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Performances of submerged membrane photocatalysis reactor during treatment of humic substances

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Abstract. During the disinfection of potable water, humic substances present in the solution react with chlorine to form potential carcinogenic compounds. This study evaluates the feasibility of using a submerged membrane photocatalysis reactor (SMPR) process for treatment of humic substances through the characterization of both organic removal efficiency and membrane hydraulic performance. A simple SMPR was operated and led to the removal of up to 83% of the polluting humic matters. Temporal rates of organic removal and membrane fouling were found to decrease with filtration time. Using tighter membrane in the hybrid process resulted in not only higher organic removal, but also more significant membrane fouling. Under the experimental conditions tested, optimum TiO_2 concentration for humic removal was found to be 0.6 g/L, and increasing initial pollutant concentration expectedly resulted in a more substantial membrane fouling. The importance of the influent nature and pollutant characteristics in this type of treatment was also assessed as various water sources were tested (model humic acid solution vs. local water containing natural organic matters). Results from this study revealed the promising nature of the SMPR process as an alternative technique for organic removal in the existing water treatment system.

Keywords: TiO_2 photocatalysis; natural organic matter; humic acid; submerged membrane process; membrane fouling.

1. Introduction

Natural phenomena and human activities continuously release organic pollutants to surface water. The major components of natural organic matters (NOM) in surface water are humic substances, especially humic and fulvic acids (HA and FA). Even at relatively low concentrations, humic substances pose not only aesthetic but also potential health problems. When subjected to chlorination, a standard disinfection technique used in treatment of surface water for domestic consumption, humic substances act as precursors to the formation of harmful carcinogenic trihalomethane by-products (Li *et al*. 2002). For the aforementioned reasons, it is essential that an effective method to remove humic substances from surface water is developed.

Advanced oxidation technologies based on UV/H_2O_2 systems are currently used in large municipal recycling operations in Australia and around the world to remove organic pollutants from surface water prior to chlorination. Even though these processes have been shown to be highly effective in eliminating trace micropollutants (Coleman *et al*. 2007), they are energy intensive and can introduce toxic peroxide into the water. Based on recent investigations (Coleman *et al*. 2007, de Lasa *et al*. 2005, Li *et al*. 2002), heterogeneous photocatalysis using suspended UV-illuminated TiO_2 has emerged

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as an attractive alternative in removing organic pollutants from surface water. Not only does photocatalysis require less energy than the other oxidation technologies, it also uses a readily available catalyst in TiO_2, which is known to be non-toxic and photostable. Detailed mechanisms of photocatalysis for NOM degradation can be found in (de Lasa *et al.* 2005).

Despite its advantages, one major drawback of heterogeneous photocatalysis is the difficulty involved in removing suspended sub-micron TiO_2 aggregates (0.5 – 1.2 μm in diameter) from the post-treated water. One solution is to immobilise the TiO_2 catalysts onto the reactor walls. However, such modification substantially decreases the contact surface area between target organic molecules and the catalyst surface, resulting in undesirably slow reaction kinetics (Coleman *et al.* 2007). Another possible solution is to utilize one of the existing industrial solid-liquid separation techniques to achieve complete isolation of TiO_2 aggregates from the treated water. Due to the decreasing cost of microporous membrane material and its operational robustness, membrane technology has emerged as a leading contender for the above solution, resulting in the development of a hybrid photocatalysis/membrane process (Le-Clech *et al.* 2006). In such a configuration, the membrane serves two simultaneous functions, acting as both an efficient barrier for the TiO_2 catalyst and a selective separation device for the organic pollutant molecules. During membrane filtration of the hybrid system, the catalyst is retained in the membrane cell for further reaction while TiO_2-free treated effluent is withdrawn from the system. Filterability of TiO_2 slurry has been previously assessed and an average pore size of 0.45 μm was found to be sufficient to completely prevent passage of TiO_2 aggregates (Degussa P25) across the membrane (Le-Clech *et al.* 2006).

Even though TiO_2-mediated photocatalysis has been extensively investigated in recent years (for NOM removal (Huang *et al.* 2008, Le-Clech *et al.* 2006); fulvic acid removal (Fu *et al.* 2006), humic acid removal (Fang *et al.* 2005, Lee *et al.* 2007, Wiszniowski *et al.* 2002)), only few studies have used continuous membrane filtration process to separate TiO_2 from the treated water. Of those that investigated the synergy of the hybrid photocatalysis/membrane process (Le-Clech *et al.* 2006, Molinari *et al.* 2006), none explored the effects that simultaneous organic photo-oxidation coupled with TiO_2 filtration might have on membrane hydraulic performance and fouling propensity. For enhanced efficiency, the experimental setup used in this study has integrated both systems (photocatalytic slurry reactor and membrane cell) in a single vessel and membranes are used in a submerged configuration.

In this study, the feasibility of using the submerged membrane photocatalysis reactor (SMPR) process to supplement a water treatment system for humic substance removal was assessed for not only organic removal efficiency but also membrane hydraulic performance. Relative effects of individual processes featured in the SMPR system (UV photolysis, TiO_2 adsorption, membrane filtration) were investigated, while a comparative study which analysed the effects of different membranes in the system was carried out. Finally, the influences of experimental parameters (TiO_2 catalyst loading and initial HA concentration) and the effects of pollutant characteristics (model solution vs. real surface water) on the performance of the SMPR were further examined.

2. Materials and Methods

2.1 Chemical reagents and membranes

Two feed waters were used in this study: HA model solution (HA powder supplied from Sigma

Aldrich) and surface water collected from local Woronora Catchments in NSW, Australia (with an average total organic carbon or TOC concentration of 10±0.5 mg/L). The HA model solution was made by dissolving a calculated amount of HA powder in de-ionized water to make a given TOC concentration. Once dissolved, HA powder dissociates to form macromolecules with size ranging from 0.1 to 10 nm (Belfort *et al.* 1994).

The TiO_2 catalyst used in the study was Aeroxide® P25 from Degussa. Once suspended in water, this type of TiO_2 forms agglomerations of variable size, ranging from 0.5 to 1.2 μm. Cellulose acetate syringe filters with an average pore size of 0.45 μm (Millipore) were used for sampling and filtering supernatant solution from the reactor. Two types of hollow fibre membranes were used: (1) polypropylene (PP) with an average pore size of 0.22 μm and (2) polyvinylidene fluoride (PVDF) with an average pore size of 0.04 μm. Both membranes were supplied by Siemens - Memcor and were potted into a 30-cm module, consisting of 24 fibres with a total active filtration area of $9.8\times10^{-3}\ m^2$.

2.2 Experimental setup

SMPR used in the experimental setup was cylindrical (14 cm diameter), and featured a total working volume of 4 L (Fig. 1). In order to ascertain maximum UV transmission, the SMPR was tested with a radiometer (International Light PMA 2200). The pyrex wall of the reactor was shown to successfully transmit more than 90% of the incident photons emitted by surrounding blacklight blue UV lamps (8×8W with peak emission at 365 nm). The membrane module was placed in the centre of the SMPR by a supporting frame.

For each complete SMPR run, membrane filtration was initiated immediately after TiO_2 powder was added to the reactor and the UV lamps were activated. All experiments were conducted under constant flux (J) filtration mode (100 L/m^2hr) and operated in a steady-state continuous mode (fresh

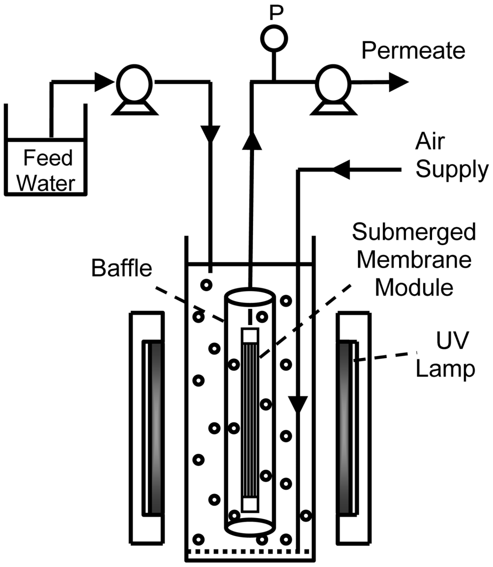

Fig. 1 Schematic of the SMPR experimental setup

feed was continuously supplied to the SMPR as permeate was withdrawn). Aeration at 5 L/min was supplied through the nozzles installed at the bottom of the SMPR. Aeration served three important purposes: it enhanced photo-oxidation of organic molecules by reducing the sacrificial recombination of electrons with activated catalyst surface, fluidized the system to ensure homogeneous mixing, and provided turbulence along the submerged membrane surface to dissipate foulant layer. The temperature during the experiments was maintained at 25±2°C.

2.3 Analytical methods

The performance of the SMPR was evaluated by two key indicators: organic removal efficiency and membrane hydraulic performance. In each experimental run, both indicators were measured and reported. The amounts of humic substances in the feed (pre-SMPR) and in the permeate (post-SMPR) were quantified by their TOC levels (TOC_{feed} and TOC_{perm} respectively, measured by Shimadzu TOC-VCSH). The organic removal efficiency (E_{ff} in %) of the SMPR was calculated according to Eq. (1).

$$E_{ff}\,(\%) = \frac{(TOC_{feed} - TOC_{perm})*100}{TOC_{feed}} \tag{1}$$

Membrane hydraulic performance was described by the change in its fouling resistance throughout filtration. Membrane's fouling resistance (R_f in m^{-1}) was calculated according to equation 2 (Lee *et al.* 2007).

$$R_f = \frac{TMP}{\mu J} - R_m \tag{2}$$

where TMP is the evolving trans-membrane pressure (in Pa), μ is permeate viscosity (equivalent to pure water at 10^{-3} Pa.s), R_m is the clean membrane resistance ($3.9\pm0.5 \times 10^{11}$ m^{-1} for PP and $7.1\pm0.6 \times 10^{11}$ m^{-1} for PVDF).

The liquid chromatography-organic carbon detector (LC-OCD) system (DOC-LABOR, Germany) was used to characterise the organic compounds present in feed waters. The LC-OCD is equipped with size exclusion column TSK 50S and online dissolved organic carbon (OC) detectors. The LC unit separates organic compounds according to their molecular size and the separated compounds are identified by online detectors.

3. Results and discussions

3.1 Preliminary results

Figs. 2 and 3 illustrate respectively typical TOC and TMP profiles obtained in complete SMPR experimental runs conducted throughout this study. In these experiments, all components of the hybrid system (UV irradiation, TiO_2 addition, and membrane filtration) were fully operated. Even though the specific values of TOC and TMP for each experiment were different depending on their operational parameters, the trend in which they evolved throughout the experimental duration had been consistently similar. From Fig. 2, it was observed that TOC declined most rapidly in the beginning of the experiment (from 10.0 to 3.2 mg/L in the first 20 mins) and that the rate of TOC

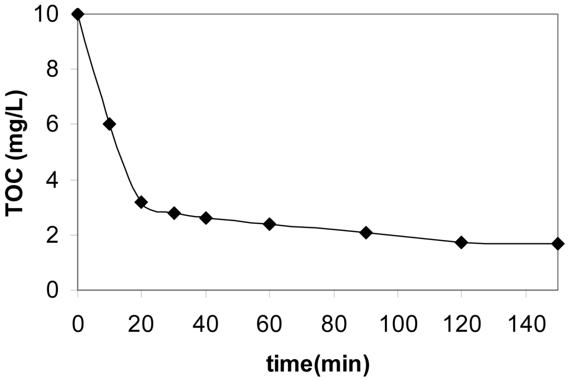

Fig. 2 Characteristic TOC profile of SMPR experiments; $[TOC]_0 = 10$ mg/L, $TMP_0 = 8400$ Pa, membrane = 0.22 μm PP, $[TiO_2] = 0.6$ g/L, feed water = HA model solution

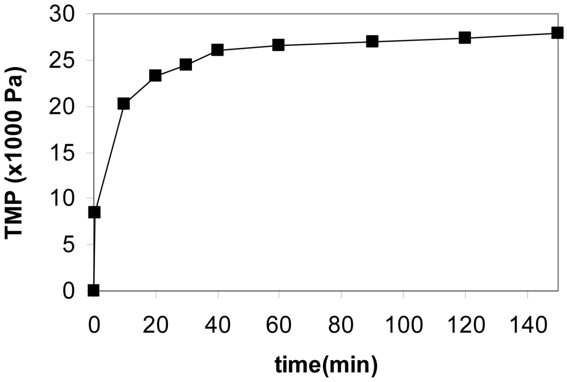

Fig. 3 Characteristic TMP profile of SMPR experiments; $[TOC]_0 = 10$ mg/L, $TMP_0 = 8400$ Pa, membrane = 0.22 μm PP, $[TiO_2] = 0.6$ g/L, feed water = HA model solution

removal continuously decreased with experimental time. TOC profile eventually reached a plateau and only little reduction in organic concentration was observed after 120 min. This pattern of TOC evolution correlated well with those reported by Li *et al.* (2002) and Huang *et al.* (2008), both of whom also noted asymptotic behaviour of TOC removal with time.

Two phenomena are suggested to explain the observed changes in TOC concentration. Firstly, as photocatalysis continued to mineralize organic molecules to CO_2, less humic substances were available for degradation. This was to be expected, even when fresh feed was constantly added to the reactor like in these experiments. The second reason was postulated based on the actual surface-bound mechanisms of heterogeneous photocatalysis. Immediately after TiO_2 addition to the feed water, rapid adsorption of organic macromolecules onto the catalyst surface took place. The active area of the catalyst became saturated with pollutants which tend to desorb during the degradation process (Huang *et al.* 2008). Upon UV-photocatalytic oxidation, a fraction of the degraded organic intermediates were desorbed and released back to the water, liberating some portions of the catalyst surface and allowing for further adsorption of organic molecules. As this cycle of adsorption and partial desorption was repeated throughout the photocatalytic experiment, the amount of catalyst surface accessible for reaction is believed to progressively decrease, resulting in the observed diminishing removal rate. The stable TOC concentration at the end of experiment partly indicated the fresh HA fed continuously into the reactor and the photo-resistant fraction of original organics which remained in the feed water (Wiszniowski *et al.* 2002).

The rate of membrane fouling (indicated by the increase in TMP values in Fig. 3) was also observed to decrease with experimental time. Even though TMP values were seen to substantially increase at the beginning of the experiment (from 8400 to 23300 Pa in the first 20 mins), such dramatic changes were not sustained and the values eventually converged to an asymptotic level with little variation (between 26000 and 27900 Pa from 40 mins onward). In the SMPR, membrane fouling resulted from both TiO_2 and humic molecules deposition on the membrane surface. Visual observation of the hollow fibre membrane after each experiment confirmed the formation of a thick cake build-up consisting of both TiO_2 and HA.

The following model is suggested to explain the evolution of TMP values in Fig. 3. During the initial adsorption process, TiO_2 aggregates combined with HA molecules to form complex laden particles. These structures lead to an immediate formation of a very dense cake and exert a fouling resistance higher than either TiO_2 or HA cake (Lee *et al.* 2001), explaining the high initial TMP increase. As the effect of photocatalysis became established, high molecular weight (MW) HA fraction was preferentially and continuously degraded to form low MW intermediate chains with more modest fouling propensity. As a consequence, the resulting laden particles formed a cake with progressively lower density and fouling rate continued to decrease with experimental time. At the end of experiment, only little fouling was observed despite the presence of residual organics (about 2 mg/L for the given experiment), confirming that most organics with high fouling tendency had been mineralized.

3.2 Relative effect of individual processes and membrane pore size

The degradation of pollutant occurring in the SMPR can be better understood if the contribution of each individual component towards the overall performance of the system can be assessed. Four sets of experiments were therefore designed

- Filtration only: without UV and TiO_2,
- UV photolysis and filtration: without TiO_2,
- TiO_2 adsorption and filtration: without UV and
- SMPR: photocatalysis (UV+TiO_2) and filtration.

Additionally, the effect of membrane pore sizes on the hybrid process was also assessed, as each of the above experiments was repeated with three membranes: 0.45 μm CA filter, 0.22 μm PP and 0.04 μm PVDF membranes. HA model solution with TOC concentration of 10±0.5 mg/L was used as feed water. When TiO_2 was used, its initial concentration was 0.5±0.05 g/L and experiments were conducted for 60 min.

From Fig. 4, membrane-filtration-only appeared effective in removing a fraction of HA macromolecules: up to 34% for PP and 73% for PVDF. With humic macromolecules (10^{-10} to 10^{-8} m) smaller than average membrane pore size (10^{-7} to 10^{-5} m), these rejection values were higher than expected. Under certain operating conditions, organic molecules are known to interact with each

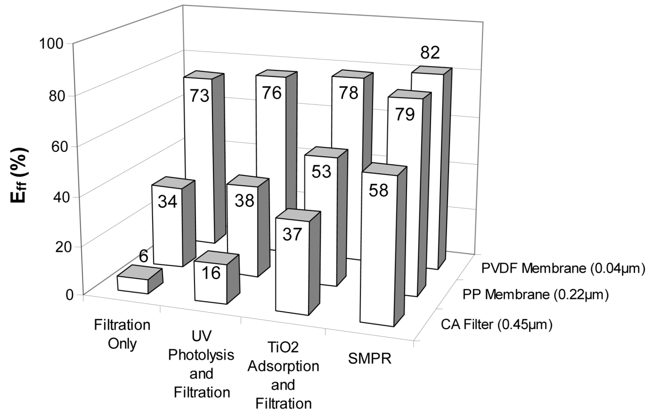

Fig. 4 Relative effect of individual processes on organic removal efficiency (E_{ff}); $[TOC]_0 = 10$ mg/L, feed water = HA model solution, duration = 60 min When used, $[TiO_2] = 0.5$ g/L

other and agglomerate into flocs larger than the membrane pore size examined in this work (Le-Clech *et al*. 2006). It was also expected that a fraction of HA adsorbed on membrane material. These results can also be used to characterise the average size distribution of HA agglomerates formed in this study: 6% of HA was larger than 0.45 μm, 28% (calculated from 34%-6%) ranged between 0.45 and 0.22 μm, 39% (from 73%–34%) featured a size between 0.22 and 0.04 μm, while the remaining 27% was smaller than 0.04 μm.

Irradiation by UV photons (without addition of TiO_2) is capable of mineralizing some organic molecules (Le-Clech *et al*. 2006). However, such additional treatment did not show a great improvement in the removal of HA. Only a slight increase of 3-10% in the E_{ff} values from filtration-only was observed when UV irradiation was used. Wiszniowski *et al*. (2002) also reported negligible TOC removal by UV illumination only. Further discussion on effect of UV illumination can be found in Section 3.5.

Adsorption of organic molecules to TiO_2 surface seemed to remove a significant proportion of TOC from the feed water. For PP membrane, the E_{ff} values increased from 34 to 53%, when TiO_2 were added. However, without UV irradiation, the adsorbed organics were not degraded, and once the catalyst surface saturated, no further organic removal is expected to take place (de Lasa *et al*. 2005). This limits the efficacy of adsorption when compared to photocatalysis, especially in a continuous process like this setup, where new feed was supplied at steady rate. Although the efficiency of adsorption was highly dependent on TiO_2 dosage and pH (Li *et al*. 2002), the TiO_2 adsorption measured here seemed to be significantly more effective than UV photolysis in eliminating HA.

As expected, the highest E_{ff} values were measured when UV was combined with TiO_2 for the photocatalysis to occur. The high E_{ff} values offered by the SMPR (up to 79 and 82% for PP and PVDF respectively) further highlighted the promising nature of this system for the removal of HA dissolved in water. In all experiments, it was observed that organic removal was strongly dependent on membrane average pore size. The E_{ff} values increased with decreasing pore size and E_{ff} for PVDF (0.04 μm) were higher than those obtained for PP (0.22 μm) and CA (0.45 μm).

In order to assess the fouling propensity obtained in these experiments, the comparison of R_f values was conducted between PP and PVDF membranes (Fig. 5). The CA filter was used for

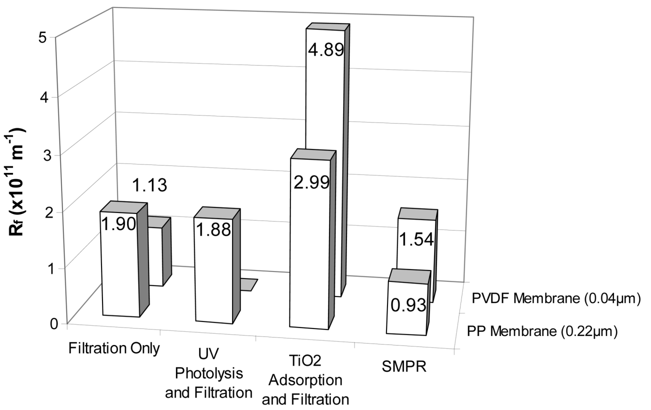

Fig. 5 Relative effect of individual processes on fouling resistance (R_f); $[TOC]_0 = 10$ mg/L, feed water = HA model solution, duration = 60 min When used, $[TiO_2] = 0.5$ g/L

sampling only, and therefore did not perform continuous filtration. During filtration-only experiments, the deposition of HA on the membrane surface generated significant fouling with R_f reaching 1.90 and 1.13×10^{11} m^{-1} for PP and PVDF respectively. These values correlated strongly with those reported by Lee *et al.* (2007) for HA fouling of 0.22 μm PVDF membrane (also with R_f around 2×10^{11} m^{-1}) and confirmed the major role played by HA on fouling propensity in potable water treatment.

Based on the modest E_{ff} results obtained for UV photolysis, R_f value for UV-photolysis- and-filtration run was expected to be similar to that obtained for filtration-only (confirmed for PP membrane). However, the PVDF membrane suffered from noticeable TMP decline ($R_f = -5.6\times10^{10}$ m^{-1}, this value is not shown in Fig. 5). Even located in the middle of the reactor, the membrane may have undergone UV illumination, resulting in pore opening and membrane degradation. The HA fouling which was still occurring during this experiment did not seem to be significant enough to counter balance the above phenomenon. Such finding is in agreement with Chin *et al.* (2006), who reported PVDF membrane to be unstable under continuous UV-irradiation.

A 0.5g/L TiO_2 suspension mixed with deionised water (with no organics) was also filtered under the same conditions to investigate the fouling propensity of TiO_2 aggregates only (results not shown). This resulted in low R_f value of around 0.92×10^{11} m^{-1} for both PP and PVDF membranes. Such results were anticipated due to the highly porous nature of TiO_2 cake. For both membranes, the TiO_2-adsorption-and-filtration experiments led to the highest R_f values (2.99 and 4.89×10^{11} m^{-1} for PP and PVDF, respectively). As mentioned before, the adsorbed (but non-degraded) NOM compounds can combine with TiO_2 to form laden particles, resulting in the formation of dense fouling cake and considerable constriction of the membrane pores (Chin *et al.* 2006, Lee *et al.* 2001). SMPR (Photocatalysis and filtration) experiments featured lower R_f values than TiO_2-adsorption-and-filtration. Once destroyed by the photocatalysis process, HA did not seem to participate any longer to the fouling mechanisms. Unlike adsorption, which only retained the long-chained organic molecules on the catalyst surface, the photocatalytic process was expected to further complete the treatment by degrading the adsorbed molecules to shorter chains with lower fouling propensity. As a result, the laden particles were suspected to form a more porous fouling layer.

With the exception of the UV-photolysis-and-filtration experiments, the PVDF membrane (0.04 μm) seemed to experience more significant fouling than the PP membrane (0.22 μm). This pattern strongly agrees with Lee *et al.* (2007) who reported tighter membranes to exhibit higher fouling resistance during organic filtration.

3.3 Effect of TiO_2 concentration

The efficiency of TiO_2-mediated photocatalytic processes has been reported to be a function of catalyst dosage (Fu *et al.* 2006, Huang *et al.* 2008, Le-Clech *et al.* 2006) and the effects of TiO_2 concentration on the performance of the SMPR were therefore investigated in this study. TiO_2 concentrations ranging from 0 to 3 g/L (a total of 8 different experiments) were tested to treat HA model solution with initial TOC concentration of 10±0.5 mg/L. All experiments used the PP membrane and lasted for 150 min.

Fig. 6 reports the positive effect of TiO_2 concentration increase on the E_{ff} values, rising from 38 to 83% for catalyst loadings of 0 to 0.6 g/L. However, increasing the TiO_2 concentration above 0.6 g/L did not benefit the removal performances of the process, as E_{ff} was observed to decrease to 71% for catalyst dosages of 1 g/L and 3 g/L. These results indicated the existence of an optimum TiO_2

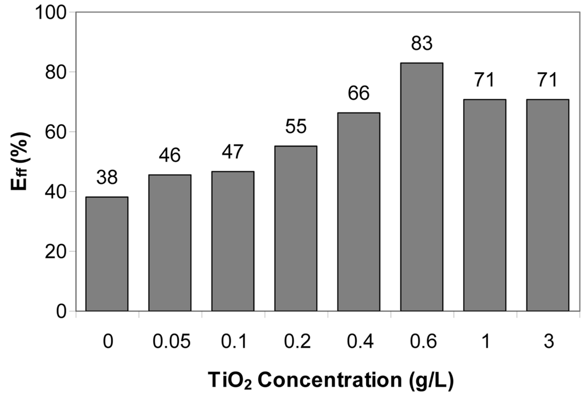

Fig. 6 Effect of TiO_2 concentration on organic removal efficiency (E_{ff}); membrane = 0.22 μm PP, $[TOC]_0$ = 10 mg/L, HA solution filtered for 150 min

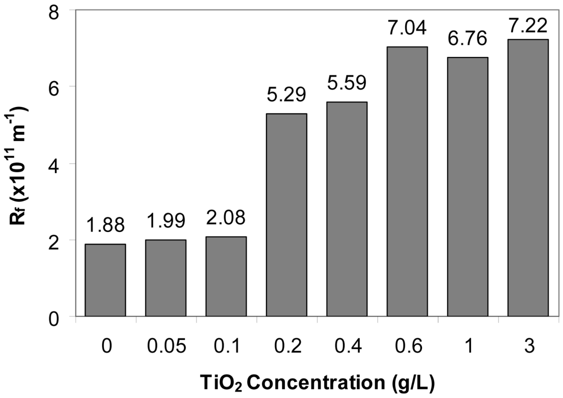

Fig. 7 Effect of TiO_2 concentration on fouling resistance (R_f); membrane = 0.22 μm PP, $[TOC]_0$ = 10 mg/L, HA solution filtered for 150 min

concentration (around 0.6 g/L) for which removal efficiency was maximal. This optimal value is the result of two competing phenomena. Firstly, additional catalyst particles provide greater surface area for the reaction to occur; however, they need to be activated by the UV radiation. Secondly, UV absorption by the catalyst particles also increases with increasing catalyst loading. Hence, additional TiO_2 beyond the optimum, whilst providing more surface area, is unable to be activated due to the limited absorption of the UV light. For humic substances, previous studies have reported a wide range of optimum dosages: 0.1 g/L for NOM (Le-Clech *et al.* 2006), 0.3 g/L for NOM (Huang *et al.* 2008), 1.0 g/L for NOM (Ho *et al.* 2009); 0.5 g/L for FA (Fu *et al.* 2006); 1 g/L for HA (Wiszniowski *et al.* 2002). The observed discrepancies can be attributed to the different experimental setups, concentration of organic substrates, and operating conditions.

It was anticipated for the degree of membrane fouling (R_f values) to steadily increase with TiO_2 concentration (Fig. 7). As more TiO_2 was present in the reactor, the fouling cake was expected to become thicker and to have higher density due to a possible compaction effect (Lee *et al.* 2007). However, this direct dependence was noted to discontinue after TiO_2 concentration exceeded 0.6 g/L. Despite the significant increase in TiO_2 concentration from 0.6 to 3 g/L, the R_f values remained relatively constant at $7.0 \pm 0.2 \times 10^{11}$ m^{-1}. As the filter cake was the result of the synergetic interaction between both catalyst particles and organic substrates (Lee *et al.* 2007), a sole increase of TiO_2 dosage above 0.6 g/L, without any simultaneous change in the amount of organic foulant, was believed to be no longer effective in further impacting the overall membrane fouling.

3.4 Effect of initial TOC concentration

Photocatalytic efficacy is known to be highly dependent on initial substrate concentration (Chin *et al.* 2007, Fu *et al.* 2006, Uyguner and Bekbolet 2005). In this section, the effects of initial TOC concentration on the performance of the SMPR were investigated. HA powder was dissolved in de-ionized water to yield a range of TOC concentrations between 5 and 50 mg/L (a total of 4 different experiments). TiO_2 concentration was maintained at 0.5±0.05 g/L, and PP membranes were used during the 150-min-long experiments.

Table 1 Effect of initial TOC concentration on TOC degradation rate and fouling resistance (R_f); membrane = 0.22 μm PP, $[TiO_2] = 0.5$ g/L, HA solution filtered for 150 min

Initial TOC concentration (mg/L)	TOC degradation rate (mg/[L.min])	R_f ($\times 10^{11}$ m^{-1})
5	0.023	1.00
10	0.055	1.98
20	0.082	2.33
50	0.192	4.76

Table 1 highlights the dependence of TOC degradation rate and R_f on the initial TOC concentration. TOC degradation rate, calculated by dividing ($TOC_{feed} - TOC_{perm}$) with experimental duration, was observed to increase with rising initial TOC concentration. This is in agreement with Li *et al.* (2002) who reported photocatalytic efficiency to increase with higher initial HA concentration. Increasing level of reactants was anticipated to result in a higher photocatalytic rate as it lead to more frequent collisions between the organic molecules and the catalyst particles, subsequently enhancing the adsorption process. However, since the system was operated under constant conditions, one of its operating parameters (TiO_2 concentration or UV intensity) was expected to eventually limit its overall capacity for organic destruction. For this reason, it was believed that, had a greater range of initial TOC concentration been experimented, a constant TOC degradation rate would eventually be obtained.

Considering the high fouling propensity of HA molecules (Ho and Zydney 2000, Yuan *et al.* 2002), it was expected for the R_f values to increase for higher initial TOC concentrations (Table 1). Higher HA concentration was believed to result in a higher concentration of organic laden particles and in the formation of a denser cake layer.

3.5 Effect of pollutant characteristics

Pollutant characteristics are known to strongly influence the performance of a photocatalytic system (Chen and Jenq 1998, Le-Clech *et al.* 2006, Yang and Lee 2006). In this section, the process efficiency assessment was carried out with two types of feed water (surface water from the Woronora dam and HA model solution, both with TOC concentration of 10±0.5 mg/L). Although both feed waters contained humic substances as their primary components, they featured different compositions of organic contaminants, as reported in the LC-OCD spectra (Fig. 8). The model solution constituted mainly of HA macromolecules and derivates (low-molecular-weight or LMW acids and neutrals), while the surface water was composed of a wider range of compounds (especially some larger biopolymeric substances at retention time of 30 min). While LC-OCD analysis of surface water revealed a typical humic acid peak (elution time around 45 min), the HA model solution appeared to be also composed of larger compounds (elution time at 40 min), indicating the presence of FA together with HA macromolecules. In this comparative study, TiO_2 concentration was maintained at 0.5±0.05 g/L, and all experiments, based on the use of PP membrane, lasted 60 min.

During the treatment of the Woronora water by UV photolysis and filtration, a modest E_{ff} value of 22% was obtained (Fig. 9), which contrasted with the results obtained previously in our group (Le-Clech *et al.* 2006). In this early study, high TOC removal efficiency of up to 70% was reported. Although both studies were based on the treatment of the Woronora water, the E_{ff} discrepancy can be explained by the more superior level of UV illumination used in the early paper (75 W lamp

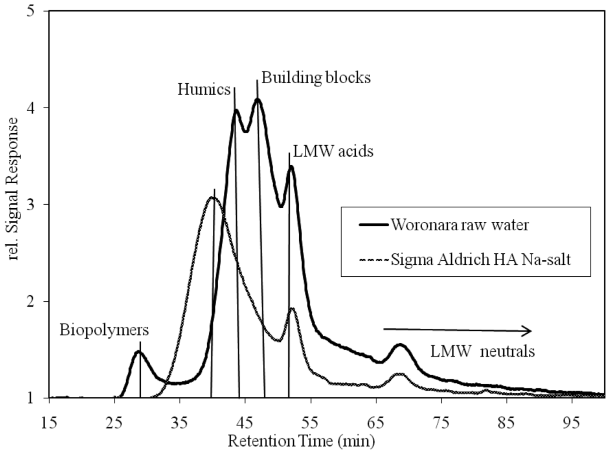

Fig. 8 LC-OCD spectra obtained for Woronora water and synthetic humic acid model solution

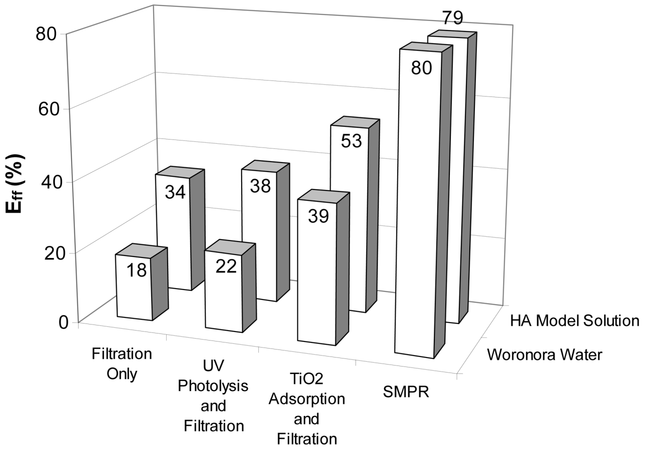

Fig. 9 Effect of pollutant characteristics on organic removal efficiency (E_{ff}); membrane = 0.22 μm PP, filtration for 60 min When used, $[TiO_2] = 0.5$ g/L

with peak emission at 254 nm). UV lamp with lower peak emission wavelength radiates photons with higher energy level and enables a more rapid transition of the photocatalyst electrons from valence band to conduction band (Chin *et al.* 2006), resulting in a higher photocatalytic rate (and higher E_{ff}). These results highlight the importance of UV illumination configuration in influencing the performance of the hybrid process.

The relative role TiO_2 adsorption in TOC removal was also assessed by comparing the E_{ff} values obtained during the filtration-only and the TiO_2-adsorption-and-filtration experiments (Fig. 9). For Woronora water, the 21% TOC removal by adsorption on TiO_2 calculated in this study correlated well with those reported in earlier work (about 20% in Le-Clech *et al.* 2006). These values were lower to those reported by Huang *et al.* (2008) who calculated 50% organic removal when Suwannee river extract was mixed with TiO_2. The difference between these results probably originates from the nature of the water sources (*i.e.*, organic characteristics).

The significance of influent characteristics was further demonstrated in this study, when the relative roles of the individual processes involved in the SMPR were compared for the HA model solution and the Woronora water. The various treatments applied to the HA model solution (filtration only, UV photolysis and filtration, and TiO_2 adsorption and filtration) generally resulted in higher E_{ff} values. Given the lower rejection of organics during the filtration-only experiments based on the Woronora water (18% against 34% for HA model solution), it can be deduced that the organic components from this surface water featured a smaller average size than the HA macromolecules in the model solution. This was confirmed with the LC-OCD results, which revealed a HA average size of 516 and 913g/mol for the Woronora and the HA model solutions respectively.

Despite the difference in composition, both waters were treated similarly when the complete SMPR was operated (with E_{ff} around 80%). Therefore, it can be concluded that, although the Woronora water constituents were less vulnerable to individual removal processes (*i.e.*, UV photolysis and TiO_2 adsorption), both waters consisted of organic components which were equally susceptible to the overall photocatalytic degradation.

Composition of humic components can vary significantly from one local source to another (Lee *et al.* 2007) and results obtained from model solution can rarely predict the behaviour of these real waters (Ho *et al.* 2009). Therefore, if the hybrid system is to be used for treatment of humic substances in surface water, optimum design of the SMPR may require to be catered specifically for each water source.

When comparing the membrane hydraulic performances of SMPR process and its components for both feed waters, it can be observed that the R_f values obtained from experiments using Woronora water (filtration only = 4.40×10^{11}, UV photolysis and filtration = 4.20×10^{11}, TiO_2 adsorption and filtration = 5.53×10^{11}, SMPR = 3.54×10^{11} m^{-1}) were generally twice higher than the corresponding values from HA model solution (PP membrane in Fig. 5). Such discrepancies further highlight the significance of pollutant characteristics on the performance of the hybrid photocatalytic/membrane system. Huang *et al.* (2008) mentioned that hydrophobic organic components, such as HA and FA, tend to be more resistant to catalyst-surface adsorption and more aggressive in fouling ultrafiltration membrane when evaluated against their hydrophilic counterparts. Compared to the HA solution, the surface water resulted in lower E_{ff} for adsorption experiment and higher R_f for filtration-only. It can be deduced that the surface water featured higher fraction of hydrophobic organic molecules than those of the HA solution.

4. Conclusions

In this study, the hybrid process coupling TiO_2-mediated UV photocatalysis with submerged membrane separation was shown to be an effective treatment process for humic substances through assessment of both organic removal efficiency (E_{ff}) and membrane fouling resistance (R_f). Once optimised, the process managed to remove up to 83% of polluting humic organics while still maintaining modest R_f values. Rate of organic removal was observed to decrease with experimental time, while a majority of membrane fouling seemed to occur at the beginning of each photocatalytic run. Both phenomena validated the SMPR's rapidity and selectivity in removing HA fractions. When the relative effect of individual components featuring in the SMPR process was evaluated, UV-photolysis only was found to be ineffective in removing humic organics (E_{ff}<10% for HA solution), while TiO_2 adsorption resulted in high R_f (2.99×10^{11} m^{-1} for HA solution and PP membrane) due to the formation of a dense fouling layer by TiO_2-and-HA-laden particles. Experimental results suggested an optimum TiO_2 concentration at 0.6 g/L for HA removal ($E_{ff} = 83\%$) while R_f values seemed to increase with rising TiO_2 concentration. Increasing initial HA concentration was found to increase both TOC degradation rate and R_f values. Both organic removal and membrane fouling resistance seemed to be highly dependent on specific pollutant characteristics, which changed significantly from one source to another. In this study, HA model solution was found to be more susceptible to the SMPR treatments than surface water obtained from local catchment.

Results from this study indicate the potential use of the SMPR as a viable polishing step to supplement a water treatment system for humic substances removal. However, fundamental operational variables, such as acclimatisation periods, life time and solid retention time of the photocatalyst, effects of waters sources and characteristics, are still largely unknown and will need to be thoroughly investigated before the process can be retrofitted to an industrial scale.

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