

# Hybrid low-pressure submerged membrane photoreactor for the removal of bisphenol A

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## Abstract

The efficiency of a hybrid system combining photocatalysis and membrane filtration in a single module was investigated. Low-pressure submerged hollow fibre membranes were used to retain the TiO<sub>2</sub> particles in the system. Bisphenol A (BPA) was used as a model pollutant. Ninety-seven per cent photodegradation and more than 90% photomineralization of 10 ppm of BPA were achieved after 90 and 120 min of UV illumination, respectively. Aeration was applied in the submerged membrane photoreactor (SMPR) to provide mixing, dissolved oxygen, mechanical agitation to prevent agglomeration of TiO<sub>2</sub> particles as well as providing shear forces to remove TiO<sub>2</sub> particles from the membrane surface. The optimum aeration rate used in our 0.8-L reactor was 0.5 L/min. It was found that intermittent permeation enhanced the sustainability of the submerged membranes but showed no effect on the photoactivity of the system. An intermittence frequency (IF) of 0.1 was sufficient to reduce the fouling rate of the membrane under the experimental conditions. The SMPR appears to be very effective and can achieve removal of low-concentration organics (such as BPA) in a compact, low-energy system.

*Keywords:* Aeration; Low-pressure submerged membrane; Photocatalysis; Intermittent permeation; Bisphenol A

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## 1. Introduction

Heterogeneous photocatalytic oxidation (PCO), based mainly on the use of TiO<sub>2</sub>, has become one

of the most promising methods for the treatment of organic pollutants at low concentrations [1]. TiO<sub>2</sub> in the form of anatase and/or rutile crystals behaves as a classic photocatalyst. When incident photons of a wavelength less than 385 nm are

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absorbed by  $\text{TiO}_2$ , electrons are promoted from the valence band to the conduction band. This excitation leaves positive holes in the valence band and electrons in the conduction band. The holes can directly oxidize the organic compounds that adsorbed onto the catalyst surface and/or react with the hydroxylated surface and adsorbed water molecules to form hydroxyl radicals (OH), which can then oxidize and mineralize toxic organic compounds. Simultaneously, the free electrons can react with oxygen to produce superoxide radicals or reduce other species that are present on the catalyst surface. However, these charge carriers may also recombine and thus reduce the overall efficiency of the photocatalytic process.

Although  $\text{TiO}_2$  is known to be a good photocatalyst in terms of its activity, physical and chemical stability, the recovery of the sub-micron-sized photocatalysts is one of the key challenges for large-scale application. Membrane technology can address this issue by enhancing the separation of particulate  $\text{TiO}_2$  from the treated water. In this case, a higher throughput of treated water may be achieved. The membrane options include high-pressure nanofiltration (NF) as used by Molinari et al. [2], or low-pressure membranes such as micro- and ultrafiltration (MF and UF). The low-pressure MF and UF have an energy benefit but are not able to retain low molecular weight species. Submerged membranes have been widely used in MF and UF processes, such as membrane bioreactors (MBR) due to the recognized advantages of lower cost of fabrication and maintenance [3,4]. The key features of the submerged membrane module include air bubbling as the main mechanical method to provide membrane cleaning action and suction to withdraw the permeate from the system to prevent overpressure of the bioreactor. The non-pressurized open system also reduces the overall operating cost of the submerged membrane system. Fu et al. [5] have described a submerged membrane photoreactor (SMPR) for the degradation of natural organic matter (NOM), fulvic acid.

Their reactor consisted of two compartments — a MF and a PCO zone. An ‘in-house’ nanoparticle of  $\text{TiO}_2$  was used which enhanced the separation of  $\text{TiO}_2$  and maintained high flux of the membrane due to its larger particle size compared to Degussa P25. It was reported that a removal of 73% of total organic carbon (TOC) was achieved within 2 h of UV irradiation.

The objective of our study is to investigate the efficiency of a low-pressure SMPR in the degradation of an endocrine disrupting chemical using commercial  $\text{TiO}_2$ , Degussa P25. The SMPR consisted of a low-pressure submerged hollow fibre membrane module which was in direct contact with the PCO medium. Careful selection of membrane material allowed integration of the membrane and the reactor. Bisphenol A (BPA) was selected as the model pollutant. The presence of BPA in low concentration can result in hormonal imbalance, male infertility and breast cancers [6]. Thus, effective remediation technologies to destroy BPA have to be developed. This study also investigated the effect of operating mode, namely continuous and intermittent, on the efficiency of the SMPR.

## 2. Experimental

### 2.1. Materials

The  $\text{TiO}_2$  (P25) used for the experiments was supplied by Degussa AG, Germany. High purity BPA (Merck-Schuchardt) was used and the pH of all suspensions was adjusted using sodium hydroxide and perchloric acid. Purified air was used as a source of oxygen in this study. Unless otherwise stated, all solutions were prepared using Millipore MilliQ water with a resistivity of 18.2 M $\Omega$ cm. A U-shaped hollow fibre membrane module of area,  $4.107 \times 10^{-4} \text{ m}^2$ , was used. The MF membranes made of poly-vinylidene fluoride (PVDF) were supplied by Bluestar China, with a pore size of 0.22  $\mu\text{m}$  and outer diameter of 1 mm. The choice of PVDF for the

membrane was made following extensive tests on membrane stability in the presence of UV and UV-H<sub>2</sub>O<sub>2</sub> [7].

## 2.2. Effect of aeration

Batch photocatalytic tests were carried out to study the effect of aeration on the kinetics of photodegradation of BPA. The air was sparged to the system through a ceramic bubble diffuser to provide good mixing and a desirable level of dissolved oxygen (DO). The aeration rate was studied in the range of 0.2–4 L/min. Samples at predefined times were taken and filtered through 0.22 µm filters for analysis.

## 2.3. Submerged membrane photocatalytic reactor (SMPR)

A photoreactor made of borosilicate glass was used to study the photocatalytic degradation of BPA. A schematic diagram of the submerged hollow fibre MF system is shown in Fig. 1. It consisted of a borosilicate glass photoreactor with a portable hollow fibre membrane module in the centre. UVA irradiation was provided

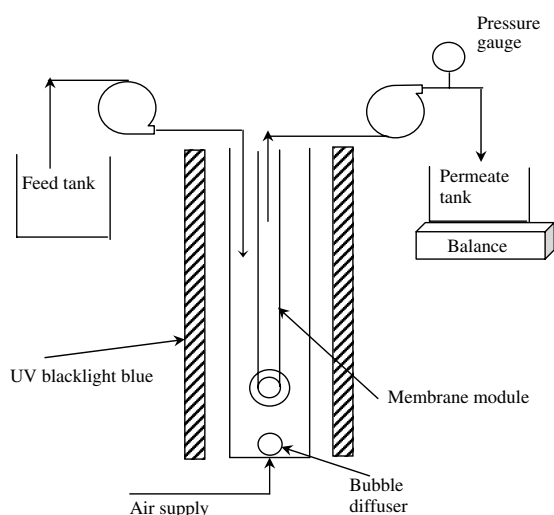


Fig. 1. Schematic diagram of the experimental setup.

by four 8 W black light fluorescent lamps (NEC FL8 BL-B) located on the four sides of the photoreactor. About 800 mL of TiO<sub>2</sub> suspension was prepared by adding pre-determined amounts of TiO<sub>2</sub> and BPA to a known volume of water followed by pH adjustment. The final solution containing 10 ppm BPA was sonicated for 10 min before charging into the photoreactor. During the experiment, a constant flux of permeate was withdrawn from the system through the suction provided by a peristaltic pump. For the intermittent permeation study, the suction pressure was applied intermittently in order to withdraw permeate in a stepwise manner. The transmembrane pressure (TMP) in all experiments was measured by a pressure gauge placed in the permeate line. A level sensor was installed and it controlled an inlet pump which pumped a solution of 10 ppm BPA into the system in order to keep the total volume of the reactor constant. The optimum aeration rate (0.5 L/min), obtained from the aeration study, was applied in subsequent experimentations. Samples were taken at predefined times from the permeate line and analysed for BPA and organic carbon concentrations. For the critical flux determination, a flux stepping method was used whereby the SMPR permeate flux was increased in increments of 20 L/m<sup>2</sup>h up to a flux of 100 L/m<sup>2</sup>h. Each flux step was maintained for a duration of 25 min. The rate of increase of TMP was used to determine the critical flux.

## 2.4. Analysis

The concentration of BPA in samples was measured using high performance liquid chromatograph (Waters Alliance) interfaced with a photodiode array detector. The separation was carried out using a Waters Xterra RP18 HPLC column (3.9 mm × 150 mm, 5 µm) with a mobile phase consisting of water–acetonitrile mixture (50%:50% by volume). The TOC present in the samples was determined by a TOC analyzer

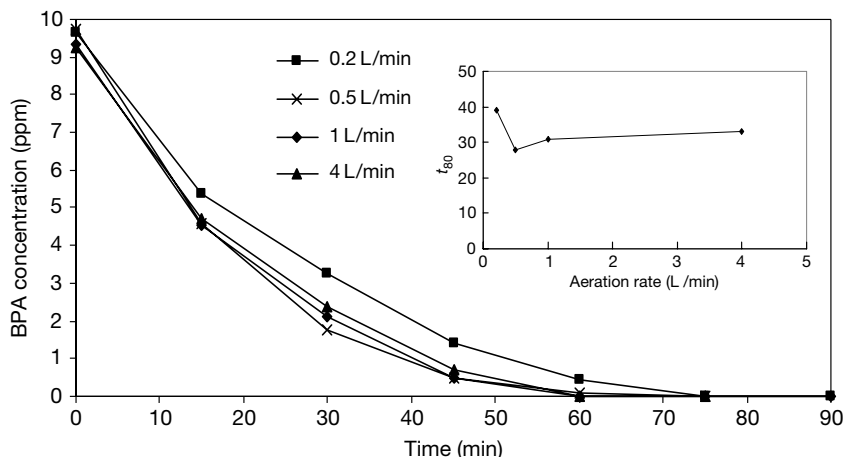


Fig. 2. Effect of aeration rates on (a) batch photocatalytic degradation of BPA (b) 80% removal of BPA [0.5 g/L TiO<sub>2</sub>, initial pH = 4, initial bisphenol A (BPA) concentration = 10 ppm].

(Shimadzu TOC-V<sub>CSH</sub>). The particle size distribution and turbidity of samples were measured by a Brookhaven ZetaPals particle sizer and a HACH 2100AN IS turbidity meter, respectively.

### 3. Results and discussion

#### 3.1. Effect of aeration rate

Aeration is important for submerged membrane systems and photocatalytic reactions. The former process requires the mechanical agitation from aeration to reduce the fouling of the membrane as well as to keep the medium in suspension; whereas the later process requires dissolved oxygen for slowing down electron hole recombination reactions. Fig. 2 shows that the reaction rate increased with an increase in bubbling rate and reached a maximum value at a bubbling rate of 0.5 L/min, beyond which no further enhancement was observed. The inset Fig. 2b shows the time for 80% removal of BPA ( $t_{80}$ ). Lee et al. [8], who performed experiments in a fluidized photocatalytic reactor, reported a similar observation. In their experiment, bubbling strongly affected the photodestruction of

methyl orange and its effect reached a plateau above a certain flow rate.

The mean size of the TiO<sub>2</sub> particle aggregates after 1.5 h of aeration are shown in Table 1. The average 50% size distribution of 0.2 and 4 L/min aeration rate are 0.75 and 0.31  $\mu\text{m}$ , respectively. Higher aeration rates produced greater shear rates which dispersed the particles well and prevented agglomeration of particles. With less agglomeration occurring, more surface area would be available for the degradation of BPA. Soparajee et al. [9] also reported the same negative effect of TiO<sub>2</sub> particles agglomeration on the photocatalytic activity.

For a three-phase reactor, the bubbling rate has to be carefully chosen. Bubbling can increase the liquid film mass transfer coefficient around

Table 1  
Average particle size of TiO<sub>2</sub> at different aeration rate

Aeration rate (L/min)	Mean particle size (nm)
0.2	757 ± 147.1
0.5	477 ± 49.5
1	491 ± 52.3
4	309 ± 32.6

the aggregates [10] but it may also provide a bubble cloud that can attenuate UV light transmission in a photoreactor. The attenuation of UV light might be the reason for the slower 80% removal rate of BPA which occurred with 4 L/min aeration (33 min) compared to 0.5 L/min (28 min) as seen in Fig. 2b (inset). The balance of the competing effects between mass transfer and light attenuation leads to an optimal bubbling rate.

Thus, an aeration rate of 0.5 L/min has been used in subsequent experiments. The use of 4 L/min aeration was avoided due to concern with the aeration energy consumption. A strategy was developed to avoid fouling under conditions of low aeration (see section 3.4).

### 3.2. Effectiveness of submerged membrane photocatalytic reactor

Fig. 3 shows the photodegradation and photomineralization efficiency of BPA using the continuous SMPR. The permeate flux used was 100 L/m<sup>2</sup> h, which was equivalent to a BPA retention time of 2 h.

Turbidity analysis of the permeate (similar to MQ water turbidity values) indicated that there was no leakage of TiO<sub>2</sub> from the SMPR. Fig. 3

shows that the concentration of BPA was reduced by 97% after 90 min of UV illumination and remained at this value until the end of the experiment.

The main objective of a photocatalytic process is the complete mineralization of all organic carbon to ensure that the substrate and any intermediates formed have been degraded. It was found by Chiang et al. [6] that some of the intermediates generated during the photodegradation of BPA were more toxic than the parent compound, especially at low pHs. Therefore, it is always important to monitor the mineralization of any PCO reaction.

As can be seen from Fig. 3, over 90% of BPA was mineralized after 120 min of UV illumination and thereafter the concentration of TOC remained at about 7% throughout the experimental duration. At 60 min, the concentration of TOC was about 3 ppm while the concentration of BPA was about 1.6 ppm (equivalent to TOC of 1.26 ppm). The difference between the concentration of TOC and BPA concentrations indicates the presence of intermediates during the PCO reaction.

The MF membrane was not able to retain BPA and its intermediate products in the

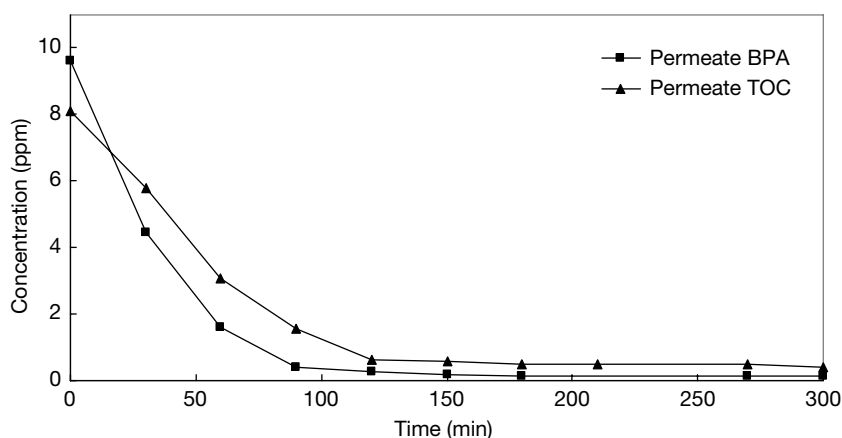


Fig. 3. Photodegradation and photomineralization of bisphenol A (BPA) in the submerged membrane photoreactor (SMPR) (Flux = 100 L/m<sup>2</sup> h, 0.5 g/L TiO<sub>2</sub>, initial pH = 4, initial BPA concentration = 10 ppm, 0.5 L/min aeration rate).

system. Therefore, it would take time for BPA to be degraded at start-up and it is recommended that the permeate line only be opened when the effluent water has met specification.

### 3.3. Intermittent permeation

Fig. 4 shows the determination of the critical flux for the SMPR  $\text{TiO}_2$  suspension and operating conditions. The TMP was constant for filtration fluxes below  $80 \text{ L/m}^2 \text{ h}$ . Defining critical flux as the flux below which fouling of membrane does not occur [11], the critical flux found in this study was  $80 \text{ L/m}^2 \text{ h}$ . Above this value, the TMP was not steady. The operation of the SMPR at a flux of  $100 \text{ L/m}^2 \text{ h}$  resulted in fouling, where the TMP steadily increased to about  $12.5 \text{ kPa}$  from the initial  $10 \text{ kPa}$  as shown in Fig. 5.

One way to increase critical flux is to increase aeration. However, this would involve more energy usage and could also attenuate UV transmission. Therefore, in order to maintain the high flux operation at low aeration, the effect of intermittent permeation was investigated and the results shown in Fig. 5. In this case, the permeation was closed for 2 min for every 5 min. The

choice of 2 min closed and 5 min open was arbitrary and further optimization is planned. When suction was stopped and no permeate was collected, there was a period for the aeration to exert shear rate on the membrane surface to facilitate the detachment of  $\text{TiO}_2$  particles. This should prevent an accumulation of  $\text{TiO}_2$  particles on the membrane. The advantages of intermittent permeation have also been reported by Hong et al. [12] and Howell et al. [4] during the operation of their MBR. Hong et al. [12] suggested that the use of intermittent suction operation could be economically feasible for controlling fouling in small-scale MBR processes treating wastewaters with high fouling potentials. For the  $\text{TiO}_2$  filtration process, intermittency should be even more effective as the  $\text{TiO}_2$  deposits are more reversible than MBR deposits.

Accumulation on the membrane indirectly indicated the loss of suspended  $\text{TiO}_2$  in the SMPR and thus reducing overall active sites of  $\text{TiO}_2$  available for PCO reaction. By mass balance, approximately  $38\% (\pm 14\%)$  of the  $\text{TiO}_2$  was found on the surface of the membrane after 5 h of continuous filtration compared to  $7\% (\pm 2\%)$  of  $\text{TiO}_2$  for the intermittent filtration.

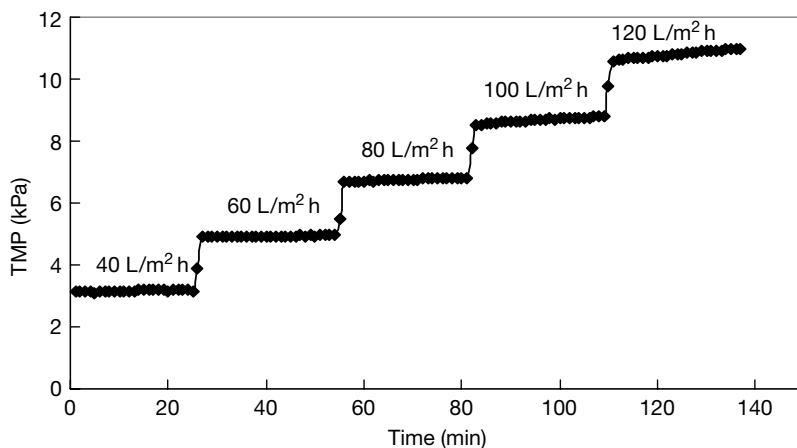


Fig. 4. The change in transmembrane pressure for different filtration flux ( $0.5 \text{ g/L TiO}_2$ ,  $0.5 \text{ L/min}$  bubbling).

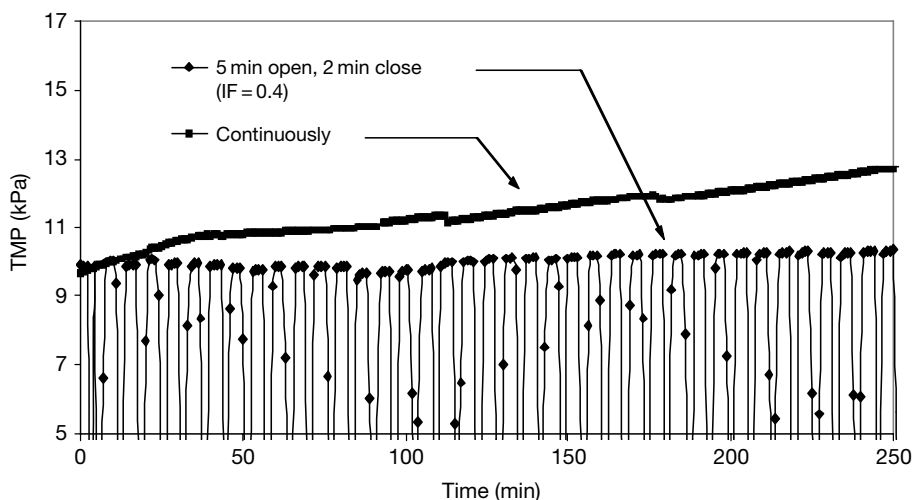


Fig. 5. Transmembrane pressure (TMP) change for continuous  $100 \text{ L/m}^2 \text{ h}$  and intermittent permeation operation (intermittency of 2 min close/5 min open).

The intermittence frequency (IF) is defined as the ratio of the off time to on time. From a practical point of view, a lower IF will mean a higher production of water. Although intermittent operation of 2 min off and 5 min on was shown to reduce the fouling tendency of the membrane as indicated in Figs. 5 and 6, it

resulted in a decrease in water production by about 30% (Fig. 6, IF = 0.4). Therefore, an experiment with IF of 0.1 (1 min close, 10 min open) was carried out.

It is worth noting that the TOC photomineralization with an IF of 0.1 was similar to that obtained with an IF of 0.4 and with continuous

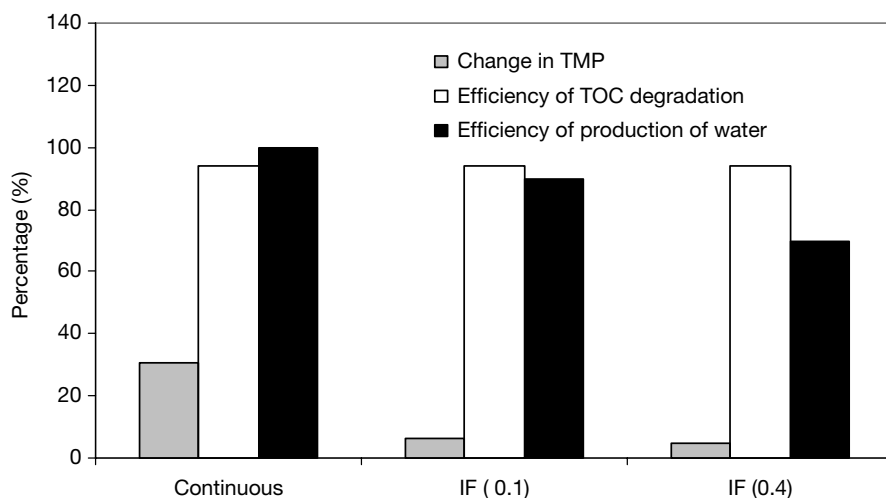


Fig. 6. Comparison of the transmembrane pressure (TMP) change, total organic carbon (TOC) degradation and production of water between continuous and intermittent permeation operation.

operations i.e. 94% BPA reduction at 250 min. The water production efficiencies with IF of 0.4 and 0.1 would be approximately 70 and 90%, respectively. Reducing the IF from 0.4 to 0.1 has increased the water production rate by about 20%. Most importantly, it was found that the TMP of the system was decreased by fivefold with IF of 0.1 compared to the continuous operation. As TMP is proportional to the filtration energy cost [13], intermittent operation would reduce the operating cost of the continuous SMPR. The use of intermittent permeation has made the operation of the SMPR at fluxes above critical flux possible, taking into account of the reversibility of the cake deposits.

#### 4. Conclusions

Aeration in a photocatalytic reactor enhanced the photodegradation rate by providing higher concentrations of dissolved oxygen (DO) and improving the mass transfer process in the system. Photoactivity was found to increase with aeration rate up to a limit of 0.5 L/min. Beyond 0.5 L/min, no significant improvement was observed in the photocatalytic process. The SMPR was able to degrade 97% of 10 ppm of BPA after 70 min of UV illumination. Furthermore, it was also capable of mineralizing more than 90% of the TOC after 100 min of UV illumination. It was found that an intermittent filtration process reduced fouling through the removal of the  $\text{TiO}_2$  layer from the membrane surface intermittently and thus allowed high flux operation of the SMPR. By varying the IF, the fouling of the submerged membrane can be controlled. It should be possible to optimize the IF to obtain maximum production of water with sustainability of membrane operation. An IF of 0.1 was found to be sufficient to stabilize the conditions at a flux of  $100 \text{ L/m}^2 \text{ h}$ . The compact and low-pressure SMPR has shown to be effective and attractive for the photodegradation of low concentrations of organics in water.

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#### References

- [1] D.S. Bhatkande, V.G. Pangarkar and A. Beenackers, Photocatalytic degradation for environmental applications — a review, *J. Chem. Tech. Biotechnol.*, 77 (2001) 102–111.
- [2] R. Molinari, L. Palmisano, E. Drioli and M. Schiavello, Studies on various reactor configurations for coupling photocatalysis and membrane processes in water purification, *J. Memb. Sci.*, 206 (2002) 399–415.
- [3] A.G. Fane, S. Chang and E. Chardon, Submerged hollow fibre membrane module — design options and operational considerations, *Desalination*, 146 (2002) 231–236.
- [4] J.A. Howell, H.C. Chua and T.C. Arnot, In situ manipulation of critical flux in a submerged membrane bioreactor using variable aeration rates, and effects of membrane history, *J. Memb. Sci.*, 242 (2004) 13–19.
- [5] J. Fu, M. Ji and L. Jin, Submerged Membrane Photocatalysis Reactor for Fulvic Acid Removal in Drinking Water by Using Nanoparticle  $\text{TiO}_2$ , Proceedings 3rd IWA Leading-Edge Conference and Exhibition on Water and Wastewater Treatment Technologies, Sapporo, Japan, 6–8 June 2005.
- [6] K. Chiang, T.M. Lim, L. Tsen and C.C. Lee, Photocatalytic degradation and mineralization of bisphenol A by  $\text{TiO}_2$  and platinumized  $\text{TiO}_2$ , *Appl. Catal. A Gen.*, 261 (2) (2004) 225–237.
- [7] S.S. Chin, K. Chiang and A.G. Fane, The stability of polymeric membranes in a  $\text{TiO}_2$  photocatalysis process, *J. Memb. Sci.*, in Press.
- [8] J.H. Lee, W. Nam, M. Kang, G.Y. Han, K.J. Yoon, M.-S. Kim, K. Ogino, S. Miyata and S.-J. Choung, Design of two types of fluidized photo reactors and their photo-catalytic performances for degradation of methyl orange, *Appl. Catal. A Gen.*, 244 (1) (2003) 49–57.
- [9] K. Soparajee, S.A. Qasim, S. Basak and K. Rajeshwar, An integrated flow reactor-membrane

- filtration system for heterogeneous photocatalysis. Part II: experiments on the ultrafiltration unit and combined operation, *J. Appl. Electrochem.*, 29 (1999) 1111–1118.
- [10] Y. Jia, R. Wang and A.G. Fane, Atrazine adsorption in water by powdered activated carbon-improved mass transfer by bubbling, *Chem. Eng. J.*, 116 (2006) 53–59.
- [11] J.A. Howell, Sub-critical flux operation, *J. Memb. Sci.*, 107 (1995) 165–171.
- [12] S.P. Hong, T.H. Bae, T.M. Tak, S. Hong and A. Randall, Fouling control in activated sludge submerged hollow fiber membrane bioreactors, *Desalination*, 143 (3) (2002) 219–228.
- [13] M. Cheryan, *Ultrafiltration and Microfiltration Handbook*, Technomic, Lancaster, PA, 1998.