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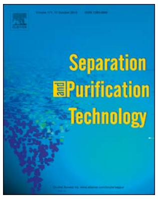

Direct contact membrane distillation for the treatment of industrial dyeing wastewater and characteristic pollutants

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ABSTRACT

In this work, the feasibility of utilizing direct contact membrane distillation (DCMD) for the treatment of industrial dyeing wastewater and their characteristic pollutants were demonstrated. Two commercial hydrophobic membranes made of polytetrafluoroethylene (PTFE) and polyvinylidene fluoride (PVDF) were comparatively studied. The results suggest that PTFE membrane always demonstrates enhanced flux and rejection performance for selected characteristic pollutants compared with that of PVDF counterpart, which can be ascribed to its enhanced hydrophobicity and reduced wettability. When challenging the industrial and synthetic dyeing wastewater, the DCMD system demonstrates different performances in terms of flux and rejection efficiency, which are closely related to the sample compositions and concentration. The relevant COD and color removal efficiency over 48 h continuous operation was, respectively, 90% and 94% for sample 1# (from discharge outlet of the dyeing vat wastewater), 96% and 100% for sample 2# (from discharge outlet of the wastewater treatment plant after physicochemical and biological treatment), and 89% and 100% for sample 3# (synthetic dyeing wastewater after bench-scale membrane bioreactor treatment). Furthermore, various advanced characterization techniques were employed to study the fouling properties and performance of the PTFE membrane. The suspended solids accumulation (*e.g.*, SiO_2 and dispersed dyes) may be responsible for the membrane wetting and fouling. These overall findings suggest that the DCMD process is a promising option for the treatment of dyeing wastewater with limited energy consumption and high performance.

1. Introduction

The textile industry is the pillar industry of China and it plays a pivotal role in the development of the national economy and people's livelihood [1]. Meanwhile, the textile industry is a heavy pollution industry [2,3]. According to the environmental statistics data of China [4], the total discharge amount of wastewater from textile industry was as high as 1.84 billion tons, ranking the third of total national industrial wastewater discharge amount. In China's "Thirteen-Five Year" plan, the textile industry has been listed as key industries needs to be rectified and improved. The complex composition, high turbidity, high pH, poor bio-degradability, huge amount and high chrominance of the textile dyeing wastewater render it one of the hardest to treat forms of industrial wastewater [5–8]. Especially, with the continuous rising of wastewater discharge standards and industry standards, the conventional physicochemical (*e.g.*, coagulation, adsorption and advanced oxidation) and biological methods cannot meet the pressing needs for environmental improvement [9–11]. Furthermore, during the degradation of dyes, various characteristic pollutants of textile industry will be produced. Their migration and transformation in aquatic environment poses serious ecological hazard [12]. It is therefore highly desirable to develop cost-effective technologies to address the issues of dyeing wastewater and their characteristic pollutants.

Currently, the pressure-driven membrane separation processes (*e.g.*, reverse osmosis, RO, and nanofiltration, NF) have demonstrated to be effective for the treatment of dyeing wastewater [13–18]. However, the high energy consumption and high cost (*e.g.*, for maintenance) has significantly restricted their wide practical engineering applications [1,19]. Alternatively, the thermally-driven membrane distillation (MD) has attracted much attention to serve as a promising technology for dyeing wastewater treatment [20–27]. MD usually employs a hydrophobic porous membrane to separate the hot feed stream and the cold permeate stream [28,29], where the temperature difference between feed and permeate creates a transmembrane vapor pressure difference that drives the vapors from the hot side to the cold side through the membrane pores. Such MD process possesses unique advantages over these pressure-driven membrane processes as well as conventional biological methods [30,31]. For instance, the MD process could utilize

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the industrial waste heat without requiring additional heating, significantly decreasing the energy consumption during operation; since the wastewater discharged from the textile industry usually maintained a temperature at 70–80 °C [32]. Additionally, like other membrane separation technologies, MD process also has advantages such as limited footprint, high efficiency, simplicity, up-scalability, and most importantly, potentially recover the dyes from concentrate [22]. An et al. have recently justified the effectiveness of MD for the treatment of selected dye model compounds using negatively charged PTFE membranes. A simple water flushing step could facilitate the recovery of flux and membrane properties. Mokhtar et al. also demonstrated the feasibility of MD process for textile wastewater treatment using a modified PVDF membrane [33]. MD combined with biofilm reactor and other advanced oxidation processes were also proposed to boost the rejection performance [34]. It is of noteworthy that most of the reports on dyeing wastewater treatment by MD were focused on laboratory synthetic dyes rather than industrial wastewater. Even for the industrial dyeing wastewater, the water quality from different fabrication sectors also vary significantly. From a more practical view, it is therefore timely to present a systematic study on the treatment of industrial dyeing wastewater and their characteristic pollutants by MD.

In this study, five typical characteristic pollutants of dyeing wastewater, laboratory synthetic dyeing wastewater and industrial dyeing wastewater (from different dyeing fabrication sectors) were employed to challenge a bench-scale direct contact MD (DCMD) test unit. Two commercial hydrophobic membranes made of PTFE and PVDF were comparatively studied. Various advanced techniques were used to study the fouling properties and the performance of this technology. The effects of several key operational parameters (*e.g.*, operational temperature, time, feed concentration and flow rate) on the treatment performance were also studied, shedding some light on the exploration of the MD technology for the industrial applications. Presented below are the details of this investigation.

2. Materials and methods

2.1. Materials

All chemicals and materials were commercially available and used without further purification. Phenol (C_6H_5OH, ≥99.0%), aniline (C_6H_7N, ≥99.5%), methanol (CH_4O, ≥99.7%), *p*-Chloroaniline (C_6H_6ClN, ≥98%), sulfanilic acid ($C_6H_7NO_3S$, ≥99.8), and 3,4-dihydroxybenzoic acid ($C_7H_6O_4$, ≥98.0%), ethanol (C_6H_6O, 95.0%), sodium chloride (NaCl, ≥99.8), and sodium sulfate (Na_2SO_4, ≥99.0) were purchased from Sinopharm Chemical Reagent Co., Ltd. Aqueous solutions were prepared using deionized water (DI-H_2O) with resistivity of 18.2 MΩ·cm.

2.2. DCMD test unit for dyeing wastewater treatment

DCMD for dyeing wastewater treatment was performed using a closed-loop test unit including a customized membrane module (effective area: 6.0 cm^2), two WT3000-1JA gear circulating pumps (Longer Precision Pump Co., Ltd), a DC-1006 chiller (Shanghai Yuming Instrument Co., Ltd) for permeate solution, and a HWS24 heater (Shanghai Bluepard Instrument Co., Ltd) for feed solution, as displayed in Fig. 1. Two 0.22 µm hydrophobic membranes made of PTFE (provided by Shanghai Minglie membrane Co., Ltd) and PVDF (provided by Haining Zhongli Filtering Equipment Co., Ltd) were comparatively studied (Fig. S1, Supporting Information) and their typical specifications were summarized in Table 1.

Feed solution with an initial volume of 1000 mL was circulated at a typical flow rate of 350 mL/min unless noted elsewhere. Likewise, the permeate solution with an initial volume of 0.2 L was circulated in opposite directions across the membrane at a constant flow rate of 250 mL/min at 20 °C. The permeate flux was controlled by adjusting the transmembrane temperature between the feed and permeate solutions. The mass change of permeate was recorded using a JS-1.5A electronic balance (Chengdu PRIS Electronic Co., Ltd) connected with a computer. Each test was repeated three times to guarantee reliable results.

To systematically study the treatment performance of dyeing wastewater by DCMD, five compounds listed as the substances of high concern in textile industry [35] were selected as model characteristic pollutants (of dyeing wastewater) to prepare the model feed. Table 2 summarizes the physicochemical characteristics of these compounds. Furthermore, two industrial dyeing wastewater samples (1# and 2#) and one synthetic dyeing wastewater sample (3#) were employed in this study. Sample 1# and 2# was collected from a dyeing & printing factory in Suzhou, China, *e.g.*, 1# was sampled from the discharge outlet of the dyeing vat wastewater and 2# was sampled from the discharge outlet of the wastewater treatment plant after physicochemical and biological treatment. As the major products of the dyeing & printing factory are chemical shell fibric, sample 1# contained certain amounts of unbroken dispersed dyes and auxiliaries (*e.g.*, alkali and surfactants). In the practical industrial process, the wastewater discharged directly from the dye vats has typical temperature of 70–90 °C. After chemical and biological treatment, sample 2# contained various intermediates derived from dyes degradation process and soluble microbial products (SMP) like polysaccharides and proteins. Sample 3# was laboratory synthetic dyeing wastewater after bench-scale membrane bioreactor (MBR) treatment (HRT = 48 h), and only one type dye was used as the substrate during the laboratory MBR operation. Table 3 summarizes the characteristics of these water samples before and after DCMD treatment.

2.3. Permeate flux and rejection efficiency

In the MD process, the permeate flux *J* (L/m²•h, LMH) was determined as follows:

$$J = \frac{\Delta W}{\Delta t \times A} \tag{1}$$

Where $\triangle W$ is the change of permeate mass, $\triangle t$ is the permeate collection time and *A* is the effective area of the membrane (*i.e.*, 6.0 cm^2).

The concentration of various characteristic pollutants (*e.g.*, phenol, aniline, *p*-Chloroaniline, sulfanilic acid, and 3,4-dihydroxybenzoic acid) was determined by an UltiMate 3000 high-performance liquid chromatography (HPLC). For the industrial water samples, the change of chemical oxygen demand (COD) and absorbance was quantified by standard dichromate method and colorimetric method. The corresponding rejection efficiency, *R* (%), was determined by the following equation:

$$R = \left(1 - \frac{C_p}{C_f}\right) \tag{2}$$

Where C_f is the initial concentration of pollutants in the feed side (mg/L) and C_p is the concentration in the permeate side (mg/L). The compositions and quantifications of industrial and synthetic dyeing wastewater samples were determined by an Agilent GC7890B gas chromatography (GC) coupled with an MS5977A mass spectrometry (MS). All these measurements (*e.g.*, permeate flux and rejection) were repeated at least three times to guarantee the reproducibility of the results.

2.4. Characterizations

The membrane morphology was examined by a HITACHI S-4800 field emission scanning electric microscopy (FESEM, Japan). The water contact angle was measured by a DataPhysics OCA15EC contact angle gniometer (Germany) using deionized water as the probe liquid to determine the surface wettability of the membranes. Fourier transform