UV-assisted surface modification of polyethersulfone (PES) membrane using TiO₂ nanoparticles

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Abstract. In this research commercial polyethersulfone (PES) membrane was modified using TiO₂ nanoparticles (P-25 Degussa) and further irradiated using UV light to overcome the hydrophobicity and fouling nature of the membrane. Further the membranes were characterized using SEM and FTIR. Contact angle measurements study confirmed the hydrophilic tendency of the modified membrane by decreasing the contact angle from 73° to 20.28°. The modified membranes showed higher flux and better anti-fouling properties as compared to the unmodified counterparts. The optimum conditions were found to be 0.5 wt% TiO₂ loading with 60 min membrane immersion and 10 min UV light illumination. The effect of different pH conditions of feed was analysed. Real wastewater filtration experiments also indicated better performance of modified membranes as opposed to neat PES membranes.

Keywords: ultrafiltration; TiO₂ nanoparticles; UV irradiation; PES membranes; Acid Blue-80 dye

1. Introduction

The rapid depletion in fresh water sources has triggered the need for reuse of wastewater after appropriate treatment. Membrane separation technology has garnered importance in the water treatment industry as it allows water purification and disinfection, leaves no by-products, has a low footprint, ensures constant permeate quality and involves a lower cost. (Ciardelli *et al.* 2000, Barakat and Schmidt 2010, Strathmann 1981, Vieira *et al.* 2001). Polyethersulfone (PES) polymer is an important polymeric material and is extensively used in separation fields. It is highly stable under high temperatures and also has high mechanical and chemical resistance. The crystalline nature of the polymer can be attributed to the benzene ring and a softer ether bond present in the structure (Rahimpour and Madaeni 2007, Luo *et al.* 2005). But its usage is stifled due to its low hydrophilicity which causes high amount of deposition of contaminants on the membrane surface leading to irreversible fouling. Membrane fouling leads to flux decline and ultimately causes reduction in membrane life (Lee *et al.* 2005, Xu *et al.* 2006, Huisman *et al.* 2000, Dizge *et al.* 2017). The hydrophobicity of the bulk membrane material is useful for maintaining structural integrity when the membrane is used in aqueous environments (Miller *et al.* 2016). The methods used to clean membranes include backwashing, chemical cleaning or sonication so as to regain the performance of the membrane but these methods require shutting down of operations or even membrane replacement causing a rise in operation costs (Strathmann 1981, Zondervan and Roffel

2007, Hillis *et al.* 1998, Lee *et al.* 2001).

Recently a number of methods have been developed to modify hydrophobic polymeric membranes which include using different metal or metal oxide nanoparticles to improve the antifouling properties, membrane lifetime, permeability and solute rejection (Lee *et al.* 2001, Rahaman *et al.* 2014, Gao *et al.* 2014, Garcia-Ivars *et al.* 2016, Vatanpour *et al.* 2016, Chan *et al.* 2015, Dong *et al.* 2015). Amongst the various nanoparticles TiO₂ has received considerable importance because of its properties such as good hydrophilicity, excellent fouling resistance and photocatalytic ability (Moghadam *et al.* 2015, Kwak *et al.* 2001, Zhang *et al.* 2013, Laera *et al.* 2011). The modification of the membrane can be achieved by (i) the phase inversion method which involves blending the nanoparticles in the membrane casting solution or (ii) via coating the surface of the membrane with the nanoparticles (Jamshidi Gohari *et al.* 2014, Zinadini *et al.* 2014, Maximous *et al.* 2010, Garcia-Ivars *et al.* 2014, Vatanpour *et al.* 2012, Yang *et al.* 2015, Rahimpour *et al.* 2008, Jyoti *et al.* 2016).

Membranes have been prepared by both entrapping of the TiO₂ and zeolite nanoparticles into the PES matrix via solution blending; and dip-coating the membranes modified by the corona air plasma technique. Further evaluation of the anti-fouling properties and the separation performance of these membranes is then reported (Moghimifar *et al.* 2015). Non-solvent induced phase separation (NIPS) technique is also used to prepare PES UF membranes containing self-assembled TiO₂ nanoparticle to reveal superior anti-fouling properties of the modified membranes (Li *et al.* 2016). PES membranes deposited with TiO₂ nanoparticles and exposed to UV light have been found to show better flux and rejection for humic acid (Vieira *et al.* 2001, Mohamad *et al.* 2013). Studies have been carried out

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Table 1 Membrane modification

Membrane	TiO$_2$ coating concentration (wt.%)	Immersion time (min)	UV exposure time (min)
M1	0	0	0
M2	0.05	60	10
M3	0.1	60	10
M4	0.5	60	10
M5	1	60	10
M6	0.5	15	10
M7	0.5	30	10
M8	0.5	90	10
M9	0.5	60	5
M10	0.5	60	15

to study the effect of different morphologies of TiO$_2$ nanoparticles on the membrane properties. PES microfiltration membranes were coated with commercial Aeroxide P25 TiO$_2$ and synthesised TiO$_2$ nanorods, further the two membranes were compared based on hydrophilicity and dye retention (Kovács *et al*. 2017). Comparison of TiO$_2$ entrapped membranes to coated membranes in terms of flux decline has revealed the performance and antifouling properties of UV-irradiated TiO$_2$-deposited membrane is higher than UV-irradiated TiO$_2$-entrapped membrane (Rahimpour *et al*. 2008). TiO$_2$ has also been deposited on the surface of a commercial PVDF membrane using DC reactive magnetic spectrum giving membranes higher flux and fouling resistance in activated sludge filtration (Tavakolmoghadam *et al*. 2014). Another technique for membrane coating known as Layer by Layer (LbL) has been explored by Kaner *et al*. to study the organic and biological fouling resistance performance of modified PES membrane with chitosan (CHI) and alginate (ALG) polyelectrolyte multilayer (PEM) alone or PEMs incorporated with sol-gel made AgCl/TiO$_2$ xerogels which imparted high water permeability, low organic fouling, low biological fouling, and long-lasting antibacterial activity to the commercial PES membrane. Corona air plasma is a technique used to alter the surface of membrane and the TiO$_2$ nanoparticles are coated on the membrane surface by immersion of the corona treated membranes into a TiO$_2$ colloidal aqueous suspension (Moghimifar *et al*. 2015).

The objective of the present research is to investigate the effectiveness of commercial PES membranes modified by coating TiO$_2$ nanoparticles on their surface using UV light and to optimize the various parameters for membrane modification. This modification helped in improving the rejection of the Acid Blue-80 dye and also improved the anti-fouling performance. The membranes are characterised using FTIR (Fourier Transform Infrared Spectroscopy), SEM (Scanning Electron Microscope). To investigate the hydrophilicity of membranes, the water contact angle is measured. Finally to check the anti-fouling property of the modified membrane - permeation of deionized (DI) water, acid blue-80 dye and real wastewater is presented. The reusability of the membrane after filtration by real wastewater is also examined by washing the membrane and repeating the filtration procedure.

2. Experimental

2.1 Materials

Sulphuric Acid, Acid Blue 80 dye, Sodium Hydroxide, Titanium dioxide nanoparticle (TiO$_2$ P25 particle size of 21 nm) were obtained from S.D. Fine Chemicals Pvt. Ltd. Commercial flat sheet PES membrane with a molecular weight cut off of 10 kDa was procured from Permionics Membrane Pvt Ltd. Vadodara. All chemicals used were of AR grade. De-ionized water (DI water) was used for all experiments.

2.2 Coating of the membrane

The commercial PES membranes were cut into discs of diameter 49 mm and placed in 0.1 Molar NaOH solution overnight at a room temperature of 28±2°C. After removing them from the solution they were placed in DI water overnight. TiO$_2$ colloidal suspensions were prepared in different concentrations (0.05, 0.1, 0.5,1 wt. %) by dissolving appropriate concentrations of TiO$_2$ nanoparticles in DI water. The suspension was then sonicated for 1 hour in an ultrasonic bath at a frequency of 20 kHz to ensure uniform dissolution of the nanoparticles and prevent settling of the TiO$_2$ nanoparticles. The membranes were further immersed in the colloidal suspension for (15, 30, 60 and 90) minutes. Further they were washed with DI water to remove excess nanoparticles from the membrane surface and exposed to UV bulb (250 W) for (5, 10 and 15) minutes. Finally the modified membranes were stored in DI water and used after 15 minutes. The membranes are numbered as M1 to M10 based on the modification conditions of the commercial PES membranes as shown in Table 1.

2.3 Membrane characterization

Fourier-transform infrared spectroscopy (MIRacle 10, IRAffinity-1, Shimadzu) was used to determine membrane surface composition. SEM was used to inspect the top surface of the membrane. The hydrophilicity of TiO$_2$ coated membranes was analyzed by measuring the contact angle between DI water and the surface of membrane using a contact angle measuring instrument (G10,KRUSS, Germany). The probe liquid in all cases was DI water. To minimize the experimental error, contact angle was measured at five different and random locations of the membrane sample and the average value was calculated.

2.4 Flux, rejection and membrane fouling analysis

The ultrafiltration experiments were carried out in an in-house manufactured 150 ml batch, unstirred, dead end ultrafiltration cell (Figure 1).

The process was carried out at room temperature (28±2°C) and a pressure of 2 kg.cm^{-2} unless stated otherwise. To maintain the upstream high pressure, nitrogen gas was used. The effective membrane area was 1385 mm^2. The cell was charged with DI water and membrane compressed for 30 min to obtain the steady state flux. After
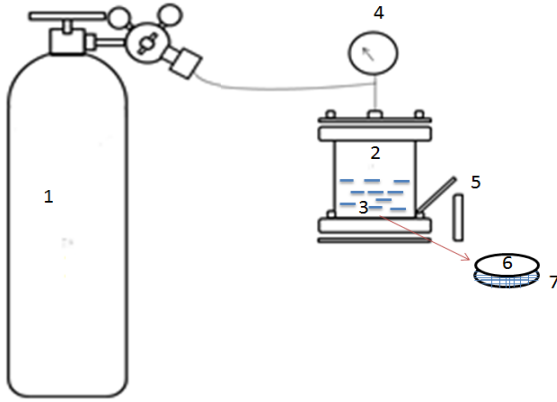
Fig. 1 Dead-End ultrafiltration setup. 1. Nitrogen Cylinder, 2. Dead End Filtration Cell, 3. Feed, 4. Pressure Gauge, 5. Permeate, 6. Membrane, 7. Membrane Support

compression the pure water flux was measured (J_{wi}). The equation used for calculating flux was as follows:

$$J = \frac{V}{A\Delta t} \qquad (1)$$

where J (l/m^2 h) is the flux, V (l) is the volume of the permeate, t (h) is the permeation time, and A (m^2) is the effective membrane area. After DI water flux measurement (J_{wi}) the cell was charged with 75 ml 20 ppm acid-blue 80 dye and the flux was measured after 8 minutes (J_p). Then the membrane was cleaned with DI water for 10 min and the cleaning flux was then measured as J_{wc}. The fouling-resistant capability of the membrane wasevaluated using the flux recovery ratio (FRR) parameter which is defined using the following expression:

$$FRR\,(\%) = \left(\frac{Jwc}{Jwi}\right) \times 100 \qquad (2)$$

Fouling resistance is described as the formation of a cake or gel layer on the surface of the membrane due to continuous deposition of contaminants in the feed. Flux (J), through the cake and the membrane, may be described by Darcy's law (Rahimpour *et al.* 2008).

$$J = \frac{\Delta P}{\mu \sum R} \qquad (3)$$

where ΔP is the transmembrane pressure (driving force), μ is the viscosity of permeate and R or (Rt) is the sum of the resistances. The intrinsic membrane resistance (Rm) can be calculated from the initial DI water flux:

$$R_m = \frac{\Delta P}{\mu J_{wi}} \qquad (4)$$

Fouling resistance caused by pore plugging and irreversible adsorption of foulants on membrane pore wall or surface (R_f) may be calculated as follows:

$$R_f = \left(\frac{\Delta P}{\mu J_{wc}}\right) - R_m \qquad (5)$$

The total filtration resistance R_t is the sum of R_m, and R_f.

In order to compare properties of the same membrane

under different conditions normalised flux J_v is used which is defined as:

$$J_v = \frac{J_p}{J_{wi}} \qquad (6)$$

A LMSP UV1900 Labman UV-Vis double beam spectrophotometer was used to determine the concentration of dye at a wavelength of 627 nm. The rejection R of the dissolved dyes was calculated as follows:

$$R(\%) = (1 - \frac{C_p}{C_f}) \times 100 \qquad (7)$$

where C_p and C_f are the permeate and feed concentrations of dyes, respectively.

Viscosity was measured using Ostwald glass viscometer. To check the efficiency of membrane for real wastewater the quantification was done using COD measurement and decolourisation. COD was measured according to the standard protocol given by ISO 6060:1989 (Mahvi *et al.* 2005), where samples were added into vial along with dichromate and sulphuric acid reagents. The vials were digested in Hanna Instrument (HI)-839800 COD thermodigester at 150°C for 2 hr. Decolourisation was observed using LMSP UV1900 Labman UV-Vis double beam spectrophotometer at a wavelength of 266 nm.

3. Results and discussion

3.1 Mechanism of coating TiO₂ nanoparticles on membrane

TiO₂ being a semi-conductor when irradiated by a light ray of energy equal to or greater than the band gap energy in ordinary conditions, causes an electron to transfer from capacity band to conduction band. This leads to the creation of electron-hole pairs on its surface. These photo-generated electrons react with the oxygen gas molecules in the surrounding and produce super-oxide radical anions (O_2^-). The photo-generated holes react with water molecules available in the environment and (OH^-) radicals are produced. Thus these two radicals have been found to be among the strongest oxidant reagents which lead to the degradation and elimination of the impurities especially organic compounds (Gupta *et al.* 2011, Sang *et al.* 2014, Emeline *et al.* 2013, Banerje, Dionysiou and Pillai 2015). This mechanism of photocatalysis is shown in figure 2 below.
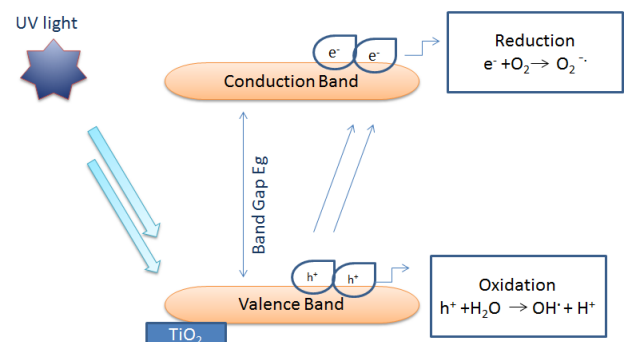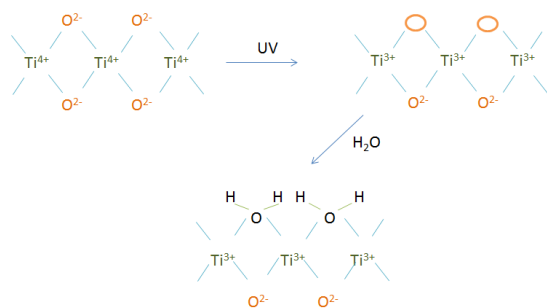

Fig. 2 The mechanism of photocatalysis

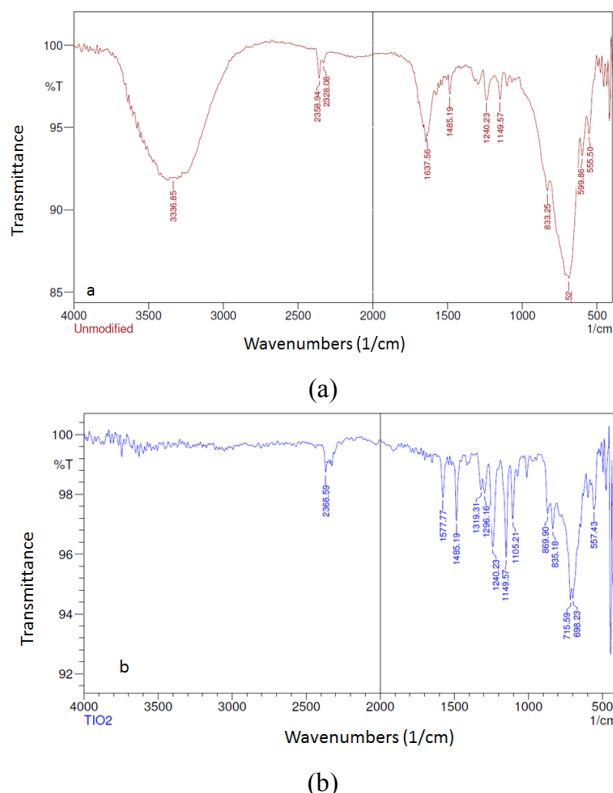Fig. 3 The mechanism of superhydrophilicity

(a)

(b)

Fig. 4 FTIR Spectra of (a) M1 (b) M4

(a)

(b)

Fig. 5 Surface SEM Images of (a) M1 (b) M4

The second phenomenon is the super hydrophilicity which is shown in Figure 3. In this case holes and electrons are also created but they react through a different mechanism. The photo-generated electrons lead to reduction of Ti(IV) cations to the Ti(III) state and the holes oxidize O^- anions. In this process, ejection of the oxygen atoms occur leading to a group of oxygen vacancies being created on the surface. Thus these empty sites create an affinity for water molecules in the environment which helps OH^- groups to become adsorbed on the surface, rendering the surface hydrophilic (Gupta *et al*. 2011, Sang *et al*. 2014, Emeline *et al*. 2013, Banerje, Dionysiou and Pillai 2015).

The PES membrane was coated with TiO_2 nanoparticles as explained in the previous section. The 0.5 wt% TiO_2 suspension was sonicated for 1 hr then neat membrane was placed in the colloidal suspension for 1 hr. After removing the membrane from the suspension it was washed with DI water and exposed to 250 W UV bulb for 10 m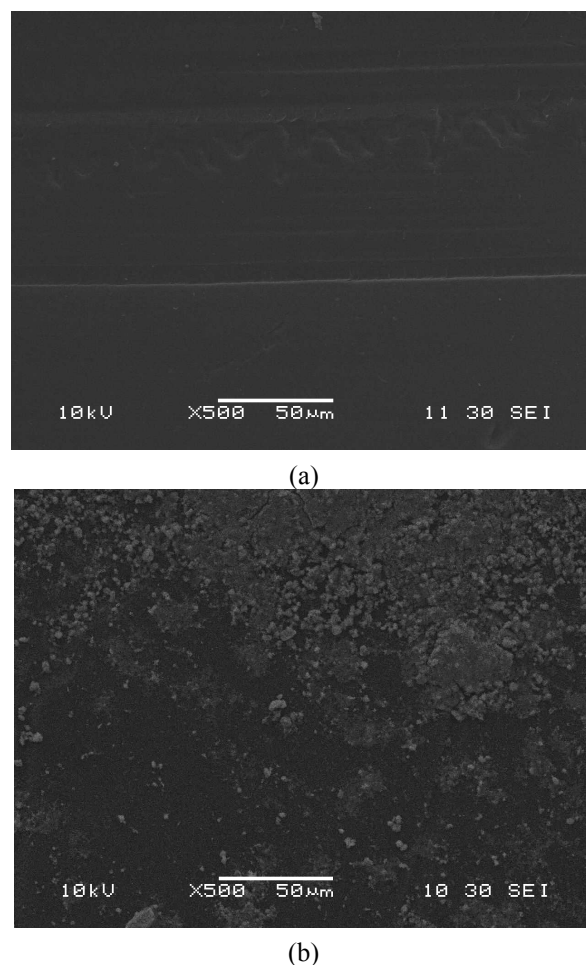in. The FTIR spectra for neat PES membrane (M1) and the TiO_2 deposited membrane (M4) is shown in Figure 4. The neat membrane had a band lying at around 3400 cm^{-1}. This peak is associated with OH stretching (Rahimpour *et al*. 2008, Belfer *et al*. 2000, Prince *et al*. 2014). This can result from water molecules being trapped in the membrane pore due to the phase inversion method of membrane manufacture. Porous materials can hold such water which becomes impossible to remove (Rahimpour *et al*. 2008, Prince *et al*. 2014). This peak has completely disappeared in the FTIR spectra for TiO_2 coated membrane indicating that the surface has been coated by the nanoparticles.

The SEM micrographs shown in Figure 5(a) for M1 and Figure 5(b) for M4 membranes indicate that the nanoparticles have deposited on the membrane surface although the deposition is not even and clusters are formed. The coating is possible due to the TiO_2 nanoparticles self-assembly with the polymer via OH bonds. The coordinate bonds between Ti^{4+} and oxygen cause strong attachment between the two (Lio *et al*. 2005, Rahimpour *et al*. 2008). This self-assembly prevents washing off of the particles from the surface of membrane. The increase in hydrophilicity of the membrane is clearly indicated by the decrease in the water contact angle which has been found to descend to 20.28° from a value of 73° for unmodified PES membrane. The values for contact angles are given in Figure 6. Lower contact angle indicates that water has spread more evenly on the surface.
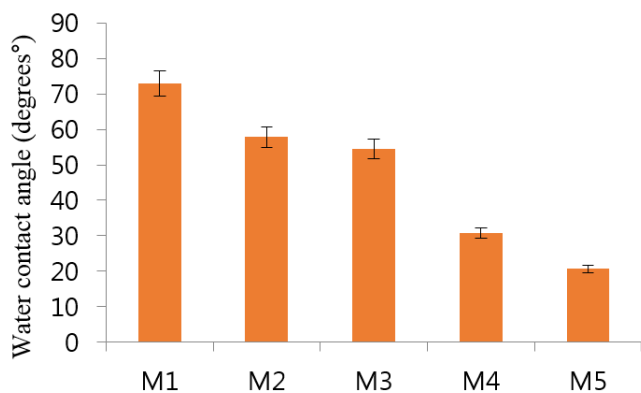
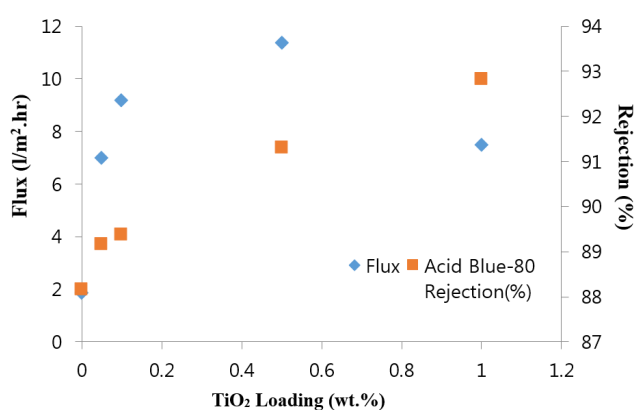Fig. 6 Water Contact Angle of neat and TiO₂ deposited membranes

Fig. 7 Acid Blue 80 Dye (20 ppm) flux and rejection vs TiO₂ loading on PES membrane

(a)

(b)

Fig. 8 Self-assembly mechanism of TiO₂ nanoparticles (a) co-ordination of sulfone group and ether bond to Ti^{4+} (b) by a H-bond between sulfone group and ether bond and surface hydroxyl group of TiO₂

Table 2 Filtration resistance and flux recovery ratio of neat and TiO₂ coated membranes

Membrane	M1	M2	M3	M4	M5
$Rm(\times 10^{13} m^{-1})$	24.4	5.75	5.15	4.38	6.26
$Rf(\times 10^{13} m^{-1})$	17.3	1.55	1.17	.889	1.7
FRR (%)	58	78	83	85	80

The DI water flux as well as acid blue-80 dye flux is found to be much higher for modified membrane as compared to unmodified membrane. The acid blue 80 dye flux and rejection of neat and TiO₂ deposited membrane during the filtration of 20 ppm concentration dye is shown in Figure 7. The loading of TiO₂ nanoparticles on the membrane is increased from 0 wt% to 1 wt%. The final stable flux increases from a value of 1.876 /m².hr for virgin membrane to 11.367 l/m².hr for a concentration of 0.5 wt%. The increase in flux can be explained by the superhydrophilicity effects of the TiO₂ nanoparticles which occurs due to the self-assembly of TiO₂ nanoparticles and the membrane polymer with OH bonds (Figure 8). The membrane surface's hydroxyl content increases due to the incorporation of TiO₂ nanoparticles on the membrane surface. The hydroxyl group has polarity and can interact well with water molecules through Van der Waals' force and hydrogen bond. A decline in flux is observed for a concentration of 1 wt% can be due to the blocking of pores by the nanoparticles. The rejection for dye also increases from a value of 88.15% for unmodified membrane to 92.82% for TiO₂ loading of 1 wt%. The increase in rejection is due to the presence of strong oxidants that can destroy impurities and also the permeation of water molecules probably increases as compared to the dye molecules. Similar results for protein rejection have been observed by Rahimpour *et al.* 2008.
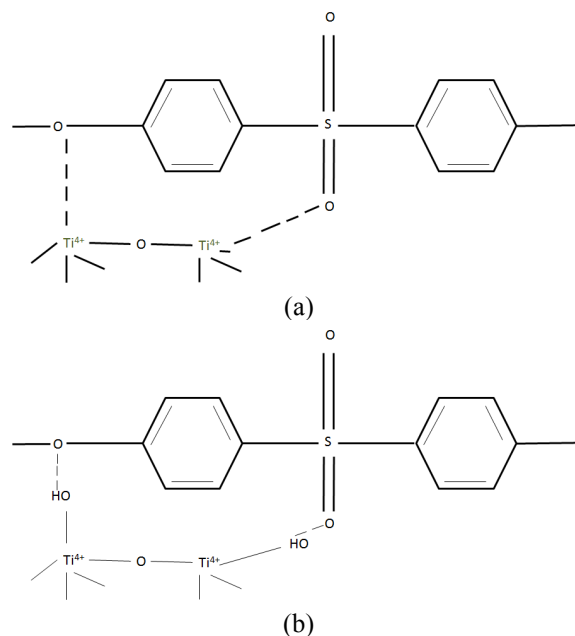
3.2 Optimum TiO₂ loading on neat PES membrane

To analyse the effect of TiO₂ loading on the membrane surface, membranes were coated with 0.05, 0.1, 0.5, and 1 wt% TiO₂ nanoparticles. After which they were exposed to 250 W UV lamp for 10 minutes. Figure 7 indicates that flux for modified membranes increases with TiO₂ loading as the coverage of the membrane surface by the nanoparticles is higher for higher concentration of TiO₂ nanoparticles. The increment in flux values is observed upto a value of 0.5 wt% TiO₂ loading i.e. M4. For a higher value of 1 wt% loading i.e M5, the stable flux value reduces to a value of 7.514 l/m².h. This can be a result of membrane pores being blocked by the TiO₂ nanoparticles. However the average dye rejection values increase linearly with TiO₂ loading as seen in Figure 7. The flux recovery ratio (FRR%) indicating the membranes anti-fouling capacity is found to be higher for TiO₂ coated membranes. The various resistances are also found to have decreased as shown in Table 2.

The flux decline for the ultrafiltration cycle of 100 minutes with acid blue-80 is shown in Figure 9. The flux decline for modified membranes is lower than that of unmodified membranes and the stable flux is much higher than that of the unmodified membrane. This is due to the improved anti-fouling of the modified membrane. The radicals (OH⁻ and O₂⁻) are present on the surface of the
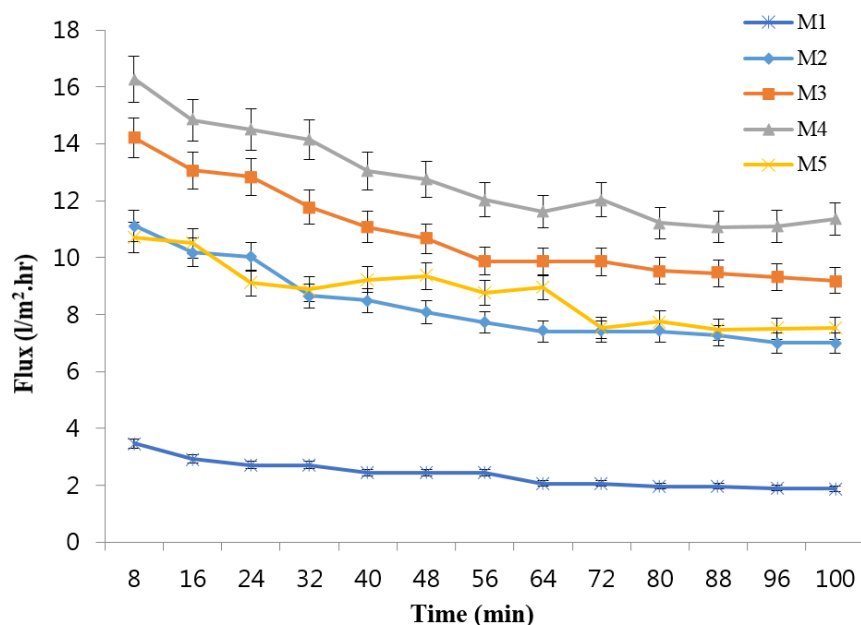
Fig. 9 Flux behaviour of neat and TiO$_2$ coated PES membrane
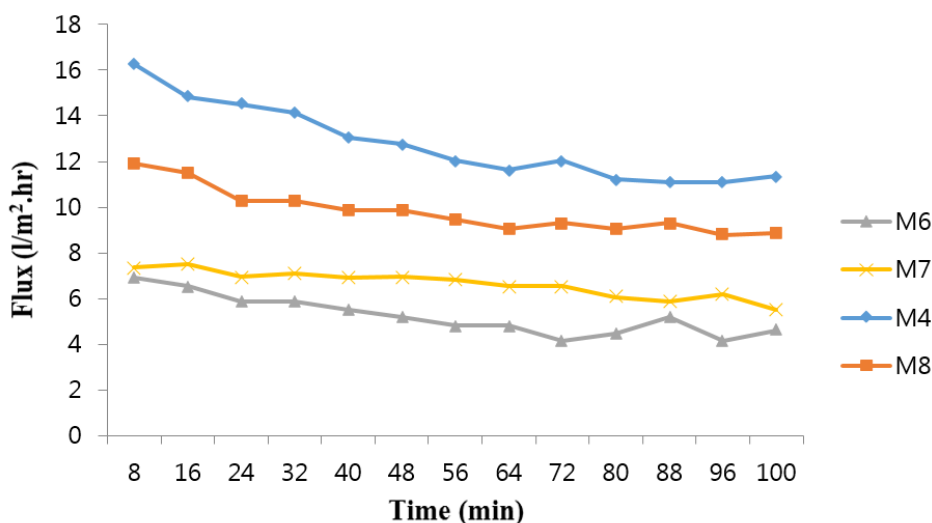
Fig. 10 Effect of membrane immersion time in 0.5 Wt% TiO$_2$ colloidal solution

Table 3 Rejection (%) of TiO$_2$ coated PES membranes

Membrane	M6	M7	M4	M8	M9	M4	M10
Rejection (%)	87	88	91.3	92	90.9	91.3	82

membrane due to the photocatalytic property of TiO$_2$ nanoparticles hence cause the decomposition of the dye molecules. The higher hydrophilicity of the modified membrane prevents the contaminants from settling on the membrane surface. The water molecules have higher preference for adsorption due to high hydrophilicity of the membrane surface hence they get preferentially adsorbed and thus prevent the contaminants from blocking the membrane surface (Rahimpour *et al*. 2012, Madaeni *et al*. 2011). The performance of M4 has been found to be most optimum as beyond this the flux reduces due to pore blockage.

3.3 Effect of immersion time on membrane properties

The effect of different times of immersion of the PES membrane in the 0.5 wt% TiO$_2$ nanoparticle colloidal suspension is shown in Figure 10. The membranes were immersed for different times of 15, 30, 60 and 90 min. After taking out they were washed and exposed to 250 W UV light for 10 min. They were labelled as M6, M7, M4 and M8 respectively. M4 was found to have the highest performance compared to the others. The higher time of membrane immersion may cause pore plugging (Rahimpour 2008). Table 3 indicates that rejection also increases with higher immersion time.

3.4   Effect of UV exposure time on membrane properties

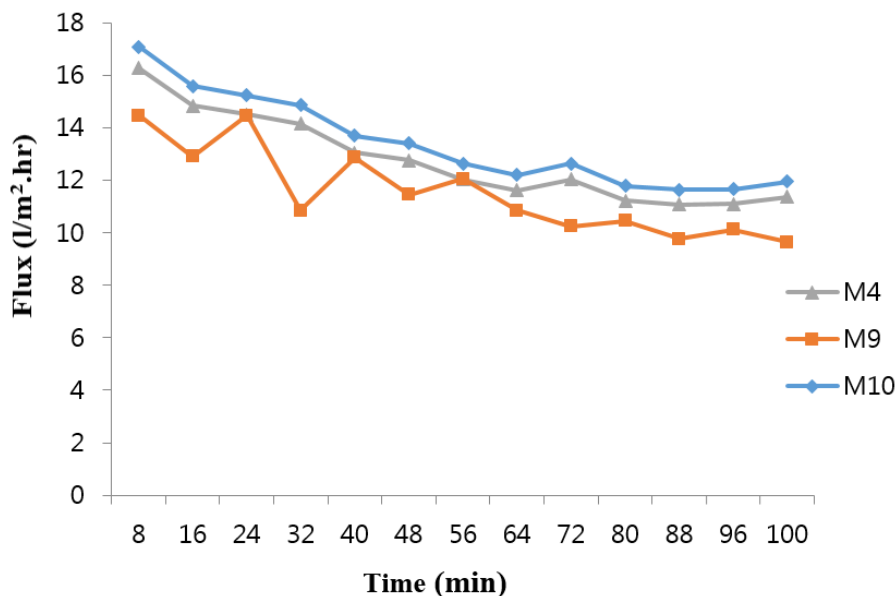To compare effect of UV exposure time PES membranes

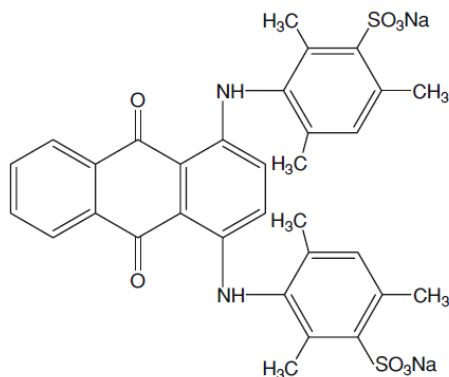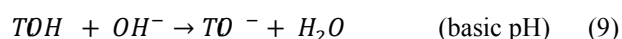Fig. 11 Effect of UV exposure time on 0.5 wt% TiO₂ coated PES membrane (60 min immersion)

Fig. 12 Acid Blue-80 Dye

were placed for 60 minutes in 0.5 wt% TiO₂ suspension, washed to remove excess of TiO₂ nanoparticles and then exposed to UV light (250W) for 5, 10 and 15 min. These membranes were labelled as M9, M4 and M10. For the nanoparticles to display their photocatalytic ability they have to be activated by UV light. Thus higher the duration of UV exposure higher will be the self-cleaning performance of membranes (Banerjee, Dionysiou and Pillai 2015). As seen in Figure 11, dye flux for M4 was somewhat higher than M9. However the flux for M10 was found to be similar to that of M4. It can be assumed that the membrane with UV exposure of 10 min has attained all the nanoparticles activation by UV rays and reached the maximum performance for a TiO₂ loading of 0.5 wt%. Thus further exposure to UV will not cause any changes in the flux. On the other hand a comparison of rejection (Table 3) shows that the rejection for M10 was lowest. This can be explained by the fact that higher UV exposure could cause bond scission and the non-availability of TiO₂ nanoparticles to bond with the membrane may cause this decline in rejection (Kilduff *et al*. 2000, Akbari *et al*. 2006). The results for flux decline and rejection are in agreement with those obtained by Rahimpour *et al*. 2008.

3.5 Effect of pH

The acid blue 80 dye (Figure 12) has a pH of 6.5 being acidic in nature, the flux decline (figure 13) and rejection (Table 4) for 20 ppm dye solution was observed. Three new membranes with the exact same modifications as M4 were prepared to be used for the three conditions. Figure 13 shows the flux decline for acidic basic and neutral conditions. The initial dye flux for a pH of 1.5 is lowest and shows a sudden drop from DI water flux. The flux decline is very high for acidic conditions. The rejection however is highest in the case of acidic conditions. Under different pH conditions TiO₂ exists as

$$TOH \;\; + \; H^+ \rightarrow TOH\;^+_2 \qquad \text{(acidic pH)} \qquad (8)$$

$$TOH \;\; + \; OH^- \rightarrow TO\;^- + H_2O \qquad \text{(basic pH)} \qquad (9)$$

In acidic condtions TiO₂ exists as $TiOH_2^+$ as shown in Figure 14 (Su *et al*. 2009, Jyoti *et al*. 2016). The acid blue 80 dye is negatively charged due to the presence of the sulfonate group (Akbari *et al*. 2006). Thus due to electrostatic interactions the dye gets adsorbed on the membrane surface causing contamination and plugging of membrane pores and hence decline in flux (Kilduff *et al*. 2000, Akbari *et al*. 2006). The rejection is also higher as along with the size exclusion by the membrane the dye molecules are also being attracted to the membranes surface. For the pH of 12 i.e. basic environment the membrane surface becomes negatively charged as TiO₂ exists as TiO⁻ (Su *et al*. 2009, Jyoti *et al*. 2016). Thus the negatively charged dye molecules are repelled and therefore not decomposed by the free radicals on the membrane surface causing a decline in rejection.

3.6 Real wastewater flux decline

Real wastewater obtained from textile industry is used to study the ability of the membranes to decontaminate
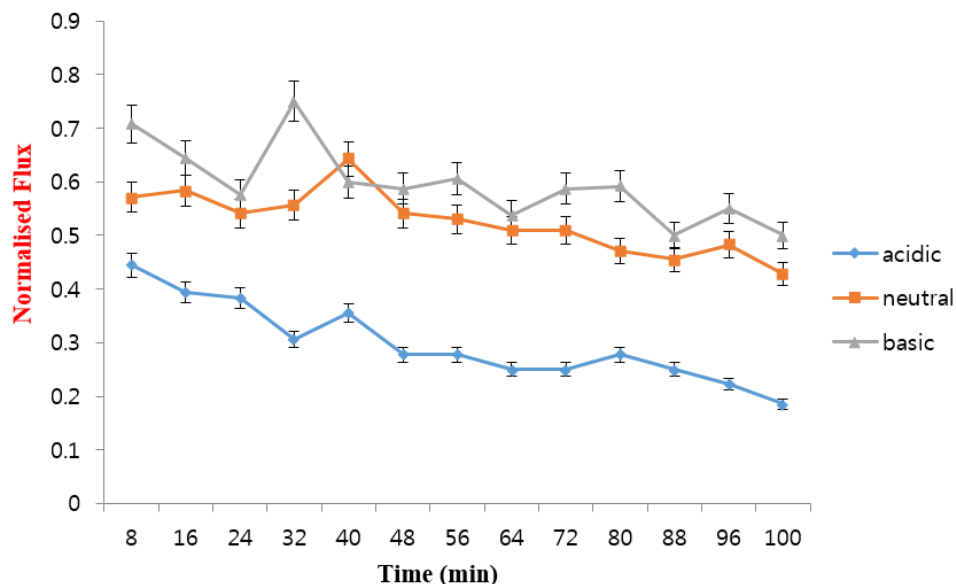
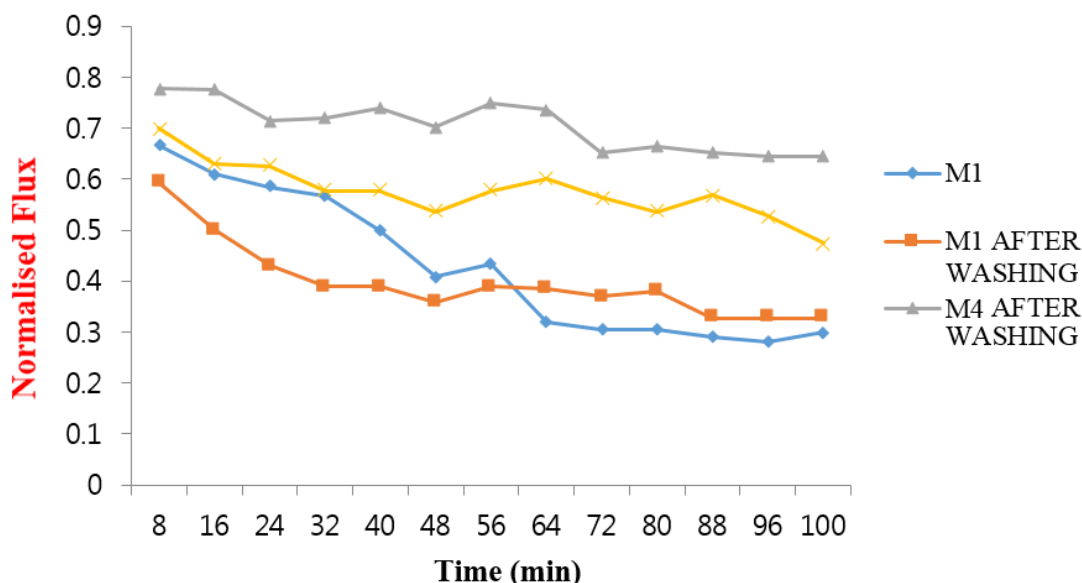Fig. 13 Normalised flux vs Time under different pH conditions for M4

Fig. 14 Flux behaviour of real wastewater

Table 4 Rejection (%) for different pH conditions

pH	Rejection(%)
1.5	93.51
6.5	92.5
12	81.45

wastewater and their ability to be reused. For this study the membrane with the same modification parameters as M4 was prepared. 65 ml real wastewater was placed in the dead end setup and analysis of permeate was performed. In order to compare membranes normalised flux was used. As can be seen from Figure 14 the flux decline for unmodified membrane is much higher as compared to the modified membrane. This can be attributed to the superior anti-

fouling property of the modified membrane which is explained in the previous sections. Figure 15 indicates the colour reduction for the two membranes. The modified membrane had a rejection of 59.9% while the unmodified had 47.18% rejection as seen in Figure 15. The higher rejection can be explained as the modified membrane having higher number of radicals on the membrane surface that can destroy the contaminants and impurities in the solution. The membrane's propensity for water molecules also increases due to the increased hydrophilicity causing an increase in the rejection. The COD reduction (%) (Figure 16) is also higher for modified membrane. To check the reusability of the membrane the membranes were washed with DI water for 10 minutes then reused with the same feed in order to check their deterioration in separation and flux performance. For the case of unmodified membrane
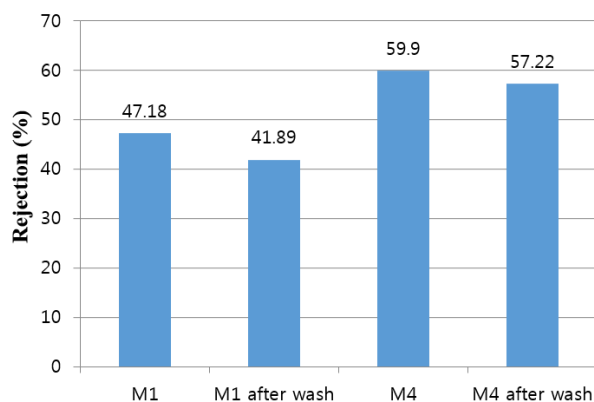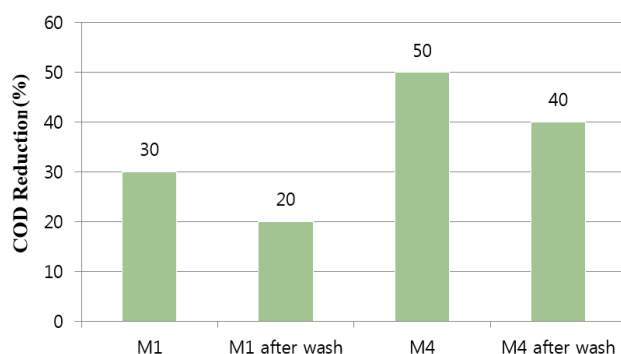
Fig. 15 Rejection (%) for real wastewater

Fig. 16 COD reduction (%) for real wastewater

deterioration in the properties of the membrane is observed as the membrane shows lower flux than the first trial and still higher flux decline. This is due to the reduction in flux for the membrane due to contaminants causing pore blocking and hence decline in the flux as well as rejection capability. On the other hand modified membranes had similar performance as the first time albeit lower which could have arisen due to the washing away of some TiO₂ nanoparticles or the loss of photocatalytic ability of the nanoparticles (Madaemi and Ghaemi 2007).

4. Conclusions

Commercial PES membranes were coated with TiO₂ nanoparticles with the help of UV light. The ability of the nanoparticles to self-assemble on the membrane was exploited. This self-assembly caused higher hydrophilicity and ultimately improved anti-fouling property for the membrane. The coating was confirmed by FTIR, SEM and contact angle measurement. The FRR(%) and resistances were much higher and lower respectively as compared to unmodified membranes.

•   **TiO₂ Loading** – Membrane immersed in 0.5 wt% TiO₂ colloidal suspension for 60 min and 10 minute UV irradiation had the highest flux and beyond this the value of flux reduces due to blockage of membrane pores.

•   **Immersion Time** – Membrane with 60 min immersion time in 0.5 wt% TiO₂ colloidal suspension with 10 min UV irradiation had the highest performance for

various different immersion times as lower times had insufficient loading while higher times caused pore blockage. Rejection increases with increased immersion time.

•   **UV exposure** – Membrane irradiated for 10 min gave the best performance as higher UV exposure had no effect on improvement on performance but caused a decline in rejection.

•   **pH** – Acidic pH of feed had highest rejection but lowest flux performance due to the positive charged gained by the TiO₂ nanoparticles on the membrane surface.

•   **Real wastewater** – TiO₂ coated membranes had superior performance as compared to the neat PES membrane.

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