Phenol Removal by Novel Choline Chloride Blended Cellulose Acetate-Fly Ash Composite Membrane

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Received: 02 April 2019, Accepted: 22 May 2019, Published online: 02 July 2019

Abstract
A novel composite membrane (CM) was prepared by coating choline chloride (ChCl) blended cellulose acetate (CA) on fly-ash based ceramic substrate for phenol removal. Different amount (0-1 g) of ChCl was blended with CA to synthesize various CMs. Amount of ChCl in CA increases the contact angle, average pore radius, permeability of CM from 55.15° to 71.55°, 1.6 to 6.83 nm and 0.0057 to 0.0152 L·m⁻²·h⁻¹·kPa⁻¹, respectively. Phenol rejection increased from 56 to 93 % while increasing ChCl amount in CA. Phenol removal decreased from 94.26-64.23 % and 91.09-78.62 % with increase in applied pressure (69-483 kPa) and feed concentration (50-200 mg·L⁻¹). However, removal rate increased from 80.46-92.47 % with increase in pH 2-12. Among all CMs, CC 5 is identified as best CM with maximum phenol removal efficiency (92.7 %) and flux (1.86 L·m⁻²·h⁻¹) at 207 kPa applied pressure and 100 mg·L⁻¹ of feed phenol concentration. The obtained results reveal that blending of 0.9 % ChCl with CA can significantly enhances the phenol removal efficiency and this could be used as potential CM for treatment of phenol bearing wastewater.

Keywords
cellulose acetate, ceramic substrate, choline chloride, composite membrane, phenol removal

1 Introduction
Phenol is a primary pollutant and it has adverse effects on human health even at very low concentration. Effluents from many industries such as petrochemical, pharmaceutical, printing press, pulp and paper, coke oven contains phenol and its derivatives [1]. The permissible discharge limit for phenol is 0.5 mg·L⁻¹ in effluent as per EPA (2002). Therefore, the phenol concentration in the effluent must be regulated prior to disposal in the environment. Several methods such as adsorption, wet air oxidation, liquid-liquid extraction, catalytic ozonation, biological degradation, electrocoagulation and deep eutectic mixture are reported for phenol removal [2-9]. However, these methods require excess amount of chemicals, high energy and post processing methods. Major drawbacks of these techniques are cost intensive and low separation efficiency. Hence, there is requisite for alternative technique which is more efficient and economical. Membrane separation by composite membranes could be a better alternative due to its high selectivity towards solute, high separation efficiency, ease to handle and energy efficient [10]. Many literatures are reported about fabrication of polymeric-ceramic CM for wastewater treatment [1, 10, 11]. However, selection of polymeric material to create a suitable active layer is an important and challenging factor. Cellulose acetate (CA) can be a good alternative for efficient coating due to its economical, good strength, solvent resistant, low fouling property and commercial viability as a desalination membrane compared with other polymers [12, 13]. However, on the other hand, fabrication of polymeric-ceramic CM is expensive due to high cost of substrate. Fabrication cost of substrate can be substantially reduced by using locally available alternative raw materials [14-16]. Mukherjee and De [13] and Hassan et al. [17] have reported merely 51 % and 64 % of phenol removal using CA-alumina nanoparticle mixed matrix membrane and CA hybrid nanofiber membrane, respectively. Phenol removal efficiency and other properties of CA membrane can be improved by using suitable additives [12]. Polyethylene amine, polyurethane and zwitterions are used as suitable blending materials with CA for efficient removal of Cu²⁺, Cr⁶⁺ and protein as reported by Chen et al. [18], Riaz et al. [19] and Wang et al. [20],
substrate. CC’s properties such as chemical stability, wettability, morphology, flux, pore radius and MWCO as well as Cellulose acetate, choline chloride (C5

2.1 Materials

2.2 Synthesis of composite membrane

2.3 Membrane Characterization

Hydrophilic or hydrophobic nature of CA active layer was examined by contact angle analyzer (Model: Phoenix 300, Make: SEO, Korea). Double distilled water was gently dropped on different sites of active layer and contact angle between active layer as well as droplet was obtained directly by sessile drop technique. Scanning electron microscopic analysis (SEM) (Model: CARL Zeiss, Germany) was performed to investigate the morphological properties of membrane. Fourier transform infrared spectroscopic (Model: Alfa, Make: Bruker, Germany) analysis was carried out to find out the functional groups present in the membrane.

Degree of swelling and chemical stability of CM was measured using gravimetric method. In this method, initially known weight of membrane was immersed in distilled water for 48 h. Then the sample was taken out and wiped gently by tissue paper. Wet and dry weight of sample was measured to estimate the degree of swelling by Eq. (1) [26].

\[ S_d = \frac{W_w - W_d}{W_d} \times 100 \] (1)

where, \( W_w \) and \( W_d \) are wet and dry weight (g) of membrane.

Chemical stability of CM was checked by analyzing permeability and dry weight of membrane before and after immersion in acidic (pH ≈ 2) and basic (pH ≈ 12) medium for 48 h. Hydraulic characteristics of CM was studied by water compaction which provides rigidity to pores and porous structure after compaction. Compaction study was conducted in a dead-end filtration set-up. This filtration set-up consists of tubular cell with 300 ml capacity and circular base plate possesses membrane holder. 5 × 0.7 cm (diameter × thickness) ChCl blended CA-fly ash composite membrane was fixed in the membrane holder and edges were sealed with sealant to avoid the leakage. The effective membrane area of this composite membrane was 18 cm². Compaction study was carried out with 250 ml distilled water which was pressurized at 483 kPa using nitrogen gas cylinder for 6 h.

Water flux was calculated for every 10 min interval till the steady state condition reached. Pure water flux of compacted CM was measured at different applied pressure (69-483 kPa). The flux (J) through the membrane was calculated by the following Eq. (2):
Flux \( J = \frac{V}{A t} \) where, \( V \), \( A \) and \( t \) are permeate volume (l), membrane area (m\(^2\)) and time (h), respectively. Molecular weight cut-off (MWCO) study was conducted with different molecular weights of PEG and BSA to obtain the MWCO and pore size of the membrane at 207 kPa and 10 g·L\(^{-1}\) solute concentration. Abbe Refractometer (Model: 135005, Make: Contech, India) was used to measure solute concentration in feed and permeate. The solute removal (\( %R \)) was calculated by using following Eq. (3):

\[
%R = \left(1 - \frac{C_p}{C_f}\right) \times 100
\]

where \( C_p \) and \( C_f \) represent permeate and feed concentration (mg·L\(^{-1}\)), respectively. Removal (%) versus molecular weight curve gives the MWCO values at 90 % rejection of solute. Average pore radius of membrane was estimated by Guerout-Elford-Ferry relation as given by Eq. (4) [13].

\[
r_m = 16.73 \times 10^{-10} M_{w}^{0.357}
\]

where \( r_m \) and \( M_w \) are the pore radius (cm) and MWCO (Da) of membrane.

### 2.4 Phenol separation from aqueous solution

Phenol separation efficiency of all CM was tested in dead-end filtration setup. Operating parameters such as feed concentration (50-200 mg·L\(^{-1}\)), operating pressure (68-414 kPa) and feed pH (2-12) were optimized to obtain high phenol separation efficiency and permeation flux. Phenol flux and phenol removal (%) was calculated by using Eqs. (2) and (3), respectively. Feed and permeate phenol concentration was determined by 4-aminoantipyrene method at 500 nm using UV-Vis spectrophotometer (Model: 1800, Make: Shimadzu, Japan) [27].

### 3 Result and discussion

#### 3.1 Contact angle, SEM and FTIR analysis

Contact angle test was performed in order to find the hydrophilic and hydrophobic nature of synthesized CMs. Fig. 1 shows the contact angle obtained between water and CMs. It can be seen in Fig. 1 that there is a slight decline in hydrophilicity of CM with addition of ChCl. SEM analysis was carried out to study the surface morphology of CM. Fig. 2 shows the SEM images of CC\(_0\), CC\(_1\) and CC\(_6\) top layer. It can be observed in Fig. 2 that porous structure and porosity of CM membranes increases with increase in amount of ChCl. CC\(_0\) top layer has stiff and tightly packed structure due to the extensive hydrogen bond in polymeric chain [12]. Addition of ChCl might reduce the hydrogen bond and increases the free volume by reducing the active cite available for polymer-polymer contact [24]. This leads to increase in contact angle and porous structure.

FTIR spectrum of CC\(_0\) and CC\(_6\) is shown in Fig. 3. The broad band obtained at 3480 and 3475 cm\(^{-1}\) for CC\(_0\) and CC\(_6\) is hydroxyl group stretching [17, 28, 29]. Bend at wavenumber of 2944.7 cm\(^{-1}\) for CC\(_0\) spectrum is attributed to stretching of –CH- of methyl groups (-CH\(_3\)), which was shifted to 2948.8 cm\(^{-1}\) for CC\(_6\) membrane [30]. The peak for CC\(_6\) at 2121.1 cm\(^{-1}\) refers to symmetrical methyl stretching due to blending of ChCl with CA [31]. The band near 1431 cm\(^{-1}\) for both the membranes indicate the deformation vibration of –CH\(_2\) [28]. Peak at 1051.37 cm\(^{-1}\) for CC\(_0\) refers to primary alcohol which is shifted to 1038.1 cm\(^{-1}\) for CC\(_6\) and that shows reduction in corresponding molecule [29]. The wavenumber at 1159.9 cm\(^{-1}\) shows the presence of secondary amine in CC\(_6\) [29]. Combination of –C-O stretching and –CH\(_2\)- vibration is also observed at 904.4 cm\(^{-1}\) for both the membrane [28].

#### 3.2 Swelling and chemical stability test

The degree of swelling for all CM was calculated by Eq. (1). Fig. 4 shows the swelling effect of different CM. It can be observed that swelling increases with increase in amount of ChCl blending in CA due to high water uptake in the enhanced porous structure of CM. This result is in good agreement with CC\(_0\) and CC\(_6\)-SEM micrographs. Chemical stability test shows that there is negligible (< 1 %) change in the weight loss when CC\(_0\) and other CC\(_0\)-CC\(_6\) were immersed in highly alkaline (pH ≈ 12) and acidic (pH ≈ 2)
media (Fig. 4). Therefore, it can be concluded that all the membranes are resistive and highly stable even in harsh chemical environment.

3.3 Pure water flux and MWCO study

Hydraulic permeability test was conducted to estimate the flux of synthesized CM at different applied pressure ranging from 69−483 kPa (Fig. 5). It can be seen in Fig. 5 that flux increases with increase in pressure and also slight increase in permeability. Permeability increases from 0.0057 to 0.0152 L·m⁻²·h⁻¹·kPa⁻¹ for CC₀ to CC₆, respectively. Applied pressure has notable effect on flux during which impermeable pore also tends to permeate with increase in pressure [32].

In order to obtain the average pore size, MWCO study was conducted with all CM (CC₀−CC₆) by using PEG (MW: 1.5, 4, 6, 10 and 20 kDa) and bovine serum albumin (MW: 64.46 kDa) at 207 kPa. Fig. 6 a) shows the average pore radius of different CMs. MWCO of CC₂ corresponding to 90 % rejection of PEG molecule is also shown in Fig. 6 b). It can be seen in Fig. 6 a) that average pore radius of CM increases from 2.86 to 6.83 nm with increase of ChCl
blending from 0.5 to 1 g whereas the CC₀ has less pore radius (1.69 nm). The results of increase in pore size with ChCl blending amount is also supported by SEM results.

3.4 Phenol separation
3.4.1 Selection of CM
Selection of appropriate CM is mainly associated with percentage removal of phenol and flux through the membrane. A preliminary phenol removal study was conducted with dead-end filtration setup at constant feed phenol concentration (100 mg·L⁻¹), applied pressure (207 kPa) and actual pH (5.8). Fig. 7 shows the % removal and flux of different CM. It can be seen in Fig. 7 that phenol removal and flux increases with increasing the amount of ChCl in CA. Increase in ChCl amount increases the number of chloride ions in the top active layer which complexes the associated phenol to retain over the membrane surface. Subsequently, only phenol free water molecules are allowed to pass rapidly through the membrane pores which increase the flux and phenol removal [22].

Moreover, increase in flux is due to the increase in pore size of membrane while increasing the ChCl amount in CA. Possible interaction mechanism of phenol with ChCl blended CA is shown in Scheme 1 [33-35]. Choline chloride OH⁻ group may attach with oxygen atom of hydroxyl group in CA and releasing hydrogen to form the H₂O during blending [24]. CC₀ CM has less phenol removal capacity than ChCl blended CA membranes which results higher concentration of phenol in the permeate side. Phenol is a hydrogen bond donor due to its partially negative oxygen atom but chloride in ChCl has large electronegativity which easily forms the strong interaction between OH⁻ group of phenol and chloride ion of ChCl blended CA (Scheme 1) [21, 36].

Hence, maximum removal of phenol was achieved by CC₆ membrane due to presence of more chloride ions which favors more removal of phenol than other CMs. Since there is no significant difference in phenol removal
between CC5 (91.72%) and CC6 (92.92%), only CC5 was chosen further for all phenol removal studies.

3.4.2 Effect of Pressure, feed phenol concentration and pH

Effect of applied pressure on phenol removal and membrane flux was studied at constant operating parameters (Fig. 8 a)). It can be seen in Fig. 8 a) that phenol removal slightly decreases from 94.26% to 92.33% while increasing the pressure from 69 to 207 kPa and thereafter removal decreases down to 64.23% for 414 kPa. However, flux gradually increases from 0.64 L·m⁻²·h⁻¹ to 2.3 L·m⁻²·h⁻¹ with increase in pressure from 69 to 414 kPa. The increases in pressure increase the driving force which results high flux and phenol concentration in the permeate side [26, 37]. Therefore, 207 kPa was considered as an optimum applied pressure to obtain the good permeation flux (1.54 L·m⁻²·h⁻¹) and phenol removal (92.33%).

Effect of feed phenol concentration on phenol removal and flux through CC5 CM was examined ranging from 50-200 mg·L⁻¹ by keeping other operating parameters constant. Fig. 8 b) shows the variation in phenol removal % and flux with respect to change in feed phenol concentration. It can be seen in Fig. 8 b) that phenol removal decreases from 91.09 to 78.62% with increase in feed phenol concentration from 50-200 mg·L⁻¹ whereas insignificant effect on flux. Increase in phenol concentration at permeate is due to the increase in concentration driving force of phenol molecules as well as molecular friction along with membrane wall surface while increasing the feed concentration [38].

The influence of feed pH on phenol removal and flux was studied in the range of pH 2-12 at constant operating conditions. Fig. 8 c) shows the effect of pH on phenol removal and flux. It can be observed in Fig. 8 c) that flux is unaffected while changing the feed pH from 2 to 10 whereas phenol removal slowly increases from 80.5 to 92.5%. At high pH phenol exists in anionic (phenolate anions) form which has electronegative repulsion with negatively charged membrane surface and leads to high phenol removal [39-41].

4 Conclusion

In this investigation, novel ChCl blended CA was coated on fly-ash based ceramic substrate to prepare the CM for effective removal of phenol. Blending of ChCl has significant effect on membrane properties such as degree of swelling, chemical stability, pore size, permeability and hydrophlicity. MWCO study showed that increase in pore radius from 16.88 to 68.32 nm which also reflected on pure water flux to increase from 2.64 to 12.16 L·m⁻¹·h⁻¹ for CC₅ to CC₆, respectively. In phenol removal study, phenol removal decreased with increasing pressure and feed phenol concentration whereas it was increased with increase in pH. Phenol permeation had increasing trend with pressure but no significant influence with pH and concentration change. The optimum applied pressure, pH and concentration
for high removal of phenol (92.7 %) and flux (1.86 L·m⁻²·h⁻¹) was identified as 207 kPa, pH 10 and 100 mg·L⁻¹, respectively for CC₃. Results obtained in this study confirm that 0.9 % ChCl blended CA can be used to fabricate the potential CM for high removal of phenol with good flux.

References

Acknowledgement
This work is supported by a grant of Department of Science and Technology (SERB), New Delhi, Government of India, under the scheme of Start-up Research Grant (ECR/2016/000435; Dated 09-09-2016).


