Photocatalytic degradation of Methylene Blue (MB) dye under UV/visible light by TiO2 nanoparticle self-assembled commercial polyethersulfone ultramembrane

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Abstract

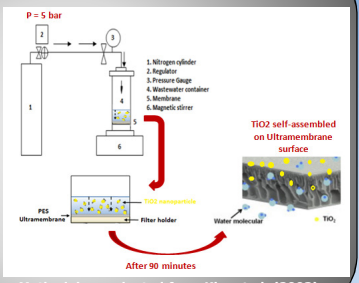
Titanium dioxide (TiO_2) in different forms such as films, fibers or particles has been the focus of numerous investigations in recent years, because of its photocatalytic effects that decompose organic chemicals, and shows good hydrophilic properties in surface of membranes. Combined with these characteristics, in this study, Polyethersulfone (PES) ultramembrane was self-assembled with TiO2 nanoparticles for the purpose of photocatalytic degradation capability of Methylene Blue (MB) dye and fouling reduction. The PES membrane with an diameter of 47 mm was dipped in the colloidal solution of 0,5% (w/v) TiO2 powder (Degussa–Hüls, P-25) for 1:30 h at 5 bar pressure to deposit TiO2 nanoparticles on the membrane surface and then washed with water. The membrane was prepared using a filtration module HP4750 StirredCell (Sterlitech ©). To evaluate the changing surface properties, the membrane before and after modification was characterized by analysis water permeability, contact angle, scanning electron microscope (SEM) and the photocatalytic activity. The photocatalytic performance of the processed samples was measured by following the degradation capability of 1.10^{-6} mol.L^{-1} MB dye solution irradiated with a high power LED source (Thorlabs, 700 mA) with an excitation peak at 365 nm (UV-A). Results showed that the TiO2 self-assembled in PES membrane demonstrated a remarkable photocatalytic activity with over 80% MB removed from the solution after 100 min of UV radiation. The SEM photographs showed TiO2 aggregates on the top surface of the modified membranes. The lower the contact angle means higher hydrophilicity of the membrane surface, however the water permeability experiments showed a decrease flow from 19.53 to 10.47 $L.h^{-1}.m^{-2}.bar^{-1}$. The reduced flow could be due TiO2 nanoparticles have entered the pores on the membrane surface. With the results, the applied method for TiO2 deposition was suitable for membrane morphology modification. The TiO2 photocatalytic properties in the MB dye degradation may indicate promising mitigation to the fouling effects of PES membrane.

TiO_2 Deposition of PES Ultramembrane

Preparation of the TiO2 nanoparticle solution

0.5 g TiO_2 (Degussa, P-25) + 100 mL of H_2O → Magnetic stirring 60 minutes → Ultrasonic 60 minutes → **TiO_2 nanoparticle solution**

Self-assembly method



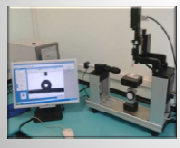
Methodology adapted from Kim et al. (2003) and Ngo et al. (2016).

Membrane Caracterization

The caracterization was realized before and after membrane modification.

Water permeability experiments

Contact angle - Characterize the hydrophobicity of the membrane



The morphology of the membranes

Ultra Scanning Electron Microscope with high resolution field emission with EDS - energy dispersive spectrometer

Photocatalytic Activity

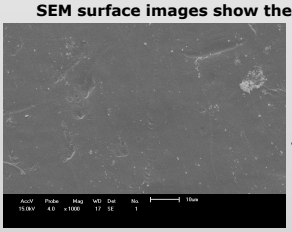
- MB (1×10^{-6} M) -> at intervals of 3 min at 663 nm on a ScanSpec UV–vis (ScanSci, 300–900 nm)
- Quartz cell was irradiated with a high-power light-emitting diode (LED) source (Thorlabs, 700 mA) at excitation peak at 365 nm (UV-A).
- The incident radiation over the sample was 4 $mW.cm^{-2}$.
- samples were placed for 30 min in the MB solution in the dark without UV irradiation.

Results

Table 1 - Summary of Results Ultrafiltration Membrane Polyethersulfone free and TiO2 coating by Self-assembly method.

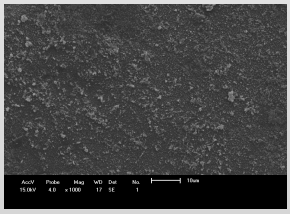
Membrane Sample	Photocatalytic Activity: Degradation Rate 10^{-3}/min	Photocatalytic Activity: Degradation Efficiency – After 6 h UV radiation %	Photocatalytic Activity: Half Life Time (min)	Photocatalytic Activity: R^2	Contact angle (°)	Water permeability (L/h.m2.bar)
Uncoated	1.0	33.9	693.14	0.996	77.32	19.53
TiO_2 coated	5.0	80.0	138.63	0.997	69.10	10.47

SEM surface images show the PES ultramembrane without and with TiO2 coated.



Uncoated membrane

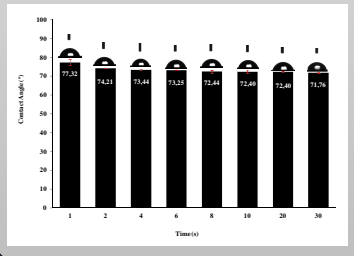
It was found that the surface of the treated membrane showed TiO2 aggregates on the top surface.



TiO2 coated on membrane

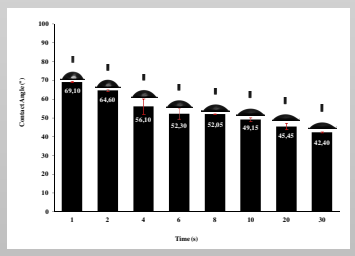
- The decrease in water permeability after treatment with TiO2 may be due TiO2 nanoparticles have blocked some of PES membrane pores.
- However, the presence of TiO2 nanoparticles causes the dye degradation rate in the presence of radiation to be 5 times faster, proving its photocatalytic property.

Contact Angle behavior versus time



Uncoated membrane

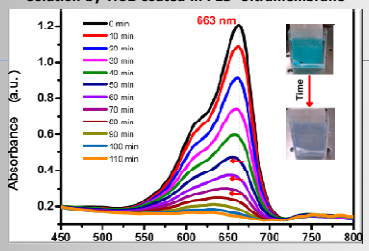
- The polyethersulfone polymer leave the membrane with hydrophobic characteristics. With the presence of TiO2 in the membrane surface becomes more hydrophilic, making the smaller contact angle.
- The contact angle decreased with respect to the time for the TiO2 coated membrane. Due to the high porous surface area of TiO2 nanoparticles, the water absorption process is higher compared to the untreated membrane.



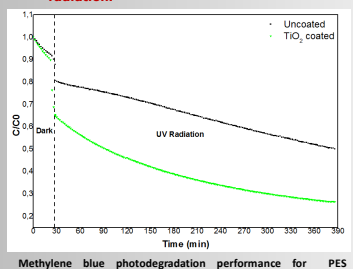
TiO2 coated on membrane

Photocatalytic Activity Results

Degradation of 10^{-6} M Methylene Blue in aqueous solution by TiO2 coated in PES Ultramembrane



- Pure PES membrane was also tested and did reveal low photocatalytic activity.
- The presence of nanoparticulate TiO2 causes the first 30 minutes in the dark adsorption process occurs due to its high surface area of pores.
- After 6 hours under UV irradiation, the MB degradation is approximately 80%. In the adsorption-migration-photodegradation process, the MB is probably adsorbed by the polymer fibres, and then migrated to the TiO_2 nanoparticles, and finally degraded by TiO_2 catalyst under UV radiation.



Methylene blue photodegradation performance for PES membrane uncoated and TiO2 coated.

Conclusions

TiO2 nanoparticles were deposited by self-assembly method onto PES ultramembrane. The characterization of these nanoparticles was investigated using SEM, contact angle and photocatalytic activity indicating that occurred the deposition of Ti and its organic compounds degradation activity as MB is efficient. With the results from the experiments we can conclude that technique for the modification of membranes is a promising process to obtain higher performance membranes.

References

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