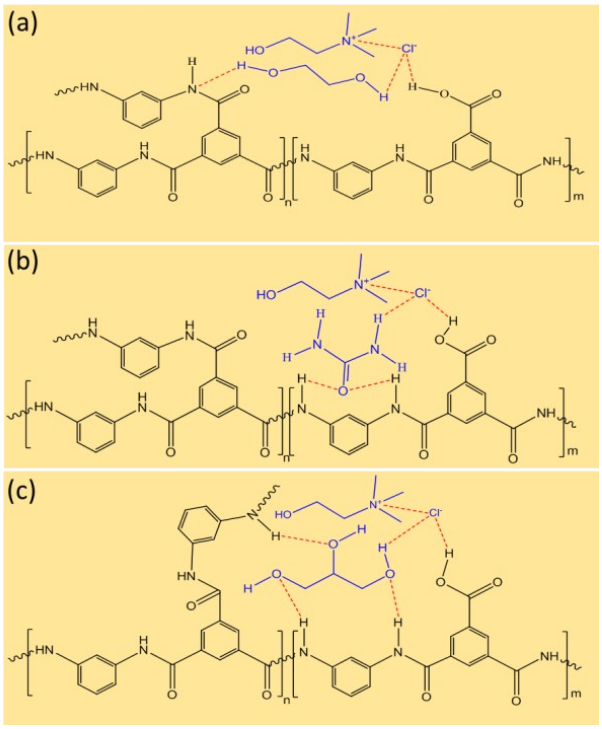


Fig S3: Chemical structure of polyamide active layer (a) hydrogen bonding interaction between the TFC-PA and ChoCl-EG (b) hydrogen bonding interaction between the TFC-PA and ChoCl-U and (c) hydrogen bonding interaction between the TFC-PA and ChoCl-Gly

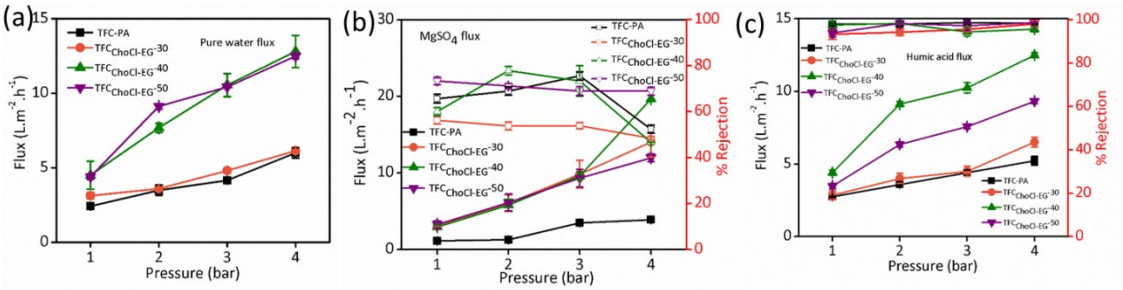


Fig S4: The flux and rejection studies for TFC-PA and ChoCl-EG treated TFC-PA membranes (a) pure water flux, (b) 2000 ppm $MgSO_4$ flux and %R and (c) 100 ppm humic acid flux and %R data.

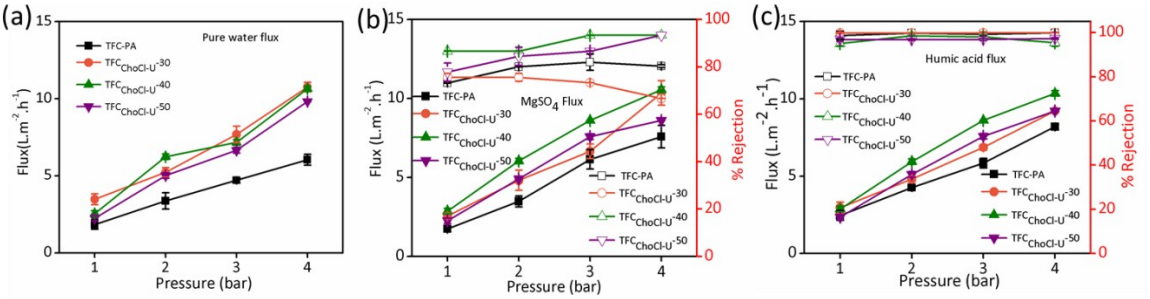


Fig S5: The flux and rejection studies for TFC-PA and ChoCl-U treated TFC-PA membranes (a) pure water flux, (b) 2000 ppm $MgSO_4$ flux and %R and (c) 100 ppm humic acid flux and %R data.

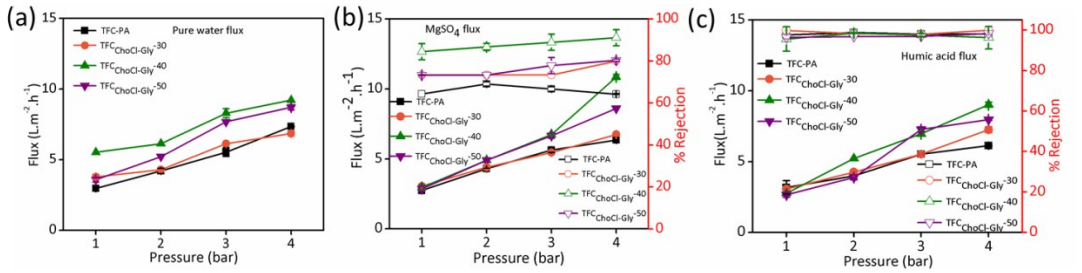


Fig S6: The flux and rejection studies for TFC-PA and ChoCl-Gly treated TFC-PA membranes (a) pure water flux, (b) 2000 ppm $MgSO_4$ flux and %R and (c) 100 ppm humic acid flux and %R data.

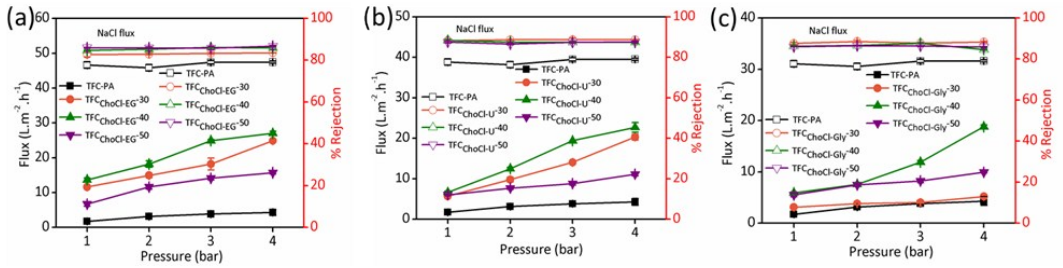


Fig S7 :NaCl flux and rejection studies for TFC-PA, (a) ChoCl-EG treated TFC-PA, (b) ChoCl-U treated TFC-PA, and (c) ChoCl-Gly treated TFC-PA

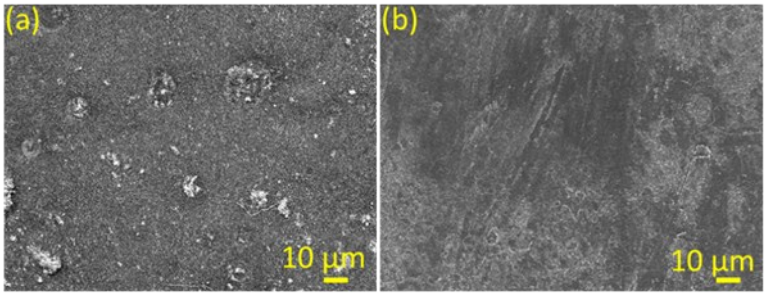


Fig S8: FESEM images of (a) TFC-PA after fouling and (b) TFC-PA after cleaning with the ChoCl-EG 40.

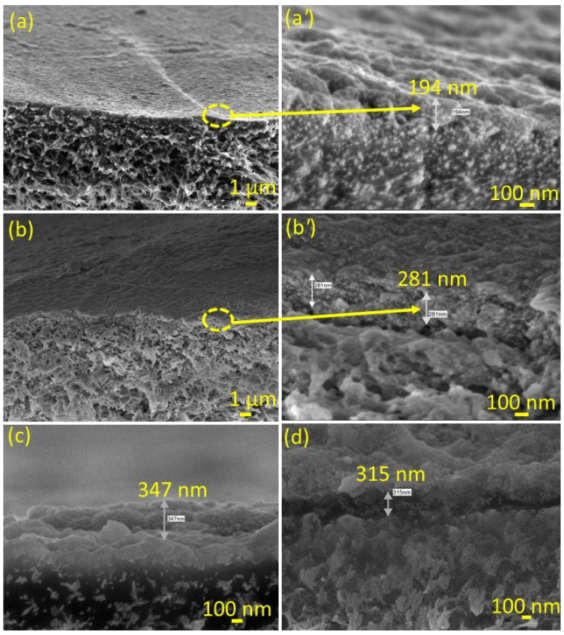


Fig S9: FESEM cross section images of (a) TFC-PA membranes before DES treatment, (a') magnified image of TFC-PA and (b-d) after treatment with different DESs. (b) $TFC_{ChoCl\text{-}EG}$-40, (b') magnified image of $TFC\text{-}PA_{ChoCl\text{-}EG}$-40, (c) $TFC_{ChoCl\text{-}U}$-40, & (d) $TFC_{ChoCl\text{-}Gly}$-40.

Table S2: Docking affinity energy and type of interactions with TFC-PA membrane and different component of DESs.

| Compound | Affinity (kcal/mol) | Type of interaction | From | TO | Distance (Å) |
|---|---|---|---|---|---|
| $[Cho]^+$ | -1.4 | Hydrogen bonding interaction (HBI) | $[Ch]^+$ - O | TFC - O | 3.56 |
| $[Cl]^-$ | -0.5 | (HBI) | - | - | - |
| Glycerol | -1.5 | (HBI) | TFC - NH | Glycerol - O | 2.51 |
| | | | Glycerol - H | TFC - O | 2.77 |

| | | | | | |
|---|---|---|---|---|---|
| | | | Glycerol - H | TFC - O | 2.84 |
| Ethylene glycol | -1.2 | (HBI) | TFC - NH | Ethylene glycol - OH | 2.50 |
| Urea | -1.3 | (HBI) | Urea - H | TFC - O | 2.29 |
| | | | Urea - H | TFC - O | 3.56 |

**References**


1. R. Rangarajan, N. Desai, S. Daga, S. Joshi, A. P. Rao, V. Shah, J. Trivedi, C. Devmurari, K. Singh and P. Bapat, *Desalination*, 2011, **282**, 68-77.
2. A. Mahto, D. Mondal, V. Polisetti, J. Bhatt, N. M. R, K. Prasad and S. Nataraj, *Industrial & Engineering Chemistry Research*, 2017, **56**, 14623-14632.
3. O. Trott and A. J. Olson, *Journal of computational chemistry*, 2010, **31**, 455-461.
4. G. M. Morris, R. Huey, W. Lindstrom, M. F. Sanner, R. K. Belew, D. S. Goodsell and A. J. Olson, *Journal of computational chemistry*, 2009, **30**, 2785-2791.