1 Title:

2 **Application of Nano TiO₂ modified hollow fiber membranes in algal membrane bioreactors**
3 **for high-density algae cultivation and wastewater polishing**

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Abstract Polyvinylidene fluoride (PVDF) hollow fiber membranes with nano-TiO₂ (5% of PVDF by mass, average size = 25 nm) additives were fabricated and applied for high-density algae (*Chlorella Vulgaris*) cultivation. At the average light intensity of 121 $\mu\text{mol}/\text{m}^2/\text{s}$, the algal membrane bioreactors (A-MBR) operated at a hydraulic retention time of 0.5 d and an average solids retention time of 25 d had an average algae biomass concentration of $2,350 \pm 74$ mg/L (in COD units) and algal biomass production rate of 6.5 ± 0.1 g/m²/d. The A-MBRs removed an average of 78% of phosphorus from the wastewater at the initial total phosphorus concentrations ranging from 3.5 to 8.6 mg/L. The nano TiO₂-embedded membranes had improved surface hydrophilicity with its total resistance about 50% lower than that of the control. This study demonstrated that PVDF/TiO₂ nanocomposite membranes had a better antifouling property for high-density algae cultivation and wastewater polishing.

Keywords: nano TiO₂; membrane fabrication; membrane bioreactor; high-density algae cultivation; wastewater polishing

1. Introduction

Integrating algae cultivation with wastewater treatment is promising for renewable energy production and beneficial to environmental sustainability. Wastewater contains nutrients such as NH_4^+ , NO_3^- , and PO_4^{3-} that are essential to algal growth. Since the early study of microalgae for wastewater treatment, many algal species have been found to effectively grow in wastewater while removing nutrients simultaneously (Abou-Shanab et al., 2013; Chong et al., 2000). One of the commonly used algae-based wastewater treatment systems is high-rate algal ponds (HRAP), which are shallow, open raceway ponds that facilitate algal growth. Problems associated with the harvest of algae from HRAPs include: (1) low biomass concentrations in the HRAP systems (around 500 g/m^3) and (2) small cell size ($5\text{-}20 \mu\text{m}$) and lack of floc structure of the algal mixed liquor (Molina Grima et al., 2003). Various harvesting methods including centrifugation, sedimentation, air flotation assisted with chemical flocculation have been developed for algal biomass harvesting (Brennan & Owende, 2010). However, these methods are still costly for large-scale applications.

Membrane technology has advantages over conventional cultivation and biomass separation methods for algae cultivation. First of all, high-density algae cultivation becomes possible through membrane bioreactor (MBR) operation. Second, membrane filtration does not require the addition of chemicals such as coagulants, thereby simplifying biomass processing and facilitating water reuse after filtration (Ríos et al., 2012). Third, membrane filtration can achieve better biomass recovery without causing significant damage to cell structure. Finally, when compared to the conventional dewatering methods, membrane filtration is a relatively lower-energy consuming process for algae harvesting.

While MBR has numerous advantages over conventional algal cultivation and biomass separation methods, membrane fouling is one major drawback limiting its use. Membrane fouling is a complex phenomenon when solute or particles deposit on membrane surfaces or inside membrane pores resulting in a decrease in membrane performance. In MBR systems, a number of fouling factors have been identified affecting membrane filtration, including membrane materials, biomass characteristics, feeding water characteristics, and operating conditions. The interactions among all these factors and their impact on membrane fouling are complex. Membranes made of polyethersulfone (PES), polysulfone (PSF) and polyvinylidene fluoride (PVDF) are widely used in filtration due to their good physical and chemical stability as well as excellent membrane formation characteristics. However, they are prone to fouling because of their hydrophobic nature, as hydrophobic interaction between solutes or microbial cells and membrane materials is considered one of the predominant fouling mechanisms (Maximous et al., 2009). A common strategy to mitigate membrane fouling is to modify membrane surface to increase hydrophilicity. Accordingly, many methods have been developed including surface coating (Madaeni & Ghaemi, 2007), plasma treatment (Kim et al., 2011), and nanomaterial incorporation (Yin et al., 2013b). For example, Madaeni and Ghaemi coated TiO₂ particles on poly vinyl alcohol (PVA) top layer of the reverse osmosis membrane, thus introducing self-cleaning mechanism under UV irradiation to minimize fouling. New PSF hollow fiber membranes (HFMs) have been successfully developed through blending with multi-walled carbon nanotubes (MWNTs) resulting in enhanced surface hydrophilicity, water flux, and antifouling properties (Yin et al., 2013b). Many other nanomaterials including zeolites, nano-

silica, and nanosilver have also been integrated in membrane structure to reduce membrane fouling (Yin et al., 2013a).

TiO₂ photocatalysis has been studied for a variety of applications and products including air and water pollution control systems and self-cleaning surfaces (Martínez et al., 2013; Yamada et al., 2013). Due to their hydrophilic characteristics and high specific surface area, the incorporation of nano-TiO₂ increases the hydrophilicity of membranes, thus reducing fouling and increasing the permeate flux (Emadzadeh et al., 2014; Moghimifar et al., 2014).

In this research, PVDF was used as the base membrane material due to its excellent chemical, thermal stability and mechanical strength (Lai et al., 2014). The objectives of this research were to determine the antifouling property of the nano-TiO₂ incorporated PVDF membranes (labeled as PVDF/TiO₂ nanocomposite membranes hereafter) and evaluate the overall performance of the algal MBRs (A-MBRs) for high-density algae cultivation and wastewater treatment/polishing.

2. Materials and Methods

2.1. Membrane fabrication materials

PVDF with an average molecular weight of 180,000 Dalton (Sigma-Aldrich, Saint Louis, MO) was used for membrane fabrication. Polyvinylpyrrolidone (PVP 10,000 Da, Sigma Aldrich) was used as an additive to increase hydrophilicity and porosity of PVDF membrane. The commercially available nanoTiO₂ (AEROXIDE TiO₂ P25) (EVONIK Industries, AG, Germany) with an average primary particle size of 25 nm and specific surface area (BET) of $50 \pm 15 \text{ m}^2/\text{g}$ was used as a nanofiller. In addition, N-Methyl-2-pyrrolidone (NMP, anhydrous, 99.5%, Sigma

Aldrich) was used as a solvent in membrane fabrication because PVDF has high solubility in NMP and NMP/PVDF has high mutual affinity to promote mixing.

2.2. Fabrication of PVDF and PVDF/TiO₂ nanocomposite membranes

The PVDF hollow fiber membranes were fabricated by the phase inversion method on a custom-designed single-head spinning machine based on our previous work (Yin et al., 2013b). The casting solution for PVDF HFMs fabrication was prepared as follows: PVDF (3.2 g) and PVP (1 g) were added into NMP (15.8 g) in a closed glass bottle. The solution was then magnetically stirred at 60 °C for 6 h. The casting solution was kept quiescent for 8 h to eliminate bubbles in the solution before it was delivered with nitrogen gas at a pressure of 35 psi, with concurrent delivery of DI water as bore liquid at a flow rate of 0.8 mL/min. Both casting solution and bore liquid flowed simultaneously through a spinneret with an outer diameter (OD) of 1.0 mm and inner diameter (ID) of 0.6 mm. Coagulation occurred when the nascent fiber was immersed in a coagulation bath with tap water as a coagulant. The fibers were later collected by a spinning wheel collector, rinsed with DI water for 2 h and cut into lengths of 30 cm for membrane module fabrication. During the fabrication of PVDF/TiO₂ membranes, nano TiO₂ (0.16 g) was dispersed in NMP solvent and ultrasonicated for 1 h to achieve dispersion before the PVDF and PVP were added to the NMP/TiO₂ mixture. The other steps were the same as that of PVDF membrane fabrication. Detailed parameters of membrane fabrication are listed in Table 1. Both PVDF and PVDF/TiO₂ HFMs were built into submerged modules (Supporting information, SI, Figure S1). Each module was made with 40 HFM strains with a total surface area of 352 cm².

Table 1.

Hydrophilicity of membrane was determined by measuring the pure water contact angle based on the sessile drop method. A video contact angle system (VCA-2500 XE, AST products, Billerica, MA) was employed to perform the test. At least eight stabilized contact angles from different sites of each sample were obtained to calculate the average contact angle and standard deviation.

A low pressure cross-flow filtration system (pressure range: 0–50 psi) developed in our previous work (Yin et al., 2013b) was used to evaluate pure water flux. The membrane module was sealed by epoxy resin, with an effective membrane area of around 50 cm². Prior to the test, membrane was compressed by DI water at a constant transmembrane pressure (TMP) of 15 psi for 3h. Pure water flux was measured by weighing the permeate water as a function of time at a fixed TMP, and recorded by a LabVIEW automated system (National Instruments LabVIEW 8.2 with Ohaus digital balance).

2.3. Algal seeding, MBR operation and monitoring

Pure algal species *Chlorella vulgaris* (Carolina Biological Supply Company, Burlington, NC) was selected for high-density algae cultivation. *Chlorella vulgaris* was selected because it is one of the fastest growing mixotrophic algae, and is a promising species for wastewater treatment and biofuel production (Beuckels et al., 2013). *Chlorella vulgaris* was cultivated aseptically in Bold's Basal Medium, which consisted of the following components per liter of water: 0.25 g NaNO₃, 0.025 g CaCl₂·2H₂O, 0.05 g MgSO₄·7H₂O, 0.10 g K₂HPO₄, 0.15 g KH₂PO₄, 0.025 g NaCl, and trace metals including Zn, Mn, Mo, Cu, and Co. Algae were first cultured under

continuous photon irradiance ($85 \mu\text{mol m}^{-2} \text{s}^{-1}$) at $25 \pm 1^\circ\text{C}$ on a solid agar plate and later in a liquid medium before they were seeded in the A-MBRs.

Two bench-scale A-MBRs (SI, Figure S2) were operated in parallel at room temperature ($23 \pm 2^\circ\text{C}$) to study both the antifouling characteristics of PVDF/TiO₂ nanocomposite membranes and the wastewater treatment/polishing performance through high-density algae cultivation. Bioreactors were made of glass (thickness was 0.8 cm), and each had a total volume of 4 L. Both bioreactors were operated at a hydraulic retention time (HRT) of 0.5 d and an average solids retention time (SRT) of 25 d through daily wasting of the mixed liquor in the A-MBR.

Each A-MBR was equipped with one PVDF module and one PVDF/TiO₂ membrane module. Continuous light exposure was provided for algal growth by placing two 40W T12 fluorescent light bulbs (Utilitech #0420865) on the front and back sides of the bioreactor, resulting in an average light intensity of $121 \mu\text{mol/m}^2/\text{s}$ measured at the surface of water by a light meter (LI-250A, Biosciences, Lincoln, NE). The algal mixed liquor in each bioreactor was well mixed through magnetic mixing at 600 rpm while intermittent air bubbling (on and off, cycling every 6 h) was provided by an air pump at 40 L/min for membrane fouling control. The mixed liquor volume in the A-MBR was maintained almost constant (with less than 5% volume change) by operating a permeate (effluent) pump through the control by upper and lower water level sensors (Cole-Palmer, Vernon Hills, Illinois). The permeate pumps (Masterflex peristaltic pumps) were operated intermittently by setting permeate/effluent flow rate to two times of the influent flow rate. All the pumps were set at a constant flux ($9.8 \pm 0.5 \times 10^{-6} \text{ m/s}$) throughout the MBR operation period. Digital pressure gauges were installed to measure the daily change in TMP as

indicator for determining fouling potential at a constant membrane permeate flux. The TMP was measured three times every day during pumping cycle.

Each A-MBR was operated as a continuous stirred tank reactor (CSTR) and it was fed with the same synthetic wastewater containing the following chemical components (in mM): NaNO₃ (0.16-0.07), NaCl (0.43), NaHCO₃ (1), MgSO₄ (0.3), CaCl₂·2H₂O (0.17), K₂HPO₄ (0.04-0.09), EDTA disodium salt dehydrate (0.01), and trace metals including Fe, Mn, Mo, Cu, Zn and Ni (Xu et al., 2014). K₂HPO₄ and NaNO₃ were used as phosphorus and nitrogen sources, respectively, with the concentrations of P and N varying in the feed to study the nutrient removal efficiency at different nutrient concentrations. Permeate water samples were collected three times every day for water quality measurement.

2.4. Membrane resistance measurement and fouling control

A relationship between permeate flux (J, m/s), TMP (N/m²), liquid viscosity (η , N s/m²) and total membrane resistance (R_t, 1/m) can be expressed in the following equation:

$$J = TMP / (\eta \times R_t) \quad (1)$$

The resistance in series model was applied to determine each resistance component contributing to the total membrane resistance as follows:

$$R_t = R_m + R_c + R_f \quad (2)$$

Where R_m is intrinsic membrane resistance, R_c is cake resistance due to cake layer formation, and R_f is irreversible fouling resistance caused by irreversible adsorption and pore plugging. R_m and R_t were calculated from the filtration of DI water with a new membrane before MBR

operation and from the filtration of algal mixed liquor at the end of the A-MBR operation, respectively. R_c were calculated from the difference between R_t and $R_m + R_f$ while $R_m + R_f$ was determined by filtering DI water through the A-MBR membrane after removing cake resistance through membrane cleaning.

At the completion of A-MBR study that lasted for about 110 d, one of the PVDF and PVDF/TiO₂ membranes were taken out of the MBRs for cleaning. Membrane cleaning was conducted following the procedure described elsewhere (Lim & Bai, 2003). Briefly, the membrane module was first rinsed and washed with tap water. Then it was submerged in a 0.05% sodium hypochlorite solution for 12 h. After rinsing with tap water, the module was soaked in 1 M HNO₃ for 12 h and rinsed with tap water again before analysis by scanning electron microscopy (SEM).

2.5. Membrane analysis by SEM/EDS

SEM was conducted on Quanta FEG 600 (FEI Company, Hillsboro, OR) to evaluate the change in the surface morphology of both PVDF and PVDF/TiO₂ membranes before and after membrane cleaning. To study the compositions of chemical aggregates on the membrane surface, energy dispersive X-ray spectroscopy (EDS) was conducted at specific aggregates through the use of Quanta FEG 600 (FEI Company, Hillsboro, OR).

2.6. A-MBR performance monitoring and statistical analysis

The influent and effluent water quality parameters, such as ammonia-N, nitrate-N, nitrite-N, orthophosphate-P, and COD concentrations were determined following the standard methods

(APHA, 2005). The pH of algal mixed liquid was monitored once a week. Algal biomass concentration was measured in COD units. One-way ANOVA analysis was conducted to assess the significance of the difference among groups, with $p < 0.05$ indicating statistical significance.

3. Results and Discussion

3.1. Nano TiO₂ modified PVDF membranes with consistently lower membrane resistance

Figure 1 shows that PVDF/TiO₂ nanocomposite membranes had consistently lower membrane resistance than PVDF membranes during more than 110 d of A-MBR operation. On average, the total resistance of the PVDF/TiO₂ membranes was $49 \pm 6\%$ lower than that of PVDF membranes, which was attributed to improved surface hydrophilicity after incorporating nano TiO₂ into PVDF membranes, as the contact angle of membrane surface decreased from $54.4 \pm 2.0^\circ$ to $46.0 \pm 1.1^\circ$. At the same time, the pure water flux of the PVDF/TiO₂ membranes increased from $106 \pm 4 \text{ L/m}^2 \text{ h}$ to $134 \pm 3 \text{ L/m}^2 \text{ h}$ at the TMP of 6 psi (Figure 2), which could be caused by the combined effects of enhanced surface hydrophilicity and increased membrane porosity after embedding nano TiO₂ (Razmjou et al., 2011).

Figure 1.

Figure 2.

Consistently, the intrinsic membrane resistances (R_m) for the PVDF and PVDF/TiO₂ membranes were $(5.8 \pm 0.2) \times 10^8 \text{ m}^{-1}$ and $(2.5 \pm 0.5) \times 10^8 \text{ m}^{-1}$, respectively. As also shown in Table 2, the cake resistance (R_c) values for the PVDF and PVDF/TiO₂ membranes were 1.3×10^8 and $0.7 \times 10^8 \text{ m}^{-1}$, respectively, suggesting that less than 20% of the total membrane resistance was removed after membrane cleaning. This could be due to the fact that both types of membranes were not severely fouled even after 110 d of operation. The irreversible fouling resistance (R_f) of

the PVDF/TiO₂ membrane was $1.8 \times 10^8 \text{ m}^{-1}$, higher than that of the PVDF ($0.8 \times 10^8 \text{ m}^{-1}$). This is probably because back flushing was not included in the membrane cleaning process, and irreversible fouling inside membrane was not recovered. .

Table 2.

By looking at the trend of membrane resistance profiles, both PVDF and PVDF/TiO₂ membranes had a rapid increase in total resistance at the beginning (from day 1 to day 20) of the operation. Such a fouling trend was consistent with previous studies (Cosenza et al., 2013), which was attributed to membrane pore clogging or cake layer formation (Wu et al., 2012). The membrane resistance started to drop from day 20 and remained relatively stable thereafter. The reason for the decrease in membrane resistance was probably linked to the floc formation of algae species as a result of the invasion of filamentous species in the A-MBRs (SI, Figure S3).

3.2. Membrane characterization by SEM and EDS

SEM analysis demonstrated that both PVDF/TiO₂ and PVDF membranes had very smooth and uniform membrane surface (Figure 3a and b) prior to their use in the A-MBRs. After more than 110 d of operation in the A-MBRs, there were visible deposits of microbes including *Chlorella vulgaris* and filamentous species, cell debris on both PVDF and PVDF/TiO₂ membrane surface, with less deposits on the PVDF/TiO₂ membrane (Figure 3c). As shown in Figure 3e and f, even after rigorous cleaning procedures (bleaching with sodium hypochlorite and acid cleaning), some aggregates still deposited on the membrane surface. The EDS result showed the existence of a variety of elements such as phosphorus, calcium, and iron, suggesting the formation of mineral foulants as a result of chemical precipitation due to the pH increase (from initial pH = 7.5 ± 0.1 to final pH = 8.5 ± 0.5) associated with algal photosynthesis. The result was consistent with

previous studies showing that the existence of a number of cations and anions such as Ca^{2+} , Mg^{2+} , Al^{3+} , Fe^{3+} , CO_3^{2-} , PO_4^{3-} and OH^- , and their high concentrations are mainly responsible for inorganic fouling, which is not easily recovered even after chemical cleaning (Shirazi et al., 2010).

Figure 3.

3.3. High-density algae cultivation

The A-MBRs were seeded with *Chlorella Vulgaris* at the initial algal biomass concentration of about 800 mg/L (in COD units). The biomass concentration gradually increased to 1,500 mg/L after about 30 d of operation at a target SRT of 25 d (Figure 4). The increase in biomass concentration was accelerated thereafter, probably due to the invasion of filamentous phototrophic species around day 20. Starting from day 40, the algal biomass concentrations were maintained at an average of $2,300 \pm 66$ mg/L and $2,328 \pm 75$ mg/L for the A-MBRs #1 and #2, respectively. The relatively constant biomass concentration conditions were achieved after around three SRTs (or 75 d) of operation. At the light intensity of $121 \mu\text{mol}/\text{m}^2/\text{s}$, the A-MBRs had an average algal biomass production rate of 6.5 ± 0.1 g/m²/d. The pH in the tank increased from initially 7.5 ± 0.1 to 8.5 ± 0.5 under steady-state operations.

Figure 4.

3.4. Nutrient removal by algae in A-MBRs

As the influent NO_3^- -N concentrations ranging from 4 to 11 mg/L (Figure 5), the average removal efficiency for the A-MBRs was 34%. As NO_3^- -N removal by algae relies on N uptake via cell assimilation and thereafter biomass wasting (Xu et al., 2014), it is not surprising that the N removal in such A-MBRs was low due to long SRT (25 d) operation. For comparison, the high-density algae cultivation resulted in good P removal, with an average removal efficiency of

78% at the influent phosphorus concentrations ranging from 4 to 9 mg/L (Figure 6). P can be removed by algae through a combination of adsorption and algae-induced chemical precipitation (Sañudo-Wilhelmy et al., 2004). High-density algal cultivation facilitates phosphate adsorption/coprecipitation resulting in improved P removal from wastewater (Xu et al., 2014).

Figure 5.

Figure 6.

Nano-toxicity of TiO₂ on algae has been studied. While some studies claimed that nano-TiO₂ has no detrimental effect on algal growth (Kulacki & Cardinale, 2012; Velzeboer et al., 2008), others have shown that nano-TiO₂ could inhibit algal growth rate due to the production of reactive oxygen species (ROS) (Ji et al., 2011; Li et al., 2015). The light source provided in this experiment had a wavelength range between 390 nm and 740 nm (SI, Figure S4), which was not suitable to active TiO₂ (Henderson, 2011; Li et al., 2006) for ROS generation. Further studies are needed to determine the influence of PVDF/TiO₂ on algal growth under sunlight.

3.5. Invasion of filamentous species during A-MBR operation and associated change in biomass settling property

Since the A-MBR was an open system, invasion of other phototrophs was observed around day 20 (presumably from tap water used in feed preparation). While *Chlorella Vulgaris* is a spherical, unicellular algae species with cell size around 5 µm (SI, Figure S3), filamentous species which had an average width of 5 µm and length over 100 µm were also observed. However, unlike in the MBR activated sludge systems where aggressive membrane fouling was associated with filamentous bacterial growth (Kim et al., 2007), *Chlorella Vulgaris* appeared to be dominant in high-density algae cultivation and the growth of the filamentous phototrophic species facilitated

biomass aggregation by forming floc-like structures (SI, Figure S3). Indeed, the invasion of filamentous species improved the algal settling properties as SI Figure S5 shows complete sedimentation of well-mixed algal biomass occurred in 100 s. Compared to a typical algal settling velocity ranging from 0.1 to 2.6 cm/h, the algal settling rate in the A-MBRs increased dramatically to about 360 cm/h.

3.6. Significance of PVDF/TiO₂ nanocomposite membrane and its application in high-density algal cultivation for nutrient removal

Membrane modification to increase membrane hydrophilicity generally results in better antifouling property (Liu et al., 2011). In this study, the improved PVDF/TiO₂ membrane property was attributed to the higher hydrophilicity of the membrane surface. It has been reported that TiO₂ surfaces become superhydrophilic with a contact angle of less than 5° under UV-light irradiation (Nakata & Fujishima, 2012). However, considering the potential toxicity of TiO₂ nanoparticles to algae, the influence of PVDF/TiO₂ membranes on algal growth under sunlight remains to be investigated.

High-density algae cultivation in the A-MBR systems is overall successfully demonstrated here for wastewater polishing, nutrient removal and algal biomass production. The A-MBR systems using PVDF/TiO₂ membranes also demonstrate excellent performance with lower membrane fouling. Further improvement in nutrient removal is possible through tank-in-series design and operation at lower SRTs for wastewater polishing and water reuse applications.

Open cultivation systems can be easily contaminated by other phototrophic species (Markou & Georgakakis, 2011). In this study, the presence of filamentous species assisted floc formation resulting in better algal biomass settling. Furthermore, formation of larger biomass flocs could reduce the tendency for algal cells to deposit onto the membrane surface thus reducing membrane fouling, as indicated by the decrease in membrane resistance from day 20 onwards (Figure 1). This finding shows the potential of culturing mixed phototrophic species including filamentous algal species to achieve good nutrient removal and settling property simultaneously. For large-scale applications (e.g., secondary wastewater polishing), some key factors such as the exposure of algae to ambient environment, a proper range of SRT, the composition of treated wastewater, and the interactions between algae and bacteria (including cyanobacteria) need to be investigated further.

4. Conclusions

PVDF/TiO₂ nanocomposite hollow fiber membranes were successfully developed with their total resistance 49 ± 6% lower than that of the control (PVDF membrane) in A-MBR operation. This study demonstrated that PVDF/TiO₂ nanocomposite membranes with low fouling property are promising for use in A-MBRs for wastewater polishing and nutrient removal. At an average SRT of 25 days, the A-MBR systems maintained a constant algal biomass concentration around 2,350 ± 74 mg/L COD while removing nutrients from wastewater. The average P and N removal efficiencies were 78% and 34%, respectively.

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Table 1. Membrane fabrication parameters

Spinneret OD/ID	1.0 mm/ 0.6 mm
Spinneret temperature (°C)	25
Spinning solution	PVDF/PVP/NMP
Concentration (wt%)	16/5/79%
TiO ₂ concentration (wt%)	5%
Membrane pore size (nm)	20
Dope solution flow rate (mL/min)	1.2
Bore fluid composition	DI water
Bore fluid flow rate (mL/min)	0.8
Range of air-gap distance (cm)	0
Coagulant	Tap water
Coagulant temperature (°C)	25
Washing bath	Tap water
Washing bath temperature (°C)	25
Take-up speed (cm/min)	450

Table 2. Membrane resistance

Module	R_t (m⁻¹)	$R_m + R_f$ (m⁻¹)	R_m (m⁻¹)	R_c (m⁻¹)	R_f (m⁻¹)
PVDF	7.9×10^8	6.6×10^8	5.8×10^8	1.3×10^8	2.1×10^8
PVDF/TiO₂	5.1×10^8	4.3×10^8	2.5×10^8	0.8×10^8	0.8×10^8

Figure Captions

Figure 1. Change in the total membrane resistance (R_t) of PVDF (●) and PVDF/TiO₂ membranes (○) with time during the study period. Errors bars indicate the standard deviation from the mean of triplicate samples.

Figure 2. Pure water flux of PVDF/TiO₂ and PVDF membranes as a function of transmembrane pressure (TMP).

Figure 3. SEM images of the surfaces of clean PVDF/TiO₂ (a) and PVDF HFMs (b); fouled PVDF/TiO₂ (c) and PVDF HFMs (d) (taken after 110 days of operation); chemically cleaned PVDF/TiO₂ (e) and PVDF HFMs (f). The inserted images at the top-right corner are membrane structure at lower magnifications.

Figure 4. Change in the biomass concentration (in COD units) with operating time in A-MBRs: #1 (●), and #2 (○) for high-density algae cultivation. Errors bars indicate the standard deviations of the mean from triplicate samples.

Figure 5. Influent (▲) and effluent NO₃⁻-N concentrations in the A-MBR #1 (●), and #2 (○) during the study period. Errors bars indicate the standard deviations from the means of triplicate samples.

Figure 6. Influent (▲) and effluent phosphorus concentrations in the A-MBR #1 (●) and #2 (○) during the study period. Errors bars indicate the standard deviations from the means of triplicate samples.

Figure 1.

Figure 2.

Figure 3.

Figure 4.

Figure 5.

Figure 6.