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Prevention of surfactant wetting with agarose hydrogel layer for direct contact membrane distillation used in dyeing wastewater treatment

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ABSTRACT

A novel approach was developed to suppress surfactant wetting during membrane distillation process for industrial wastewater treatment. In this work, a thin layer of agarose hydrogel was attached to the surface of hydrophobic porous Teflon membrane. This composite membrane was tested against aqueous NaCl solution containing various surfactants to determine the effectiveness for preventing surfactant wetting. These surfactants included sodium dodecyl sulfonate (SDS), Tween20, and Tween85. The results showed that no wetting occurred during the 24 h period of membrane distillation against 10 mg/L of SDS or Tween20. On the other hand, surfactant still penetrated through the hydrogel when the concentration was above the critical micelle concentration (CMC) of the surfactant. Even so, the wetting occurred to a lower extent at a slower pace. In addition, no wetting was observed when testing against dyeing wastewater. A model to explain this phenomenon was proposed based on the entrapment of surfactant at the interface between water and hydrogel. Although the attachment of agarose hydrogel layer would reduce the flux to about 71% of the flux using bare membrane, this approach did make membrane distillation able to recover high purity water from dyeing wastewater.

1. Introduction

Membrane distillation (MD) can be used for recovering high-purity water through a hydrophobic membrane by the temperature gradient as the driving force [1–4]. The advantages of applying MD to wastewater treatment are the utilizing of waste heat and the production of high-purity water. The membrane distillation technique was proposed by Bodell in 1963 [5] but began to develop rapidly until the 1990s. The critical factor of the performance of MD is the membrane characteristics including high liquid entry pressure (LEP), high permeability and low thermal conductivity [6]. The hydrophobic membranes currently used in microfiltration system, such as polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF) and polypropylene (PP) are often employed in MD.

After nearly 50 years of development, MD technology has not yet achieved widespread commercial use. There are only a few larger commercial cases still under testing [7]. One of the main reasons is the deterioration of membrane functions that causes decrease in the performance. The issues of membrane fouling and wetting were frequently discussed for improving the MD performance. Membrane fouling can be divided into two categories: biological fouling and inorganic fouling (scaling) [8]. Membrane wetting may be caused by membrane damage due to continuous heating and cooling, and the adhesion of bio-organisms [9] and membrane degradation due to long time operation [10].

Due to shortage of water resources, wastewater recycling has become an important application in the development of membrane technology. Owing to the excellent permeate quality, MD has been paid attention gradually for wastewater treatment in addition to desalination.

There are some studies using MD for wastewater treatment, encountering membrane fouling and wetting problems. Membrane distillation bio-reactor (MDBR) is integrated from membrane bio-reactor (MBR) and MD technology and can be used for wastewater treatment. But the problem of biological fouling and scaling was severe, so that the flux was too low [11–13]. In general, most of wastewater contained substances causing membrane fouling or pore wetting such as proteins, biomass, oily substances, surfactants, wherein the proteins [14–15] and oily substances [16] and biomass readily adsorbed on hydrophobic membrane and surfactants strongly wetted membranes causing membrane fouling more easily and deteriorating permeate quality. There are many factors about membrane wetting including the concentration of surfactants [17] and membrane properties such as pore size, pore size distribution, pore structure and porosity [18]. Membrane degradation because of long time operation [10] also increased the possibility for wetting.

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The most common method to improve membrane anti-fouling property is hydrophilic modification, including surface coating and surface grafting [19]. Peng et al. adopted a composite membrane with PVA/PEG hydrophilic dense layer on a hydrophobic PVDF membrane by the coating method [20] which can be used for 25% ethanol solution in MD system without membrane wetting. Mansouri et al. used PVA-coated membrane preventing wet-out for oily feed [21]. Xu et al. used alginate and alginic acid-silica coated microporous PTFE membrane against oily feeds to protect the membrane from wet-out [22,23]. Chanachai et al. used chitosan-coated hydrophobic PVDF hollow fiber membrane to treat oily feed for protection against wetting [24]. Zuo et al. developed a novel membrane surface modification method to graft hydrophilic polyethylene glycol (PEG) on PVDF hydrophobic membrane by plasma treatment with subsequent deposition of TiO_2 to enhance anti-oil fouling property and reduce wetting effects [25].

Dyeing wastewater is a voluminous and high temperature industrial wastewater, thus it is a potential target for MD technology [26]. However it contains several chemicals such as leveling agents, softeners, and other organic compounds that lead to fouling or wetting on the membrane. As mentioned earlier, hydrophilic modification method can reduce membrane fouling and wetting problems caused by oily substances [25], whereas wetting problem caused by surfactants had not been extensively studied. In particular, the surfactants can reduce surface tension, thus reducing the liquid entry pressure (LEP) and impairing the processing performance.

This study aims to explore a novel approach, hydrogel-covered membrane distillation (HcMD), by using a hydrogel layer to reduce membrane wetting, and to investigate the impacts of hydrogel properties on the membrane wetting during MD process with surfactants and dyeing wastewaters. The membrane wetting phenomena was detected by the change of permeate conductivity and flux. In addition, the influence of surfactant concentration was also investigated for comparing the wetting behavior due to micelle formation. The results of this study would be expected to reveal the mechanisms of membrane wetting by surfactants in order to prevent membrane wetting in MD process for treating industrial wastewater with low surface tension.

2. Experimental

2.1. Materials

The porous hydrophobic membranes used in this study were the PTFE membranes supplied by EF-Materials Industries Inc., Taiwan. These membranes were made from Teflon® with stereo asymmetry structure, exhibiting chemical and biological resistance, and operable up to 270 °C. The thickness of the membrane was 130 μm (PTFE layer was 20 μm and PET support layer was 110 μm, the porosity for both two layers was 85%), and the pore diameter was 0.2 μm. The water contact angle of the membrane was 127°. Sodium dodecyl sulfonate (SDS) was purchase from Laborate GmbH, Germany. Tween20 and Tween85 were purchased from Sigma, USA. Sodium chloride (NaCl) was purchased from Merck, USA. All the chemicals were of reagent grade. Agarose was purchased from Laboratorios, Spain. Agarose is a linear polymer with a molecular weight of about 120 kD. The deionized water was produced in our laboratory (Lotun Ultrapure Water System) with a conductivity of 4.4 μS/cm. Dispersive dyeing leveling agent (Sinonate LAT) and acidic dyeing leveling agent (Sinopol 410), both were used commonly for dyeing process, were supplied by Sino-Japan Chemical Co., Taiwan. Table 1 summarizes the characteristics of all surfactants, 2 leveling agents and agarose. Polyester dyeing wastewater was obtained from Fu-Shun dyeing Co. Ltd., Taiwan. The characteristics of the polyester dyeing wastewater were 1000 mg/L as COD, pH 6.0, turbidity: 500NTU, conductivity: 975 μS/cm. The surface tension of solutions was determined using an automatic surface tensiometer (model CBVP-A3, Kyowa Interface Science Co., Ltd., Japan).

2.2. Membrane distillation performance tests

Fig. 1(a) shows the set-up for membrane distillation, which was a direct contact membrane distillation (DCMD) system composing of a feed reservoir, a cold reservoir and the membrane distillation module. The actual volumes of the feed and permeate were both 10 L in the 20 L tanks. The architect of the module was illustrated in Fig. 1b. The dimensions of the membrane were $20 \times 20\ cm^2$. The specification of the spacer was shown in Table 2. The hydrogel layer and the PTFE membrane were held together by a flame illustrated in Fig. 1(b), similar to the spacer and membrane in a filter module. The inlets and outlets of the MD module were equipped with thermometers and flow meters to monitor the temperatures and flow rates. The increase of the cold water in the reservoir was determined with an electronic balance. During the experiment, the temperature of the hot side was fixed at 60 °C, while that of the cold-side was fixed at 21 °C. The flow rates were 2 L/min for both the hot-side and the cold-side.

Membrane distillation was terminated once the hydrophobic membrane was wetted by the surfactant in the solution. At this point, the solutes in the hot stream would penetrate through the membrane into the cold stream. To measure the degree of wetting, the hot stream was added with NaCl such that the electrical conductivity was 1400 μS/cm. The concentration of NaCl was determined using an electrical conductivity meter (Multi 3420, WTW GmbH, Germany) installed on the cold reservoir.

2.3. Diffusion tests

Fig. 2 shows the diffusion test system to determine the effect of CMC on the penetration of Tween 20 through the hydrogel layer. This system was similar to the membrane distillation system, consisting of a feed reservoir (1 L), a permeate reservoir (1 L), and a hydrogel film. The hydrogel film was placed between these two reservoirs. The temperatures of these two reservoirs were controlled at 25 °C through water jacket. Surfactant was added into the feed reservoir while the permeate reservoir contained only deionized water. Both reservoirs were stirred with magnate bars. The surface tension of the permeate was determined using an automatic surface tensiometer at fixed period to detect the permeation of surfactant from the feed through the hydrogel film.

2.4. Agarose hydrogel preparation

Agarose was dissolved completely in hot water (95–100 °C) to attain a concentration of 6.0 wt%. Then the agarose solution was poured onto a glass plate, scrubbed by a coating bar, and cooled to form a hydrogel layer, followed by refrigerating at 5 °C before using. The thickness was 200 μm measured with a thickness gauge.

2.5. Surface analysis of the membranes

The presence of surfactant on the surface of PTFE membrane was detected using a Fourier Transform Infrared spectrometer (FTIR/ATR, Nicolet iS50, Thermo Scientific, USA).