Effect of titania nanotubes on the flux and separation performance of polyethersulfone membranes

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Abstract. The improvement of membrane performances in terms of separation and permeation is a constant research problem. In this study, polyethersulfone (PES) hollow fiber nanocomposite membranes were fabricated with titania nanotubes (TNT) synthesized via hydrothermal method used as inorganic filler to improve separation and membrane permeation. The membranes were prepared using dry/wet phase inversion process. The concentration of PES was fixed at 18\% and TNT was added at concentration of 0.1\% wt. The membranes were characterized in terms of pure water permeation rate (PWP), proteins (BSA) rejection, porosity and water contact angle. The results showed that addition of TNT improves the water flux and rejection rate as well as increasing hydrophilicity of the membrane. The flux of membrane is improved more than 20\% while the rejection has been improved from 79\% to 96\%. The addition of TNT into the membrane matrix has shown that photocatalytic property can be introduced to a normal membrane.

1. Introduction
The demand for cheaper and reliable ways to purify products or remove waste generated by industrial processes is ever present. Cost and simplicity are two things that are always taken into consideration when it comes to new technologies. This is where membrane technology can come into the fore to provide a cheap and reliable system that can filter out impurities.

Membrane is universally described as a selective layer of barrier that only allows certain particles to go through it. With the developing technology in the membrane industry, researchers are able to tailor the structure and characteristics of the membrane to fit the profile of whatever feed they intend to use it for. This is where incorporation of non-organic materials comes into play in current study trends. Many different types of inorganic fillers have been added into membranes to improve the performance of membrane in terms of permeance and selectivity [1].

In light of this, titanium dioxide nanotubes (TNT) in particular has been receiving strong interest from researchers as a nanomaterial that not only improve the permeance of membrane, but also incorporate photocatalytic activity it is renowned for into the membrane as a dual functioning membrane [2]. Titanium dioxide is environmentally friendly and has good photocatalysis properties. The synthesis of TNT has many methods, template-assisted method, the electrochemical anodic

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oxidation method and hydrothermal treatment are among popular choices [2]. In this study, hydrothermal method is used to synthesize the TNT as they are environmentally friendly, easy to handle, and able to produce nanotubes with minimal issues [3]. Furthermore, they are easily modifiable and produce nanotubes in random alignment [4]. The downside of this method is their relatively long reaction time and the difficulty to obtain nanotubes with same sizes [3]. Hence, in this study, TNT, which is synthesized using the hydrothermal method with the appropriate reaction time and temperature, is incorporated into PES hollow fiber membranes via physical blending in which polyvinylpyrrolidone (PVP) is used as pore former. The effects of TNT on the membrane performance and characteristic such as water permeance, salt and molecular weight cut off are investigated. Furthermore, morphological studies will be done on both nanotubes formed and membranes fabricated to observe the changes brought about by the addition of TNT into membrane.

2. Experimental

2.1 TNT synthesis

The starting material used for the synthesis of TNT were rutile commercial Titanium Dioxide TiO₂ P25 Degussa supplied by Evonik Industries. The PES used was from Radel®, polyvinylpyrrolidone (PVP) from Fluka Analytical. Both hydrochloric acid (HCl) and sodium hydroxide (NaOH) used in the synthesis of TNT was from Merck & Co, while the solvent used for the preparation of polymer dope solution was from Across Chemicals. All the chemicals were used as received without further modification or purification. For the synthesis of TNT, 10 M of NaOH was mixed with TiO₂ and stirred for 12 hours using a magnetic stirrer. The blended solution was then transferred into a Teflon-lined autoclave container and placed into an Autoclave block and sealed tightly. The sealed autoclave was then placed into an oven and was heated at 180°C for 24 hours. The heated autoclave was allowed to cool down to room temperature before the content was removed for further treatment. The sample was washed with 0.1M of HCl, and then washed with tap water until the pH of the residual water reached 7. The sample was then filtered and placed in an oven at 60°C to remove any moisture, and then ground into powder form. The sample was analyzed using transmission electron microscope (TEM), x-ray diffraction (XRD) and brunauer–emmett–teller (BET) to determine its morphology and characteristic.

2.2 Preparation of PES/TNT hollow fiber membranes

The PES/TNT dope solution was prepared by dispersing 0.1wt% of TNT into n-methylpyrrolidone (NMP) solvent and placed into a sonicator for 60 minutes to ensure 100% dispersion of TNT in the solvent. Next, pvp K90 was added into the dope solution. Then, 18 wt% of PES polymer pellets were added into the dope solution and blended until homogeneous using a mechanical stirrer. Finally, 10wt% of ethanol was added into the dope solution drop wise. The hollow fiber membrane was spun using an annular spinneret with an internal diameter of 0.5m and an outer diameter of 1.15mm. Water was used as the bore fluid and external coagulant. The fabricated membrane was then immersed in water for one day to ensure complete removal of solvent and then treated with glycerol to improve integrity of membrane. A neat membrane was also fabricated without the addition of TNT to study the effect of TNT on membrane performance and characteristics.

2.3 Fabrication and performance analysis of fabricated membranes

The membranes were fabricated using the same spinning parameters, with a spinneret dimension of 1.15mm outer diameter and 0.50mm inner diameter, H₂O used as inner and outer coagulation agent, and the membrane were finally treated with glycerol to strengthen its structure. Finally, the membrane was air dried for 48 hours and then underwent performance testing. Pure water flux, bovine serum albumin (BSA) rejection, Contact angle, porosity and pore volume of the membrane fabricated.
2.4 Contact angle
Membrane contact angle test was done via sessile drop method, using distilled water to determine the hydrophilicity and wettability of the membrane. The test was done for 10 times and the results were averaged to improve accuracy.

2.5 Membrane porosity
Membrane porosity can give some information on the performance of the membranes fabricated. Select amount of membranes were cut and the ends were closed using epoxy resin. Then, they were immersed in water for 3 hours and the weights were taken after removing superficial water on its surface using tissue. Then, the membranes were air dried in oven for a night and weighed again. The porosity of the membranes was calculated using equation 1 below:

$$\varepsilon = \frac{W_0 - W_1}{V}$$  \hspace{1cm} (1)

where $\varepsilon$ is the membrane porosity, $W_0$ and $W_1$ is the weight of wet and dry membrane in grams, and $V$ is the membrane volume in cm$^3$.

3. Experimental results

3.1 Characterization of TNT
Three different characterizations were done on the fabricated TNT, namely x-ray diffraction to determine the crystallinity of the nanotubes, TEM to determine the morphology and dimensions of the nanotubes, and finally BET to determine the surface area and porosity of the nanotubes formed. The XRD analysis shows that the nanotubes formed are in anatase form, which is similar to the crystallinity of the starting material used. Figure 1 is the crystallinity graph obtained from XRD analysis.

![Figure 1. X-Ray Diffraction result on the titania nanotubes (24 hours) formed via hydrothermal method.](image)

As shown in figure 1, few significant peaks appear at angles of 10.85°, 24.5° and 48.5° evidenced the formation of anatase TNT. The XRD patterns are in agreement with recent publications on the
formation of TNT [5,6]. Since the crystallinity of the nanotubes formed is similar with the starting material used, TiO\textsubscript{2} P25 Degussa, it can be deduced that the alkaline hydrothermal treatment does not affect the crystallinity of the nanotubes.

However, looking into the surface area of the nanotubes formed, there was an increase of up to 500\%, where the BET analysis on the TNT formed is 197.7021 m\textsuperscript{2}/g, in agreement with literatures published elsewhere [5-7], while the commercial TiO\textsubscript{2} P23 Degussa has a surface area of only 40.0 m\textsuperscript{2}/g to 50.0 m\textsuperscript{2}/g. This massive increase is attributed to the tubular form of TNT, which increases the surface area greatly compared to the nanoparticles which is grain shaped.

Figure 2 shows the results of TEM analysis done on the morphology and structure of the TNT fabricated. Both images show the diameter of the nanotubes formed is at the range of around 29 nm, while the images also shows the inner wall of the nanotubes formed. Furthermore, both images indicate that the tubes formed are open ended. However, clear images of single images were not taken as the nanotubes faced agglomeration due to their high surface area, with high surface area increases the collision frequency among nanoparticles, which promotes agglomeration among nanoparticles [8].

3.2 Pure water flux and Bovine Serum Albumin (BSA) rejection test

The neat and mixed matrix membrane (MMM) fabricated was tested to determine the changes in pure water flux and the BSA rejection.

| Membrane | Pure water flux | BSA Rejection | Contact Angle | Porosity |
|----------|----------------|---------------|---------------|----------|
| Neat     | 15.70 L/m\textsuperscript{2}h | 79.71\% | 87.4 ± 2.0 | 69.77 g/cm\textsuperscript{3} |
| TNT 0.1%| 19.61 L/m\textsuperscript{2}h | 96.79\% | 69.0 ± 2.4 | 67.79 g/cm\textsuperscript{3} |

The first test done was to see the difference in the pure water flux of the membrane. As seen in the table 1, the pure water flux of the membrane added with TNT as an additive is higher compared to the neat membrane fabricated, with an improvement of nearly 20\%. The addition of TNT in the PES membrane has improved the flux as the structure of TNT has hydroxyl groups which are polar in nature. The presence of hydroxyl group has improved the pure water flux of the membrane [9]. The molecular weight cut off (MWCO) of the membrane shows that the addition of TNT into the polymer matrix improved the rejection from 79.71\% to 96.79\%. This indicates that the addition of smaller sized nanoparticles into the polymer matrix enhances its permeability and its separation property [10].
3.4 Contact angle of membrane
The contact angle analysis shows that the contact angle reduced from 87.4° ± 2.0° to 69.0 ± 2.4°, supporting the fact that the addition of TNT has increased the hydrophilicity of the membrane. This result is similar to the work done by [11] where contact angle of the membrane was reduced after the introduction of TNT into the polymer matrix. This is due to the fact that the addition of TNT has introduced higher amount of hydroxyl radicals, which enhances the hydrophilicity of the membrane.

3.5 Membrane porosity analysis
Membrane porosity analysis was done to determine how the addition of TNT into the polymer matrix affects the membrane porosity. The porosity of the neat membrane was calculated at 69.77 g/cm³ while the porosity of the MMM reduced to 67.79 g/cm³. This can be explained by the fact that the addition of TNT into the polymer matrix hinders the phase inversion process, hence the slight addition of the inorganic TNT has reduced the porosity of the membrane by a small amount [10]. This also explains why the addition of TNT has improved the rejection performance of the membrane compared to neat PES membrane.

4. Conclusion
This study has shown that addition of TNT as a nanocomposite into membranes have the ability to improve the performance of PES based membranes in terms of its pure water flux and also its rejection ability. The unique tubular structure of the TNT also is an upgrade compared to nanoparticles in terms of its higher surface area. Furthermore, the OH hydroxyl group that is present in the TNT also improves the hydrophilicity of the membranes incorporated with it.

5. References

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