Effect of Photocatalysis on the Membrane Hybrid System for Wastewater Treatment

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ABSTRACT

An integrated photocatalysis-membrane hybrid system was investigated for wastewater treatment with the main focus on improving the cross flow microfiltration permeate (MF) flux. Photocatalysis with TiO_2 (P25 degussa) suspension as photocatalyst was applied both as pre-treatment and as inline treatment with MF. The TiO_2 slurry was found to have significant effect in permeate flux for wastewater with lower dissolved organic carbon concentration. The MF flux decline due to TiO_2 slurry cake on the membrane surface was minimized by allowing the TiO_2 slurry to settle and by using only the supernatant for further treatment using the hybrid system. The investigation also included the study on the effect of photocatalytic reaction time and the slurry settling times on the MF permeate flux. The irradiation of ultraviolet on the MF surface in presence of TiO_2 catalyst in suspension yielded in an increase in permeate flux.

Keywords: Photocatalysis, microfiltration, pre-treatment, wastewater, TiO_2 suspension, flux decline

1. INTRODUCTION

With the continuous growth of population in the cities and towns, service utilities are under pressure to provide for the increasing demand for wastewater and water supply services. But with limited freshwater resources in many areas, alternative water sources needs to be explored. Wastewater reuse is increasingly seen as an option to augment fresh water resources but to win public confidence the reliability of the technology to produce safe reusable water must be demonstrated. Reuse of wastewater will help maintain environmental quality and help relieve the unrelenting pressure on natural freshwater resources. The existing methods of wastewater treatment do not produce effluent of safe and reusable quality and therefore advanced treatment technology needs to be further developed. The various effluent organic matters (EfOMs), pathogenic micro-organisms and persistent organic pollutants (POPs) present in the effluent from the wastewater treatment plant must be removed before reuse.

Membrane technology has been already established as one such reliable technology but it has its limitations. Besides the high power consumption, the fouling of the membranes significantly reduces permeate flux and results in high O&M cost. Membrane fouling is mainly caused by the solute content in wastewater although it may also depend on factors such as membrane property itself and operating conditions [1]. Amongst the number of theoretical models available, resistances in series model is one model that can explain the fouling mechanisms of the membrane systems [2-4]. Although numerous techniques such as intermittent chemical cleaning, process optimisation, etc. have been found to improve membrane efficiency, most of these techniques suffer from decreased net productivity and also generates secondary pollution. With time, membrane fouling by organic matter is converted into bio-fouling caused by extracelluar enzyme produced by various micro-organisms and bacteria. Eventually bacteria fouling will be dominant [5]. Also, the increased concentration of the retentate will constantly accelerate membrane fouling and decrease membrane life.

Heterogeneous photocatalytic oxidation processes have been increasingly seen as an innovative and green technology for water and wastewater treatment especially for the removal of trace organics [6]. In photocatalysis, metal oxide catalysts used such as titanium dioxide (TiO_2) generate hydroxyl radicals in the presence of ultraviolet (UV) light (photons) which in turn can attack organic matter (OM) present as pollutants in water and wastewater. Photocatalytic oxidation allows complete degradation of organic pollutants into harmless species such as CO_2 and H_2O without the use of chemicals thus avoiding sludge production and the associated management problems [7, 8]. TiO_2 photocatalysis is commonly used because it is able to remove a wide range of pollutants. Its photochemical stability, low toxicity and low cost are its other advantages [9, 10]. Nanocrystalline anatase TiO_2 powder or colloidal form in aqueous solution has been observed to have high photocatalytic property although their separation and recovery from water and wastewater after serving its purpose has been one major obstacle [11]. TiO_2 in immobilised form has been tried but found to have decreased photocatalytic activity [7].

An integrated photocatalysis membrane hybrid system leads to a near-zero fouling system [12]. Photocatalytic reaction degrades and modifies the organic foulant in wastewater and if UV is irradiated directly on the membrane surface, the photocatalytic reaction can convert the foulant on the membrane surface consisting of aromatic organics to aliphatic compounds thereby reducing membrane fouling. This study included experimental assessments of photocatalysis-MF hybrid system for wastewater treatment with the main aim of improving permeate flux of the membrane. Photocatalysis was tried as pre-treatment, inline treatment as well as on the membrane surface. Photocatalytic pre-treatment removes organic foulants, inline photocatalysis to MF targets the removal of increased organic concentration of retentate. The use of MF not only acts as selective permeation to organic matter but also acts as a barrier in recovering the TiO_2 photocatalyst.

2. MATERIALS AND METHODS

2.1 Materials: P25 Degussa TiO_2 powder was used as the photocatalyst [13, 14] and its properties are shown in Table 1. The zeta potential analysis showed that the isoelectric point of TiO_2 suspension is near pH 4 [15].

MF membrane used in this experiment consisted of a flat sheet polyvinyl chloride (PVC) (Pure-Envitech Co. Ltd., South Korea) with a pore size of 0.4 µm and contact angle of 90^o

(hydrophobic membrane) and an effective membrane area of 43.12 cm^2. The pure water (distilled water) flux was between 7.5 x 10^3 and 8.8 x 10^3 $Lm^{-2}day^{-1}kPa^{-1}$. The membranes were fully soaked in distilled water for more than 24 hours before use.

UV lamps of 15W each (manufactured by Helios Italquarz (Milan)) which emit radiation in the 300–400 nm range were used to irradiate both the slurry reactor and the membrane surface. Three UV lamps with a total surface area of 890 cm^2 encased within transparent glass were placed within the liquid in the photocatalytic reactor. Only one lamp was placed above the membrane surface at a distance of 1.5 cm.

Table 1: Properties of TiO2 photocatalyst

Specification	P25 Degussa TiO_2
Structure	Non-porous
Components	80% anatase, 20% rutile
Average aggregate particle diameter	Non-porous
Primary crystal size	3 μm
Mean pore diameter	6.9 nm
Band gap	3.03 (from 500 to 300 nm) with UV-Vis
Apparent density	130 kg/m^3
Surface area	42.32±0.18 m^2/g
Type	Powdered
Product code	Degussa P25, Frankfurt am Main, Germany

2.2 Photocatalysis-Microfiltration Hybrid System: The hybrid set up shown in Figure 1 consisted of an inline slurry photocatalytic reactor and cross flow MF membrane unit. Flat sheet PVC MF membrane was placed between the transparent quartz cases which were clamped between the metal base at the bottom and the metal lid at the top with an opening for light. The water tightness was provided by rubber seal between the quartz casings. The membrane unit is enclosed in a box with one 15W UV lamp above. The photocatalytic slurry reactor with a feed volume of 4 litres was mixed thoroughly by a motorized mechanical stirrer placed at the centre.

2.3 Experimental Procedures: Synthetic wastewater which represents the biologically treated sewage effluent was used in all experiments and its composition is presented in Table 2. The hybrid system was operated under different conditions. Firstly to examine the effect of TiO_2 slurry in MF permeate flux, the hybrid system was operated with feed water containing different TiO_2 slurry concentration and the permeate flux was observed at regular time interval. This experiment was carried out using both pure water (distilled water) and synthetic wastewater. The optimum slurry concentration was chosen for subsequent experiments. In the second experiment, wastewater was pre-treated by photocatalysis in the photo reactor. The slurry was allowed to settle before the supernatant was used as feed water for further inline photocatalysis-MF hybrid treatment. All membrane filtration tests were carried out in batch photoreactor where both the permeate and the retentate were recycled back to the reactor. The continuous recirculation of retentate maintained uniform concentration and temperature of the catalyst suspension. It has been reported that the reuse of TiO_2 suspension does not decrease the degradation efficiency of the photocatalyst. Two parameters were varied during the pre-treatment:

photo reaction time/duration and slurry settling time. The effect of these two parameters on the permeate fluxes were studied in order to obtain optimum reaction time and slurry settling time. In the third experiment, UV light was irradiated directly on the MF surface and the results were compared with the optimum conditions in the second experiments. The performance of the hybrid system was monitored through two main output parameters: permeate flux and dissolved organic carbon (DOC) removal.

In all the experiments, MF was first stabilized with pure water (distilled water) filtration and the stabilized pure water flux was used as initial MF flux (J_0). The permeate fluxes were observed at different time intervals and samples were taken out every one hour for DOC analysis. The samples were analysed using a UV persulfate DOC analyser. All the samples were filtered using 0.45 μm Millipore filter prior to DOC analysis. The permeate flux was recycled back to the feed tank. The effect on the results due to change in the slurry concentration was considered negligible. The membranes were operated at transmembrane pressure (TMP) of 30 to 50 kPa, cross flow velocity of 0.5 m/s and room temperature of about 30^oC. TMP was adjusted with the help of bypass valve, pressure valve and the flow rate indicator which was maintained at 0.5 l/min throughout. The pH of synthetic wastewater was observed in the range of 6.3 to 7.5.

To avoid the effect of residual TiO_2 particles in the pumps and conduits on membrane flux, the cleaning method adopted was a combination of hydraulic and chemical (acid and base) cleaning before the start of the next experiment. Each time a different experiment was performed and a new membrane was used.

Table 2: Constituents and characteristics of the synthetic wastewater.

Compounds	Concentration (mg/L)	Main molecular weight (dalton)	Fraction by DOC
Beef extract	1.8	298, 145, 65	0.065
Peptone	2.7	34265, 128, 80	0.138
Humic acid	4.2	1543, 298	0.082
Tannic acid	4.2	6343	0.237
Sodium lignin sulfonate	2.4	12120	0.067
Sodium laury le sulphate	0.94	34265	0.042
Arabic gum powder	4.7	925, 256	0.213
Arabic acid (polysaccharide)	5.0	38935	0.156
$(NH_4)_2SO_4$	7.1	-	-
K_2HPO_4	7.0	-	-
NH_4HCO_3	19.8	-	-
$MgSO_4 \cdot 7H_2O$	0.71	-	-

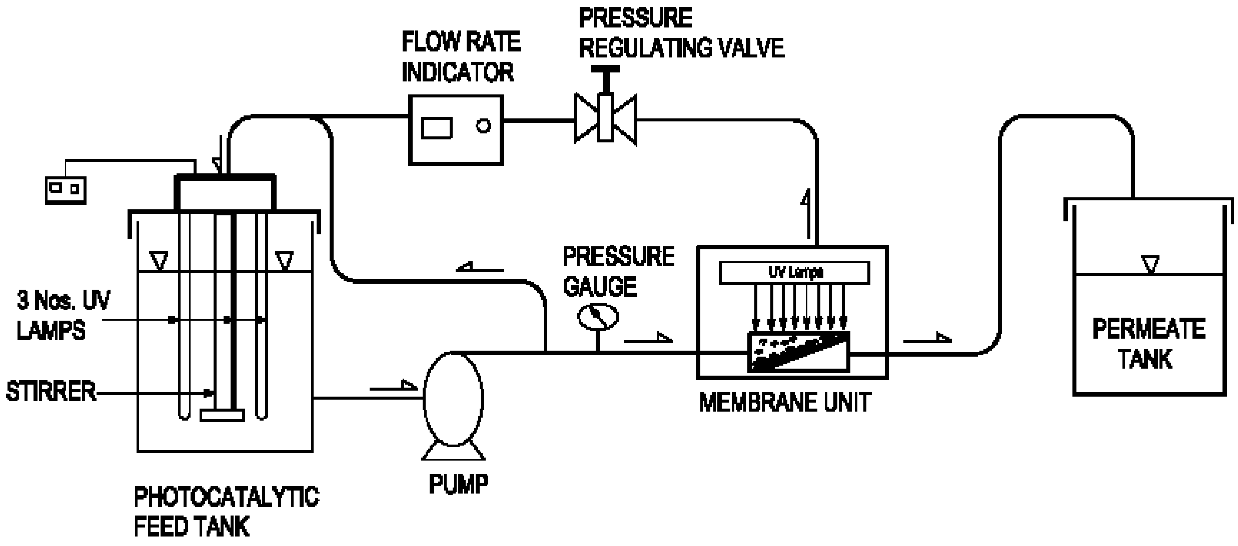


Figure 1: Schematic drawing of photocatalysis cross-flow membrane filtration unit

2.4 Membrane Resistance

Resistance in series model was used in this study. The flux decline and their relationship with the resistances can be represented as in equation 1.

$$J = \frac{\Delta P}{\mu(R_m + R_c + R_g + R_a)} \tag{1}$$

where μ is the dynamic viscosity (kPa•sec), R_m: resistance due to membrane, R_c is the resistance due to concentration polarization, R_g is the resistance due to the gel layer and R_a is the resistance due to adsorption of organic matter (all resistance in m^{-1}).

To determine the membrane resistance, pure water was first filtered through the membrane until a constant flux was obtained. Wastewater was next filtered through the same membrane and the permeate flux was monitored at regular time intervals. Once constant flux was achieved, the wastewater was replaced by pure water. The transmembrane pressure released to remove concentration polarisation. The fouled membrane was then rinsed with pure water so that the gel layer (highly concentrated organic layer) was removed from the membrane surface and pure water filtration was again performed.

3. RESULTS AND DISCUSSION

3.1 Effects of TiO_2 slurry concentration

Pure water flux with different TiO_2 slurry concentrations (0.001, 0.01, 0.1, 1.0 g/L) was measured and compared with the pure water flux without TiO_2 slurry. The results are shown in the form of normalized flux in Figure 2. Negligible flux decline was observed when 0.001 g/L TiO_2 slurry was used but the flux decline increased at higher TiO_2

concentrations (15%, 64% and 94% with 0.01, 0.10 and 1.00g/L TiO_2 respectively after 2 hours operation). Observation of the membrane with the naked eye after the experiment revealed the formation of a layer of TiO_2 cake on the membrane surface with its thickness proportional to the TiO_2 slurry concentration used. The cake on the membrane surface eventually reached a (quasi) steady-state thickness where the particle convection to the cake surface was balanced by the back-transport of the particles away from the surface of the cake layer due to cross flow interference. At this condition the filtration flux reached its (quasi) constant value after continuously declining with the rising of the particle cake resistance [16].

Similar experiments were carried out using wastewater and the results are shown in Figure 3. A slight improvement in permeate flux was observed when higher TiO_2 concentration was used (Figure 3 (a)) but the TiO_2 slurry in wastewater did not have a very significant effect on the flux decline as the permeate flux even without TiO_2 slurry was generally low. This is in contrast to the significant slurry effect observed for pure water flux (Figure 2). In the presence of OM TiO_2 formed larger diameter clusters thereby increasing the porosity of the TiO_2 cake layer formed on the membrane surface. TiO_2-cluster diameter varied as a function of its zeta potential and thus as a function of pH and electrolyte concentration [15]. The DOC variation in the permeate is shown in Figure 3 (b). It was observed that higher TiO_2 slurry concentrations lead to higher DOC removal.

It may also be noted that the crossflow filtration is influenced by a number of parameters such as cross-flow velocity, transmembrane pressure, membrane resistance, size distribution of the suspended particles, particle form, agglomeration behaviour and surface effects of the particles, pH and temperature of the solution, etc. [17, 18]. Therefore it is postulated that the effect of TiO_2 slurry on the MF permeate flux depends on the initial DOC concentration of the feed water. The lower the OM content in the wastewater the more significant is the TiO_2 slurry effect on the membrane flux.

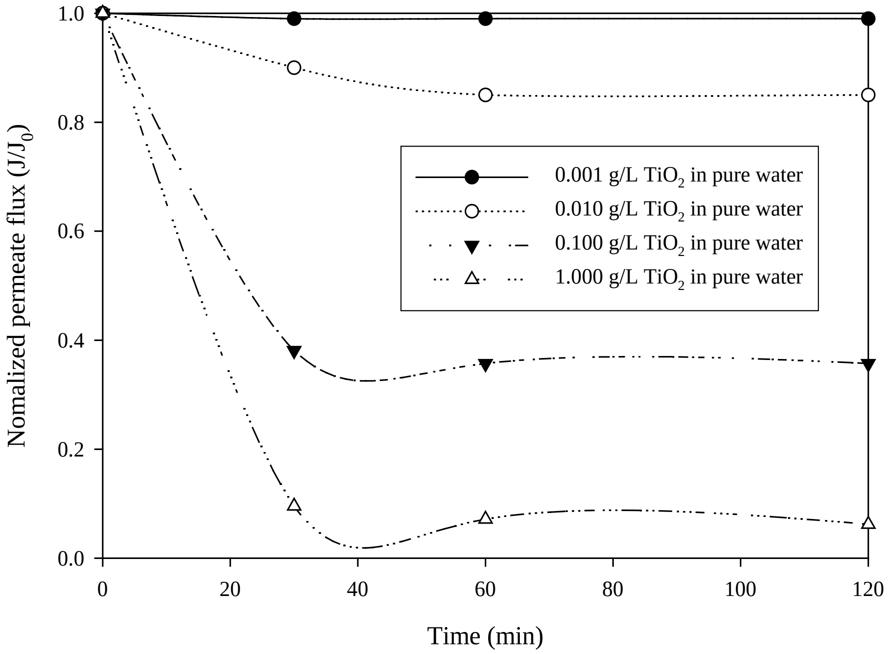
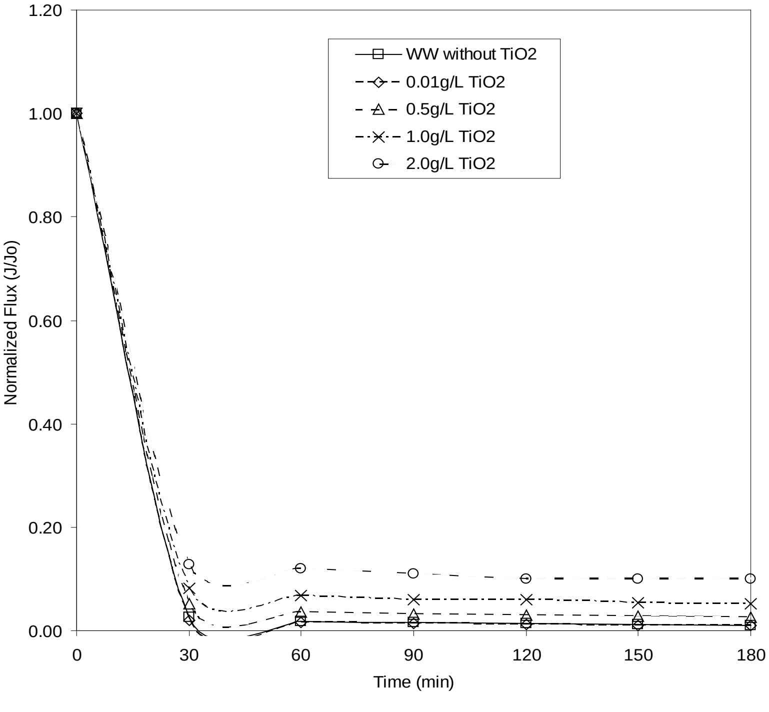
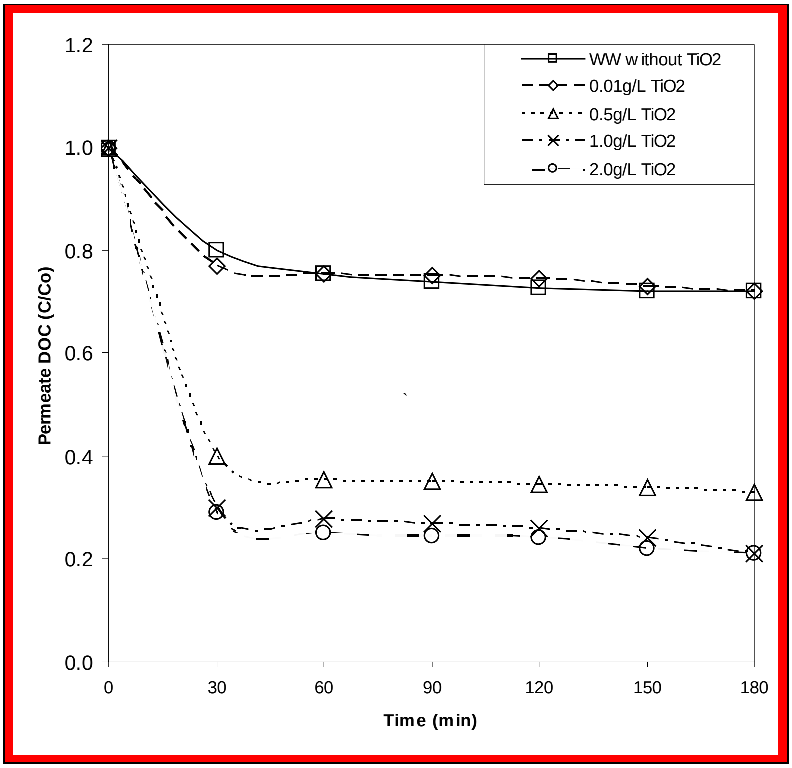


Figure 2: Normalized flux (J/Jo) of MF with different TiO_2 slurry concentration in pure water (TMP = 20 kPa, cross flow velocity = 0.5 m/s, Temperature = 30°C, effective membrane filter area = 43.12 cm^2. Where J: Observed flux and Jo: initial pure water flux = 8.3188 x 10^3 Lm^{-2} day^{-1} kPa^{-1}).



(a)



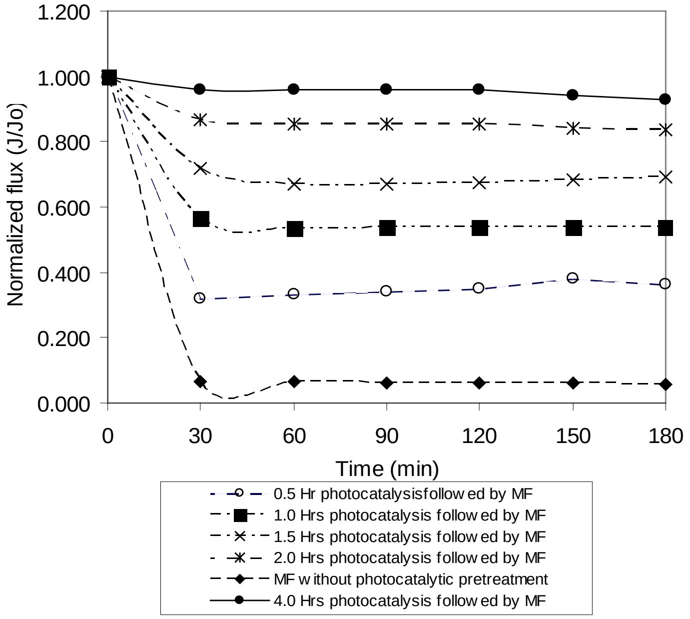
(b)

Figure 3: Variation of (a) permeate flux and (b) permeate DOC (in terms of C/C_0) with different TiO_2 slurry concentrations in synthetic wastewater (TMP = 20 kPa, cross flow velocity = 0.5 m/s, Temperature = 30^oC, effective filter area = 43.12 cm^2. Where J: Observed flux, Jo: initial pure water flux of 8.3 x 10^3 L $m^{-2}day^{-1}kPa^{-1}$, C: observed DOC and C_0: initial DOC of 9.4 mg/L).

3.2 Effects of photocatalytic reaction time

The effect of photocatalytic duration (reaction time) on the MF flux and DOC removal during the pre-treatment was observed. Wastewater with 2.0 g/L TiO_2 slurry underwent photocatalysis for 0, 0.5, 1.0, 1.5, 2.0, and 4.0 hours and the supernatant after 1 hour settling was used for subsequent photocatalysis-MF treatment. The results in Figure 4 show an increased permeate flux and OM removal when the duration of photocatalysis is increased. Two hours of photocatalytic pre-treatment removed up to 55% of the OM and the post treatment by photocatalysis-MF hybrid system removed another 30%, Figure 4 (b). Four hours of photocatalytic pre-treatment removed more than 90% OM and the post treatment by hybrid system removed up to 97% of the OM. Although photocatalysis-MF hybrid system removed 97% of the OM in wastewater, the permeate flux was still observed lower than the pure water flux because of the resistance due to TiO_2 cake layer as explained in the earlier section. Le-Clech *et al* [18] observed a synergetic effect when

TiO_2, UV and membrane processes were used together for water treatment. The organic matter in the water in this system can be removed by two processes: interfacial effect of particles enhancing adsorption on TiO_2 particle surface and the photo oxidation of organic matter due to TiO_2 in presence of UV light. The NOM adsorption on TiO_2 surface has not been observed in this study but the study by Le-Clech *et al* [18] reported a small amount of OM removal (5%) due to absorption on the surface of this photocatalyst powder.



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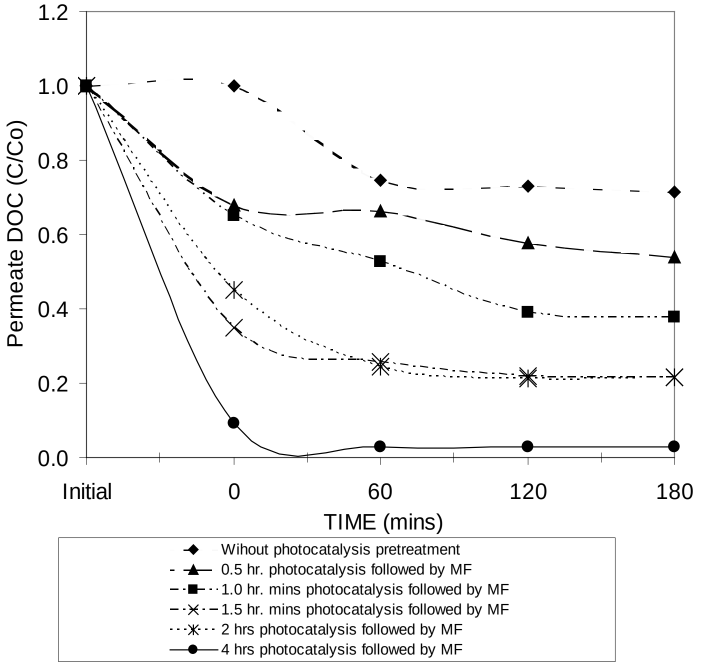


(b)

Figure 4: Effect of photocatalytic reaction time on the (a) permeate flux and (b) DOC variations in synthetic wastewater using photocatalysis-membrane system. Time interval between Initial and 0 in the x-axis indicates the photocatalytic reaction time during the pre-treatment. TMP = 20 kPa, cross flow velocity = 0.5 m/s, Temperature = 30^{o}C, effective filter area = 43.12 cm^{2}. Where J: Observed flux, Jo: initial pure water flux = 7.5 x 10^{3} L m^{-2}day^{-1}kPa^{-1}, C: observed DOC and Co: initial DOC in mg/L = 8.0 mg/L.

3.3 Optimum settling time for TiO_2 slurry

As postulated earlier, the effect of TiO_2 slurry on the permeate flux became more significant at lower OM concentration. As inline photocatalysis continuously removed OM in wastewater the effect of TiO_2 cake might become more significant on the permeate flux. In order to reduce this cake effect on the permeate flux, the slurry after two hours of photocatalytic pre-treatment in 2.0 g/L TiO_2 was settled for different durations 15, 30, 45, and 60 minutes before collecting the supernatant for post hybrid treatment. The results in Figure 5 clearly show that the settling time had a significant effect on the permeate flux. The longer the TiO_2 slurry was allowed to settle, the higher the permeate flux observed. The flux decline after 3 hours of operation was 53%, 42%, 32% and 16% with 15, 30, 45, and 60 minutes of settling time respectively. Therefore 1 hour settling time has been used in the subsequent experiments.

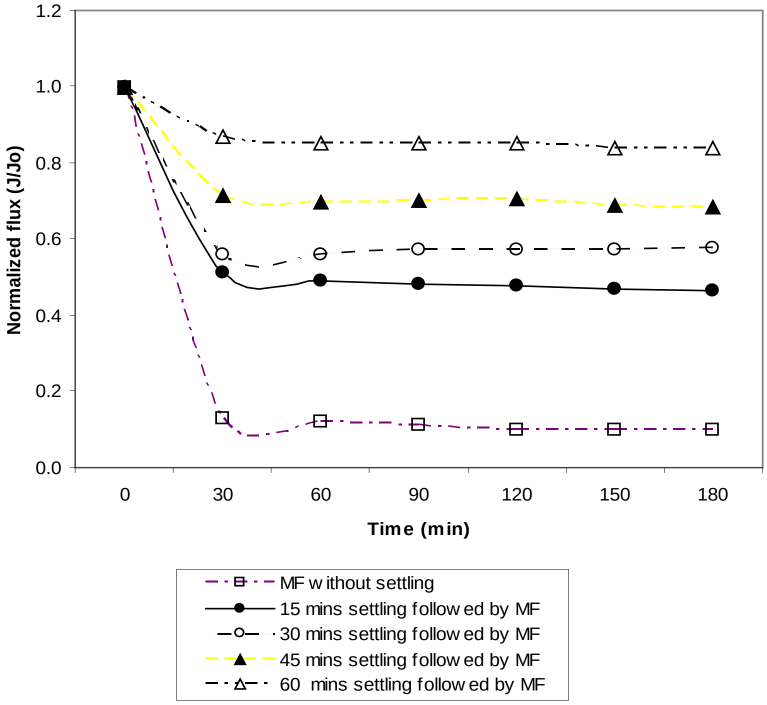


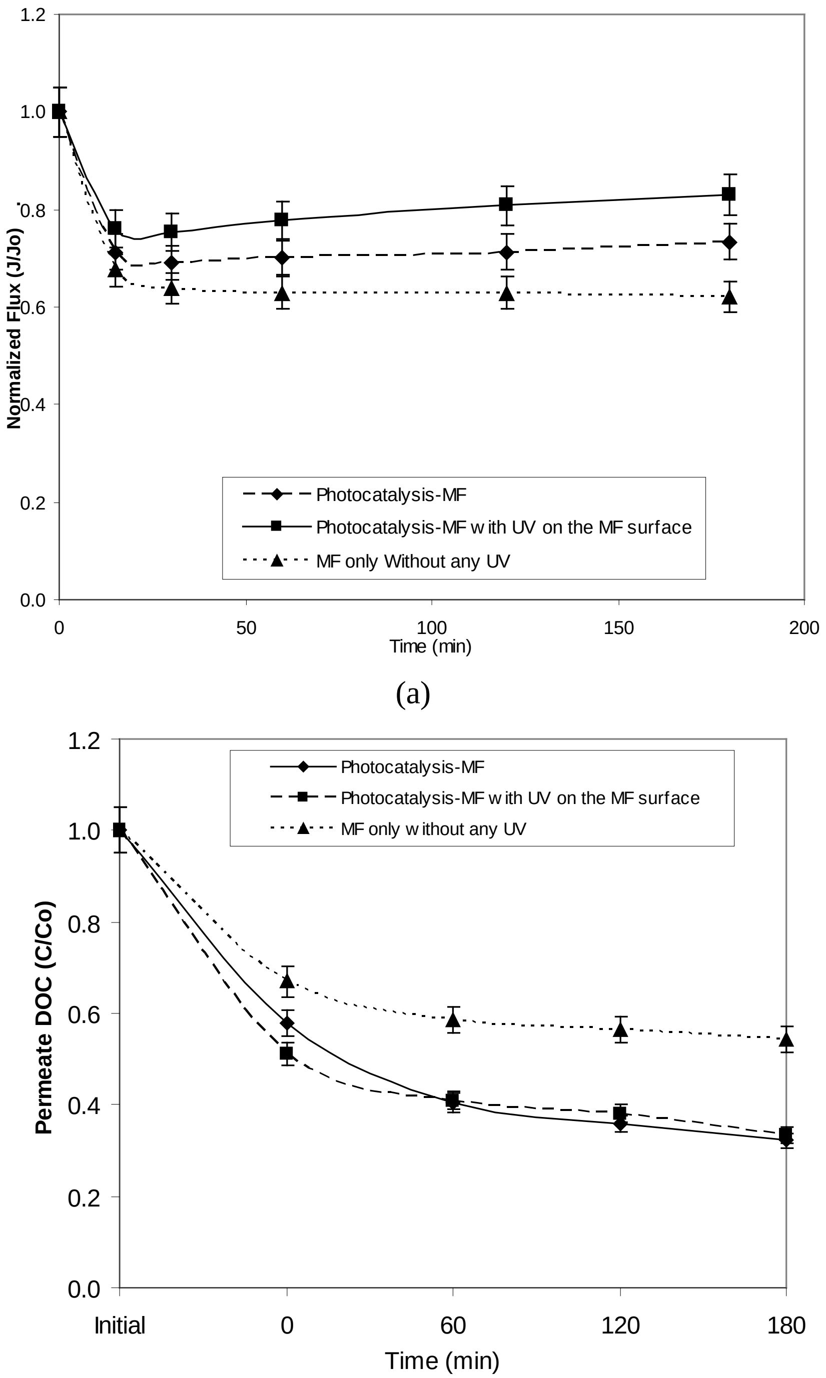
Figure 5: Effect of settling time on the permeate flux using inline photocatalysis-membrane system. Photocatalytic pre-treatment with 2 g/L TiO_2 followed by 1 hour settling. TMP = 20 kPa, cross flow velocity = 0.5 m/s, Temperature = 30°C, effective filter area = 43.12 cm^2. Where J: observed flux and Jo: initial flux with pure water = 7.5139×10^3 L $m^{-2}day^{-1}kPa^{-1}$.

3.4 Effects of UV irradiation on the membrane surface

This experiment was carried out to investigate whether the photocatalytic reaction on the membrane could be effective in preventing membrane fouling. The wastewater was first pre-treated by photocatalysis for 2 hours with 2.0 g/L TiO_2 slurry. The supernatant collected after 1 hour settling was used for further inline photocatalysis-MF hybrid treatment, this time with UV irradiation on the membrane surface. The results are shown in Figure 6(a) and 6(b). The permeate flux decline is lower when the hybrid system was operated with UV irradiation on the membrane surface. The flux decline was of the following order:

MF alone > photocatalysis-MF hybrid system > hybrid system with UV on MF surface

The other notable observation from this experiment was the gradual increase of permeate flux when MF was irradiated with UV on its surface which is contrary to the other two conditions. The results are shown in Figure 6(a). This increase in permeate flux may be due to the following reasons: continuous decrease of OM in the batch reactor over time due to photocatalytic degradation, increase of temperature on the membrane surface due to UV irradiation (high temperature increases permeate flux), and the removal of membrane foulants by photocatalytic action under UV irradiation. The results in Figure 6(b) did not indicate any change in the release of DOC but it may be wrong to assume at this point that the polyvinyl alcohol membrane is stable to UV irradiation on the basis of DOC release alone as other parameters such as change in membrane resistance [6] may indicate the membrane structural damage due to UV. Also the membrane stability needs to be observed for a longer duration. This observation is significant because the photocatalytic reaction on the membrane surface could be effective in removing organic foulants responsible for the flux decline but one must be careful in selecting the membrane as not all polymeric membranes are stable to UV light [6, 19]. Although there is no literature covering the study of PVC membranes to UV/photocatalysis reported, PVC degradation using photocatalysis has been reported [20, 21]. This observation covers only PVC membranes but is assumed comparable with membranes made of other materials although more research may be necessary.



(a)

(b)

Figure 6: (a) Permeate flux variation and (b) DOC variations using photocatalysis-membrane hybrid system. Photocatalytic pre-treatment with 2 g/L TiO_2 followed by 1 hour settling. TMP = 20 kPa, cross flow velocity = 0.5 m/s, Temperature = 30^{o}C, effective filter area = 43.12 cm^2, UV irradiation influencing membrane surface = 14.4 cm^2. Where J: Observed flux and Jo: initial pure water flux = 7.8478 x 10^3 L $m^{-2}day^{-1}kPa^{-1}$, C: observed DOC and Co: initial DOC of 8.95 mg/L.

3.5 Interpretation of Permeate Flux, DOC and the resistance

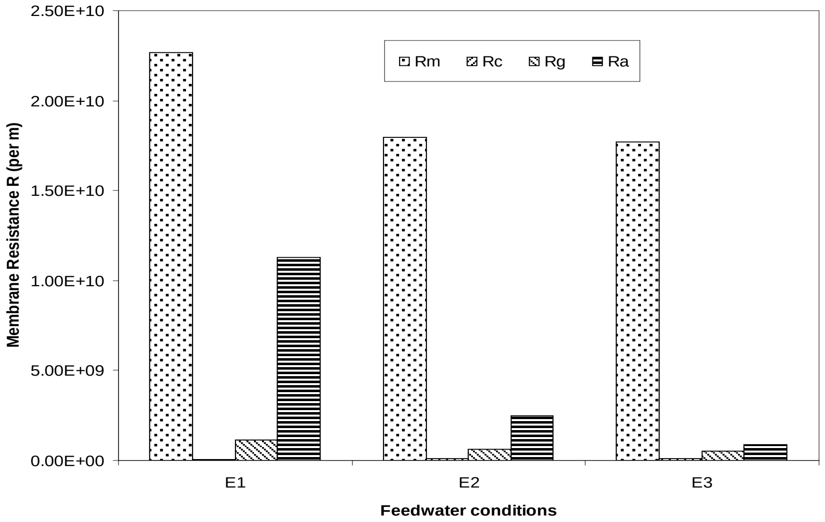
The optimum condition from each configuration has been selected and their corresponding normalised permeate flux and DOC removal efficiency are shown in Table 3. The membrane resistance calculated for some selected conditions using equation 1 is also been presented in Figure 7.

It may be noted here that for all selected optimum conditions under each effect, permeate flux was always lower than the pure water flux although the rate of flux decline is different for each effect. The permeate flux for wastewater with 2.0 g/L TiO_2 slurry without any photocatalysis had the greatest rate of flux decline. Out of the optimum conditions studied (omitting slurry effect in pure water), the four hours photocatalytic pre-treatment followed by hybrid system was observed to give the best permeate flux. The irradiation of UV on the membrane surface was observed to keep the rate of flux decline to a minimum which may prove to be a very promising technique for reducing membrane fouling. But more research is required since all the membranes may not be stable to UV.

Three different feed water conditions were selected and their membrane resistance due to concentration polarization, gel layer and adsorption was determined as shown in Figure 7. The permeate flux decline was caused mainly by resistance due to adsorption of organic matters in the membrane taking into account that R_m is inevitable. The fouling caused by gel layer was small but the resistance caused due to concentration polarization was observed to be negligible. A large part of the fouling caused by adsorption is reversible as it can be removed by desorption during chemical cleaning [22, 3, 2].

Table 3: Normalized flux and its OM (DOC) removal efficiency of each process after 3 hrs. of operation.

Operation Conditions	Normalized flux (J/J_0)	DOC Removal efficiency (%)
MF of wastewater for optimum TiO_2 slurry concentration of 2.0 g/L	0.2	79
Photocatalysis-MF of WW after 4 hours of photocatalytic pre-treatment with 2.0 g/L TiO_2 slurry and 1 hour settling	0.93	97
Photocatalysis-MF of WW for optimum slurry settling time of 1 hr. following 2 hrs. photocatalytic pre-treatment	0.84	79
Photocatalysis-MF of WW with UV on MF surface. WW after 2 hrs. photocatalytic pre-treatment and 1 hr. settling.	0.83	67



R_m: *Resistance due to membrane*
R_c: *Resistance due to concentration polarisation*
R_g: *Resistance due to gel layer*
R_a: *Resistance due to adsorption*

E1: MF using WW only
E2: Photocatalysis-MF: 2 hrs. photocatalytic pretreatment with 2 g/L TiO2, 30 mins settling
E3: Photocatalysis-MF: 2 hrs. photocatalytic pretreatment with 2 g/L TiO2, 1 hr settling, UV on the MF surface

Figure 7: Membrane resistances of the selected feed water conditions.

4. CONCLUSIONS

An integrated photocatalysis-MF hybrid system was investigated in wastewater treatment with the main focus of reducing membrane fouling and improving permeate flux. The hybrid system was operated under various conditions and combinations of feed water and UV irradiation and the results was studied in terms of their effect on the membrane permeate flux and the DOC variations. The effect of TiO_2 slurry on the membrane permeate flux depends on the initial DOC concentration of the feed water and the concentration of slurry itself. The lower the OM contents in wastewater the more significant is the TiO_2 slurry effect on the membrane flux. Removal of organic matters from wastewater depends on photocatalytic reaction time. More than 90% DOC was removed within 4 hours reaction time and the post treatment by the hybrid system removed almost all OM from the wastewater. Although photocatalysis-MF hybrid system removed

97% of the OM in wastewater, the permeate flux was still observed lower than the pure water flux indicating the flux decline caused by TiO_2 slurry. The flux decline due to TiO_2 slurry can be minimised by settling the TiO_2 slurry following photocatalysis pre-treatment. Using only the supernatant and one hour settling has been observed to be optimum settling time for producing optimum flux. It was also observed that an integrated photocatalysis-membrane hybrid system could be an effective technology in reducing flux decline. UV irradiation directly on the membrane surface could be an attractive method in removing organic foulants

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REFERENCES

1. Hu, X., E. Bekassy-Molnar, and A. Koris, *Study of modelling transmembrane pressure and gel resistance in ultrafiltration of oily emulsion.* Desalination, 2004. 163(1-3): p. 355-360.
2. Tansel, B., W.Y. Bao, and I.N. Tansel, *Characterization of fouling kinetics in ultrafiltration systems by resistances in series model.* Desalination, 2000. 129(1): p. 7-14.
3. Cho, J., G. Amy, and J. Pellegrino, *Membrane filtration of natural organic matter: factors and mechanisms affecting rejection and flux decline with charged ultrafiltration (UF) membrane.* Journal of Membrane Science, 2000. 164(1-2): p. 89-110.
4. Derradji, A.F., S. Taha, and G. Dorange, *Application of the resistances in series model in ultrafiltration.* Desalination, 2005. 184(1-3): p. 377-384.
5. Shon, H.K., S. Vigneswaran, H.H. Ngo, and J.H. Kim, *Chemical coupling of photocatalysis with flocculation and adsorption in the removal of organic matter.* Water Research, 2005. 39(2005): p. 2549-2558.
6. Chin, S.S., K. Chiang, and A.G. Fane, *The stability of polymeric membranes in a TiO2 photocatalysis process.* Journal of Membrane Science, 2006. 275(1-2): p. 202-211.
7. Molinari, R., M. Borgese, E. Drioli, L. Palmisano, and M. Schiavello, *Hybrid processes coupling photocatalysis and membranes for degradation of organic pollutants in water.* Catalysis Today, 2002. 75(1-4): p. 77-85.

8. Sagawe, G., B. R.J., B. D., and C. A.E., *Photocatalytic reactors for treating water pollution with solar illumination. I: a simplified analysis for batch reactors.* Chemical Engineering Science, 2003. 58(12): p. 2587-2599.
9. Arana, J., J.A.H. Melian, J.M.D. Rodriguez, O.G. Diaz, A. Viera, J.P. Pena, P.M.M. Sosa, and V.E. Jimenez, *TiO2-photocatalysis as a tertiary treatment of naturally treated wastewater.* Catalysis Today, 2002. 76(2-4): p. 279-289.
10. Blount, M.C., D.H. Kim, and J.L. Falconer, *Transparent thin-film TiO2 photocatalysis with high activity.* Environmental Science and Technology, 2001. 35(14): p. 2988-2994.
11. Chin, S.S., K. Chiang, and A.G. Fane, *The stability of polymeric membranes in a TiO2 photocatalysis process.* Journal of Membrane Science, 2006. 275(1-2): p. 202-211.
12. Shon, H., *Ultrafiltration and Nanofiltration Hybrid Syatems in Wastewater Treatment and Reuse: PhD. Thesis, University of Technology, Sydney.* 2006.
13. Molinari R., Grande C., Drioli E., Palmisano L. and Schiavello M., *Photocatalytic membrane reactors for degradation of organic pollutants in water***.** Catalysis Today, 2001. 67 (1-3): p. 273-279.
14. Al-Rasheed, R. and D.J. Cardin, *Photocatalytic degradation of humic acid in saline waters: Part 2. Effects of various photocatalytic materials.* Applied Catalysis A: General, 2003. 246(1): p. 39-48.
15. Al-Rasheed R. and Cardin D. J.. 2003. *Photocatalytic degradation of humic acid in saline waters. Part 1. Artificial seawater: influence of* TiO_2*, temperature, pH, and air-flow.* Chemosphere, 2003. 51, 925-933.
16. Xi, W. and S.-U. Geissen, *Separation of Titanium dioxide from pohotocatalytically treated water by cross flow microfiltration, Water Research.* Water Research, 2001. 35(5): p. 1256-1262.
17. Altmann, J. and S. Ripperger, *Particle deposition and layer formation at the crossflow microfiltration, Journal of membrane science.* Journal of Membrane Science, 2002. 124(1997): p. 119-128.
18. Le-Clech, P., E.-K. Lee., and V. Chen., *Hybrid photocatalysis/membrane treatment for surface waters containing low concentrations of natural organic matters.* water research: IWA publishing, 2006. 40(2006): p. 323-330.
19. Ollis, D.F., *Integrating photocatalysis and membrane technologies for water treatment.* Annals of the New York Academy of Sciences, 984, 65., 2003.
20. Horikoshi, S., N. Serpone, Y. Hisamatsu, and H. Hidaka, *Photocatalyzed Degradation of Polymers in Aqueous Semiconductor Suspensions. 3. Photooxidation of a Solid Polymer: TiO₂-Blended Poly(vinyl chloride) Film.* Environ. Sci. Technol., 1998. 32(24): p. 4010-4016.
21. Gesenhues, U., *Influence of titanium dioxide pigments on the photodegradation of poly(vinyl chloride).* Polymer Degradation and Stability, 2000. 68(2): p. 185-196.
22. Shon, H.K., P.J. Smith1, S. Vigneswaran., and H.H. Ngo., *Effect of a hydrodynamic cleaning of a cross-flow membrane system with a novel automated approach.* 2000.