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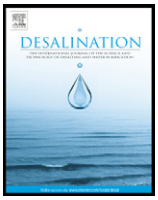

Comparison of two different UV-grafted nanofiltration membranes prepared for reduction of humic acid fouling using acrylic acid and *N*-vinylpyrrolidone

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ABSTRACT

UV-photografting using two different monomers, acrylic acid and *N*-vinylpyrrolidone, with different concentrations in an aqueous solution and various irradiation times were studied. Irreversible fouling of both the un-grafted polyethersulfone and the UV-grafted membranes have been studied using humic acid model solutions at two different pH values; 7 and 3. It was observed that the UV-grafted membranes exhibited practically less tendency to be irreversibly fouled by humic acid molecules at pH 7. However at the acidic condition of pH 3, some membranes exhibited a higher degree of fouling more than the un-grafted membrane, especially for membranes with higher roughness values. The smaller pore size generated after UV-grafting of polyethersulfone membrane did not significantly affect humic acid removal due to the larger humic acid molecular size.

1. Introduction

Selection of suitable material and the formation of a membrane with a desired specific structure are very important to enhance membrane performance for a specific application. In addition, it is often necessary to modify the membrane material and/or its structure to enhance the overall performance of the fabricated membrane. Generally, the objectives for modifications are i) increasing flux and/or selectivity and ii) increasing chemical resistance (solvent resistant, swelling or fouling) [1]. In the literature, several physical and chemical techniques of modification were carried out for bulk modification (i.e., polymer blend) or on membrane surface.

Bulk modification by blending polymer materials is normally used to produce a new functional membrane to achieve a specific target. Lau and Ismail [2] investigated the effect of sulfonated poly (ether ether ketone), SPEEK, polymer on polyethersulfone (PES) membrane performance. A good performance of the SPEEK blended PES membrane with high permeability and high rejection of salt/neutral solutes was achieved. The increase of water permeability and the obtained high rejection were explained based on the hydrophilicity nature of the SPEEK polymer and its electrical properties, respectively. SPEEK polymer was also used by Bowen et al. [3] and blended with polysulfone (PS). AFM studies revealed that the SPEEK-PS membrane had low adhesion force interaction between membrane surface and a silica sphere particle of colloid probe. This force interaction decreased as the SPEEK content was increased due to low adhesion forces resulting in membranes with high tendencies to reduce fouling. Poly (acrylic acid) (PAA) and PES were successfully blended to produce membranes with high pH sensitive and ion-exchange capacity [4]. The blended PAA/PES membrane has pH reversibility between 3 and 8 and also a high capability to be used as an ion-exchange membrane since it can bind ion metal (i.e. Cu^{2+}) [4].

Besides bulk modification of polymers, surface modification of membranes is a promising approach to provide membranes with tailor-made separation properties and a reduced tendency for fouling [5]. In fact, surface chemistry and morphology of membranes play an important role in the transmembrane transport of components, as well as on the efficiency of the membrane process [6].

Several procedures have been studied to chemically modify the membrane surface of a previously formed porous membrane in order to increase its hydrophilicity or to allow functionalization and incorporation of polymer segments. These membrane surface modifications include chemical oxidation, plasma treatment, classical organic reaction and grafting polymerization [7]. Among the graft polymerization methods, UV-initiated grafting is the most used technique [8–19] for the UF membrane surface modification. For example, Susanto et al. [8] modified PES ultrafiltration (UF) membrane using UV-photografting and found that the UV-modified membrane has a lower tendency of natural organic matter (NOM) fouling than the unmodified membrane. It is worth quoting that very few studies have been reported for the modification of nanofiltration (NF) membranes [20–23].

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The main objective of this paper is to study the UV-photografting modified membranes with improved NF anti-fouling properties by using two different hydrophilic monomers, acrylic acid (AA) and *N*-vinylpyrrolidone (NVP). Different UV-irradiation times and monomer concentrations in water were employed. Humic acid has been used as a model organic foulant and different humic acid aqueous solutions at different pH values have been tested.

2. Experimental

2.1. Materials

The monomers acrylic acid (AA) and *N*-vinylpyrrolidone (NVP) were purchased from Acros Organics Co. Their chemical structures are shown in Fig. 1.

Humic acid (Sigma-Aldrich Co.) was chosen as a model organic foulant. Hydrochloric acid (HCl, Sigma-Aldrich Co.) and sodium hydroxide (NaOH, Acros Organics) were used to adjust the pH of the feed humic acid solutions to the required values.

For membrane pore size determination, polyethylene glycol (PEG, Sigma-Aldrich Co.) of different molecular weights in the range 200–3350 g/mol were used.

The asymmetric commercial membrane NFPES10 purchased from Hoechst Company (Germany) with 75 µm thickness (based on SEM image without backing material) was used for UV-grafting.

2.2. UV irradiation

UV-light system of wavelength 365 nm using a B-100 lamp (Ultra-Violet Products Ltd) with a radiation intensity of 21.7 mW/cm^2 was used to modify the membrane surface following the immersion method [22]. The UV-light intensity was measured by the light intensity meter (Cole Parmer Instrument Co., VLX-3W). The reactor system and the modification protocol were described elsewhere [22]. For both AA and NVP monomers, the membrane was modified with different monomers concentrations (5, 15, 30 and 50 g/L) and irradiation times (1, 3 and 5 min).

2.3. Membrane characterisation

Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR-FTIR Bruker model Tensor 27) was used to characterise both the unmodified NFPES10 and the UV-modified membranes.

The surface of both the unmodified and the modified membranes were characterised by a multimode AFM (Veeco Instruments (USA)). Comprehensive reviews on membrane characterisation by AFM are available in the literature [24,25]. The images were obtained over different areas of each membrane sample. In this study, tapping mode was used and the same tip was employed to scan the surface of all membranes. Finally, all captured images were treated in the same way. From the obtained AFM images, the root mean square roughness, RMS, was determined considering the same scan range, 5 µm × 5 µm, for all images.

NF experiments have been carried out using a membrane module with an effective area of 12.6 cm^2, which can be operated under the transmembrane pressure in the range of 1 up to 9 bar. The feed solution was circulated through the membrane module by a pressure pump. In all NF experiments, the feed and retentate flow rates were maintained at 0.4 L/min. The permeate flux (J) of each membrane sample was determined by weighing the obtained permeate during a predetermined time using an electronic balance (Precisa, Model XB3200C) connected to a computer and calculated by the following equation:

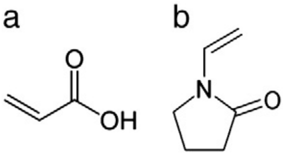

Fig. 1. Structure of monomers (a) acrylic acid (AA) and (b) *N*-vinylpyrrolidone (NVP).

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

where W is the weight of the obtained permeate during a predetermined NF operation time Δt and A is the membrane area.

The concentration of humic acid in the feed, retentate and permeate aqueous solutions were determined by Shimadzu UVmini-1240. The humic acid rejection factor (α) was calculated as follows:

$$\alpha = \left(1 - \frac{C_p}{C_f}\right) \times 100 \tag{2}$$

where C_p and C_f are the humic acid concentrations in the permeate and in the feed solutions, respectively.

Before all NF experiments, each membrane was pressurised at 7 bar for at least 2 h using deionised water to reduce compaction effect. Subsequently, the pure water experiments were conducted at different transmembrane pressures, ΔP (4, 5, 6 and 7 bar), in order to determine the pure water permeation flux (J_w) using Eq. (1). The membrane permeability, P_m, was determined from the slope of the straight line that can be obtained by plotting the permeate flux (J_w) against ΔP using the following equation:

$$P_m = \frac{J_w}{\Delta P} \tag{3}$$

Humic acid aqueous solutions were used and the product permeate rate (J_t) as well as the rejection factor (α), were determined as a function of time applying a transmembrane pressure of 6 bar. In this study, the pH of humic acid feed solution with a concentration of 15 mg/L was adjusted using 0.1 M NaOH or 0.1 M HCl. For both the un-grafted and the UV-grafted membranes, before and after NF experiments with humic acid solution, the system was washed with deionised water and the pure water permeation flux (J_{wf}) was measured again in order to evaluate the irreversible fouling in terms of pure water flux reduction, called hereafter irreversible fouling factor (FR_w). This is determined as follows [26,27].

$$FR_W = \frac{J_{w0} - J_{wf}}{J_{w0}} 100 \tag{4}$$

The pore size and pore size distribution of the un-grafted and the UV-grafted membranes were determined using feed aqueous solutions containing 200 ppm PEG and operating at a pressure of 6 bar. The feed solution temperature was maintained constant at room temperature. Each membrane was initially subjected to pure water experiments to determine the pure water permeation flux (*PWP*). Then, the PEG aqueous solution was circulated through the membrane module for about 1.5 h. The solute concentration in the feed, concentrate and retentate were measured by the total organic carbon (TOC) analyser (Model TOC-V$_{CPH}$, Shimadzu) and the solute separation was calculated using Eq. (2). Stokes radius was used to characterise the size of the solute. The Stokes diameter of PEG is determined from its molecular weight using Eq. (5) [28–30]:

$$a_d = 33.46 \times 10^{-10} M^{0.557} \tag{5}$$

where a_d is Stokes diameter (cm), and M is the molecular weight of PEG (g/mol).