

# Photocatalytic degradation of a basic dye in water by nanostructured HPEI/TiO<sub>2</sub> containing membranes

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A photocatalytically active membrane was synthesized through the embedding of HPEI/TiO<sub>2</sub> nanocomposite in PES membrane for the removal of methyl orange (MO) dye from water. Membranes were characterized using scanning electron microscopy coupled with energy dispersive X-ray, atomic force microscopy, water contact angle measurements and water flux analysis. PES/HPEI/TiO<sub>2</sub> membranes showed improved hydrophilicity and were effective in the photodegradation of MO. The reaction rate for MO degradation was  $11.6 \times 10^{-3} \text{ min}^{-1}$ , and the degradation was accompanied by the generation of sulphate ions as degradation by-products.

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## INTRODUCTION

The use of a photocatalytically active membrane has received attention of late in the degradation of dyes (e.g. methyl orange, MO) in water. A multi-functional system that incorporates the attractive qualities of both membrane filtration and photocatalysis will synergistically achieve physical separation by membrane filtration and organic degradation in a single unit (Xu et al., 2018; Li et al., 2019). The utilisation of photocatalytic membranes promotes photocatalyst separation from treated water and thus enhances this application (Bellardita et al., 2020).

Titanium dioxide (TiO<sub>2</sub>) is mostly used because of its high stability, low cost, non-toxicity, high turnover number, flexibility, strong oxidizing power, stability against photocorrosion and chemical resistance (Anwer et al., 2019; Dhanasekar et al., 2018). TiO<sub>2</sub> based photocatalysts possess a large surface area, which can signify high photocatalytic efficiency (Hoseini et al., 2017). The TiO<sub>2</sub> band gap is approximately 3.2 eV and its photocatalytic activity is restricted to the ultraviolet region since it cannot absorb visible light (Han et al., 2017). There are different crystal structures of TiO<sub>2</sub>, anatase, brookite and rutile. The anatase phase has gained more recognition owing to its increased photoactivity (Leong et al., 2014). To achieve its maximum efficiency, TiO<sub>2</sub> nanoparticles have previously been immobilised on polymer films (Yan et al., 2017; Kuvarega et al., 2018; Pereira et al., 2015).

In this study, polyethersulfone (PES) and hyperbranched polyethyleneimine (HPEI) were used as immobilizers for anatase TiO<sub>2</sub> to form a photocatalytically active membrane. HPEI was used as a template and dispersing agent for the synthesis of TiO<sub>2</sub> nanoparticles. HPEI has cavities that act as hosts for nanoparticle synthesis through electrostatic attractions between the nitrogen groups, thus producing uniform and well-dispersed nanoparticles (Koloti et al., 2018; Mathumba et al., 2017). In our previous study HPEI played a significant role in the production of small and well-dispersed TiO<sub>2</sub> nanoparticles (Mathumba et al., 2017). Moreover, these nanocavities accommodate the catalyst and act as adsorption sites for degradation and removal of organic pollutants. Moreover, the amine groups on the peripheral region of HPEI induce hydrophilicity on the membrane (Vlotman et al., 2018; Mosikatsi et al., 2019).

Introduction of PES in the system induces membrane properties such as hydrothermal, mechanical and chemical stability (Safarpour et al., 2016; Rajabi et al., 2015; Nasrollahi et al., 2019). The use of HPEI/TiO<sub>2</sub> nanocomposite embedded in PES for the removal of MO in water has not previously been reported. Thus, this study is aimed at fabricating and applying PES/HPEI/TiO<sub>2</sub> for the photocatalytic degradation of MO dye under ultraviolet (UV) light.

## EXPERIMENTAL

### Materials

HPEI (Lupasol WF, Mw:25 kDa) was supplied by Caltech (California, USA) and used as received. Solvay provided PES (Mw 3000 P, India). Other chemicals and reagents used in this study were used as received.

### Fabrication of PES/HPEI/TiO<sub>2</sub> photocatalytic membrane

TiO<sub>2</sub> nanoparticles were prepared according to a previously reported method by Mathumba et al. (2017). To prepare the HPEI/TiO<sub>2</sub> composite, HPEI (9.83 mmol) was first dissolved in deionised water (5 mL). From this solution, varying concentrations of HPEI:TiO<sub>2</sub> were prepared by adding TiO<sub>2</sub> nanoparticles

to the HPEI solution. The solutions were stirred for 2 h and consequently sonicated for another 2 h. The resulting slurry was then heated for 5 h at 60°C to remove the solvent and then dried in an oven for 2 h at 90°C to remove excess moisture.

Flat sheet membranes were prepared by using the phase inversion method. PES powder (16 wt%) was dissolved in NMP and stirred for 2 h. HPEI/TiO<sub>2</sub> nanocomposite (0.05%, 0.10%, 0.50% and 1.00 wt%) was added into the PES dope solution under continuous stirring to attain varying concentrations of PES nanocomposite polymer. The solution was stirred overnight at a temperature of 80°C and further degassed using nitrogen gas to remove air bubbles formed during the reaction. A casting knife set at an air gap of 200 µm was used to cast the membranes on a glass plate. The casting solution was poured on the edge of the glass plate and spread on the glass plate using the casting knife. The glass plate was immediately placed into a non-solvent coagulation bath containing deionised water at 4°C for 30 min. The resulting membranes were dried at room temperature and stored in between sheets of paper.

## Characterization of membranes

### Morphological assessment

To assess the surface and cross-section (CS) of the membranes, SEM (TESCAN Vega TC instrument, VEGA 3TESCAN software) was utilised. For CS image analysis, the membrane samples were frozen in liquid nitrogen, fractured and coated with gold. Scanning electron microscopy (SEM) images were analysed at an accelerating voltage of 2 kV using a TESCAN Vega TC instrument (VEGA 3TESCAN software), equipped with X-ray detector for energy dispersive X-ray analysis (EDX) operated at 5 kV. The surface morphology and the roughness (Rq) of the membranes were measured using a Veeco Dimension 3100 atomic force microscopy (AFM) equipped with Nanoscope V530 r3sr3 software. Prior to analysis, the samples were mounted on a carbon tape and coated with carbon for enhanced images.

### Water contact angle

Surface wetting properties of the membranes as a function of the concentration of TiO<sub>2</sub> nanoparticles were evaluated through water contact angle measurements. Contact angle measurements were conducted using the sessile drop method on a Data Physics Optical instrument (SCA20 software) using water as a probe. An average of 10 measurements was conducted per sample at room temperature.

### Water intake capacity (WIC) measurements

The extent of water absorption by membranes was determined through sorption experiments. Membrane samples (25 cm<sup>2</sup>) were soaked in distilled water for 24 h, and thereafter mopped with blotting paper and weighed to give the wet weight (*w<sub>w</sub>*). The membranes were then dried at 60°C for 24 h in an oven to obtain the dry weight (*w<sub>d</sub>*) of the membranes. The analyses were performed in replicate.

The water intake capacity was calculated using Eq. 1.

$$\text{Water intake capacity (\%)} = \frac{w_w - w_d}{w_w} \times 100\% \quad (1)$$

where: *w<sub>w</sub>* and *w<sub>d</sub>* are the weights of wet and dry membranes, respectively.

### Membrane flux studies

Membrane flux studies were conducted on a Sterlitech corporation CF042SS316 S/NJC164 207613 cross flow instrument. The membranes were compacted for 12 h at 250 Pa for stabilization of flux before analysis. Four different pressures were used for the pure water flux studies, namely, 50, 100, 150 and 200 Pa. The analyses

were performed in replicate. The flux was calculated using Eq. 2:

$$J_w = \frac{V}{T \times A} \quad (2)$$

where: *J<sub>w</sub>* (L·m<sup>-2</sup>·h<sup>-1</sup>) is the pure water flux, *V* is the volume of the permeate (m<sup>3</sup>), *T* is the permeation time (h) and *A* is the effective membrane surface (36 cm<sup>2</sup>).

## Photocatalytic degradation of methyl orange using PES/HPEI/TiO<sub>2</sub> membranes and degradation by-products

Photocatalytic tests were performed using batch experiments. Photocatalytic degradation of MO dye was conducted by cutting small pieces of membranes (25 cm<sup>2</sup>). The membranes were individually immersed into 500 mL beakers covered with parafilm, containing MO dye (10 mg/L, 250 mL) solutions and equilibrated for 1 h in the dark while stirring. The UV light source for the excitation of TiO<sub>2</sub> was set at a wavelength of 365 nm. Aliquots (5 mL) of the samples were collected at 10 min interval for a maximum period of 2 h using a syringe. The photocatalytic studies were conducted at different pH values (2, 5, 7, 9 and 12) and these were adjusted using 0.1 M NaOH and 0.1 M HCl. The degradation of MO dye was monitored by measuring the absorbance at λ = 464 nm, as a function of irradiation time, using a UV-Vis spectrophotometer (Shimadzu UV-2450). All measurements were done in replicate. The photocatalytic degradation was calculated using Eq. 3:

$$\% \text{ removal} = \left(1 - \frac{C_t}{C_0}\right) \times 100\% \quad (3)$$

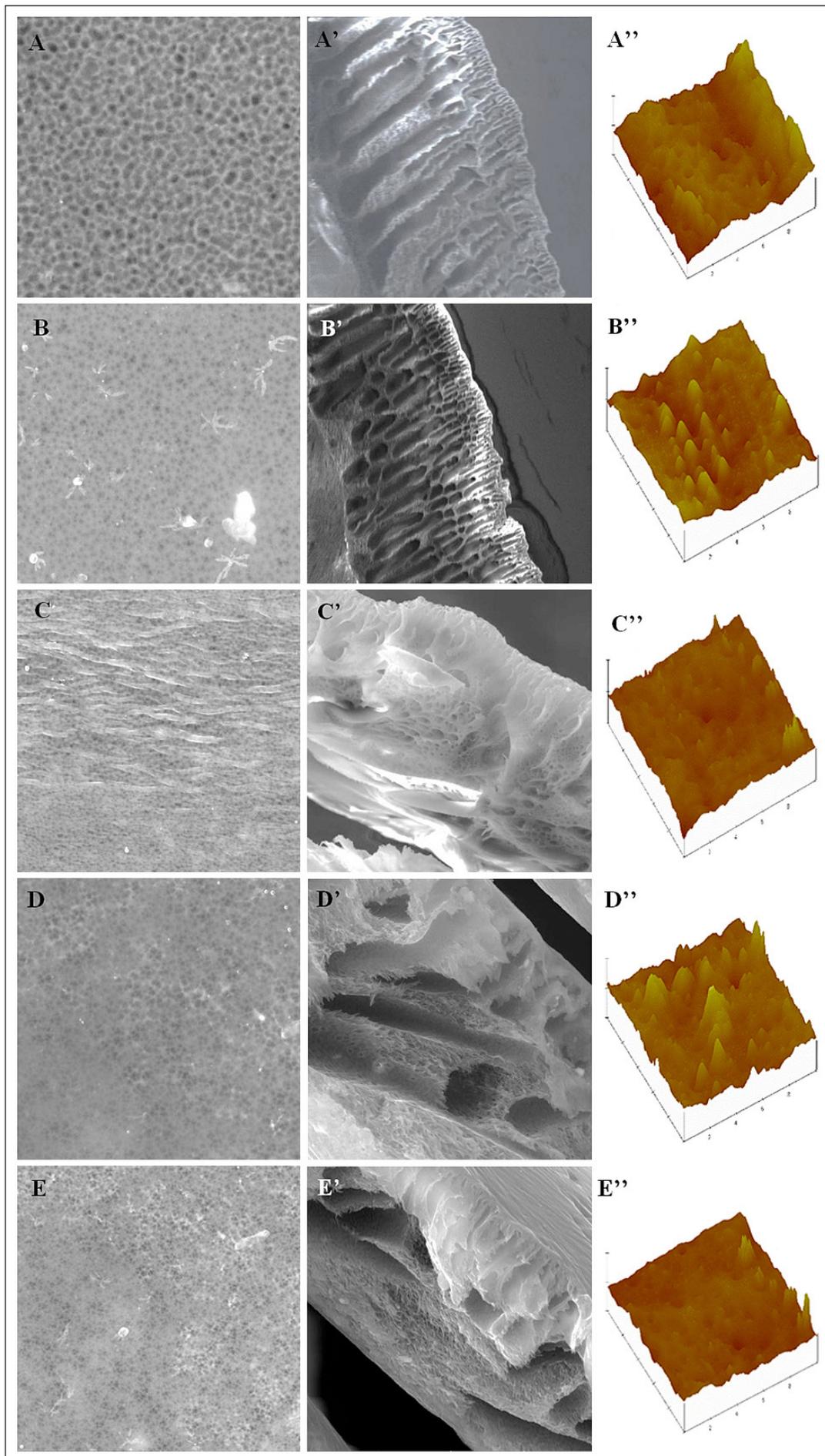
where: *C<sub>0</sub>* and *C<sub>t</sub>* are the initial and final concentrations of the dyes at *t* = 0 minutes and *t* = *t* min, respectively. The resulting degradation by-products of MO, i.e., SO<sub>4</sub><sup>2-</sup> ions, were analysed using ion chromatography (IC-Dionex-IC2000). The eluent solution was 30.00 mM KOH. The pump pressure was set at 1630 psi, column heater at 30°C and run time was 11 min/sample.

## RESULTS AND DISCUSSION

### SEM analysis

Figure 1 represents the surface, CS and AFM images of the membranes. The pristine PES exhibited a highly porous surface, uniform finger-like structure with a thin skin layer and large ridges (Fig. 1 A, A', A''). Upon addition of HPEI/TiO<sub>2</sub> the pores became reduced due to the accumulation of the HPEI/TiO<sub>2</sub> nanocomposite (Fig. 1 A–E). The CS images (Fig. 1 A'–E') show a sponge-like structure with a dense skin layer for the blended membranes as opposed to the pure PES membrane. As the composition of HPEI/TiO<sub>2</sub> was increased in the membranes, the macrovoids in the sponge-like membrane became more pronounced (Fig. 1 B'–E'). The addition of HPEI/TiO<sub>2</sub> composite changes the kinetics and the thermodynamics of the phase inversion process by reducing the hydraulic resistance due to its hydrophilicity. The increased affinity of the HPEI/TiO<sub>2</sub> nanocomposite resulted in a faster exchange between the solvent and non-solvent during phase inversion thus leading to the formation of a sponge-like structure with macrovoids (Xu et al., 2017; Ayyaru and Ahn, 2018).

It was observed from the AFM images (Fig. 1 A''–E'') that the surface properties of the PES membranes improved due to blending with HPEI/TiO<sub>2</sub>. As the concentration of HPEI/TiO<sub>2</sub> increased, the ridges decreased in size, indicating a decrease in surface roughness of the blend membranes. The roughness measurements illustrated in Table 1 showed a decrease from 40 nm (pristine PES) to 18.9 nm for the modified membranes. The migration and accumulation of HPEI/TiO<sub>2</sub> nanocomposites on the surface pores leads to the reduction of surface pores and roughness (Liu et al., 2007). A similar trend was observed by Parvizian et al. (2020), where TiO<sub>2</sub> was functionalized with oleic acid and embedded on a PES membranes via phase inversion. AFM measurements decreased from 24 nm (unmodified membrane) to 4 nm (modified membrane).



**Figure 1.** SEM surface, CS and AFM images of PES (A, A' and A'') 0.05% HPEI/TiO<sub>2</sub> (B, B' and B''), 0.10% HPEI/TiO<sub>2</sub> (C, C' and C''), 0.50% HPEI/TiO<sub>2</sub> (D, D' and D'') and 1.00% HPEI/TiO<sub>2</sub> membranes (E, E' and E'')

**Table 1.** Contact angle, water intake capacity and membrane roughness studies

| PES/HPEI/TiO <sub>2</sub> membrane (%) | Contact angle (°) | Water intake capacity (%) | Membrane roughness (nm) |
|--|-------------------|---------------------------|-------------------------|
| 0.00                                   | 76.5              | 8.32                      | 40.3                    |
| 0.05                                   | 69.0              | 26.67                     | 37.5                    |
| 0.10                                   | 65.3              | 38.82                     | 28.0                    |
| 0.50                                   | 62.8              | 41.86                     | 34.3                    |
| 1.00                                   | 66.2              | 35.28                     | 18.9                    |

This was attributed to the nanoparticles that migrate to fill in the pores and the free volume in the surface of the membranes due to the migration of OA-TiO<sub>2</sub> to the membrane surface.

### Water permeation studies of PES/HPEI/TiO<sub>2</sub> membranes

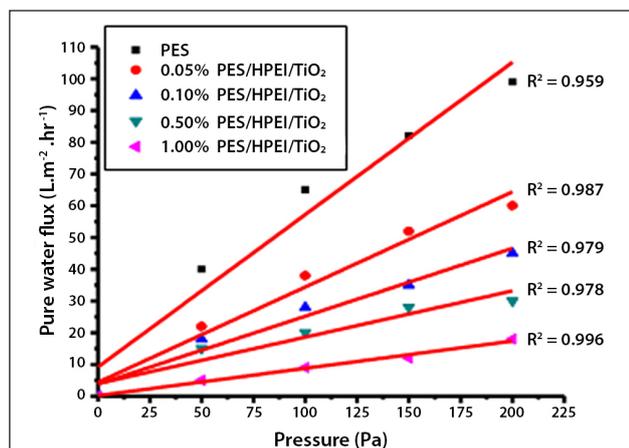
The contact angle measurements were performed to evaluate the hydrophilicity of the membrane. Generally, the contact angle of PES/HPEI/TiO<sub>2</sub> membranes decreased as the HPEI/TiO<sub>2</sub> loadings were increased from 0.05% to 0.10% (Table 1). The presence of hydrophilic TiO<sub>2</sub> and HPEI enhanced hydrophilicity of the membranes, due to the NH<sub>2</sub> and -OH groups from HPEI and TiO<sub>2</sub>, respectively (Xu et al., 2018; Wang et al., 2017). This increase in contact angle at high HPEI/TiO<sub>2</sub> content may be attributed to the migration of hydrophobic cavities of the HPEI polymer to the surface of the membrane during the drying process (Safarpour et al., 2016). The WIC for modified membranes increased with increasing nanocomposite loading (Table 1). The WIC values for the neat PES membrane were low, due to its hydrophobic nature.

### Water flux analysis

The pure water flux was measured at different applied pressures and the results showed a good linear relationship between the two parameters ( $R^2 \approx 0.98$ ). The flux increased with an increase in operating pressure. The PES membrane showed higher water flux as compared to PES/HPEI/TiO<sub>2</sub> membranes (Fig. 2). The low water permeability of the modified membranes could be due to the HPEI/TiO<sub>2</sub> nanocomposites blocking the surface pores of the membranes. This creates a dense membrane surface layer, thus resulting in high resistance to water passing through the membrane resulting in reduced permeability. Tavakolmoghadam and Mohammadi (2019) observed a decrease in water flux with the increase of TiO<sub>2</sub> in PVDF membrane. This was due to the agglomeration of TiO<sub>2</sub> nanoparticles thus blocking the surface pores of the membranes.

### Photocatalytic activity of PES/HPEI/TiO<sub>2</sub> membranes

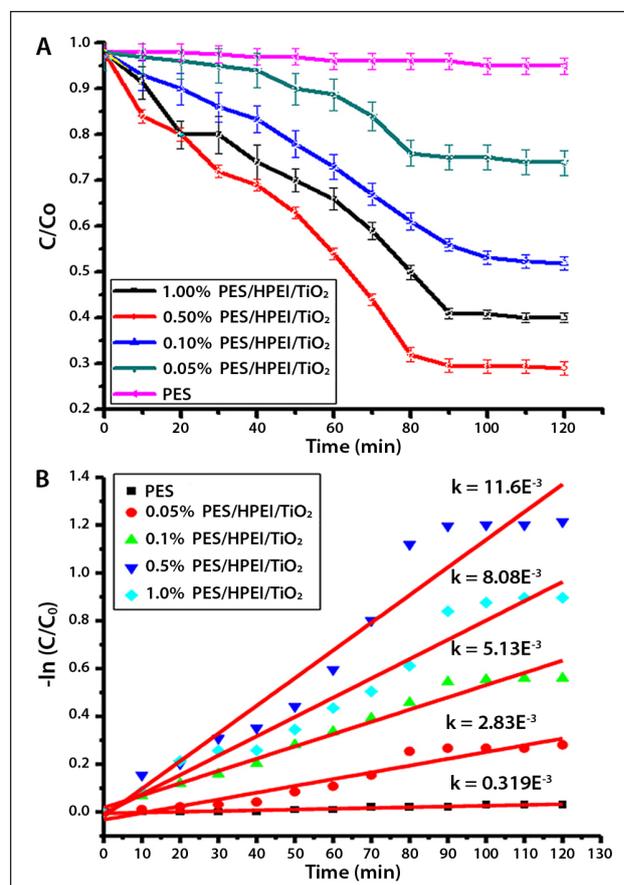
The PES/HPEI/TiO<sub>2</sub> membranes were evaluated for their ability to degrade MO at different pH conditions under UV light radiation. It was observed that the neat PES membrane exhibited low dye removal (less than 5% in acidic, neutral and alkaline conditions) since the polymer is not photocatalytically active.

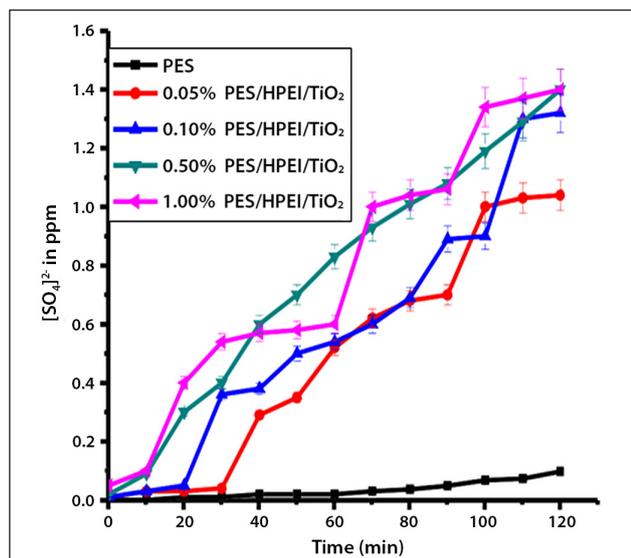
**Figure 2.** A plot of pressure versus pure water flux

Faster degradation rates were observed in the first 5 min of the reactions for all modified membranes. The rate then decreased with time up to 80 min due to the saturation of membrane reactive sites. However, all the membranes showed optimal activity at pH 2 for degradation of MO dye. For comparison, the kinetics of MO degradation at pH 2 were evaluated for all the membrane samples (Fig. 3A). It was observed that the PES membrane shows 4.26% removal of 10 mg/L MO. However, the percentage removal of MO increased upon introduction of HPEI/TiO<sub>2</sub> nanocomposites on the PES membranes, which then reached the highest removal of 70.3% at 0.50% HPEI/TiO<sub>2</sub> loading and a decline to 59.2% at 1.00% HPEI/TiO<sub>2</sub> loading. This is an indication that nanocomposite percentage loadings above 0.50% on the membranes result in membrane saturation and, therefore, are not effective for the degradation of dyes. It can be observed from Fig. 3B that the photodegradation of MO under UV light radiation follows pseudo-first order reactions and the kinetics can be described by the general Eq. 4:

$$-\ln \frac{C}{C_0} = kt \quad (4)$$

where  $k$  is the reaction constant,  $C_0$  and  $C$  are the initial and final concentrations of MO and  $t$  is time respectively. Among these photocatalytically active membranes, the 0.50% PES/HPEI/TiO<sub>2</sub> membrane showed the highest reaction rate ( $11.6 \times 10^{-3} \text{ min}^{-1}$ ) when illuminated with UV light, thus exhibiting the highest percentage removal of MO as compared to the other membranes.

**Figure 3.** Degradation of MO by PES/HPEI/TiO<sub>2</sub> membranes at pH 2 (A); Reaction kinetics of MO dye degradation initiated by UV light irradiation (B)



**Figure 4.** Generation of sulphate ions from the degradation of MO using PES/HPEI/TiO<sub>2</sub> photocatalytic membranes at pH 2

### Photodegradation by-products

Figure 4 illustrates the generation of degradation by-product of MO dye (SO<sub>4</sub><sup>2-</sup>) as a function of time. The degradation of MO was confirmed by the liberation of SO<sub>4</sub><sup>2-</sup> ions using IC. The sulphite ion can be oxidized to sulphate, a more stable (+6) oxidation state of sulphur, and hence it was more reasonable to measure than the sulphite ion. Studies reveal that sulphates adsorb irreversibly on TiO<sub>2</sub> surfaces, and this might have accounted for the low amounts of sulphate ions detected (Liao et al, 2013; Sonawane et al, 2004; Han and Bai, 2010).

### CONCLUSION

Photocatalytically active PES/HPEI/TiO<sub>2</sub> membranes were synthesized using varying concentrations of HPEI/TiO<sub>2</sub> nanocomposite. The PES/HPEI/TiO<sub>2</sub> membranes showed improved hydrophilicity, water intake capacity and ability to degrade MO dye in water under UV radiation as compared to pristine PES membrane. The PES/HPEI/TiO<sub>2</sub> (0.50%) membrane exhibited the highest dye removal ability. Thus, these membranes could be applicable in the photocatalytic degradation of organic compounds in highly acidic, neutral and alkaline wastewater.

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### DISCLOSURE STATEMENT

No potential conflict of interest was reported by authors.

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