A controlled wet-spinning and dip-coating process for preparation of high-permeable TiO₂ hollow fiber membranes

Qi Zhang, Hua Wang, Xinfei Fan, Shuo Chen, Hongtao Yu and Xie Quan

ABSTRACT

In order to improve the permeate flux of photocatalytic membranes, we present an approach for coupling TiO₂ with ceramic hollow fiber membranes. The ceramic hollow fiber membranes with high permeate flux were fabricated by a controlled wet-spinning process using polyethersulfone (PESf) and ceramic powder as precursors and 1-methyl-2-pyrrolidinone as solvent, and the subsequent TiO₂ coating was performed by a dip-coating process using tetra-n-butyl titanate as precursor. It has been found that the PESf/ceramic powder ratio could influence the structure of the membranes. Here the as-prepared TiO₂ hollow fiber membranes had a pure water flux of 4,450 L/(m²·h). The performance of the TiO₂ hollow fiber membrane was evaluated using humic acid (HA) as a test substance. The results demonstrated that this membrane exhibited a higher permeate flux under UV irradiation than in the dark and the HA removal efficiency was enhanced. The approach described here provides an operable route to the development of high-permeable photocatalytic membranes for water treatment.

Key words | hollow fiber membrane, permeate flux, photocatalysis, TiO₂

INTRODUCTION

Fresh water resources available on earth account for only about 0.26% of the total water resources. Unfortunately, part of the surface water has been polluted by the drainage of industrial wastewater, the emissions of an agricultural nonpoint source, or the discharge of domestic sewage effluent (Sujaul et al. 2013; Miao et al. 2015; Schreiber et al. 2015). Recently, TiO₂ photocatalysis has attracted great interest because it is environment-friendly and provides a promising pathway for potential applications in breaking down many kinds of organic pollutants, such as persistent toxic substances, dyes, pesticides, and herbicides under UV light irradiation. (Hoffmann et al. 1995; Chen & Mao 2007; Yu et al. 2009a, b; Chong et al. 2010). However, there are issues with TiO₂ photocatalysis involving the recycling and reuse of the TiO₂; these are inherent drawbacks that restrict practical application of this technology (Yu et al. 2001; Zhang et al. 2006).

Membrane separation achieves the separation, purification, and concentration of different components by using membrane selectivity; this has the advantages of high efficiency, energy savings, and convenient operation (Molinari et al. 2002; Sholl & Johnson 2006). However, the traditional membrane has the drawback of rapid membrane fouling. Considering the advantages of combining TiO₂ photocatalysis and membrane separation, a TiO₂-based photocatalytic membrane has been proposed as a possible solution that would provide the dual functions of membrane separation and photocatalytic pollutant degradation concurrently (Choi et al. 2006; Zhang et al. 2006; Albu et al. 2007).

In particular, the photocatalysis function could greatly reduce membrane fouling. (Ma et al. 2009; Zhang et al. 2014).

Until now, most of the reported TiO₂-based photocatalytic membranes have been limited to single-channel tube membranes or flat sheet membranes (Wang et al. 2008; Ma et al. 2010), whose permeate flux is relatively low. Hollow fiber membranes with high specific surface area have shown more promise in increasing the permeate flux of membranes (Kingsbury & Li 2009; Yu et al. 2009a, b; Leo et al. 2011; Haworth et al. 2012; Wu et al. 2013; Fan et al. 2015). For instance, Razmjou et al. (2012) reported that the pure water flux of a TiO₂ nanoparticle-modified polyethersulfone ultrafiltration hollow fiber membrane was

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about 60 L/(m²·h). Zhang et al. (2014) reported that a nanostructured TiO₂ hollow fiber photocatalytic membrane exhibited the membrane flux of 87.7 L/(m²·h). Especially, a porous yttria-stabilized zirconia hollow fiber membrane, although without the photocatalytic property, has been reported to show a extremely high pure water permeate flux of 10.89 m³/(m²·h·bar) at a transmembrane pressure difference of 1.5 bar (Zhang et al. 2015). Motivated by this finding above, we expect that the permeate flux of TiO₂ hollow fiber membranes could still be enhanced by optimizing the hollow fiber formation process. Therefore, in the present work, the TiO₂ hollow fiber membrane was prepared by dry-jet wet-spinning and dip-coating, and the photocatalytic activity of this membrane was evaluated using humic acid (HA) as a test substance.

**MATERIALS AND METHODS**

**Chemicals and materials**

Ceramic powder and polyethersulfone (PESf) were provided by Shanghai Kaidu Industrial Development Co., Ltd. 1-Methyl-2-pyrrolidinone (NMP), tetra-n-butyl titanate ([CH₃(CH₂)₃O]₄Ti), ethanol (C₂H₅OH), and diethanolamine (NH(C₂H₄OH)₂) were obtained from Tianjin Fuyu Fine Chemical Co., Ltd. HA was provided by MP Biomedicals, Inc. (Eschwege, Germany).

**Preparation of ceramic hollow fiber membranes**

The ceramic hollow fiber membranes were fabricated by a dry-jet wet-spinning process. To prepare the dry-jet wet-spinning solution, the ceramic powder was added to the mixed solution of PESf and NMP; the ratio of PESf to ceramic powder was set at 13%, 14%, 17% and 20%, respectively. This mixture was continuously stirred for about 2 h. As shown in Figure 1, the spinning solution was then extruded using a tube-in-orifice spinneret (outer diameter = 750 μm and inner diameter = 510 μm) to form a hollow fiber; the air gap between the spinneret and the coagulation bath used for the spinning process was 20 mm. Either spinning dope or pure water was used as the bore fluid at a rate of 25 mL/min or 12 mL/min, respectively. To eliminate the influence of NMP, the as-prepared ceramic hollow fiber membranes were dipped in pure water for 24 h, and the phase inversion formed completely on the inner side of the ceramic hollow fiber membranes. Finally, the ceramic hollow fiber membranes were calcined at 1,200 °C for 2 h with a heating/cooling rate of 5 °C/min.

**Coating TiO₂**

The TiO₂ hollow fiber membranes were obtained by coating TiO₂ on the ceramic hollow fiber membranes using a dip-coating process. A TiO₂ colloidal solution was prepared by adding 17 mL of tetra-n-butyl titanate and 4.5 mL of diethanolamine to 67 mL of absolute ethyl alcohol, and continuously stirring for 2 h. Subsequently, a mixture of 10 mL anhydrous ethanol and 1 mL pure water was added, and continuously stirred for 1 h (Yu et al. 2001). A dip coater (SYDC-100, Shanghai SAN-YAN Technology Co., Ltd, China) was used for coating TiO₂ on the ceramic hollow fiber membranes. The dipping time was set to 15 min and the lifting speed was 1 mm/s. In this study, the impregnation of ceramic hollow fiber membranes with TiO₂ solution was repeated 5, 7 or 9 times. The final products were calcined at 500 °C for 2 h with a heating/cooling rate of 2 °C/min.

![Figure 1 | Schematic diagram of experimental set-up for controlled wet-spinning.](https://iwaponline.com/wst/article-pdf/73/4/725/463700/wst073040725.pdf)
Characterization

The morphology of the as-prepared products including ceramic hollow fiber membranes and TiO$_2$ hollow fiber membranes was characterized using a scanning electron microscope (SEM; Quanta 200 FEG). The crystallinity of the prepared samples was determined by X-ray diffraction (XRD) using a diffractometer with Cu K$_\alpha$ radiation (Shimadzu LabX XRD-6000). A three-point bending test performed on an Instron 5543 universal material testing machine was used to measure the mechanical strength of the TiO$_2$ hollow fiber membranes. In order to determine the flux of the membranes, one end of the membrane was sealed using silicone gel and the other end was connected to a permeate collector, which was connected to a vacuum pump. The absolute pressure at the mouth of the pump was 75 kPa as a driving force. The pure water flux of the TiO$_2$ hollow fiber membranes was measured without and with UV irradiation. A 300 W high-pressure mercury lamp was used as the UV light source with a principal wavelength of 365 nm. The incident UV light intensity was 1.5 mW/cm$^2$, which was measured by a radiometer (model UV-A). The flux of the hollow fiber membrane was calculated depending on the volume variation of the solution on the basis of the following equation (Zhang et al. 2014):

$$ J = \frac{V_0 - V_t}{A \times t} $$

Here, $J$ is the flux; $V_0$ is the initial volume of the feed solution; $V_t$ is the volume of the feed solution at time $t$; and $A$ is the membrane surface area. The porosity of hollow fiber membranes with different ratios of PES/f/ceramic powder is calculated based on the following equation:

$$ P = \frac{m_a - m_\beta}{\rho \pi (R^2 - r^2) L} $$

where $P$ is the porosity of the hollow fiber membranes; $m_a$ and $m_\beta$ are the weight of the hollow fiber membrane before and after dipping in pure water, respectively; $\rho$ is the density of pure water; $R$ and $r$ are the outer and inner radii of the hollow fiber membrane, respectively; and $L$ is the length of the hollow fiber membrane. The TiO$_2$ mass-to-area ratio was calculated based on a previous report (Ma et al. 2009). The performance of the membrane was evaluated for treating HA (initial concentration of 10.5 mg/L) using a dead-end filtration unit (as shown in Figure 2). The removal rate of HA was calculated based on the variation of total organic carbon (TOC) in the solution. TOC was measured with a TOC analyzer (TOC-V CPH, Shimadzu). The rejection of HA was calculated using the formula (Jyothi et al. 2014):

$$ \text{rejection} \% = \left(1 - \frac{C_p}{C_f}\right) \times 100 $$

where $C_p$ and $C_f$ are the permeate and the feed concentrations of HA, respectively.

RESULTS AND DISCUSSION

Figure 3 shows the SEM images of the cross-section of the ceramic hollow fiber membranes with the ratio of PES/ceramic powder ranging from 13 to 20%. Upon increasing the PES/ceramic powder ratio from 13 to 20%, the shape of the inner profile gradually became asymmetrical. It also can be seen from Figure 3 that finger-like macrovoids formed within the membrane, which could serve as channels during membrane filtration. As shown in Figure 3(d), when the ratio of PES/ceramic powder reached 20%, the inner profile of the ceramic hollow fiber membrane was not circular and the inner wall displayed an inward bulge.
Figure 4 shows the porosity of the ceramic hollow fiber membrane with different ratios of PESf/ceramic powder. The porosity was approximately 50%, 57%, 63%, and 80% for ceramic hollow fiber membranes with PESf/ceramic powder ratios of 13%, 14%, 17%, and 20%, respectively. This result is consistent with the morphologies shown in Figure 3 in that the porosity increased with increasing of finger-like macrovoids.

The permeate flux of the ceramic hollow fiber membranes was evaluated using pure water. As shown in Figure 5, the pure water flux increased as the PESf/ceramic powder ratio increased. The pure water flux was 4,600 L/(m²·h) (75 kPa) at a PESf/ceramic powder ratio of 13%, and it increased to 7,400 L/(m²·h) (75 kPa) at the ratio of 14%, followed by additional increases to 10,200 and 31,900 L/(m²·h) (75 kPa) at the ratios of 17% and 20%, respectively.

Figure 6 presents the maximal bending strength of the ceramic hollow fiber membrane as a function of the...
PESf/ceramic powder ratio. The PESf/ceramic powder ratio had a significant influence on the mechanical strength. Figure 6 shows that the mechanical strength increases as the PESf/ceramic powder ratio decreases. The mechanical strengths were 490, 590, 720, and 1,170 kPa for ceramic hollow fiber membranes with PESf/ceramic powder ratios of 20%, 17%, 14%, and 13%, respectively. Meanwhile, as shown in Figure 5, the pure water flux decreased with the decreasing PESf/ceramic powder ratio. Therefore, although the ceramic hollow fiber membrane with a PESf/ceramic powder ratio of 13% had excellent mechanical strength, the pure water flux was relatively low. Compared to the membranes with PESf/ceramic powder ratios of 17 and 20%, the membrane of 14% has better mechanical strength. Considering both permeate flux and mechanical strength, the ceramic hollow fiber membrane with a PESf/ceramic powder ratio of 14% was adopted as the substrate for the fabrication of TiO2 hollow fiber membranes.

During the TiO2 dip-coating process, the dip time in the TiO2 solution was a key parameter influencing the mass/area ratio of the TiO2 hollow fiber membrane. The TiO2 mass/area ratio as a function of TiO2 dipping time is shown in Figure 7. As can be seen from Figure 7, the TiO2 mass/area ratio increased from 16 to 21 g/m2 as the dipping time increased from 1 to 15 min, and then leveled off from 15 min to 25 min. Therefore, the dip time was fixed at 15 min for this study.

The XRD pattern of a TiO2 hollow fiber membrane is shown in Figure 8. Five distinctive peaks appeared at 20 angles of 25.31°, 37.91°, 48.01°, 54.61°, and 62.81°, which correspond to the reflections of crystalline anatase-TiO2 planes (JCPDS 21-1272); this result is consistent with a previous study (Goei & Lim 2014).

Figure 9 shows the variation of pure water flux as a function of different numbers of impregnation cycles of the TiO2 hollow fiber membranes; the flux decreased slightly as the number of coating cycles increased. When the impregnation was repeated 5, 7, and 9 times, the pure water flux was 3,175 L/(m²·h), 2,955 L/(m²·h), and 2,790 L/(m²·h), respectively. It can be concluded that the pure water flux decreases as a result of the increased thickness of the TiO2 functional layer.

Figure 10 presents the cross-section images of TiO2 hollow fiber membranes for various numbers of impregnation cycles; the thickness of the TiO2 layer gradually increased as the number of coating cycles increased. The thickness of TiO2 was about 480, 730, and 1,110 nm, corresponding to repetitions of 5, 7, and 9, respectively. Based on the results of Figures 9 and 10, the hollow fiber membrane dipped 7 times in the TiO2 sol was employed for the rest of this study.

As shown in Figure 11, the pure water flux of the TiO2 hollow fiber membranes was different with or without UV irradiation. Without UV irradiation, the pure water flux of the TiO2 hollow fiber membrane was 2,955 L/(m²·h), while in the presence of UV (at UV light intensity of 1.5 mW/cm²), the pure water flux of TiO2 hollow fiber membranes reached 4,450 L/(m²·h), which is approximately 1.5 times greater. The influence of light intensity on the pure water flux was also investigated. As expected, the pure water flux increased as the UV light intensity increased. This could be attributed to the hydrophilicity of the TiO2, which has a UV-sensitive hydrophilic surface conversion agent. The hydrophilicity of TiO2 was created by the formation of a layer of adsorbed hydroxyl and multiple layers
of water molecules (Lee et al. 2013). It has been reported that the photo-induced hydrophilic reaction of the TiO$_2$ surface was enhanced by the UV illumination increasing (Banerjee et al. 2015; Kim et al. 2015). This indicates that the pure water flux of the TiO$_2$ hollow fiber membranes could be improved with the increasing of UV light intensity.

The permeate flux of the TiO$_2$ hollow fiber membrane during the HA treatment (initial concentration 10.5 mg/L) with or without UV irradiation was investigated and the result is shown in Figure 12. In the absence of UV irradiation, the permeate flux declined from 290 to 85 L/(m$^2$·h) in 30 min, and remained constant at 80 L/(m$^2$·h) for an additional 30 min. In the presence of UV irradiation, the permeate flux reached 410 L/(m$^2$·h) after 10 min, and then stabilized at 250 L/(m$^2$·h) after an additional 30 min. In other words, the average permeate flux increased from 80 to 250 L/(m$^2$·h) with UV irradiation, and the improvement in HA permeate flux was approximately 210%. Here, it is obvious that HA molecules could be adsorbed on the membrane surface and rejected, followed by decrease of the permeate flux of the membrane. Meanwhile, under UV illumination, TiO$_2$ could absorb UV light to generate...
hydroxyl radicals and other reactive oxygen species, which further accelerate the process of photocatalytic decomposition of HA. Generally, the photocatalytic degradation of HA could produce some intermediates that ultimately could be converted to CO₂ and H₂O (Ma et al. 2010; Xue et al. 2011). Since the HA adsorbed on the membrane surface could be destroyed by TiO₂, the permeate flux would be enhanced.

Although the membrane shows attractive prospects for water treatment, the fouling often restricts its practical application. The degree of membrane fouling could be investigated by monitoring the permeate flux variation. As shown in Figure 12, the fouling of the TiO₂ hollow fiber membrane could be demonstrated by the changes in permeate flux of HA without and with UV irradiation. In the case of without UV irradiation, the permeate flux of HA declined from 290 initially to 85 L/(m²·h) after 30 min, suggesting the cake layer of HA formed due to surface adsorption by filtration alone. However, the permeate flux reached 250 L/(m²·h) with UV irradiation, indicating the coating of TiO₂ was beneficial to resist fouling, due to its distinguished photocatalytic ability to mineralize HA, ensuring the attractive performance of the TiO₂ hollow fiber membrane.

Figure 13 shows the TOC of HA before and after treatment with the TiO₂ hollow fiber membrane with and without UV irradiation. The initial TOC value of HA was set at 10.5 mg/L; it decreased to 7.2 mg/L under TiO₂ hollow fiber membrane treatment in absence of UV irradiation and decreased to 1.7 mg/L in presence of UV irradiation. This indicated that HA could be partially rejected by filtration alone, whereas HA removal by filtration and concurrent photocatalysis was remarkable. It could be calculated that the 51.4% rejection of HA was observed by filtration alone, whereas 83.8% of HA was removed by filtration and concurrent photocatalysis, suggesting a typical synergistic effect by integration. Consequently, compared with the filtration alone, the HA removal efficiency was dramatically increased by the contribution of both rejection and photocatalysis.

CONCLUSIONS

A TiO₂ hollow fiber membrane was fabricated by a controlled wet-spinning process, followed by a subsequent dip-coating process. It is shown that the optimized fabrication
process is very effective in controlling membrane performance. In this study, using the TiO2 hollow fiber membrane, the pure water flux reached 4,450 L/(m2·h). The permeate flux was significantly enhanced in the presence of UV irradiation, and increasing the UV light intensity resulted in increased pure water flux. Meanwhile, the TiO2 hollow fiber membrane was applied for treating an aqueous HA solution. Compared with the 31.4% rejection of HA by filtration alone, 85.8% of HA removal efficiency was achieved. The HA removal was improved under UV irradiation, likely due to enhanced performance of filtration along with photocatalytic degradation of HA simultaneously. In addition, the use of TiO2 hollow fiber membranes provided a better reduction of membrane fouling in the presence of UV light irradiation. Considering the high permeate flux and enhanced performance, the TiO2 hollow fiber membranes may find various applications in water treatment.

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