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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 TiO_2 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 TiO_2 and 65 °C. The permeate flux decreased by 15.8% when the TiO_2 dose increased from 0.5 to 6.0 g/L. The permeate flux of the SPMDR in the presence of 2.0 g/L TiO_2 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 (SO_4^{2-}, NH_4^+ and NO_3^-). The SPMDR produced high quality water because dye, TiO_2 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 TiO_2 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.

1. Introduction

Titanium dioxide (TiO_2) 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 TiO_2 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 TiO_2 and byproducts and thus enables the continuous separation of TiO_2 [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 TiO_2 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 TiO_2 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 TiO_2 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 ($C_{26}H_{21}N_5Na_4O_{19}S_6$) 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 ($C_{o,RB5}$), 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, L/m^2 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

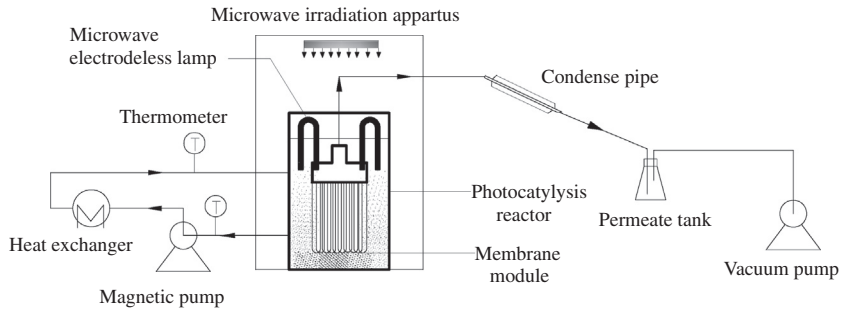

Fig. 1. Schematic diagram of the submerged photocatalytic membrane distillation reactor.