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Choline chloride-Glycerol (1:2 mol) as draw solution in forward osmosis for dewatering purpose

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Abstract. Choline chloride-glycerol (1:2 mol), a natural deep eutectic solvent (NADES) is examined as a draw solution in forward osmosis (FO) for dewatering application. The NADES is easy to prepare, low in toxicity and environmentally benign. A polyamide thin film composite membrane was used. Characterization of the membrane confirmed porous membrane structure with good hydrophilicity and a low structural parameter (722 µm) suitable for FO application. A dilute solution of 20% (v/v) NADES was enough to generate moderate water flux (14.98 L $m^{-2}h^{-1}$) with relatively low reverse solute flux (0.125 g $m^{-2}h^{-1}$) with deionized water feed. Application in dewatering industrial wastewater feed showed reasonably good water flux (11.9 L $m^{-2}h^{-1}$) which could be maintained by controlling the external concentration polarization and fouling/scaling mitigation via simple periodic deionized water wash. In another application, clarified sugarcane juice could be successfully concentrated. Recovery of the draw solute was accomplished easily by chilling utilizing thermo responsive phase transition property of NADES. This study established that low concentration NADES can be a viable alternative as a draw solute for dewatering of wastewater and other heat sensitive applications along with a simple recovery process.

Keywords: forward osmosis; flux; ionic liquid; membrane; wastewater

1. Introduction

The continuous growth of industrialization and Forward osmosis (FO) has triggered a renewed interest in the basic and applied research of membrane based wastewater technologies, despite being old in its concept. FO has created its own niche in the reclamation of high-fouling complex wastewater feed either as a stand-alone system or in integration with other hydraulic pressure driven membrane processes (Chekli *et al*. 2016, Dutta and Nath 2019, Sun *et al*. 2017). Selection of an efficient membrane and that of a draw solute stand out to be the two most significant prerequisites for the success of FO process and a proper combination is required to maintain a balance between permeability and selectivity (Shaffer *et al*. 2015). Membrane development has taken a long stride in the directions of improved water flux, better reusability and reasonably low level of reverse solute flux (RSF) (Awad *et al*. 2019, Ghadiri *et al*. 2019). On the other hand, a wide spectra of draw solutes of different types has been assessed for their amenability in FO applications with respect to the issues mentioned above (Cai and Hu 2016, Doshi and Mungray 2020, Dutta *et al*. 2020, Sudeeptha and Thalla 2017). Deep eutectic solvents (DES) which belong to a family of ionic liquids (IL) are considered to be environment friendly and are extensively used as solvents in a range of separation processes, entrainer in azeotropic separation, absorbents, catalyst in reaction and various other applications (Dutta and Nath 2018a, Taghizadeh *et al*. 2021). DESs have similar characteristics to ILs but are comparatively cheaper, low in toxicity and often biodegradable (Paiva *et al*. 2014). They are typically formed by mixing choline chloride (ChCl) with hydrogen bond donors such as amines, acids, and alcohols. DESs demonstrate close physico-chemical properties (viscosity, density, conductivity, among others) to those of conventional ILs. In addition, like ILs, the physico-chemical properties of DESs can be tuned more or less substantially by altering the nature of the quaternary ammonium salt ($-N(CH_3)_3)^+$ and the hydrogen-bond donor, thereby facilitating the synthesis of task-specific DESs. Compared to ILs, DESs have remarkable benefits in the form of: (i) expedient synthesis (100% atom economy), (ii) very low cost as most of DESs can be prepared from readily available chemicals and (iii) little toxicity, particularly DESs derived from ChCl and renewable chemicals. Obviously, these notable ecological and economical footprints of DES nowadays unlock optional routes for the emergence of ionic fluids at a larger scale. It should also be further noted that though mechanisms of DESs are potentially reactive chemicals, their auto-association by a hydrogen bond drastically limits their reactivity, allowing their use in many fields of research (Zhang *et al*. 2012). When natural compounds like primary metabolites comprise the DES it is termed as natural deep eutectic solvents (NADES).

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ILs have demonstrated great prospects when tried as draw solutes in the FO process (Dutta and Nath 2018a). Some interesting work using IL and DES as draw solutes in the FO process has been cited in literature (Cai *et al*. 2015, Mahto *et al*. 2017, Mok *et al*. 2013, Mondal *et al*. 2015, Nakayama *et al*. 2014, Noh *et al*. 2012). Being thermally responsive, the IL/DES-water separation required for recovery of draw solute from diluted draw solution is accomplished by increasing or decreasing the temperature of dilute draw solution depending upon the type of IL/DES. In the case of lower critical solution temperature (LCST) type mixture the temperature of dilute draw solution is increased and phase separation occurs at temperature above the LCST point (Inada *et al*. 2019, Mok *et al*. 2013, Nakayama *et al*. 2014, Noh *et al*. 2012), while in the case of upper critical solution temperature (UCST) type mixture the temperature of dilute draw solution is decreased and the phase separation occurs at temperature below the UCST point (Mondal *et al*. 2015, Zhong *et al*. 2016). The phase separation results in an IL rich phase and water rich phase. The water rich phase may need further polishing to produce good quality water. One of the main reasons for using IL or DES as a draw solute is the ease and possibility of energy efficient recovery. Considering the vast world of IL/DES, only a few have been tried as a draw solution which keeps the area wide open.

Choline chloride-glycerol (1:2 mol) is an UCST type NADES. The impetus for choosing this NADES is that both its components are easily available, low in cost, non-toxic and environmentally benign compared to other ILs. ChCl is a dietary component extracted from biomass and is used as additives in bird and animal feed to boost productivity. Glycerol, on the other hand, is often used as a solvent, sweetener, preservative etc. in the food and beverage industry and also a common ingredient in pharmaceutical and personal care preparations. Contrary to most DESs, ChCl-glycerol (1:2 mol) is less acidic in nature, pH ranging from 4.5-5 between 20-60°C. Moreover, preparation of the NADES by heating method is simple. High osmotic potential of 317 atm. and low water activity of ≤ 0.1 render it worthy of study as a draw solute in FO process. Considering that the NADES and its water mixture have low toxicity profile (Hayyan *et al*. 2016), may be particularly suitable for dewatering of sensitive products such as pharmaceutical and food products. The relative high cost of NADES can be compensated by keeping concentration low for FO application. Moreover the ease of draw solute recovery may make them competitive against inexpensive inorganic salt draw solutes that require complex recovery processes (Dutta and Nath 2018b, 2019).

The objective of the present work was initially to synthesize ChCl-Glycerol (1:2 mol) NADES draw solute and study its interaction with water. The NADES draw solute, thus prepared, was used in a bench scale FO unit for dewatering of industrial wastewater and sugarcane solution using an indigenously developed FO membrane by the Indian Institute of Chemical Technology (IICT), Hyderabad under Council of Scientific and Industrial Research (CSIR), India. Suitability of using low concentration NADES as a draw solute was explored and applied for dewatering of wastewater and other heat sensitive applications with subsequent recovery by chilling. Altogether, this study aims to shed some light on the viability of low concentration NADES induced FO processes and to disseminate further the idea of an integrated forward osmosis system with easy recovery of draw solute.

2. Materials and methods

2.1 Membrane

The membrane used in the present study was developed and kindly provided by the Indian Institute of Chemical Technology (IICT), Hyderabad under Council of Scientific and Industrial Research (CSIR), India. The thin film composite (TFC) type membrane was manufactured by interfacial polymerization technique. It has a polyamide active layer with polyethersulfone (PES) support substrate over polyester fabric having total membrane thickness of 70 µm. Dimethyl sulfoxide (DMSO) was added to increase pore size and number of pores during interfacial polymerization to promote water flux. More details about the membrane synthesis and other details can be found in literature (Madhumala *et al*. 2017).

2.2 Forward osmosis system

A specially designed and indigenously fabricated bench scale unit with a flat sheet membrane module having an active area (A_m) of 14.5 cm^2 was used for FO experiments (Fig. 1). All the experiments were conducted in batch mode using a pre soaked fresh membrane piece every time in active layer (AL) facing feed solution (FS) i.e., AL-FS orientation (FO mode). The feed and draw solution (1 L each) were kept in storage tanks and were circulated using submerged centrifugal pumps of low capacity (12 W, 15 L min^{-1} maximum). The flow rate was maintained using flow control valves and maintained at 1 L min^{-1} on both sides. All the experiments were performed at ambient conditions (20 ± 0.5°C). The water transport was measured by weight reduction of the feed solution using a digital weighing balance. Weight was noted at 30 s intervals for the first 10 min, 1 min interval for the next 20 min and 5 min interval from then on. The water flux was calculated as shown in Eq. (1);

$$J_w = \frac{\Delta W_t}{\rho\, A_m \Delta t} \tag{1}$$

where J_w denotes the water flux, W_t is the weight of the FS at any time t, ρ is the density of the FS. The initial and final concentration of FS was measured to calculate the RSF as shown in Eq. (2):

$$J_s = \frac{\Delta(C_t\, V_t)}{A_m \Delta t} \tag{2}$$

where C_t is the solute concentration and V_t the volume of the FS at any time t. All the batch experiments using deionized (DI) water and industrial wastewater feed were

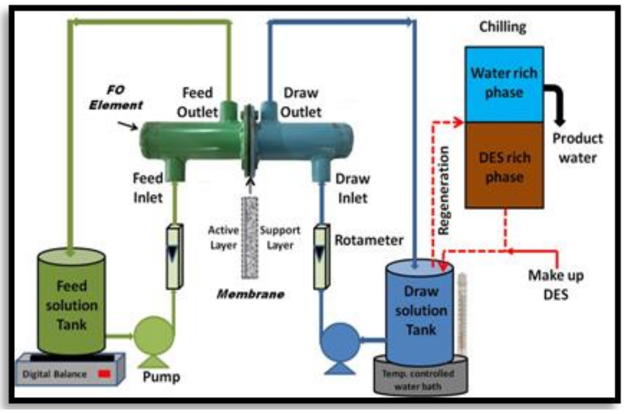


Fig. 1 Schematic representation of the experimental setup

Table 1 Industrial wastewater analysis

Parameters	
pH	7.99
Total dissolved solid	4626.9 mg L^{-1}
Total suspended solid	101.2 mg L^{-1}
Chemical oxygen demand	722.2 mg L^{-1}
Biological oxygen demand	250.3 mg L^{-1}
Chloride as Cl^-	505.7 mg L^{-1}
Sulphate as SO_4^{2-}	58.2 mg L^{-1}
Flouride as F^-	0.002 mg L^{-1}
Ammonical N (NH_3-N)	34.4 mg L^{-1}

conducted for 4h and no makeup draw solute was added. A digital thermometer was used to measure the temperature of the solution.

For dewatering of industrial wastewater with membrane cleaning, two separate tanks containing feed solution and DI water with necessary piping and valve arrangement were used. FO operation of 4h followed by DI water washing for 1h was carried out in cyclic manner by valve operation. Required quantity of makeup draw solute was added after each cycle to maintain the draw solution concentration.

2.3 Chemicals

DI water (Merck Ltd) of conductivity (5-10 µS cm^{-1}), sodium chloride and choline chloride (Luba Chemie), glycerol (S. D. Finechem) and sugarcane were procured from local suppliers. All the chemicals were of standard laboratory reagent (LR) grade and were used as-received without any further purification. The industrial wastewater was acquired from a local dye manufacturing unit producing a range of dyes with different chemistries. The sample was collected from the outlet of the effluent treatment plant after primary treatment. The analysis of the industrial wastewater is provided in Table 1.

2.4 Preparation of NADES (ChCl-glycerol, 1:2 mol)

The NADES was prepared by heating method. Required choline chloride (ChCl) and glycerol was weighed at a molar ratio of 1:2. ChCl was dried in a drying oven at 50°C for 24 h for moisture removal before weighing. Glycerol was heated up to 80°C in a round bottom flask with reflux condenser on a constant temperature hot plate fitted with a mechanical stirrer. ChCl crystals were added and the mixture was maintained at 80°C for 2 h with continuous stirring until homogeneous pale yellow liquid was formed. For NADES-water mixture preparation, the necessary quantity of DI water was added with continuous stirring.

2.5 Characterization

The Raman spectra were recorded at room temperature under the backscattering geometry using a Jobin Yvon Horiba LabRam, HR 800 single monochromator coupled with a Peltier cooled charge coupled device (CCD) and a 488 nm argon (Ar^+) laser was used for excitation. The samples were analyzed using the microscope and a 50 × objective was used. Spectra were collected in the range of 800 to 2000 cm^{-1}. The spectra were acquired using scan time settings of 50s for composite fabric analysis. Raman data acquisition and data processing were achieved through Thermo Electron’s OMNIC software. Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR, VERTEX 80, Bruker Corp., Germany) was used for analysis of the bonds and functional groups on the near-surface region of membrane. IR spectra of the membranes were recorded in the wave number range of 500–4000 cm^{-1} at 28°C. The scanning electron microscope (SEM) images were taken using JSM-6010LA InTouch scope (JEOL, USA). A dry fresh membrane piece was used which was sputter coated prior to taking images. The wettability of the FO membrane was analyzed by measuring the contact angle using the sessile drop method with an optical Tensiometer. A digital refractometer (Hanna Instruments) was used to measure the refractive index of NADES at various concentrations. The chilling of 20% (v/v) NADES solution was carried out in a 490 L laboratory freezer (temperature up to –25°C). The sugarcane juice concentration was measured by using a well calibrated digital refractometer and measuring the refractive index at various concentrations.

For wastewater characterization, the pH of all the solutions was measured by a standard pH meter (Hanna Instruments, Taiwan). The total dissolved solids (TDS) of all the streams were measured by an auto-ranging conductivity/TDS meter (Hanna Instruments, Taiwan) with automatic temperature compensation. Total suspended solids (TSS) was measured by filtering a known volume of wastewater sample using a glass fiber filter, drying the filter containing captured solids at 104°C, followed by determining weight differential by a microbalance. Chemical oxygen demand (COD) was measured by closed reflux method measuring the oxygen consumed during oxidation of organic matter using potassium dichromate as an oxidizing agent. The BOD_5 was measured by 5 days incubation at 20°C following standard procedure. All other elemental analyses were performed as per APHA 23rd edition and IS 3025 standards.

Table 2 Properties of choline chloride, glycerol and NADES

Parameters	Unit	Choline Chloride	Glycerol	NADES
IUPAC name		2-hydroxy-N,N,N-trimethylethanaminium chloride	propane-1,2,3-triol	-
Molecular formula		$C_5H_{14}NOCl$	$C_3H_8O_3$	-
Molecular weight	g mol^{-1}	139.62	92.094	107.9
pH	-	6.5–8	7	6.2
Density	g cm^{-3}	1.1*	1.261	1.18
Viscosity	cP	21*	954	259
Water activity	-	-	-	0.1
Conductivity	mS cm^{-1}	-	-	4.05
Osmotic Potential	atm.	-	-	317
Melting point	°C	302	18.2	– 40
Boiling point	°C	#	290	-

All properties at NTP

* 70 ± 1 % choline chloride, 30 % water, less than 0.05 % impurities; measured; BASF AG (1974).

\# not applicable due to decomposition on heating

3. Results and discussion

3.1 Properties of choline chloride-glycerol (1:2 mol) NADES

The structure of ChCl-glycerol NADES has been investigated by ATR-FTIR. Also to determine the influence of water presence on the interactions between different terminal groups in the ChCl-glycerol (1:2 mol) NADES, FTIR spectra of the NADES of varying composition (10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, 100%) were recorded (Fig. 2), and the corresponding wavenumber (cm^{-1}) of the vibrational modes and their associated terminal groups. It can be noted that, approximately, the characteristic spectrum of the NADES is an overlap of those of glycerol and ChCl. In addition, the bands associated to ChCl, such as ρ CH_3, ρ CH_2, ν_{as} CCO and δ CH appeared in the spectrum of NADES. These results divulge that the structure of Ch+ was not destroyed in the NADES. Particularly, the absorption bands of Glycerol at 3448 cm^{-1} and 3359 cm^{-1}, which can be ascribed to the stretching mode of -NH_2 (ν_{as} NH_2 and ν_s NH_2), moved towards the lower wavenumber region to 3421 cm^{-1} and 3349 cm^{-1} and changed to broader bands. This could be attributed to the forming of more hydrogen bonds between glycerol and ChCl. The additional hydrogen bonds maybe exist as O-H⋯N-H, O-H⋯O and O-H⋯OH, as illustrated in Fig.3 (A-D). The water had a marginal effect on the vibration frequency of the groups in NADES by studying systematically various compositions (10 – 100%), the increasing composition NADES. At this point, the spectrum of the NADES containing 100% ChCl-glycerol H_2O shifted to higher % transmission. The absorption bands of glycerol ascribed to the stretching mode of –OH at 2990 cm^{-1}and 3200 cm^{-1}moved towards the lower wavenumber region due to absorbing water. Meanwhile, its absorption bands ascribed to the bending mode of –NH_2 (δ_{as} NH_2 and δ_s NH_2) moved to the higher wavenumber area, and which can be attributed to the formation of more hydrogen bonds with increasing % composition from 10–100% NADES.

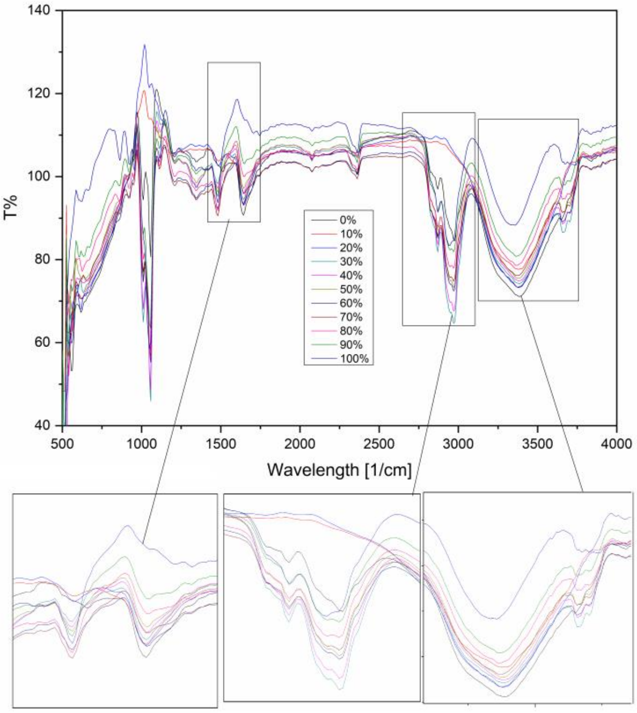


Fig. 2 ATR FTIR spectra for Choline chloride and glycerol composition (1:2 mol) + water at different (0 - 100%) concentration

The excess hydrogen bonds may exist as O–H⋯N–H, O–H⋯O and N–H⋯O, as depicted in Figs. 3(c) and 3(d). In addition, a band at 1580 cm^{-1} ascribed to the bending vibration of –OH (δ_{as} OH) appeared given the co-existence of water as a result of hydration whereas, water has a leading impact on the shape of the spectrum of ChCl. Two individual absorption bands of ChCl at 3126 cm^{-1} and 3460 cm^{-1} assigned to the stretching mode of –OH, were merged into a broad peak with a maximum peak value at 3126 cm^{-1} after absorbing water (shown in Fig. 3(b)), illustrating that the water existed as flocks or aggregates. It can be predicted that

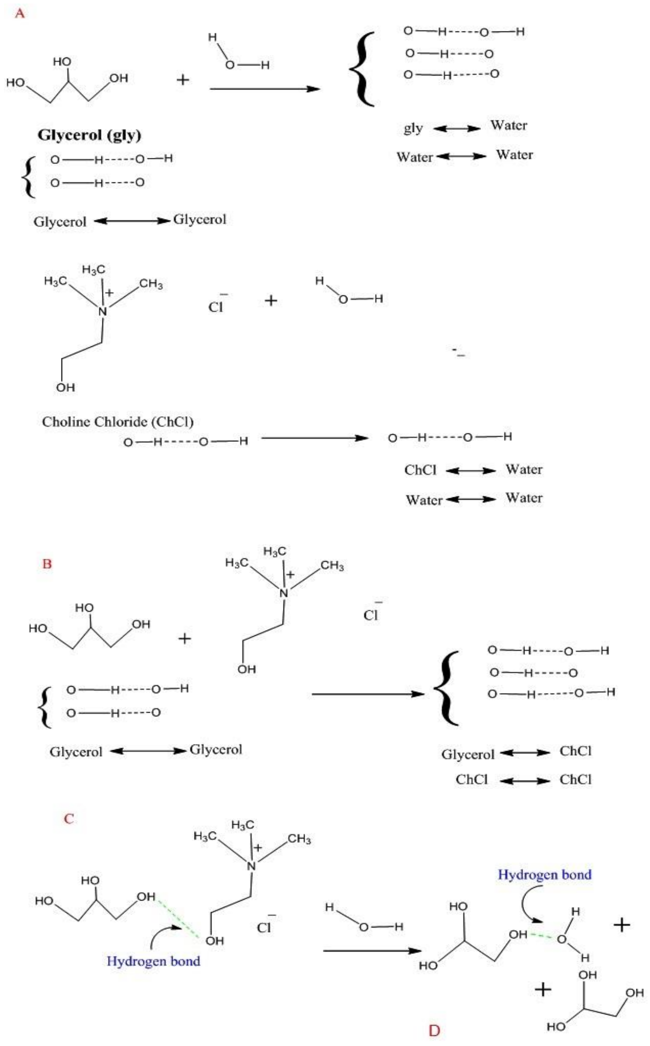


Fig. 3 Proposed mechanism of hydrogen bonds formed between glycerol and ChCl and water

water molecules preferentially pooled with other water molecules rather than ChCl according to their structural resemblance (Figs. 3(a)-3(c)).

The structure of ChCl-glycerol NADES has been investigated by ATR-FTIR but that particularly didn't focus on the water presence. Notably, the FTIR spectrum of the glycerol in the reference is in agreement with that of the glycerol containing 10 – 100 wt.% water in the present study. It implies that extraordinary care should be taken regarding the analysis of NADES due to its high hygroscopicity. Based on the above analysis, the water will preferentially combine with glycerol molecules but not ChCl once NADES absorbs water from the environment through hydrogen bonds.

Hence, the decomposition of water can be suppressed and the electrochemical window could be persisted due to the strong hydrogen bond, as revealed by the cross validation (CV) tests in Fig. 3. On the other hand, the fact that a fraction of the ChCl linked with glycerol through hydrogen bonds were replaced by water molecules will produce more free Ch+ and in turn result in a high ionic dissociation. This is due to the fact that water can interfere with the coulombic force between Glycerol and ChCl through interacting with the –OH group, which may be the intrinsic reason why the ionic dissociation was promoted by water in Fig. 4(b). It has been proposed that hydrogen bonds were formed preferentially with –OH when water was added into the similar protic ILs.

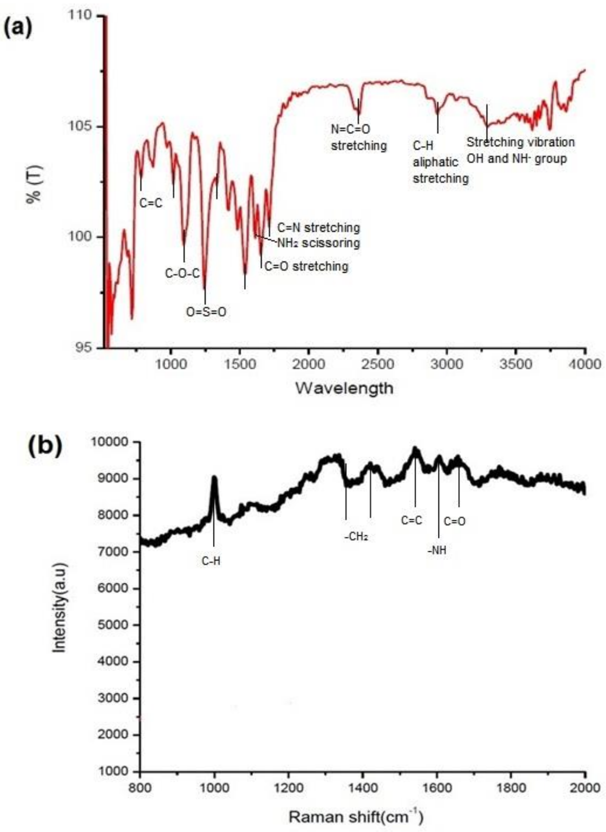


Fig. 4 (a) FTIR and (b) Raman spectroscopy of thin film composite FO membrane

Further, ChCl-Glycerol could generate very high osmotic pressure of 317 atm. The osmotic potential could be retained ($\pi > 150$ atm.) after 50% dilution and ($\pi > 60$ atm.) even after 80% dilution (similar to approximately 1 mol L^{-1} NaCl). Similar observation is also reported in literature (Mondal *et al*. 2015). Taking into account the above observations, due to (i) retention of osmotic potential, (ii) low viscosity, (iii) good ionic activity, and (iv) reduction in cost, 10 – 30% (v/v) ChCl-Glycerol was tested as a draw solute for FO application.

3.2 Membrane study

3.2.1 ATR-IR spectroscopy analysis

ATR-IR spectroscopy was used for surface analysis because of its unique ability to estimate the content of various functional groups present on the membrane surface. Fig. 4(a) depicts the IR spectrum of cross linked thin film composite membrane with polyamide active layer over polyethersulfone support substrate with polyester support fabric. The common adsorption bands typical for all grafted polymers at 980 cm^{-1} (C=C bending, alkene), 1290 cm^{-1} (C–O stretching, alkyl aryl ether), 1670–1680 (C=N stretching, imine/oxime), 1725–1705 (C=O stretching, aliphatic ketone) and 2275–2250 cm^{-1} (N=C=O stretching) were displayed in the ATR-FTIR spectrum. The sharp peaks

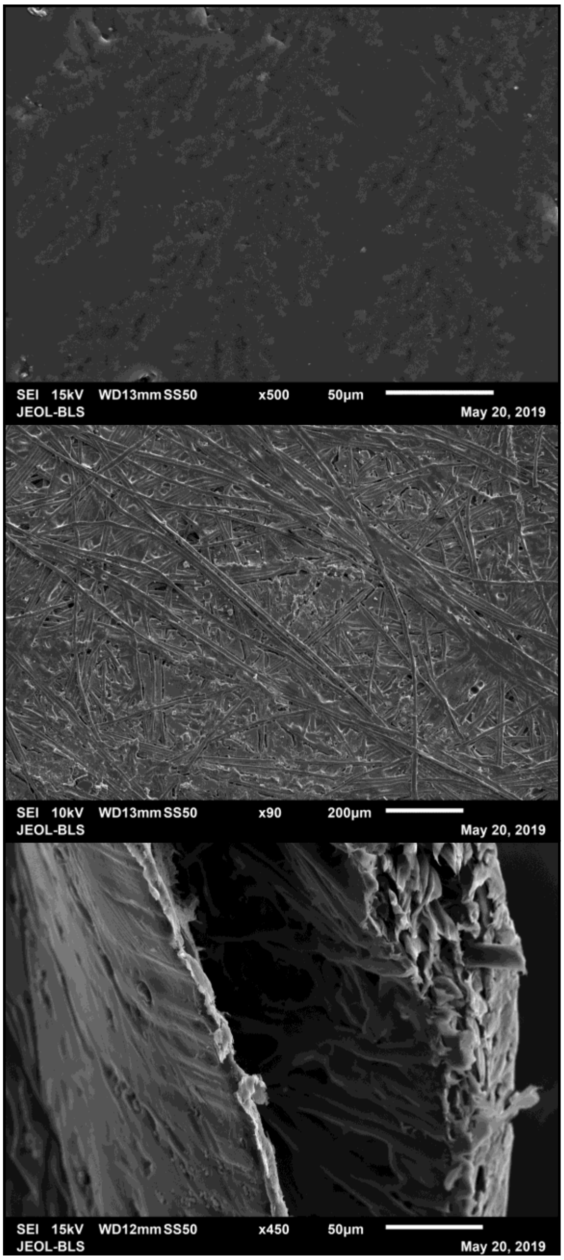


Fig. 5 SEM micrographs of thin film composite FO membrane (a) top layer (500×), (b) polyester support layer bottom surface (90×) (c) cross section showing the differentiated active and support layers (450×)

at (2921–2875cm^{-1}) are due to C–H aliphatic stretching vibration presence in the polyamide active layer. The peaks at 2965 cm^{-1} represent =CH stretching vibrations in both polyamide and polyethersulfone. The wide absorption band at 3300 cm^{-1} might be due to overlapping of the bending vibration of –OH group of water and –NH group of amide (Madhumala *et al*. 2017). Comparison with DMSO FTIR analysis from literature (NIST Chemistry WebBook), the peaks particularly around 1050–1100cm^{-1}, 1290–1310 cm^{-1} and 2800–3000 cm^{-1} in both DMSO (sharp) and membrane (broad) indicates presence of DMSO.

3.2.2 Raman spectroscopy

Raman spectroscopy was used for surface analysis because of its unique ability to estimate the content of various functional groups present on the membrane surface. The data in Raman spectroscopy is provided in the form of intensity over wavelength of the scattered photons (Raman shift) as shown in Fig. 4(b). The peaks at 1355, 1420 and 1610 cm^{-1} are representative of -CH_2 wagging, -CH_2 bending and amide respectively, the characteristics of polyamide layer over polyethersulfone support substrate.

3.2.3 SEM analysis

The SEM images of the FO membrane are shown in Fig. 5. The surface morphology of the TFC polyamide membrane exhibited a ridge-and-valley structure. Cross-sectional image shows presence of a dense nanoporous polyamide layer over the ultraporous PES substrate which is attached to a polyester non-woven fabric layer. The upper polyamide layer is a selective forbidding movement of solute molecules (active layer), whereas both PES and polyester layer act as a support layer to provide the necessary mechanical strength and allow passage of both solvent and solute molecules. The thickness of the support layer is optimized to the extent required for non-pressurized application. Addition of DMSO also caused disruption in the pore structure of PES substrate to a small extent creating bigger voids that enable increased solvent permeation. No agglomeration or cluster formations were observed anywhere in the multilayered polymer materials. Additional information about the same membrane can be found in the literature (Madhumala *et al*. 2017).

3.2.4 Contact angle measurement

The contact angle of the membrane was found to be 68.7° which shows good wettability of the membrane surface and is responsible for providing high water flux. This may be attributed to the addition of DMSO which causes disruption in the pore structure of PES substrate during interfacial polymerization creating bigger voids that enhances solvent permeation through the membrane (Kim *et al*. 2005).

3.2.5 Membrane parameters

Membrane parameters water permeability coefficient (A), solute permeability coefficient (B) and membrane structural parameter (S) was determined numerically using NaCl-DI water system by FO based test method (Tiraferri *et al*. 2013)). A and B value was 4.11 L m^{-2}h^{-1}bar^{-1} and 0.65 L m^{-2}h^{-1} respectively and the S value of the membrane was found to be 722 µm. The lower value of the structural parameter indicated a porous and less tortuous support layer. Hence, it was possible for the membrane to attain higher water flux as the draw solute faced less resistance in the support layer, a prime requirement for non-pressurized FO application.

3.3 FO performance

The performance of ChCl-glycerol (1:2 mol) NADES as a draw solute was assessed using DI water as a feed solution in AL-FS orientation using the TFC FO membrane. The temperature and flow rate of DI water feed and draw solution was maintained constant. The water flux first increased and then decreased within a range of 12 – 15 L m^{-2}h^{-1} with increase in concentration of NADES draw solute from 15 –

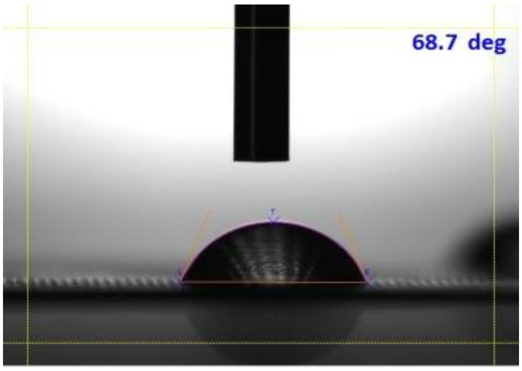


Fig. 6 Contact angle measurements of FO membrane depicting the hydrophilicity of the membrane

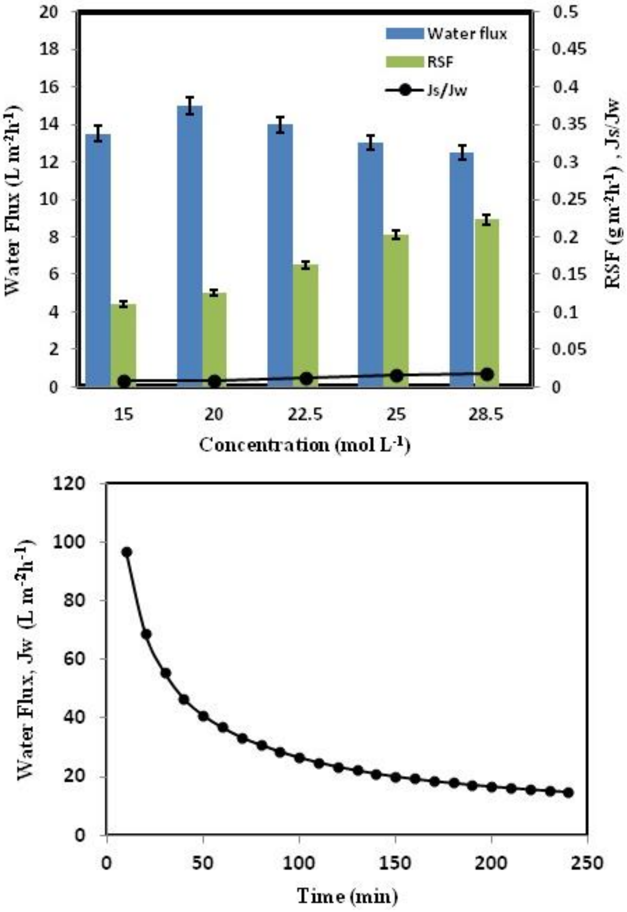


Fig. 7 (a) Water flux and reverse solute flux (RSF) in forward osmosis process with DI water as feed solution and 20% (v/v) choline chloride-glycerol (1:2 mol) NADES as draw solution at various concentrations for 4h operation. (b) Water flux with time for 4h operation using 20% (v/v) choline chloride-glycerol (1:2 mol) NADES draw solution and DI water feed solution in AL-FS orientation

28.5% (v/v). The direct correlation of concentration of NADES solution with osmotic potential was the primary reason for increase in water flux. On the other hand, increase in the viscosity of solution with concentration posed a detrimental effect on diffusivity of solutes inside the support layer causing dilutive ICP. As a result, the water flux peaked at around 20% (v/v) and then reduced gradually. The RSF also increased with draw solute concentration which led to loss of valuable draw solute and put in additional replenishment cost. Furthermore it contaminated the feed solution rendering it unsuitable for pharmaceutical, food and other sensitive applications. At 20% (v/v) NADES concentration the ratio of J_s/J_w was found to be the lowest – an observation based on which NADES concentration was selected for further experimentation.

The profile of water flux as a function of time using 20% (v/v) NADES as a draw solution for a run time of 4 h is shown in Fig. 7. Significant decline in the water flux was observed during the first hour of operation (about 62% of initial flux) which, however was mitigated eventually maintaining the steady flux for a long duration of the operating period. Initially the effect of full osmotic potential across the active layer, which is presumed to be the sole driving force, could be realised. But gradually the dilutive internal concentration polarization (ICP) effect became noticeable. Dilutive ICP occurred as the porous support layer acted as a diffusive boundary layer restricting the movement of draw solute in the support layer. In addition, water transport from the feed side to the draw side diluted the draw solution near the active layer. Combined effects of these two were responsible for gradual reduction of the available osmotic pressure over the active layer. Due to usage of DI water as feed, concentrative external concentration polarization (ECP) could be plausibly ignored. The membrane did not act as a perfect barrier under the present experimental conditions. This could be established by measuring the RSF at 0.125 g $m^{-2}h^{-1}$ for DI water feed after 4h of operation. The sharp decline in the initial water flux may be attributed to complex solute membrane interaction at the membrane interface. The greater part of reverse draw solute transport from the draw side to feed side occurred initially because of the highest osmotic pressure differential across the membrane selective layer. It might be possible that the solutes which diffused through the membrane were retained close to the active layer instead of promptly diffusing into the bulk feed solution due to the initial high water current. Occurrence of some complex ionic interaction between the membrane and draw solute, which prevented the quick liberation of the solute ions cannot be overruled. A combination of all the factors might have led to the dramatic decrease in the available osmotic potential over the active layer resulting in the initial steep decline of the water flux.

Additionaly increase in the temperature of draw solute resulted in increase in water flux up to 19.15 L $m^{-2}h^{-1}$ at 50°C. Increase in temperature reduced the viscosity of the draw solution thereby increasing the diffusivity of solute inside the support layer lowering dilutive ICP effect. Solar energy can be utilized by putting the draw solution tank in an open area especially in hot countries. However, temperatures beyond 50°C could be detrimental for the polymeric membranes as it might cause morphological changes in the pore structure of the membrane.

3.4 Dewatering application

3.4.1 Dewatering of industrial wastewater

The performance of the FO system using 20% (v/v) NADES as a draw solute for dewatering of industrial

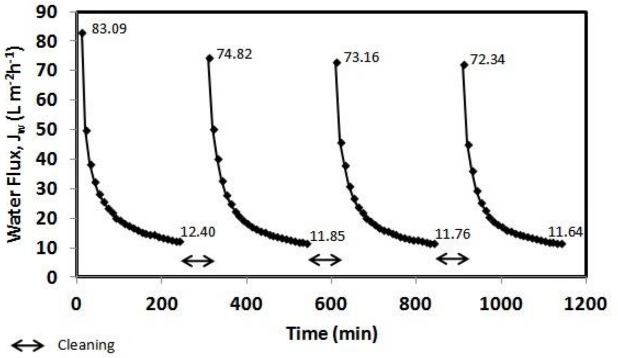
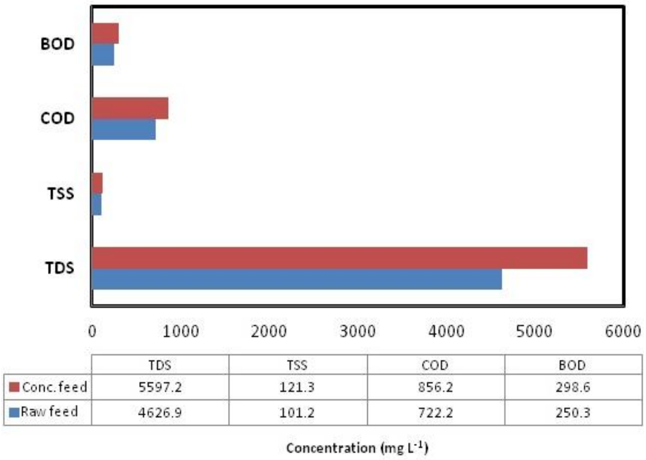


Fig. 8 Water flux with time in FO process with industrial wastewater as feed solution and 20% (v/v) choline chloride-glycerol (1:2 mol) NADES as draw solution after 4 h FO operation followed by 1 h DI water circulation in feed side (multiple washing cycles)



	TDS	TSS	COD	BOD
🟥 Conc.feed	5597.2	121.3	856.2	298.6
🟦 Raw feed	4626.9	101.2	722.2	250.3

Fig. 9 Increase in concentration of wastewater parameters after dewatering by FO operation using 20% (v/v) choline chloride-glycerol (1:2 mol) NADES as draw solution after 24h operation with multiple washing cycles

wastewater was checked. The water flux was found to be reasonable at 11.9 L m^{-2}h^{-1} when operated for 4h. This was around 21% less compared to DI water feed. This might be due to the fact that the industrial wastewater had high TDS (4627 mg L^{-1}) which contributed to the osmotic potential of feed solution. Also feed solutes induce additional concentrative ECP effect. Both these factors contributed to the diminution of the osmotic potential differential across the active layer of the membrane thereby lowering the water flux. Additionally high COD value indicates there may be presence of organic foulants which may form cake layer providing additional resistance (Xia *et al*. 2015). After 4 h of operation the water flux could be fairly maintained for a long period and the average water flux after 24h was 5.6 L m^{-2}h^{-1}. Post the initial drop in water flux the complex interaction amid the membrane and solutes developed some sort of equilibrium ensuing an almost stable system which is also highlighted in other research papers (Giagnorio *et al*. 2019).

A separate study was carried out using the same system for dewatering of industrial wastewater with an additional mechanism for membrane cleaning. A 4 h FO operation followed by 1h DI water wash cycle was followed. After the first cycle, the flux recovery was low in the second cycle (89.5%) which might be because of the pristine membrane piece used and undeveloped dilutive ICP which resulted in initial high flux. Restoration of water flux to prior levels could be achieved with a minor loss (~ 2%) (Fig. 8). The average water flux including cleaning time increased to 9.54 L m^{-2}h^{-1} which was substantially higher than 5.6 L m^{-2}h^{-1} without cleaning for the same time period. The detailed analysis of the raw and concentrated industrial wastewater (Fig. 9) showed an increase in TSS, TDS, BOD and COD which indicated that water was drawn out thereby concentrating the feed solution.

During the course of operation there was a gradual accumulation of feed solute combined with a minor amount of draw solute caused by RSF over the membrane active layer. This resulted in concentrative ECP on the feed side which over a long time reduces the water flux. It has been shown that the concentrative ECP effect is much lower than the dilutive ICP effect in AL-FS orientation, still it can reduce up to 10% of the total osmotic pressure drop (Suh and Lee 2013). The DI water wash might have facilitated and enhanced the reverse flow of the accumulated solutes towards the bulk feed due to concentration difference. Also the use of industrial wastewater feed might have resulted in foulants/scale deposition on the active layer which also contributed to gradual decrease of water flux during long hours of operation. DI water wash at regular interval with occasional back flushing further ascertained that the foulants/scale deposition on the membrane surface was loose in nature and was possible to remove without difficulty. Addition of DMSO to increase hydrophilicity also might be responsible for demonstrating lower fouling propensity (Chun *et al*. 2017). The results showed that the average water flux can be substantially increased by controlling the ECP and fouling/scaling mitigation by a simple cleaning mechanism for wastewater feed. Minor adjustment of the cleaning cycle can be done to increase the average water flux. The membrane was found usable after multiple cycles in spite of using wastewater feed. At this point, it is pertinent to mention that after multiple recycling; imperfect rejection of feed solutes by the membrane may result in slow accumulation of the feed ions in the draw solution and will require purging.

3.4.2 Concentration of sugarcane juice

Cane sugar mills produce sugar from sugarcane which contains about 70% water. After crushing and extracting juice, it is concentrated (using evaporators) before crystallization. FO could be a viable alternative to evaporation for the concentration of sugarcane juice. Freshly crushed sugarcane juice was procured from a local vendor. The sugarcane juice was clarified by adding a small amount of activated charcoal. Suitable quantity of lime water was added to adjust the pH (~ 7). 1L of the same was used as a feed solution and 20% (v/v) NADES as a draw solution. The water flux was 12.4 L m^{-2}h^{-1} after 4 h operation. Compared to DI water feed, there was only a 17% reduction in water flux, all other conditions remaining the same. About 110 ml of water was removed from 1 L clarified sugarcane juice with DI water wash at an average water flux of 9.92 L $m^{-2}h^{-1}$. The initial and final concentration of sugarcane juice was measured at 16.8 °Brix and 18.3 °Brix respectively.

3.5 Product water recovery by chilling

Recovery of the draw solute after FO process is absolutely essential to facilitate reuse of precious draw solutes and simultaneous separation of water having high level of purity. The thermo responsive UCST behaviour of ChCl-glycerol (1:2 mol) NADES (freezing point = – 40°C) was exploited for recovery of draw solute. 100 ml of 20% (v/v) NADES was taken and refrigerated in a normal refrigerator at 4°C for 4 h to avoid any sudden phase change of water leading to ChCl entrapment. The cold mixture was then chilled in a laboratory freezer at –10°C for 8 h. The water part in the form of ice was physically separated out whereas the NADES remained in the form of liquid. Analysis of 78 ml of ice after phase change to water showed around 5% of NADES which required further polishing to generate potable water. The Institute of Medicine, USA has set the upper limit for choline at 3500 milligrams per day for adults (The National Academics - Institute of Medicine, 2003). The recovered NADES in liquid form had around 75% NADES content which could be reused as draw solute. Though clear separation of water and ice was observed physically, there is a good possibility of trapped ChCl at the ice-water interface. Further research is required for improving the efficiency of separation which can minimize the loss of draw solute and increase the purity of product water. Even if generation of potable grade water seems challenging, industrial grade water/non-potable water for other uses appears to be highly probable.

3.6 Energy consumption and future applicability

FO process requires nominal energy in the form of pumping of the feed and draw solutions which can be further reduced if renewable energy is used. Low fouling tendency of FO system may eliminate the need of pre-treatment or extensive membrane cleaning protocols which may be beneficial compared to RO/NF specifically for handling high fouling wastewater. Dewatering the effluent will reduce the load on effluent treatment unit down the line. As this technology does not use harsh process conditions like heat and pressure, and uses low concentration NADES as draw solute, hence the chances of deterioration of the dewatered product are very less. Hence where the product is sensitive to heat, FO can be a viable alternative to conventional methods like evaporation. For example, in case of protein enrichment, usage of pressure driven membrane process like ultra and microfiltration results in severe protein denaturation and destabilization whereas FO process showed promising results (Mondal *et al*. 2015). However the regeneration of draw solute consumes energy. Phase separation by chilling gives relatively a high degree of separation resulting in good quality of product water. In cold countries sub-zero temperature ambient conditions can be utilized for phase separation aiding to low energy consumption. Evaporative losses are also minimized at lower temperatures. The proposed process tenders noteworthy technological gains germane to pharmaceutical, biomedical and food processing industries where mild process conditions are benign to the products.

4. Conclusions

ChCl-glycerol (1:2 mole), a natural deep eutectic solvent (NADES) was examined as a draw solute in forward osmosis process using a hydrophilized polyamide TFC FO membrane with added dimethyl sulfoxide. The membrane displayed good hydrophilicity and a highly porous support substrate which helped in achieving a lower structural parameter at 722 µm and consequently high water flux. ChCl-Glycerol was effective as a draw solute at 20% (v/v) concentration by way of retention of osmotic potential, low viscosity, good ionic activity, and being inexpensive. A reasonable water flux of 14.98 L $m^{-2}h^{-1}$ with low RSF of 0.125 g $m^{-2}h^{-1}$ with DI water feed was observed at ambient condition. At 50°C, the higher water flux of 19.15 L $m^{-2}h^{-1}$ could be achieved. With industrial wastewater feed, the water flux declined only 21% at 11.9 L $m^{-2}h^{-1}$ with good solute rejection. When operated for 24h, it was possible to maintain the water flux at 9.54 L $m^{-2}h^{-1}$ by controlling the ECP and fouling/scaling mitigation via simple periodic DI water wash. In another application, clarified sugarcane juice could be successfully concentrated at an average water flux of 9.92 L $m^{-2}h^{-1}$. Utilizing the thermo responsive UCST nature of the draw solute, it could be easily recovered by chilling. The proposed process revealed that low concentration NADES may be a viable alternative as a draw solute for dewatering of wastewater and other applications requiring mild process conditions together with a simple recovery process.

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