

INVESTIGATION OF TITANIUM-DIOXIDE COATINGS ON MEMBRANE FILTRATION PROPERTIES

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ABSTRACT. In this study, synthesized TiO₂ nanorods and commercial Aeroxide P25 TiO₂ nanoparticles were deposited on polyethersulfone (PES) membrane surfaces to compare their photocatalytic activity and effects on membrane surface and filtration properties. The catalysts were deposited on the membrane surface by physical deposition. The effect of the TiO₂ amount on the stability of the catalyst layer and its effect on membrane resistance in presence and absence of UV irradiation were investigated. 1.2 mg/cm² catalyst coverage proved to be a minimal appropriate coverage to prevent membrane damage during UV irradiation. The catalysts formed hydrophilic layers on the surface, and in case of both catalyst the surface free energy increased compared to the neat membrane. The photocatalytic activity and retention of the modified membranes were tested spectrophotometrically by using Acid Red1, azo dye.

Keywords: *membrane filtration, TiO₂ coated membranes, photocatalysis, azo dye, Acid Red 1*

INTRODUCTION

Polyethersulfone (PES) is a widely-used material in asymmetric membrane manufacturing, because of its good performances [1]; it has high mechanical strength, thermal stability, environmental endurance, and

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processing [2, 3]. However, it has low permeability and high fouling tendency due to its inadequate hydrophilic property [1–3]. This limits its application as a membrane material. To overcome these flaws, it is possible to modify PES membranes to improve their hydrophilicity [2], since back-flushing and chemical cleaning are not providing a permanent solution against membrane fouling and require serious optimization [4].

Some authors specifically investigated approaches to modify PES membrane with TiO_2 to increase its hydrophilicity and to decrease its tendency to fouling. TiO_2 is favoured over other semiconductors due to its good physical and chemical properties, availability, photocatalytic activity, desirable hydrophilic and potential antifouling properties [5–7].

PES composite membrane modified by self-assembly of TiO_2 nanoparticles showed good separation qualities and higher water flux compared to the unmodified membrane, improved thermal stability, and increased hydrophilicity [2, 8]. Three different modified PES membranes were compared by Rahimpour and co-workers [1]: TiO_2 -entrapped membranes, UV-irradiated TiO_2 -entrapped membranes, and UV-irradiated TiO_2 -deposited membranes. It was found that by adding TiO_2 to the casting solution changes the morphology of the membrane, by making a more hydrophilic and porous structure that has photocatalytic activity. However, the TiO_2 -deposited membranes had superior characteristics in terms of fouling mitigation.

The membrane fouling properties are determined by the interactions between foulants and the membrane surface. These interactions are weak secondary forces such as van der Waals, hydrogen and electrostatic forces. The strength of these forces depends on the characteristics of the membrane such as wettability or surface free energy. Generally, it can be stated that higher hydrophilicity and lower surface free energy leads to lower fouling property [6, 9, 10].

In this work PES microfiltration membranes were coated with commercial Aeroxide P25 TiO_2 and synthesised TiO_2 nanorods. The aim of the work was to examine and compare the two layers made of catalysts of different geometry and different hydrophilicity. Contact angle measurements were carried out to determine the effect of the catalyst layer on the membrane surfaces wettability and surface free energy. Acid Red 1 (AR1, Azophloxine) dye was used as a model pollutant to determine the photocatalytic activity of the TiO_2 P25 and TiO_2 NR layers. AR1 is a reactive azo dye belonging to the largest class of dyes commonly employed in textile industry [11].

RESULTS AND DISCUSSION

Characterization of the used photocatalyst. For the membrane coating a commercial and a self-prepared titanium dioxide photocatalyst was applied. The synthesised TiO_2 “nanorods” (TiO_2 NR, Figure 1) can be characterized with $\sim 50\text{--}70$ nm length, $\sim 20\text{--}30$ nm width and a $\sim 54\text{ m}^2\text{g}^{-1}$ specific surface area (determined by nitrogen adsorption at 77 K, using BET method). Based on the XRD diffractogram of TiO_2 NR (Figure 2) it consists of 100% anatase phase. Commercial Aeroxide P25 titanium dioxide (produced by Evonik Industries) was also used for our experiments, which have spherical shape with a primer particle size of ~ 25 nm [12]; however, it should be noted that in a suspension it forms aggregates nearly $1\text{ }\mu\text{m}$ in diameter [13]. This titania is a mixture of anatase (90%) and rutile (10 %) phase, and it has similar specific surface area ($49\text{ m}^2\text{g}^{-1}$) like our self-prepared TiO_2 NR.

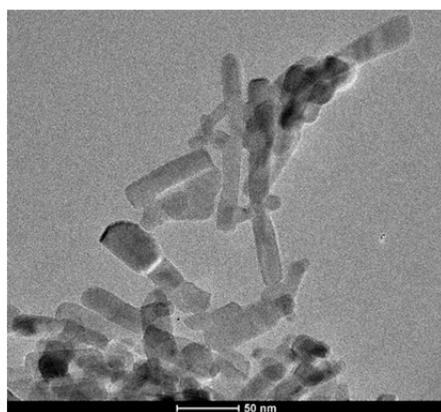


Figure 1. TEM image of titania nanorods (TiO_2 NR)

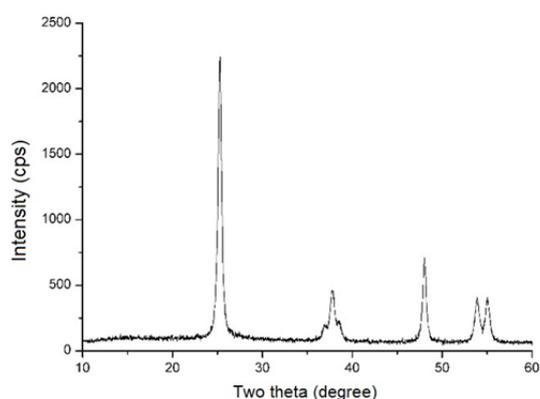


Figure 2. XRD of titania nanorods (TiO_2 NR)

Neat and TiO₂ Coated Membrane Surface Property. To investigate the effect of the catalyst layer on the membrane surface, TiO₂ suspension was filtered through the membrane in a dead-end stirring cell to provide a specific cake layer. The SEM images of top surface of 0.6 g cm⁻² TiO₂ P25 coated and the 0.6 g cm⁻² TiO₂ NR coated membranes are shown in Figure 3. In case of both catalysts the aggregates are larger than the membrane pores, thus depositing on the surface, this amount of the catalysts does not provide a full coverage of the membrane and are not distributed uniformly. TiO₂ P25 forms a thick layer of uniform aggregates on the membrane surface. TiO₂ NR deposits on the surface forming different sized aggregates. To achieve better coverage of the membrane to protect from UV damage the amount of the catalyst was doubled, and its effect was investigated in further experiments.

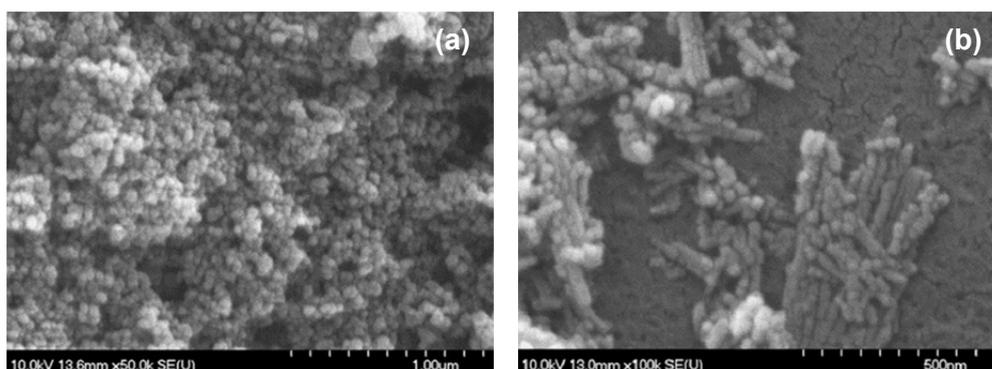


Figure 3. SEM images of top layers of (a) 0.6 g cm⁻² TiO₂ P25 coated, and (b) 0.6 g cm⁻² TiO₂ NR coated membranes

To characterize the wettability of the modified membrane surfaces, contact angles (with distilled water and glycerol) were measured and the surface free energy values were calculated. Figure 4 shows the contact angles of water and glycerol and the surface free energies. The contact angles of the TiO₂ P25 coated membrane show that the catalyst forms a hydrophilic layer on the surface. The hydrophilicity of TiO₂ NR coated membranes also increased compared to the neat membranes. Reportedly, the reactivity of TiO₂ surface and its affinity toward water is dependent on TiO₂ crystal phase [14].

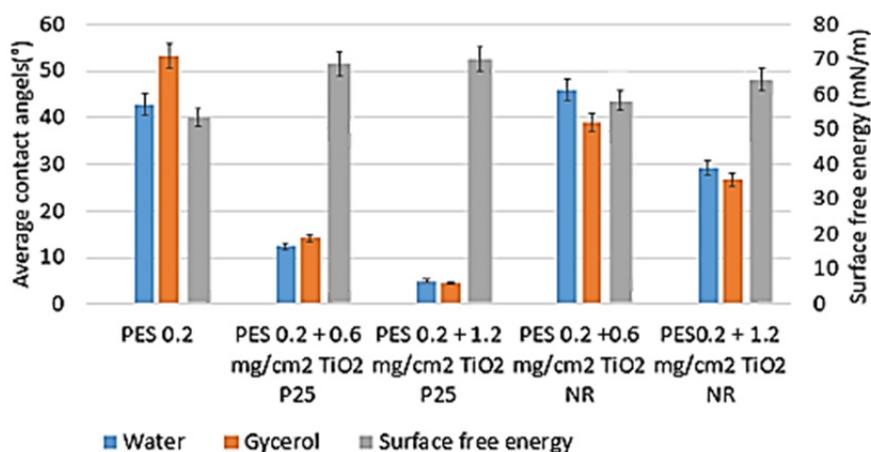


Figure 4. Contact angles of water and glycerol and surface free energies of neat and TiO₂ coated membranes

Investigation of the membrane stability under UV irradiation. To investigate the effect of UV irradiation on the membrane stability, the membrane flux changes were measured and the membrane resistances were calculated before and after UV irradiation of the neat and coated membranes. It was found that the neat PES 0.2 membrane resistance (calculated by Equation (2)) decreased 30% after 1 hour UV ($\lambda = 254$ nm) irradiation (Figure 5) due to its sensitivity to UV. According to the literature, similar decrease in membrane resistance was achieved after 24 hours of UV-A light irradiation of an ultrafiltration PES membrane [15, 16]. This was attributed to the fact that PES contains sulphur that is highly susceptible to UV light. In the next series of experiments the effect of the amount of the catalyst on membrane stability under UV irradiation was examined. By coating the membrane with higher amounts of catalyst layer the decrease of membrane resistances were less extensive after 1 hour UV irradiation, since the catalyst layer absorbs the UV light. The 1.2 mg/cm² catalyst layers in case of both types of TiO₂ provided a sufficient coverage to be used for investigating the photocatalytic activity of the catalyst layer without extensive damage of the membrane during the irradiation.

To investigate the stability of the catalyst layer on the membrane surface, all coated membranes were left overnight in the stirring cell. 100mL distilled water with 300rpm for 24 hours was stirred over them to check if the layer would wash off during operation. It was found that the turbidity of the distilled water did not change; the catalyst did not resuspend thus the TiO₂ coating did not wash off.

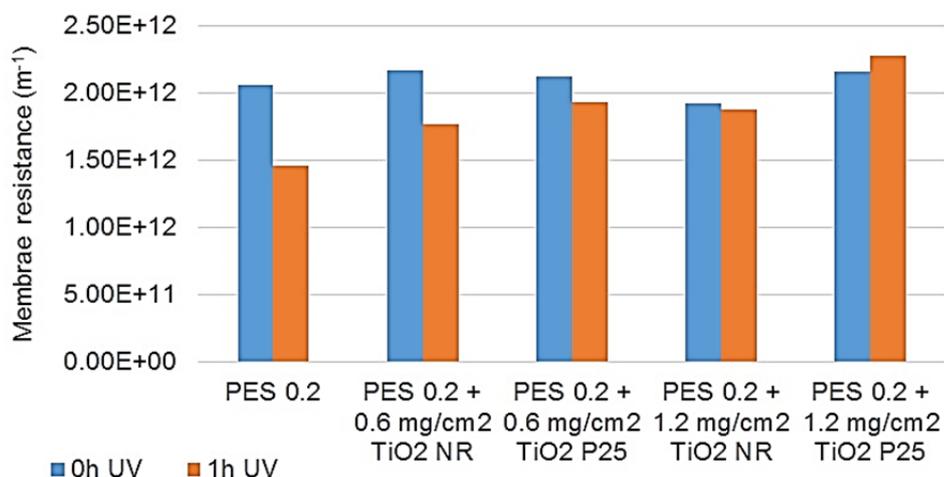


Figure 5. Changes of resistances of neat and TiO₂ coated PES 0.2 membranes before and after UV irradiation

Photocatalytic activity of the catalyst coated membranes. The photocatalytic efficiencies of the catalyst layers were characterized by the decolourization of Acid Red 1 dye solution. In the first series of experiments the effect of UV irradiation on the decolourization of Acid Red1 was examined. During these experiments 100mL of 15mg/L Acid Red 1 solution was UV irradiated for an hour, and it was found that the irradiation alone did not result in colour intensity change of the solution. The photocatalytic activity of the coatings was examined in two different experimental arrangements. First, a 1 hour UV irradiation was used as a pre-treatment in the presence of the coated membrane, which was followed by the filtration. Secondly, the photocatalysis was performed during the filtration.

First, the retention of the neat membrane was measured and calculated by filtering the dye solution through it, using Equation (3). The TiO₂ coated membranes had different retention values compared to the neat membrane (Figure 6). The TiO₂ P25 coating resulted in a 26% increase of the retention, which can be explained with the dense structure of the TiO₂ layer [17], the layer behaves as an additional filtration layer which can adsorb the positively charged dye ions, due to its hydrophilic character. The TiO₂ NR coating resulted in a 62% retention decline compared to the neat membrane. The TiO₂ NR coating prevents the dye molecules from adsorbing on the membrane surface, due to its lower surface free energy compared to TiO₂ P25, which means that this surface is less prone to fouling.

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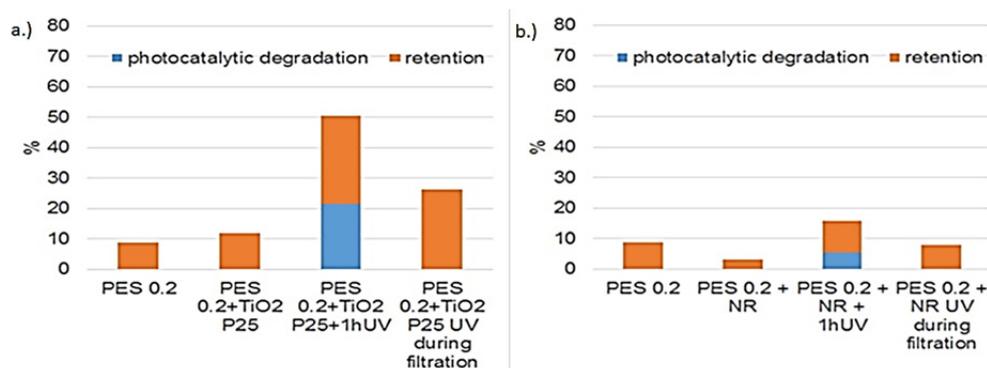


Figure 6. Neat and TiO₂ P25 (a.) and TiO₂ NR (b.) coated membrane dye retention

It was found that as a pre-treatment, irradiating the solution in the presence of the TiO₂ P25 coated membrane for an hour resulted in a 22% decolourization of the dye; this was only 8% in case of the TiO₂ NR coating. These results prove that the catalyst layers have photocatalytic activity, which means that the reactive species generated by heterogeneous photocatalysis react with the dye molecules. These results show that the efficiency of the photocatalytic degradation depends on the adsorption ability of the organic molecules on the catalyst surface: since the dye is less prone to adsorb on the surface of the TiO₂ NR coated membrane the efficiency of photocatalytic reaction is lower.

Filtering of the pre-treated solution through the TiO₂ P25 coated membrane resulted in a nearly 50% dye retention. In case of the TiO₂ NP coated membrane the membrane retention was significantly higher than the neat membrane retention, but significantly lower compared to the TiO₂ P25 coated membrane. In the case of continuous irradiation during filtration through the TiO₂ P25 and TiO₂ NP coated membranes the retention was lower compared to the pre-treatment that was followed by the filtration due to shorter exposure to the UV irradiation. In case of the pre-treatment the irradiation time was 1 hour while the simultaneous irradiation and filtration lasted for only 6 minutes.

CONCLUSIONS

Polyethersulfone microfiltration membranes were coated with commercial TiO₂ P25 and synthesized TiO₂ NR. The minimal appropriate catalyst coverage of the membrane surface was determined to be 1.2 mg/cm²,

to create a stabile coating which adsorbs the UV making the membrane withstand the irradiation. The coated membrane surfaces become more hydrophilic compared to the neat membrane, and the catalyst layer resulted in a higher surface free energy. The results showed that the surface hydrophilicity and the surface free energy determined the adsorption ability of the dye particles; the more hydrophilic TiO₂ P25 coating adsorbed higher amount of dye. Based on the results the surface free energy is in relation with the photocatalytic activity of the catalyst coating; the TiO₂ NR coated membranes have lower surface free energy, which means that it is less prone to adsorb dye particles, and this type of modified membrane showed lower photocatalytic activity, even though the specific surface area was similar in both cases.

EXPERIMENTAL SECTION

TiO₂ (anatase) (BA01-01), TiO₂ P25 (AEROXIDE) and Acid red1 were supplied by UNIVAR, EVONIC Industries and Synthesia respectively. The concentration of AR1 solution used in membrane filtration measurements was 15 mg/L.

The preparation of TiO₂ nanorods were as follows: in 1 L of a 10 M NaOH solution 250 g TiO₂ (anatase) was suspended, then for 24 hours the suspension was stirred in a rotating autoclave at 3 rpm and 155°C. Then the resulting product was washed and protonated with 0.1 M HCl, after maintaining a pH value between 3 and 4 for 30 minutes the product was washed with 0.01 M HCl for 3 days than with distilled water to remove the remaining chloride ions. The resulting TiO₂ nanotubes were dried at 80°C for a day. The TiO₂ nanotubes (NT) were than heat treated at 600°C for 6 hours. As a resulting product TiO₂ nanorods (TiO₂ NR) arose.

Polyethersulfone membranes (PES-MF (NEW LOGIC Research INC, USA) with a 0.2 µm were coated with commercial TiO₂ P25 and synthesized TiO₂ NR. The membranes were coated by filtering through the membrane 50 mL and 100 mL 0.4 g/L catalyst suspension in a dead end cell, at 0.1 MPa without stirring, that resulted in 0.6 and 1.2 mg/cm² TiO₂ coating respectively. The filtration was carried out with a Millipore batch filtration unit (XFUF04701, Solvent-resistant Stirred Ultrafiltration Cell, Millipore, USA). For the photocatalytic tests were carried out by the presence of the catalyst coating and UV irradiation, the stirring cell cap was modified and a UV light source was fitted in it (Fig. 7). This way a photocatalytic membrane reactor was set up. The UV light source was a low pressure mercury-vapour-lamp (GERMIPAK LightTech, Hungary, 40W, λ=254nm). The filtrations of the dye

solution were carried out at 0.1 MPa transmembrane pressure, without stirring at 20°C. In case of every filtration 100 mL water or dye solution was filtered to volume reduction ratio 5 (VVR=5). VRR [-], was defined as:

$$VRR = \frac{V_F}{V_F - V_P} \quad (1)$$

where V_F and V_P is the volume of the feed and permeate [m^3] respectively at any time.

The membrane resistance (R_M) was calculated as [18]:

$$R_M = \frac{\Delta p}{J_w \eta_w} [m^{-1}] \quad (2)$$

where Δp is the transmembrane pressure (Pa), J_w is the water flux of the clean membrane and η_w is the viscosity of the water (Pas).

The retention values were calculated by the following equation:

$$R = \left(1 - \frac{c}{c_0}\right) 100\% \quad (3)$$

where c is the concentration of the permeate phase, and c_0 is the concentration of the feed, both calculated from the absorbance of the solutions.

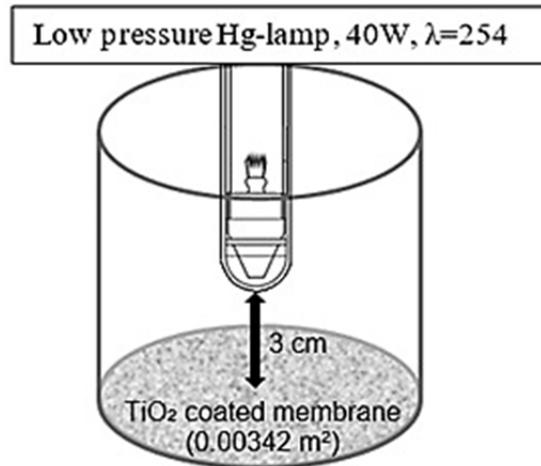


Figure 7. Schematic of the photocatalytic membrane reactor

UV irradiation of certain samples was done in the dead end cell before the filtration as a pre-treatment for 60 minutes and during the filtrations for as long as the filtration lasted.

Transmission electron microscopy (TEM; Philips CM10) images were recorded to determine the morphology and size of the TiO₂ NT and TiO₂ NR. The nitrogen adsorption isotherms were recorded at 77 K using a QuantaChrome Nova 2000 surface area analyzer. Before the nitrogen adsorption, the samples were outgassed at 423 K for 1 h to remove any adsorbed contaminants. The specific surface areas were calculated from multipoint BET method.

During XRD measurements, titania nanorods were registered in the $2\theta = 10\text{--}60^\circ$ range on a Rigaku Miniflex II instrument, using Cu K α ($\lambda = 1.5418 \text{ \AA}$) radiation.

The concentration of the dye was measured by spectrophotometer (Nanocolor® UV/Vis, Macherey-Nagel GmbH, Germany) at $\lambda=532 \text{ nm}$.

Membrane hydrophobicity was quantified by measuring the contact angle that was formed between the (neat and coated) membrane surface and distilled water. 10 μL water was carefully dropped on the top of the membrane surface and immediately measured, within 30 seconds. Contact angles were measured using the sessile drop method (Dataphysics Contact Angle System OCA15Pro, Germany). The measurements were repeated five times and the average value was calculated and is presented in this work. The surface free energies of membranes were calculated by the Owens, Wrndet, Rabel, and Kaelble (OWRK) method, using the OCA15 software package (Dataphysics).

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