Synthesis and characterisation of TiO₂ nanofibre/cellulose acetate nanocomposite ultrafiltration membrane

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ABSTRACT
Nanofibres of TiO₂ were synthesised by hydrothermal routine. Cellulose acetate/TiO₂ nanofibre composite membranes were synthesised via blending TiO₂ nanofibre in cellulose acetate solutions in 1-methyl-2-pyrrolidone. In order to study the effect of addition of nanofibre, membranes with various composition were synthesised, first by keeping cellulose acetate to 1-methyl-2-pyrrolidone ratio constant and second by decreasing cellulose acetate concentration with increasing addition of TiO₂ nanofibre. The membranes were characterised using scanning electron microscope and X-ray diffraction. Hydrophilicity of the membranes was evaluated in terms of contact angle measurements and water uptake study. Permeation characteristics were determined in terms of pure water flux and bovine serum albumin rejection. Antifouling property was studied in terms of flux recovery after rejection. Remarkable improvement in membrane flux and antifouling properties is achieved by the addition of TiO₂ nanofibres.

KEYWORDS
TiO₂ nanofibres; cellulose acetate; composite; permeation; antifouling

1. Introduction
Rapid industrialisation and population explosion have overburdened our water resources. Limited fresh water resources and rising environmental concerns have intensified global research in water treatment [1–3]. Adsorption of dissolved impurities has been a widely used technique for water purification [4–8]. Photocatalytic degradation is another promising field to completely eliminate organic impurities using a suitable photocatalyst in presence of light radiation [9–14]. Both these water treatment methodologies are efficient and eco-friendly but protracted. With the dawn of nanotechnology, various novel materials are being developed for efficient water purification [15–21]. The need for immediate and continuous water supply has made membrane filtration a significant option for water treatment although being an energy-intense operation. Membrane filtration units have low installation and operational costs, flexibility in scale-up, wide range of separation selectivity and environmentally friendly operation. Membrane filtration has its applications in production of pure water, desalination of sea water and also in treatment of effluents [22]. An ideal membrane must possess high rejection of solute, high flux and good antifouling property [23]. Among the different polymeric membrane materials, cellulose
Acetate (CA) has been widely used in aqueous-based filtration due to its good hydrophilicity, toughness, permeate flux and film-forming properties. Also, CA is comparatively inexpensive and environment friendly [24–26].

There are several reports on modification of CA membranes which include blending with other additives and pore formers [27,28]. Current studies indicate that using nanocomposite membranes, i.e. incorporation of nanomaterials into polymeric membranes, is an effective method to improve the separation performance of membranes and enhance thermal and mechanical characteristics [29]. TiO₂ is a widely used photocatalyst; it is also a good inorganic additive in membranes owing to its good physical and chemical properties [30–32]. Abedini et al. incorporated TiO₂ nanoparticles in CA membranes and obtained enhanced permeation [33]. Vatanpour et al. revealed that higher surface area of nano-additive plays a very important role in determining membrane hydrophilicity and antifouling properties [34].

Titanium dioxide nanofibres (TNF) are one-dimensional nanomaterials with length in microscale and diameter in nanoscale [35]. They have very high specific surface area and along with its larger length can significantly affect the composite properties [36]. The increased surface area provides greater interfacial area for interaction with the polymer matrix in a composite. Our previous study on polysulfone (a hydrophobic polymer) showed that TNF is an effective additive to achieve superior permeation and antifouling properties [37]. The properties of nanocomposite membranes depend on individual constituent properties, their relative amounts and also the geometry of dispersed phase. To the best of our knowledge, CA/TNF composite membranes have not been reported. It would be interesting to study the extent to which TNF can improve the properties of a hydrophilic polymer like CA. In this work, the effect of varying filler concentration on the performance of the membrane and the interaction between filler polymer ratios is studied.

2. Experimental

2.1. Materials

TiO₂ anatase nanopowder (TNP, Dia-21 nm), CA having a molecular weight of 35,000 Da and Bradford Reagent were purchased from Sigma Aldrich Chemical Co. Bangalore. NaOH, dil. HCl (37%), and 1-methyl-2-pyrrolidone (NMP) were purchased from Merck chemicals. Bovine serum albumin (BSA) was purchased from Central Drug House (CDH), New Delhi, India.

2.2. Preparation of TiO₂ nanofibres

TiO₂ anatase nanopowder was dispersed in 30 ml of 10 M NaOH and stirred for 12 h. This dispersion was transferred into a teflon-lined stainless steel autoclave and kept in a hot air oven at 170 °C for three days. The residue obtained was washed with distilled water several times and with dilute HCl until the pH became neutral and subsequently filtered. The filtered sample was dried in a hot air oven at 60 °C for 24 h [37].
2.3. Preparation of TNF blend CA membranes

CA/TNF blend membranes were prepared via phase inversion method with different compositions as given in Table 1. In brief, the polymer CA was dissolved in NMP by stirring for a period of 12 h at room temperature and kept undisturbed for 12 h at room temperature to remove air bubbles. Suitable amount of TNF was added to the above solution and stirred for 1 h at room temperature. The solution was uniformly casted over a glass plate with the help of a finely polished glass rod and the glass plate was immersed in distilled water at 25 °C. All membranes were kept immersed in water for 24 h prior to use [33].

3. Characterisation

3.1. FT-IR analysis

The Fourier transform infrared (FT-IR) spectra of membranes were obtained using Shimadzu FTIR-8400S spectrometer in the range of 400–4000 cm⁻¹. The direct spectra of using TNF and composite membranes were analysed at room temperature.

3.2. XRD analysis

X-ray diffraction was done using Rigaku Miniflux 6000, X-ray diffractometer equipped with monochromatised high-intensity Cu Kα radiation (λ = 1.54178 Å). The diffractograms were obtained at a scanning rate of 0.06°/s in the 2θ scanning range of 10°–60°.

3.3. SEM analysis

Scanning electron microscope (Jeol JSM-6380LA) was used to obtain SEM images of membranes and fibres. The membrane samples were dipped in liquid nitrogen and then cut in to small pieces. The cryogenically fractured samples were then used for cross-sectional images. All the samples were sputtered with gold before scanning using a sputter coating machine.

| Table 1. Blending compositions of membranes. |
|--------------------------------------------|
| Membrane                                   | CA (wt.%) | TNF (wt.%) | NMP (wt.%) |
| CA series membranes (addition of TNF to a fixed CA:NMP cast solution) |          |            |            |
| CA0                                       | 17.5      | 0          | 82.5       |
| CA1                                       | 17.32     | 0.99       | 81.683     |
| CA5                                       | 16.66     | 4.76       | 78.57      |
| CA10                                      | 15.9      | 9.09       | 75         |
| M series membranes (decreasing CA concentration with respect to increasing TNF addition); CA + TNF fixed at 17.5 wt.% |          |            |            |
| M1                                        | 13.125    | 4.375      | 82.5       |
| M2                                        | 10.9375   | 6.5625     | 82.5       |
| M3                                        | 8.75      | 8.75       | 82.5       |
3.4. Contact angle measurement

FTA-200 dynamic contact angle analyser was used to estimate the contact angle of membranes using the sessile droplet method. Rectangular pieces of membrane samples were pasted on glass slides using a thin double side tape. The slides were loaded on the stage of dynamic contact angle analyser. A drop of water was loaded on the membrane surface using a syringe. The contact angle of the droplet after 60 s was measured. In order to minimise experimental error, the contact angle values were obtained as an average of three trials at different locations.

3.5. Water uptake study

In order to quantify the pore volume, percentage water uptake was calculated with the help of equation as given below:

\[
\% \text{ Water uptake} = \left(\frac{\text{Wet weight} - \text{Dry weight}}{\text{Wet weight}}\right) \times 100.
\]

Dry membrane pieces were soaked in distilled water for 24 h. The wet samples were wiped with blotting paper and then weighed. These membranes were placed in a drier for 48 h at 75 ºC and dry weights were noted to calculate % water uptake [38].

3.6. Permeation properties

High water flux is an essential parameter for any membrane. The pure water flux (PWF) study of the membranes was done using Sterlitech HP4750 stirred dead end filtration cell with an effective membrane area of 14.6 cm² at 25 ºC. All the membranes were placed in distilled water for 24 hours and subjected to compaction prior to the permeation study. The permeate sample collection was started after 20 min of exposure to 0.5 MPa transmembrane pressure (TMP) at 25 ºC. The time-dependent PWF of membrane was determined.

The PWF \( J_w \) is calculated using the following equation:

\[
J_w = \frac{Q}{\Delta t A},
\]

where \( J_w \) is expressed in L/m² h and \( Q \) is the amount of water collected for \( \Delta t \) (h) time duration using a membrane of area \( A \) (m²).

3.7. Protein rejection

Rejection studies were carried out using BSA as a typical protein [16]. Protein solutions with concentration 0.8 g/L was prepared using distilled water and filtered through each membrane individually for 90 min. The BSA permeate concentration, collected over 10-min time interval was estimated by UV-spectrophotometer at a wavelength of 595 nm only after treating the collected samples from each membrane using Bradford Reagent.
The BSA rejection (%R) of the membrane was determined using the following equation:

\[
%R = \left( 1 - \frac{C_p}{C_f} \right) \times 100, \tag{3}
\]

where \( C_p \) (mg/mL) and \( C_f \) (mg/mL) are the BSA concentrations in permeate and feed, respectively.

### 3.8. Antifouling properties

The ability of a membrane to resist fouling was determined in terms of flux recovery ratio (FRR) [39]. After BSA rejection, the membranes were washed with distilled water for 20 min and subjected to pure water flux study once again. The ratio of initial pure water flux to the recovered flux indicates the recycling potential of the membrane. FRR was evaluated using the following expression:

\[
\text{FRR} \% = \frac{J_{w2}}{J_{w1}} \times 100. \tag{4}
\]

### 4. Results and discussion

#### 4.1. Characterisation of TiO₂ nanofibres

TiO₂ nanofibres with diameter of around 80–120 nm and lengths of around 2–4 μm were obtained (Figure 1).

![SEM image of TNFs](image)
Figure 2(a) shows the FTIR spectrum of TNF, the broad peak between 3300 and 3400 cm$^{-1}$ corresponds to O–H stretching vibration of hydroxyl groups. The peak at 1640.64 cm$^{-1}$ represents an O–H distorting vibration due to water molecules. The peak at 894.8 cm$^{-1}$ corresponds to anatase phase of TiO$_2$. The decrease in transmittance beyond 900 cm$^{-1}$ is attributed to Ti–O stretching vibration and O–Ti–O lattice [40]. In the XRD diffractograms, the peaks around 25.4°, 38.5°, 48° and 53.8° confirm the anatase (A) phase of TNP (Figure 3) [41].

4.2. Membrane characterisation

4.2.1. ATR-IR analysis

In Figure 2(b,c), peaks at 2939 and 2871 cm$^{-1}$ correspond to the asymmetric and symmetric C–H stretching, 1744 cm$^{-1}$ corresponds to C=O stretching, 1168 cm$^{-1}$ (asymmetric stretching of the C–O–C bridge) and 1215 cm$^{-1}$ (carboxylate C–O stretch) is also observed [42]. These peaks were also observed for the hybrid M-1 membrane. Significant deviation in transmittance is seen for the hybrid membrane due to the effect of TNF addition. The elevation of transmittance around 1140 cm$^{-1}$ and reduction in transmittance around 2360 cm$^{-1}$ is the indication of merging of TNF and polymer peaks, indicating a good additive polymer interaction [43].

4.2.2. XRD analysis

A comparison of the XRD pattern of TNF, CA0 and M3 can be seen in Figure 5. XRD of CA0 shows peaks around 13.4°, 14.9° and 18.3°, which corresponds to the crystalline peak of CA. In M-3 membrane, the characteristic peaks of anatase can be clearly seen at a lower intensity. The crystalline peaks of CA have become more dominant in the composite M3.
4.2.3. Morphology of the membrane

SEM analysis of the cross section of membranes with different concentrations of TNF is shown in Figure 4. The membranes depict asymmetric structure, typically the dense top layer, porous sub-layer and fully developed macropores layer. It is apparent from SEM cross-sectional images that the increase in concentration of TNF resulted in a decrease in finger-like projection with reduced length. The formation of spongy structure in the sub-layer was favoured with higher additive content [44,45].

Figure 5 depicts the contact angle and water uptake values of various membranes. It was observed that contact angle of the membranes decreased with an increase in TNF content. M-3 had the lowest contact angle of 51°, indicating a good increase in hydrophilicity [46]. M series membranes showed a drastic decrease in contact angle, whereas CA series membranes showed a gradual decrease. Although addition of hydrophilic TNF is the prime reason for drop in contact angle, the simultaneous decrease in polymer content magnifies the effect of TNF in the M series. Also water uptake increased with greater TNF content. This significant increase in water uptake can be attributed to the presence of more TNF in the interconnected polymer matrix, thereby creating void spaces in the polymer network. Greater water uptake was seen for the M series when compared to the CA series membranes.
Figure 4. Cross-sectional SEM images of membranes: (a) CA0; (b) CA1; (c) CA5; (d) CA10; (e) M1; (f) M2 and (g) M3.
4.2.6. Permeation studies of CA/TNF membranes

To determine the permeation properties of the modified CA membranes, PWF study was carried out at transmembrane pressures of 0.5 and 0.1 MPa. The PWF of the membranes is shown in Figures 6 and 7, respectively, at both the pressures.

As shown in Figure 6, the lower PWF for CA1 and CA5 membranes can be associated with the entrapment of TNF in the pores without getting dispersed in the bulk or to rheological hindrance of the system which affects the mutual diffusivities.
of the solvent and nonsolvent during phase inversion process, eventually forming a closed structure with lesser pore volume relatively. The contact angle decreases for CA1 and CA5; therefore, the chances of TNF blocking pores can be omitted. In case of CA10, the TNF concentration is high enough to increase hydrophilicity to a greater extent and thus accelerates the indiffusion of water during phase inversion [47]. For M series membranes, the decrease in polymer phase and simultaneous increase of hydrophilic TNF mitigate any chances for delayed demixing during phase inversion. The superior hydrophilicity achieved due to presence of higher TNF content resulted in a sweeping increase in water flux. The hydroxyl content of the membrane increases due to TNF addition. The presence of polar hydroxyl group enables better interaction with water molecules via hydrogen bond and van der Waals’ force [29]. Greater hydrophilicity thus enables higher diffusion of water through the membrane, with M-3 showing a flux increase almost 25 times that of nascent CA0 membrane. The high-flux membranes were operated at lower trans-membrane pressure of 0.1 MPa and exhibited good water flux as shown in Figure 7.

4.2.7. Protein rejection studies
Flux reduction was observed for all membranes during BSA rejection due to fouling (Figure 8). The observed BSA rejection values are 82%, 88.61%, 90.375%, 85.55%, 92%, 83.55%, and 83.025% for the membranes CA0, CA1, CA5, CA10, M1, M2 and M3, respectively. It was obvious that relative delay in demixing process during phase inversion resulted in more symmetric structure originating from low flux and hence rejection was high for CA1, CA5 and M1 membranes.

4.2.8. Anti-fouling properties
Fouling is a major shortcoming in membranes; it is the deposition of impurities on the membrane surface. For the effective long-term usage of membranes, good anti-fouling properties are necessary. Reusability of the membrane can be evaluated using FRR (Figure 9). The addition of hydrophilic TNF to the membrane imparts polar
nature to the membrane surface due to presence of hydroxyl groups. When the membrane surface becomes more hydrophilic, it weakens the interaction between BSA protein particles and membrane surface. Due to improved hydrophilicity, the membrane surface has an affinity towards aqueous media, making the membrane surface easily washable [48]. It was observed that in CA series membranes, there was an initial decrease in FRR, but at 10% addition, good FRR was obtained. In M series membranes, since the polymer content was less and TNF content is high, the increase in hydrophilicity resulted in good increment in FRR.
5. Conclusions

Titanium oxide nanofibres were successfully synthesised and incorporated into CA to give nanocomposite membranes. The M series membranes showed tremendous improvement in flux and flux recovery without compromising rejection. M3 membrane exhibited a remarkable 25 times rise in pure water flux. The M series membranes could give good water flux at lower operating pressures. The increase in membrane hydrophilicity due to TNF resulted in significant improvement in antifouling property. M3 gave a superior FRR of 83%. Thus, TNF proved to be a good modifier for CA membranes. M series membranes showed superior performance when compared to their CA series counterparts. It became evident that decreasing polymer content with a simultaneous increase in additive content proved more effectiveness than adding the nanomaterial to a constant polymer solvent ratio solution.

Acknowledgments

The authors thank Prof. K. Narayan Prabhu, Metallurgical and Materials Engineering Department of NITK Surathkal, India for providing contact angle measurement facility.

Disclosure statement

No potential conflict of interest was reported by the authors.

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