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Characterization of surface-modified porous PVDF hollow fibers for refinery wastewater treatment using microscopic observation

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ABSTRACT

Microscopic observation was made to investigate the surface structure of porous polyvinylidene fluoride hollow fiber membranes. Field emission scanning electron microscopy (FESEM), atomic force microscopy (AFM), and the Guerout–Elford–Ferry equation applied for pure water permeation rate were used to determine the average pore sizes. As well, surface roughness parameters and nodule sizes were determined by AFM. The observed unmodified and modified PVDF hollow fiber membranes were prepared by dry-jet wet spinning method from spinning dope mixtures containing 19 wt.% PVDF, 0.98 wt.% lithium chloride ($LiCl.H_2O$) and 0, 1.95, and 3.85 wt.% titanium dioxide (TiO_2). Significant difference of spun fibers surface morphology was observed between inner and outer surface by AFM and FESEM. Higher TiO_2 concentration formed rougher surfaces, increased average nodule sizes, and decreased the pore size, resulting in lower permeation flux. Pore size obtained from AFM was intermediate between FESEM and the method based on the Guerout–Elford–Ferry equation.

1. Introduction

Investigation of the physical properties of a membrane is one of the most important recent developments in the membrane separation process. To allow the optimum separation performance the membrane has to possess physical properties giving appropriate interactions with solutes in the process stream. The most effective investigation of physical properties is being made by microscopic observation. These properties are surface morphology, the minimum attachment of solutes and dispersed materials to the membrane surface, which affect the membrane fouling phenomenon [1]. Among these, in-depth study on the surface pores of membranes can be made by using field emission scanning electron microscopy (FESEM), scanning electron microscopy (SEM), atomic force microscopy (AFM), transmission electron microscopy (TEM), and scanning tunneling microscopy (STM) [2]. AFM and FESEM/SEM are the most widely used among these various techniques, but samples for both FESEM and SEM must be prepared by metal coating to determine pore size distributions by image analysis. AFM, on the other hand, requires no initial metal coating; thus, it offers higher resolution. In addition, AFM makes three-dimensional observation possible and provides information on the surface roughness and power spectral density. Recently, the presence of pores on the membrane surface was successfully confirmed using AFM [3–10].

Many studies have been reported on the surface morphology [11–19]. While the porous surface acts mainly as a mechanical support in the thin film composite membrane, it may also provide high permeation capability. The fabrication of hollow fibers by the phase inversion method is intrinsically connected to the porous membrane structure and allows the tailoring of the very distinct structures upon variation of the spinning dope composition. Hwang and Lin [20] reported the SEM observations of different microfiltration membranes pores with a cut-off of 0.1 μm. They also observed that the major drawback of this technique was the sample preparation by gold metallization, which entailed a less accurate pore size determination.

Moreover, various modified hydrophilic membranes have been investigated as active layers for membranes for refinery wastewater treatment [21–23]. Typically, the substrate of modified membranes for refinery wastewater treatment needs low permeation resistance as well as good mechanical strength. For instance, Zularisam et al. [24] found that the addition of high-molecular weight PEG or PVP enlarged the pore size and enhanced the water permeation of poly(ether sulfone) (PES) ultrafiltration membranes. Chakrabarty et al. [25,26] observed an increasing tendency for flux in polysulfone (PSf) ultrafiltration membranes with increase in the PEG molecular weight from 400 to 20,000. The effect of hydrophilic additives, i.e. LiCl and PVP, on the thermodynamic/kinetic relations during the phase inversion process in the preparation of PVDF-based membranes was investigated by Fontananova et al. [27]. These additives were soluble

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both in DMAc and H_2O, and were leached out of the solution during phase inversion process. The presence of finely dispersed inorganic particles in the polymer matrix has proven very useful in the improvement of the membrane surface and membrane performance.

In this study, surface-modified and unmodified PVDF hollow fiber membranes were fabricated for refinery wastewater treatment with an inside diameter of approximately 0.55 mm. The surfaces of the hollow fibers were observed by AFM and FESEM, and they were further characterized by the average pore sizes calculated by the Guerout–Elford–Ferry equation. The observations were used to assess the effect of surface-modified on surface membrane morphology, which overcome the serious problems in the refinery wastewater treatment.

2. Experimental

2.1. Material

Commercial PVDF polymer pellets (Kynar®740) were supplied by Arkema Inc. Philadelphia, USA. *N*,*N*-dimethylacetamide (DMAc, Aldrich Chemical) (synthesis grade, Merck, >99%) was used as solvent without further purification. Lithium chloride monohydrate ($LiOH.H_2O$) (Sigma Aldrich) and titanium dioxide (TiO_2) (Sigma Aldrich) were used as inorganic additives. Glycerol was purchased from Merck (Germany) and used as non-solvent for post-treatment of membrane. In all cases, tap water was used as the external coagulation bath medium in the spinning process. Distilled water and refinery wastewater were used as feed in ultrafiltration experiments.

2.2. Fabrication of PVDF hollow fiber membranes

PVDF hollow fiber membranes were spun employing the dry-jet wet spinning technique by adding 0.98 wt.% lithium chloride ($LiCl.H_2O$) and various amounts of titanium chloride (TiO_2) (0, 1.95, and 3.85 wt.% in concentration) to the spinning dope. The spinning system used is schematized in Fig. 1. In this study, all spinning parameters were constant (Table 1).

The PVDF polymers pellets were dried at 50 °C in a vacuum oven for 24 h to remove moisture content in order to prepare the spinning dope. The spinning dope was prepared by mixing PVDF and inorganic additives at 50 °C under vigorous stirring until the mixture became homogenous. The spinning dope was degassed using ultra-sonic and maintained for 12 h at room temperature before subjected to spinning. The details of the hollow fiber spinning apparatus by the dry-jet wet phase inversion process were given elsewhere [28]. Table 1 lists the detailed spinning parameters.

Table 1
Detailed spinning parameters for preparation of PVDF hollow fibers.

Spinning dope composition	
PVDF-T0	PVDF (19 wt.%), $LiCl.H_2O$ (0.98 wt.%), TiO_2 (0 wt.%) in DMAc
PVDF-T1	PVDF (19 wt.%), $LiCl.H_2O$ (0.98 wt.%), TiO_2 (1.95 wt.%) in DMAc
PVDF-T3	PVDF (19 wt.%), $LiCl.H_2O$ (0.98 wt.%), TiO_2 (3.85 wt.%) in DMAc
Dope extrusion rate (ml/min)	4.20
Bore fluid	Distilled water
Bore fluid flow rate (ml/min)	1.40
External coagulant	Tap water
External bath temperature	25 °C
Air gap distance (cm)	1 cm
Spinneret o.d./i.d. (mm)	1.10/0.55
Coagulation temperature (°C)	25
Wind up drum speed	13.7 cm/s

The spun hollow fibers were immersed in the water bath for a period of 3 days, with daily change of the water, to remove the residual DMAc and the additives. The hollow fibers were then post-treated in 10 wt.% glycerol aqueous solution for 1 day in order to minimize fiber shrinkage and pores collapse. After the fibers were dried for 3 days, they were ready for the construction of hollow fiber test bundles.

2.3. Refinery wastewater ultrafiltration experiment

The permeation flux and rejection of PVDF hollow fiber membranes were measured by submerged ultrafiltration experimental equipment. The equipment is shown schematically in Fig. 2. An in-house assembled U-shape hollow fiber bundle, with a filtration area of 11.42 cm^2, was submerged in the prepared suspension in a membrane reservoir with a volume of 14 L. A cross-flow stream was produced by air bubbles generated by a diffuser situated underneath the submerged membrane bundle for mechanical cleaning of the membrane surface. The air bubbling flow rate was set to 1.8 L/min in order to maintain proper turbulence. Permeate flow rate was continually recorded using a flow meter.

The flux test was carried out with synthetic refinery wastewater with a mixed liquor suspended solids (MLSS) concentration of 3 g/L and constant pH of 6.9. All experiments were conducted at 25 °C using a vacuum pump on the permeate side. Firstly, the pure water permeation flux (J_w) was measured at reduced pressure (0.5 bar absolute) on the permeate side. Then, the permeation flux for the refinery wastewater (J_R) was measured. Both J_w and J_R were determined after the steady state was reached, and the flux was calculated as

$$J = \frac{V}{At} \tag{1}$$

where J is the flux (l/m^2 h), V is the permeate volume (l), A is the membrane surface area (m^2), and t is the time (h).

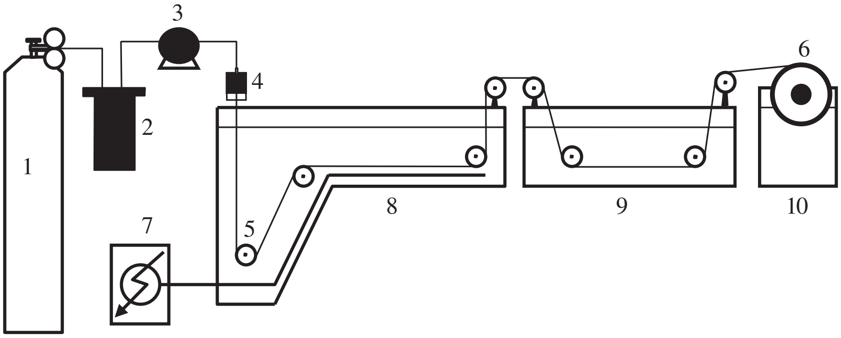

Fig. 1. Schematic diagram of the spinning system: (1) high purity nitrogen, (2) storage reservoir, (3) gear pump, (4) spinneret, (5) roller, (6) wind-up drum, (7) refrigeration unit, (8) coagulation bath, (9) washing bath, and (10) collecting drum.