TiO$_2$-nanoparticles Coated Forward Osmosis Membranes for Enhanced Filtration of Textile Effluent

Kaung Ko KoSint$^{1,*}$ and Chavalit Ratanatamskul$^{2,*}$

$^1$Department of Environmental Engineering, Faculty of Engineering, Chulalongkorn University, 254 Phayathai Road, Patumwan, Bangkok 10330, Thailand.
$^2$Research Unit on Innovative Waste Treatment and Water Reuse, Faculty of Engineering, Chulalongkorn University, 254 Phayathai Road, Patumwan, Bangkok 10330, Thailand.

$^*$E-mail: kaungkokosintt@gmail.com Tel: +66(6)2-9256344
$^{*}$E-mail: dr_chawalit@yahoo.com; Fax: +66(0)2-2186678; Tel: +66(0)2-2186678

Abstract. Textile wastewater has been recognized as one of significant industrial wastewater sources due to its complex composition and the presence of reactive constituents such as heavy metals and salts as well as nutrients, e.g. nitrogen, sulphate and phosphate. In this research, the combination of forward osmosis with photocatalytic method was analytically considered for the recycling of textile effluent after biological treatment process. The research aims to study the feasibility in application of TiO$_2$-nanoparticles coated on two commercially accessible FO membranes; an aquaporin (AqP) membrane and a cellulose triacetate (CTA) membrane by the way of a specially designed 3-(trimethoxysilyl) propyl methacrylate–polymethyl methacrylate–bromide (MEMO–PMMA–Br) monomer chain as a novel forward osmosis treatment method. High efficiency of reactive dye rejection of 99.9% could be achieved with this novel FO process with the use of 1 M NaCl as the draw solution, while varying reactive dye (black) at concentrations of 200, 400, 600, 800 ppm in the synthetic textile effluent. The obtained water fluxes of both FO membranes suggested that the achievement of the CTA membrane was incredibly improved after surface modification than that of AqP membrane with the increase in average fluxes of 18.03% and 11.83%, respectively. The experiments also suggested that CTA membrane gives higher water flux than aquaporin membrane for forward osmosis filtration for synthetic textile effluent. Moreover, effect of interferences in terms of dissolved anions on reactive dye removal efficiencies by the TiO$_2$-nanoparticles coated FO membranes were also investigated.

1. Introduction

Large amount of wastewater from textile industry can result in significant water pollution problem when sufficient treatments are employed. Since this type of wastewater has colour regardless of holding only small amount of dyes. These dyes are harmful, difficult to be biodegraded as well as they are resistant to various wastewater treatment processes [1]. Most of the ongoing development in the FO process dedicated to the improvement of membrane materials to enhance the performance FO membranes for water and wastewater application. CTA Membranes are considerably less expensive than other types of FO membranes, have a longer life time of usage, require less chemical cleaning, and are much more resistant to chlorine. While Aquaporin (AqP), another type of FO membrane, empowers high removal of various contaminants and utilizing just simple osmotic pressure in system
Various strategies in surface modification techniques have been accounted for including grafting macromolecules preparing antifouling surfaces by functionalization with photocatalytic nanoparticles and carbon-based nanomaterials and using biocidal Nanoparticles whichever consolidated into the support layer or connected to the surface of the TFC membranes [3]. Among the various possible photocatalysts, titanium dioxide (TiO$_2$) is one of the most widely used chemical oxidizing agent since it is commercially available, inexpensive, chemically stable and less toxic [4]. The objectives of our research are to develop novel TiO$_2$ nanoparticle coated commercial FO membranes and to investigate the suitability in application of these hybrid FO membranes for treatment of textile effluent after biological treatment processes. The surface morphology, chemical components, and properties were also evaluated to confirm the success of the TiO$_2$ coating brought by the new technique of surface modification [5]. Changes of water permeation performance and fouling phenomena were analysed in a laboratory scale FO filtration framework with a light-emitting diode (LED) light connected rather than UV illumination to additionally lessen the impact to the polymer membranes. By comparing the properties and performance between membranes with and without TiO$_2$ nanoparticles coating, the mechanisms of enhanced filtration performance due to TiO$_2$ nanoparticles coating will be discussed.

2. Materials and methods

2.1 FO membranes

The morphological characterizations, fundamental performances and antifouling performances were studied using the two commercial FO membranes with the surface modification technique for TiO$_2$ nanoparticle coating, which are already described in our previous work [5]. Here, the CTA membranes were commercially available from The Hydration Technology Innovations (Albany, OR, USA). The performance and properties of CTA membrane were examined and reported in previous literature[6]. The CTA membrane is made out of a cellulose triacetate active layer with an installed woven support labyrinth [6]. The AqP membrane was purchased from Aquaporin A/S (Copenhagen, Denmark) which is produced by installing biomimetic aquaporin protein channels into a polyamide active layer [7]. Deionized water (Millipore, USA) was used to immerse the membrane sheets for 24 hours to expel remaining additive reagents before the filtration tests.

2.2 Laboratory-scale FO setup and operation

The laboratory scale FO system was performed in this research. The flow diagram of the system was already described in our previous research work. A cross flow filtration membrane test cell unit can hold a flat sheet membrane having an effective area of 60cm$^2$ (C10-T, Nitto Denko, Japan). Peristatic pumps (BT100-2J, Longer Pump, China) controlled the co-current circulation of draw solution and feed solution. The crossflow velocity of 8.3 cm per second was set for all set of filtration tests. During the filtrations, a LED light (5watt) was installed to illuminate the TiO$_2$ nanoparticles. A digital mass balance connected to a computer data logging system was employed to analyse the weight in order to calculate the membrane permeate flux at regular time intervals (UW4200H, Shimadzu, Japan), by:

$$J_W = \frac{\Delta V}{A \Delta t}$$

The water flux of FO is $J_W$, L m$^{-2}$ h$^{-1}$; the permeate volume is $\Delta V$, over a predetermined time interval, $L$; $\Delta t$ which is the predetermined time interval, h; and the effective filtration area of the membrane is $A$, m$^2$.

2.3 Synthetic Textile Effluent with Interference

The synthetic textile effluents were prepared from the commercial reactive dyes (Reactive Black 5) (Sigma-aldrich) through this research. Reactive dye concentrations of the feed solutions were varied from 200 to 800 ADMI (common range of colour unit found in industrial textile effluent) to know effect of reactive dye concentration on treatment performance of TiO$_2$-coated FO membrane system.
Reactive Black 5 was obtained from SIGMA-ALDRICH company. 1M NaCl (reagent grade) was used for draw solution. Additional trace ions commonly found in textile effluent were also added to the synthetic textile wastewater as follows: Phosphorus prepared from potassium phosphate K$_2$HPO$_4$ for 2 mgP/L, sulphate prepared from Magnesium sulfate MgSO$_4$ for 300 mgSO$_4$-L and nitrate prepare from sodium nitrate for 200 mgN/L. DI water (Millipore purification system) was used to prepare the dye solution by dissolving DI with requisite quantity of dye and abovementioned ions. H$_2$SO$_4$ and NaOH solutions were used to adjust the pH of the reaction. pH meter was used to checked pH of the solution.

In operation the FO system, the feed water and draw solution were pumped in to the FO membrane unit. The permeate was collected after the steady state condition. (3 hrs. or steady state time). When possible, all samples were analysed immediately after being withdrawn from the reactor; however, some samples were preserved in accordance with standard methods 1998 [8]. The filtrate was collected in a clean container and further be prepared for the analysis. The permeate quality was measured for TOC, colour (ADMI) and all anions were measured by Ion Chromatography (IC) machine.

3. Results and discussion

3.1 FO membrane surface modification and characterization

In our previous work [5], we investigated the effects of TiO$_2$ coating on membrane surface and its characteristics were measured by the following analysis and experiments. During surface modification, Fourier-transform infrared spectroscopy (FT-IR) analysis was used to figure out the variation in functional groups. To approve that the TiO$_2$ nanoparticles were firmly coated onto the active layers of CTA and AqP membranes and to figure out the variation of surface roughness before and after modification, Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy (SEM-EDX) and Atomic force microscopy (AFM) were used.

3.2 Performance of TiO$_2$ coating FO membranes on colour, TOC and Ions removal filtration of synthetic textile effluent

Figure 1 illustrates the performance of colour removal with both types of the TiO$_2$ nanoparticles coated FO membranes (modified CTA and aquaporin membranes). With initial colour units of 200, 400, 600 and 800 ADMI in the feed textile effluent, very high colour rejection efficiencies with two novel FO membranes with TiO$_2$ nanoparticles coated FO membranes could be achieved.

![Figure 1](image_url)

**Figure 1.** (a) Removal efficiencies for color (ADMI value) with modified CTA and Aquaporin membranes. (b) Comparison of effluent TOC, while varying ADMI values of synthetic textile effluent with original CTA and modified CTA membrane.

According to Figure 1.(a), all ADMI values in the membrane permeate of the modified membranes of both AqP and CTA membranes were lower than 10 at pH 7, with color removal efficiencies of 99.6%. Since FO membranes have very fine pore sizes that can separate reactive dye due to sieving mechanism at low pressure operation in osmotic pressure range. Through this study, raw wastewater
TOC was averagely 4 mg/L. Figures 1(b) and 2(a) show the comparison of effluent TOC values in the permeate water with and without TiO$_2$ coating CTA and AqP membranes, while varying with the initial ADMI values of synthetic textile effluent with the application of FO membrane. In all cases, our modified FO membranes with TiO$_2$ nanoparticles coating could show higher reliable removal performance for TOC. Effluent TOC concentrations, obtained from two novel modified FO membranes were apparently lower than those of the original FO membranes without surface modification. The effluent TOC concentrations were 0.72 ± 0.16 mg/l and 0.43 ± 0.18 mg/l, with original and modified CTA membrane respectively. Also, the effluent TOC concentration, obtained with original and modified AqP membranes were 1.87 ± 0.5 mg/l and 1.41 ± 0.6 mg/l respectively. Therefore, the TiO$_2$ nanoparticles coated FO membranes could yield better performance in terms of TOC removal due to the photocatalytic reaction with TiO$_2$ that was coated on membrane surface with the photo UV assistance.

![Figure 2](image_url)

**Figure 2.** (a) Comparison of effluent TOC values, while varying the initial ADMI values of synthetic textile effluent with (a) original AqP and modified AqP membrane. (b) Sulphate removal percentage for the modified FO membrane, while varying the initial ADMI values of modified CTA and AqP membrane.

3.3 Rejection of anions having different initial ADMI in synthetic textile effluent

The anion removal studies using the TiO$_2$ nanoparticle coated membranes are illustrated in Figures 2(b)-3(b). High efficiencies for sulphate, nitrate and phosphate removal with the modified CTA and AqP membranes are shown, while varying the initial ADMI values. The maximum removal percentages for sulphate were found to be around 99.84% and 99.71% with the modified CTA membrane and the modified AqP membrane, respectively; similarly, for nitrate removal up to 99.71% and 99.9% were achieved with the modified CTA and modified AqP membranes, respectively. Phosphate ions were completely removed within experimental time with all set of experiments with the modified FO membranes.

After grafting MEMO–PMMA–BR, the mean effective pore radius of modified membranes are declined, indicating a larger size exclusion impact. Likewise, modified membranes decrease membranes fouling greatly due to the mechanism of negatively charged and Donnan repulsion. Therefore, molecular sieving and electrostatic repulsion are main mechanisms for solute rejection [9, 10]. The higher molecular weights and hydrated ion diameters for NO$_3^-$ are 62.01 g/mole and 0.3 nm; for SO$_4^{2-}$ are 96.06 g/mol and 0.52 nm; and for PO$_4^{3-}$ are 94.97 g/mole and 0.4 nm, leading to higher rejection rates as a result of decreased transfer that ions across the membrane. Negatively charged ions may have higher rejection abilities, compared to the negatively charged MEMO–PMMA–BR membrane [11]. Therefore, the MEMO–PMMA–BR grafted membrane can incredibly reject anions in the complex feed solution with various anions.
Figure 3. Nitrate removal percentage (a) and phosphate removal percentage for the modified FO membrane (b), while varying the initial ADMI values of modified CTA and AqP membrane.

3.4 Effect of TiO$_2$ coating on enhancement of membrane filtration performance

The fluxes of original and modified FO membranes were determined using 1 mol L$^{-1}$ NaCl as the draw solution and varying concentration of reactive dye (black) in synthetic textile effluent. The results are illustrated in Figure (4) and Figure (5). The CTA membrane exhibited the water flux of 12.44 ± 1.52 L m$^{-2}$ h$^{-1}$ with original membrane and 21.23 ± 0.32 L m$^{-2}$ h$^{-1}$ with the modified TiO$_2$ coated one. Obviously, CTA membrane could yield higher flux than that of the AqP membrane. The obtained fluxes were 10.21± 1.25 L m$^{-2}$ h$^{-1}$ with original AqP membrane and 11.37 ± 0.31 L m$^{-2}$ h$^{-1}$ with modified one. The water flux of modified FO membranes was measured with the AL-FS orientation. The increase in water flux up to 71.2% and 11.36% were obtained with the CTA and AqP membranes after the surface modification, accordingly. Therefore, this is worth observing that the water flux of the CTA membrane was significantly enhanced by TiO$_2$ nanoparticle modification, which is consistent with the enhanced surface hydrophilicity.

Figure 4. Membrane flux variation during synthetic textile wastewater with different ADMI values (reactive black) of (a) modified AqP membrane, (b) original AqP membrane.

Figure 5. Membrane flux variation during synthetic textile effluent filtration with different ADMI values (reactive black) for (a) modified CTA membrane, (b) original CTA membrane.
4. Conclusion
According to the colour removal performances for both modified AqP and CTA membrane, high efficiencies up to 99.61% removal were observed. The CTA membrane exhibited a water flux of $12.44 \pm 1.52$ L m$^{-2}$ h$^{-1}$ with original membrane and $21.23 \pm 0.32$ L m$^{-2}$ h$^{-1}$ with the modified one, apparently higher flux than those of AqP membrane ($10.21 \pm 1.25$ L m$^{-2}$ h$^{-1}$ with original and $11.37 \pm 0.31$ L m$^{-2}$ h$^{-1}$ with modified one). The maximum removal percentages of sulphate were found to be around 99.71% and 99.84 % and the maximum removal percentages of nitrate were found to be around 99.93% and 99.91% using modified CTA and AqP membrane respectively. The higher molecular weights and hydrated ion diameters for $\text{NO}_3^-$, $\text{SO}_4^{2-}$ and $\text{PO}_4^{3-}$ lead to in higher rejection rates as a result of decreased transfer that ions across the membrane. The negatively charged MEMO–PMMA–BR membrane might have higher rejections to negatively charged ions. Phosphate was almost completely removed after experiment. Accordingly, the rejection of the MEMO–PMMA–BR grafted membrane increases due to the complex feed anions. this is worth observing that the water flux of the CTA membrane was significantly enhanced by TiO$_2$ nanoparticle modification, which is constant with the enhanced surface hydrophilicity after coating. And the AqP membrane's flux performance was lower than that of the CTA membrane due to the it’s biomimicry molecular design, the performance of the modified CTA membrane became surpassed that of the AqP membrane in this study.

Acknowledgement.
This research is financially supported by the Rachadapisek Sompote Fund, Chulalongkorn University for promoting Research Unit purpose.

References
[1] Rahman, F., The treatment of industrial effluents for the discharge of textile dyes using by techniques and adsorbents. Journal of Textile Science & Engineering, 2016. 6: p. 242.
[2] Huang, L. and J.R. McCutcheon, Impact of support layer pore size on performance of thin film composite membranes for forward osmosis. Journal of Membrane Science, 2015. 483: p. 25-33.
[3] Soroush, A. and W. Ma, Surface modification of thin film composite forward osmosis membrane by silver-decorated graphene-oxide nanosheets. Environmental Science: Nano, 2015. 2(4): p. 395-405.
[4] Lu, S.-y., et al., Photocatalytic decomposition on nano-TiO$_2$: Destruction of chloroaromatic compounds. Chemosphere, 2011. 82(9): p. 1215-1224.
[5] Xue, W., et al., Binding TiO$_2$ nanoparticles to forward osmosis membranes via MEMO–PMMA–Br monomer chains for enhanced filtration and antifouling performance. RSC Advances, 2018. 8(34): p. 19024-19033.
[6] Xue, W., et al., Seawater-driven forward osmosis for enriching nitrogen and phosphorous in treated municipal wastewater: effect of membrane properties and feed solution chemistry. Water research, 2015. 69: p. 120-130.
[7] Ye, W., et al., Enhanced performance of a biomimetic membrane for Na$_2$CO$_3$ crystallization in the scenario of CO$_2$ capture. Journal of Membrane Science, 2016. 498: p. 75-85.
[8] Standard, A., Methods for the Examination of Water and Wastewater. 1998: American Public Health Association.
[9] Alturki, A.A., et al., Removal of trace organic contaminants by the forward osmosis process. Separation and Purification Technology, 2013. 103: p. 258-266.
[10] Hancock, N.T. and T.Y. Cath, Solute coupled diffusion in osmotically driven membrane processes. Environmental science & technology, 2009. 43(17): p. 6769-6775.
[11] Bodnar, J., L. Hajba, and A. Guttman, A fully automated linear polyacrylamide coating and regeneration method for capillary electrophoresis of proteins. Electrophoresis, 2016. 37(23-24): p. 3154-3159.