Degradation of Reactive Black 5 in a submerged photocatalytic membrane distillation reactor with microwave electrodeless lamps as light source

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ABSTRACT

A novel submerged photocatalytic membrane distillation reactor (SPMDR) was developed and microwave electrodeless lamps were applied as the source light. Reactive Black 5 was used as a model dye with an initial concentration of 400 mg/L. The effects of TiO₂ dose and feed temperature on the photodegradation efficiency and permeate flux were first investigated. The highest degradation rate was observed at 2.0 g/L TiO₂ and 65 °C. The permeate flux decreased by 15.8% when the TiO₂ dose increased from 0.5 to 6.0 g/L. The permeate flux of the SPMDR in the presence of 2.0 g/L TiO₂ was higher than the pure water flux using conventional heating, which confirms the enhancement of microwave irradiation to the membrane distillation mass transfer. The SPMDR achieved a high color (100%) and TOC (80.1%) removal efficiency after 300 min reaction. The byproducts identified in the feed included aliphatic acids (formic, acetic and maleic) and inorganic ions (SO₄²⁻, NH₄⁺ and NO₃⁻). The SPMDR produced high quality water because dye, TiO₂ and inorganic ions were completely retained in the feed side. Formic and acetic acids were detected in the permeate side with amounts of 0.08 and 0.25 mg (i.e., 1.83 and 5.29 mg/L), respectively. Scanning electron microscope (SEM) images showed that a loose TiO₂ cake layer was formed on the membrane surface, which decreased the membrane porosity and contact angle to some extent. However, the module efficiency, porosity and contact angle could be largely recovered after 30 min of washing with distilled water.

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1. Introduction

Titanium dioxide (TiO₂) is generally used as one of the most popular photocatalysts because of its good photocatalytic activity, high stability, nontoxicity, chemical inertness, and low cost [1]. However, the separation and reuse of TiO₂ powder remain a big challenge for its practical application. Photocatalytic membrane reactors (PMRs) combine the photocatalysis and membrane processes together, in which the membrane acts as a barrier for TiO₂ and byproducts and thus enables the continuous separation of TiO₂ [2]. Most PMRs described in the literature adopt a pressure-driven membrane process such as microfiltration (MF) [2–5], ultrafiltration (UF) [2,6,7] and nanofiltration (NF) [2,8–11], which leads to a severe permeate flux decline because of TiO₂ particles. Furthermore, the permeate has an unsatisfactory quality because small molecules can pass easily through the membrane, even in the case of NF.

Recently, a new type of PMR that combines photocatalysis with hydrophobic membrane distillation (MD) has been reported [8, 12–17]. Since the MD is a thermally driven process, only volatile components in the feed can pass through the pores of the hydrophobic membrane to the permeate side. This enables the production of pure water if the feed only contains non-volatiles. Compared with the pressure-driven membrane process, the MD is less prone to fouling because it is operated at an ambient pressure [18].

Mozia et al. developed a photocatalytic membrane distillation reactor (PMDR) for azo dye degradation, which combined hybrid photocatalysis with direct contact membrane distillation (DCMD) [8,12–17]. Low-pressure mercury vapor UV lamps were positioned above the feed tank in which photocatalytic degradation took place. The mixture of a synthetic dye wastewater and TiO₂ particles in the feed tank was pumped through a heat exchanger to the membrane module for separation. The feed flowed inside the hollow fibers whereas the permeate flowed outside. The results showed that the MD process was effective in separating TiO₂ particles with an insignificant flux decline and a high quality permeate.

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In this study, a novel submerged photocatalytic membrane distillation reactor (SPMDR) was developed using microwave electrodeless discharge lamps (MEDLs) as the light source. The MD process selected was vacuum membrane distillation (VMD). The MEDLs, powered by microwave, have been widely used in photocatalytic processes because of its low cost, simple equipment, and high photochemical efficiency [1,19–21]. In addition to the benefits of a conventional PMDR, such as high quality permeate and alleviated membrane fouling, a significant advantage of the developed SPMDR is that microwave irradiation can enhance both the photocatalysis efficiency and the VMD mass transfer. Temperature polarization widely exists in the MD process, which will decrease the mass transfer efficiency. Microwave irradiation can provide homogeneous heating to increase a local temperature, which compensates for the temperature decrease caused by evaporation and temperature polarization. Ji et al. reported that microwave irradiation could increase the mass transfer coefficient by 27.7% during a VMD process and enabled high permeate fluxes even at a low feed flow rate [22].

Reactive Black 5 (RB5) with a high concentration was used as a model azo dye to be degraded by the developed SPMDR. The effects of TiO_2 dose and feed temperature on the photodegradation efficiency and permeate flux was investigated. The decolorization and mineralization of RB5 as well as the rejection of VMD toward TiO_2 , dye and photodegradation byproducts were assessed. Moreover, membrane fouling was examined.

2. Experimental

2.1. Materials and reagents

RB5 ($\text{C}_{26}\text{H}_{21}\text{N}_5\text{Na}_4\text{O}_{19}\text{S}_6$) was purchased from Beijing Dongxiyi Ltd., Co. (China). A commercially available TiO_2 (Aeroxide P25, Evonik, Germany) was used as the photocatalyst. U-shaped quartz MEDLs (Jimin Illumination Equipment Factory, Shanghai, China), filled with 20 mg Hg and 5.0 Torr Ar, were used as the light source. The MEDLs emitted UV and visible lights upon microwave irradiation. The irradiation spectrum showed peaks at 254, 312, 365, 405 and 435 nm, and the main UV wavelength was 254 nm (provided by the manufacturer). The hydrophobic polyvinylidene fluoride (PP) hollow-fiber membrane was obtained from Hangzhou Kaijie Membrane Company (China), with an average pore size of 0.2 μm , a porosity of 40–45%, and an inside and outside diameter of 400 and 500 μm , respectively. The membrane module consisted of 60 hollow fibers, with an effective area of 0.039 m^2 (calculated from the outside diameter).

2.2. The submerged photocatalytic membrane distillation reactor (SPMDR)

The SPMDR is schematically illustrated in Fig. 1. A cylindrical glass reactor (outer diameter 150 mm and height 250 mm) was housed in

a modified microwave oven (1300 W, 2.45 GHz). The membrane module was submerged in the working solution. The MEDLs floated on the solution with approximately 60% of immersion. The feed temperature was controlled by circulating the solution through a cooler (DC 510, Xinzhi Biotechnology, China) via a magnetic pump (MP-20RM, Seisun Pump, China). A vacuum pump (DOA-P504-BN, GAST, USA) was used as the driving force and the transmembrane vapor was condensed and collected in a permeate reservoir.

2.3. The degradation of RB5 in the SPMDR

The effects of TiO_2 dose and feed temperature on the photodegradation efficiency and permeate flux were first investigated under the following experimental conditions: 400 mg/L of initial RB5 concentration ($C_{0,\text{RB5}}$), 1500 mL of reaction solution, -75 kPa of vacuum pressure (P_{vac}), and 300 min of reaction time. The feed samples (10 mL each) were taken every 30 min and filtered through 0.45 μm membrane filters before analysis. The UV–vis spectra of the samples were scanned over a wavelength range of 200–900 nm using a Hitachi UV-2600 spectrophotometer (Japan). The RB5 concentration in the feed was determined by measuring its absorbance at 600 nm. Total organic carbon (TOC) was analyzed with a Shimadzu TOC-VCSN analyzer (Japan). Aliphatic acids and inorganic ions were detected with ion chromatograph (IC 3000, Dionex, USA). The permeate conductivity was measured by a DDS-307 conductivity meter (China). The permeate flux was calculated by the following equation:

$$J = \frac{V}{Ant} \quad (1)$$

where J is the permeate flux, $\text{L}/\text{m}^2 \text{ h}$; V is the permeate volume, L; A is the area of one hollow fiber, m^2 ; n is the number of hollow fibers; and t is the elapsed time, h.

2.4. Characterization of the hollow-fiber membrane

The outer surface morphology of the PP membrane was viewed with a scanning electron microscope (SEM, S-3000N, Hitachi, Japan). Membrane samples were frozen in liquid nitrogen, fractured to obtain fragments, and then sputtered with platinum by using a HITACHIE-1010 ion sputtering device. Membrane porosity was determined gravimetrically by weighing the liquid contained in membrane pores [23]. The contact angle (θ) of the hollow fiber was measured by a tensiometer (DCAT 11, Dataphysics, China).

3. Results and discussion

3.1. Effect of TiO_2 dose on photodegradation efficiency and permeate flux

In the SPMDR, the feed volume decreased continuously because of water vapor transferring to the permeate side. Since the

Fig. 1. Schematic diagram of the submerged photocatalytic membrane distillation reactor.

permeate flux varied under different conditions, the change in the RB5 amount, instead of its concentration, was plotted as a function of time at different TiO_2 doses. Fig. 2 shows that the RB5 removal efficiency reached approximately 75% in the absence of TiO_2 within 300 min, most probably due to the destruction of azo bonds by UV light emitted by the MEDLs [1]. The addition of TiO_2 (0.5–6.0 g/L) could enhance dye degradation, and a complete removal was achieved for all runs within 300 min. The maximum reaction rate of RB5 was observed at a TiO_2 dose of 2.0 g/L, while further increasing the TiO_2 dose (i.e., 4.0 and 6.0 g/L) led to a decrease in the reaction rate. That was because a high TiO_2 dose would decrease the solution transmittance to UV light and thus reduce the photocatalytic reaction rate [24]; and moreover, the TiO_2 particles would agglomerate and thus lose partially the available photocatalytic surface area [25].

The permeate flux as a function of time at different TiO_2 doses is shown in Fig. 3. The permeate flux decreased slightly with an increasing TiO_2 doses. The average permeate flux at 0.5 g/L TiO_2 was 4.56 L/m² h, which was close to that measured with pure water (4.64 L/m² h). However, it decreased to 3.74 L/m² h at 6.0 g/L TiO_2 . It is noted that the permeate flux increased gradually during the initial 60 min of each run and thereafter remained approximately stable. During the initial reaction period, the feed temperature was increased gradually from an ambient value to 65 °C, thus leading to an increase in the permeate flux. After the feed temperature reached stable (i.e. 65 °C), a steady-state permeate flux was achieved.

Fig. 2. Change in the RB5 amount in the feed during the photodegradation process at different TiO_2 doses ($C_{0,\text{RB5}} = 400 \text{ mg/L}$, $T = 65^\circ\text{C}$, $P_{\text{vac}} = -75 \text{ kPa}$).

Fig. 3. Change of the permeate flux during the photodegradation process at different TiO_2 doses ($C_{0,\text{RB5}} = 400 \text{ mg/L}$, $T = 65^\circ\text{C}$, $P_{\text{vac}} = -75 \text{ kPa}$).

Mozia et al. reported that the TiO_2 dose (0.1–0.5 g/L) had no impact on the permeate flux in the DCMD process [8,12,13]. However, membrane fouling was observed in the current study. The permeate flux decreased by 15.8% when the TiO_2 dose increased from 0.5 to 6.0 g/L. To investigate the membrane fouling, the PP membrane module had been operated continuously for 25 h at various TiO_2 doses, and then it was washed with distilled water for 30 min. The permeate flux was restored to 4.05 L/m² h after washing. In comparison, severe membrane fouling was observed in the pressure-driven membrane processes. For example, during an MF process with TiO_2 suspension, the permeate flux declined significantly by 15%, 64% and 94% at TiO_2 doses of 0.01, 0.1 and 1.0 g/L, respectively [4]. Additionally, in a hybrid photocatalysis-NF system, the permeate flux decreased quickly from 54 to 33 L/m² h in the presence of suspended TiO_2 [10]. Therefore, the developed SPMSR is more resistant to membrane fouling than the conventional PMRs with pressure-driven membrane processes.

3.2. Effect of feed temperature on photodegradation efficiency and permeate flux

Fig. 4 compares the photodegradation efficiencies of RB5 at different feed temperatures. The results indicate that in the temperature range of 55–70 °C under microwave irradiation, the removal efficiency of RB5 for all runs reached 100% within 300 min. In addition, the photodegradation efficiency first increased with an increasing temperature below 65 °C, and then decreased as the feed temperature was further raised to 70 °C. This was attributed to the properties of MEDLs whose emission spectrum changes substantially with the feed temperature. The UV light of 254 nm dominates at a temperature below 65 °C; while at a temperature above 70 °C, the MEDLs will emit less UV light and even turn off [26]. In the present work, occasional lamp fails were also observed at 70 °C, which decreased the photodegradation efficiency.

The feed temperature also influenced notably the VMD process. Table 1 shows the effect of feed temperature on the pure water flux (PWF) with conventional thermostatic bath or microwave irradiation heating and the SPMDR flux in the presence of 2.0 g/L TiO_2 . The results indicate that a higher flux was observed with microwave heating or in the SPMDR than with conventional heating. It is seen that the VMD mass transfer was enhanced by microwave irradiation. Microwave irradiation led to a local temperature increase, which compensated for the temperature decrease caused by evaporation and temperature polarization. This is an obvious advantage of the developed SPMDR.

Fig. 4. Change in the RB5 amount in the feed during the photodegradation process at different feed temperatures ($C_{0,\text{RB5}} = 400 \text{ mg/L}$, TiO_2 dose = 2.0 g/L, $P_{\text{vac}} = -75 \text{ kPa}$).

Table 1

Comparison of permeate fluxes under different conditions.

Flux (L/m ² h)	Feed temperature (°C)			
	55	60	65	70
PWF (conventional heating)	0.85	1.88	3.62	5.43
PWF (microwave heating)	1.52	2.84	4.64	6.25
SPMDR (TiO ₂ dose = 2 g/L)	1.32	2.46	4.14	5.72

3.3. Decolorization and mineralization of RB5

Fig. 5 shows the change of the solution absorption spectrum during the photodegradation process. The absorption peaks of RB5 appearing at 230, 310 and 600 nm could be attributed to the benzene ring, naphthalene ring and azo bond, respectively. The absorption peak at 600 nm (denoting the azo bond) disappeared completely after 180 min, demonstrating an effective decolorization efficiency of the SPMDR.

The decolorization of the RB5 solution was mainly associated with the cleavage of the azo bonds. The subsequent photodegradation would break down the benzene and naphthalene rings and lead to the formation of low molecular-weight aliphatic acids, which could be further mineralized to H₂O, CO₂ and inorganic anions [16].

The amounts of TOC, aliphatic acids and inorganic ions in the feed were determined at various reaction times, as shown in Fig. 6. The TOC removal showed three phases: (1) in the initial 30 min, a relatively rapid TOC removal (12%) was observed probably because RB5 was adsorbed onto TiO₂ particles besides its photodegradation; (2) in the time period of 30–180 min, the TOC removal slowed down (only with a 10% increase), which arose from the continuous formation of aliphatic acids; and (3) in the final time period (180–300 min), the TOC was removed more quickly due to the mineralization of the aliphatic acids and a high TOC removal efficiency (80.1%) was observed at 300 min. The amounts of formic, acetic and maleic acids reached maximum at 210–240 min, and then decreased to 7.2, 8.6 and 21.1 mg at 300 min, respectively.

Fig. 7 shows the generation of inorganic ions (SO₄²⁻, NH₄⁺ and NO₃⁻) in the feed during the RB5 photodegradation process. The amount of SO₄²⁻ slightly increased to 8.2 mg in the initial 150 min, and then increased sharply to 102 mg at 300 min. Although much less NH₄⁺ and NO₃⁻ ions were formed than SO₄²⁻, their amounts in the feed exhibited a similar increasing trend. The amount of NH₄⁺ was approximately three times that of NO₃⁻, indicating that the oxidation of NH₄⁺ to NO₃⁻ was a slow process.

Fig. 5. Change of the solution absorption spectrum during the photodegradation process ($C_{0, \text{RB5}} = 400 \text{ mg/L}$, TiO_2 dose = 2.0 g/L, $T = 65^\circ\text{C}$, $P_{\text{vac}} = -75 \text{ kPa}$).

Fig. 6. Change in the amounts of TOC and aliphatic acids in the feed during the photodegradation process ($C_{0, \text{RB5}} = 400 \text{ mg/L}$, TiO_2 dose = 2.0 g/L, $T = 65^\circ\text{C}$, $P_{\text{vac}} = -75 \text{ kPa}$).

In addition, the high feed temperature (65°C) would reduce the water solubility of oxygen gas, thus retarding the oxidation of NH_4^+ to NO_3^- [16].

The initial dye concentrations were usually not higher than 100 mg/L in the conventional PMRs using UV lamps as the light source [12–17]. In comparison, the developed SPMDR could achieve an effective color and TOC removal at an initial RB5 concentration as high as 400 mg/L. This may be attributed to two reasons: (1) more hydroxyl radicals ($\cdot\text{OH}$) could be generated in the SPMDR by photocatalysis assisted with microwave irradiation [27]; and (2) the partially immersed MEDLs could shorten the optical path and transfer more light energy into the solution [1].

3.4. Permeate quality analysis

The permeate quality of the SPMDR was analyzed, including the concentrations of RB5 and inorganic ions (i.e., SO_4^{2-} , NO_3^- and NH_4^+), turbidity, pH, conductivity, and the amounts of TOC and aliphatic acids. The results indicate that neither RB5 nor the target inorganic ions were detected in the permeate. The permeate turbidity was kept in a low range of 0.10–0.18 NTU, similar to that of tap water (i.e., 0.15 NTU). The hydrophobic PP membrane was only permeable to volatile chemicals, so the RB5 dye, TiO_2 and inorganic ions were completely retained in the feed side as expected. However, in the PMRs utilizing pressure-driven membranes, complete rejection of non-volatile chemicals could not be achieved, even utilizing NF [9,10].

Fig. 7. Change in the amounts of inorganic ions in the feed during the photodegradation process ($C_{0, \text{RB5}} = 400 \text{ mg/L}$, TiO_2 dose = 2.0 g/L, $T = 65^\circ\text{C}$, $P_{\text{vac}} = -75 \text{ kPa}$).

The variations of permeate conductivity and pH as a function of time are shown in Fig. 8. The permeate conductivity increased from 4.2 to 28.7 $\mu\text{S}/\text{cm}$, while the permeate pH decreased from 6.5 to 4.2 during the entire photodegradation process. This result implies that some organic acids could penetrate the PP membrane to reach the permeate side. As confirmed in Fig. 9, formic and acetic acids were detected in the permeate, which made a main contribution to the TOC. Maleic acid was not detected in the permeate because of its low volatility. The amount of acetic acid was always higher than that of formic acid, which is in correspondence with their concentrations in the feed (Fig. 6). The amounts of formic and acetic acids and TOC kept increasing till a maximum was reached at 201–240 min and started to decrease thereafter, which agreed well with their variations in the feed (Fig. 6). After 300 min of photodegradation, the amounts of formic and acetic acids and TOC in the permeate were determined to be 0.08, 0.25 and 0.52 mg (or 1.83, 5.29 and 10.6 mg/L), respectively. Additionally, the CO_2 generated from organic mineralization in the feed may also transfer to the permeate side and change the permeate pH and conductivity.

Although a complete rejection of organic compounds was not achieved in the SPMDR, the permeate had only a low TOC concentration. Therefore, the SPMDR could produce a higher quality permeate than the PMRs utilizing pressure-driven membranes.

3.5. Membrane fouling

In the previous experiments examining the effect of TiO_2 dose (0.5–6.0 g/L) on RB5 removal and permeate flux, each experiment was conducted for 300 min (5 h) by using the same membrane module. Therefore, the membrane module had been working for 25 h. The SEM images of a fresh PP membrane, the fouled membrane after 25 h reaction, and the rinsed membrane after 30 min washing with distilled water are compared in Fig. 10. During the photodegradation process, membrane samples at different reaction times (5, 15 and 25 h) were also collected for porosity and contact angle analysis.

As described above, the average permeate flux decreased from 4.56 to 3.74 $\text{L}/\text{m}^2 \text{ h}$ when the TiO_2 dose increased from 0.5 to 6.0 g/L (Fig. 3). The flux decline was attributed to a TiO_2 cake layer formed on the membrane surface, as visible in Fig. 10b. This fouling layer would not only reduce the surface area available for water evaporation, but also decrease the heat transfer. After washing the fouled membrane with distilled water for 30 min, the TiO_2 cake layer was partially removed and some micropores were regenerated. The permeate flux increased notably to 4.05 $\text{L}/\text{m}^2 \text{ h}$ after membrane washing, although was not fully recovered.

Fig. 8. Variation of the permeate conductivity and pH during the photodegradation process ($C_{0,\text{RB5}} = 400 \text{ mg/L}$, TiO_2 dose = 2.0 g/L, $T = 65^\circ\text{C}$, $P_{\text{vac}} = -75 \text{ kPa}$).

Fig. 9. Variation in the amounts of TOC and aliphatic acids in the permeate during the photodegradation process ($C_{0,\text{RB5}} = 400 \text{ mg/L}$, TiO_2 dose = 2.0 g/L, $T = 65^\circ\text{C}$, $P_{\text{vac}} = -75 \text{ kPa}$).

Fig. 10. SEM images of: (a) a fresh PP membrane; (b) the fouled membrane after 25 h reaction; and (c) the rinsed membrane (30 min washing with distilled water).

The changes in porosity and contact angle of the fouled membrane were also examined. The porosity of the fresh PP membrane was measured to be 40.5%, and it decreased slightly to 38.7%, 38.5% and 38.0% after 5, 15, and 25 h of reaction, respectively. After rinsing with distilled water, the membrane porosity was recovered to 40.2%, 39.9% and 40.0%, respectively. The contact angle of the fresh PP membrane was 97.65°, confirming its hydrophobic nature. After reaction for 5, 15, and 25 h, it decreased to 94.43°, 92.24° and 89.87°, respectively. The contact angle was recovered to 97.15°, 95.69° and 95.08° after membrane washing.

The above results show that a TiO₂ layer was formed at high TiO₂ doses, which decreased the membrane porosity and contact angle to some extent. However, simple membrane washing with distilled water could recover most of the permeate flux and the membrane porosity and contact angle as well. This denotes indirectly that the formed TiO₂ cake layer was quite loose because of the hydrophobicity of the PP membrane used. By contrast, a compact TiO₂ cake layer was usually formed on the surface of a pressure-driven membrane even at a low TiO₂ dose.

4. Conclusions

In this study, a SPMDR with MEDLs as light source was developed and applied to degrade a synthetic dye wastewater containing 400 mg/L RB5. The results show the SPMDR was more resistant to membrane fouling than the conventional PMRs with a pressure-driven membrane process, especially in the case of a high TiO₂ dose. In addition, the enhancement of microwave irradiation to the VMD mass transfer was confirmed. The SPMDR flux in the presence of 2.0 g/L TiO₂ was higher than the PWF with conventional heating, which exemplifies an obvious advantage of the SPMDR.

A high color (100%) and TOC (80.1%) removal efficiency was achieved after 300 min photodegradation of 400 mg/L RB5 synthetic wastewater by the SPMDR. Identified byproducts included aliphatic acids (formic, acetic and maleic acid) and inorganic ions (SO₄²⁻, NH₄⁺ and NO₃⁻). The permeate was high quality water, containing only a low TOC concentration (10.6 mg/L) and a low turbidity (≤0.18 NTU). RB5, TiO₂ and inorganic ions were completely retained in the feed side. A loose TiO₂ cake layer formed on the membrane outer surface decreased module efficiency, membrane porosity and contact angle to some extent. However, they could be largely recovered after 30 min of washing with distilled water.

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