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A comprehensive physico-chemical characterization of superhydrophilic loose nanofiltration membranes

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ABSTRACT

Nanofiltration (NF) membranes, especially loose NF membranes, trigger a growing interest for the fractionation of concentrated organic matters/salt mixtures in addition to the production of pure water. This study presents an in-depth characterization of two superhydrophilic loose NF membranes (Sepro NF 6 and 2A, Ultura). The physical characterization included the determination of the molecular weight cut-off (MWCO), pore size distribution, membrane morphology, surface charge, roughness and hydrophilicity. This was combined with a chemical characterization, i.e., by Fourier-transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS), to determine the intrinsic membrane properties. The chemical characterization demonstrates that both Sepro NF membranes are poly(piperazineamide) based, showing the modification chemistry for the top layer through XPS measurement. Specifically, Sepro NF 6 and NF 2A membranes were found to have a superhydrophilic surface (contact angle for Sepro NF 6: $14.3 \pm 0.9°$; that for Sepro NF 2A: $21.7 \pm 1.4°$) with a low roughness, offering a potential advantage over conventional NF membranes in minimizing membrane fouling. Sepro NF 6 and NF 2A membranes had a mean effective pore size of 0.64 ± 0.03 nm and 0.52 ± 0.01 nm (corresponding to MWCOs of 862 ± 80 Da and 493 ± 53 Da), respectively. In terms of filtration performance, Sepro NF 6 showed a high permeability of 16.7 L m^{-2} h^{-1} bar^{-1} with 88.9% salt transmission for 0.01 mol L^{-1} NaCl solution, and a slightly lower permeability and salt transmission was obtained for Sepro NF 2A, which is desired for an effective fractionation of target organic matter/salt mixtures.

1. Introduction

Nanofiltration (NF), with its characteristic pore size in the order of 1 nm, is a burgeoning pressure-driven membrane process [1,2]. NF membranes can generally separate molecules with a molar mass of 200–1000 Da along with partial salt rejection, which make NF attractive for water purification, water softening, wastewater treatment, and desalination [3–7]. Furthermore, due to the selective separation through the mechanisms of size exclusion and electrostatic repulsion, NF membranes are promising for the fractionation of organic matter/salt mixtures in the textile industry [8], mixed organic matter systems in food [9], agriculture and pharmaceutical industries [10,11], and binary ions (SO_4^{2-}/Cl^- and F^-/Cl^-) for drinking water production [12]. However, the use of NF membranes in these applications is hindered by the occurrence of membrane fouling, resulting from the interaction between feed constituents (e.g., colloids, dissolved organic matter, proteins, and bacteria) and the membrane surface [13–16]. Fouling may deteriorate the permeate quality and increase the operational costs.

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Although different pretreatment strategies, such as coagulation [17,18], ozone oxidation [19,20], UV/H_2O_2 and Fenton oxidation [21], have been shown to alleviate membrane fouling, these could involve significant additional costs. A potentially more effective way is to improve membrane antifouling properties.

Characterization of the physico-chemical properties of NF membranes is vital for understanding their separation performance as well as antifouling properties [22,23]. In general, a hydrophobic top layer decreases the flux [13]. In addition, the hydrophobic interactions between the membrane surface and the constituents of the feed solution may overcome the electrostatic forces to result in severe membrane fouling. Therefore, one of the most common strategies for preparing antifouling membrane surfaces is to enhance the surface hydrophilicity, e.g., by incorporating hydrophilic monomers or nanoparticles [24–26]. Besides hydrophilicity, surface roughness and charge properties also play critical roles in membrane fouling [27]. Colloidal particles have a strong propensity to accumulate in the "valleys" of rough membranes in the initial stage of fouling [28,29]. Surface roughness can further influence the membrane hydrophilicity as well [30,31]. The surface charge characteristics of NF membranes are also important in determining the foulant-membrane electrostatic interactions as well as the permselectivity to the charged solutes [32,33]. Due to the increasing diversity of NF membranes, such as positively charged NF membranes [34,35], and hollow fiber NF membranes with double repulsion effects [36], more applications of NF membranes in industry are being explored, requiring a more in-depth characterization of NF membranes, not only in terms of purification but also as tools for fractionation.

In our previous work, commercial loose NF membranes (Sepro NF 6 and NF 2A, Ultura) were evaluated for the separation of dye/salt aqueous streams, demonstrating that loose NF membranes can be an excellent alternative to conventional denser NF membranes (such as NF 90 from Dow Film Tec [37] and DK from GE Osmonics [38]) to allow a high retention of dyes ($>99.6\%$) and a high transmission ($\sim 97.5\%$) of NaCl (in a 40 g L^{-1} solution) [39]. The intensive work from Zhang's group and Xue's group confirmed the excellent fractionation performance of dye/salt mixtures of loose NF membranes [40–44]. The combination of a low salt rejection and high dye retention for loose NF membranes demonstrates the potential for fractionation of organic system/salt mixtures (examples including separating glyphosate [11], stevioside [45], heterocyclic drug derivatives [46], soy sauce [47], iminodiacetic acid [48], and/or organic acids from salty aqueous solutions) while avoiding the penalty of a high osmotic pressure of feed solutes due to their partial salt retention [39]. Nevertheless, the material–structure–performance relationship of such high performance membranes has not yet been well documented. Therefore, it is of paramount importance to perform a comprehensive physico-chemical characterization to provide deep insights of the role of membrane chemistry and structure on NF performance.

In this study, the physico-chemical properties of the loose NF membranes mentioned above were comprehensively characterized. The chemical nature of the membranes was studied by Fourier transform infrared (FTIR) and X-ray photoelectron spectroscopy (XPS). Membrane morphology, roughness, hydrophilicity, pore size, surface charge, permeability, and salt rejection were also characterized. The intrinsic correlation between various membrane properties and surface chemistry was analyzed and may facilitate the understanding of their potential for treatment of other industrial streams as a guideline for membrane end user, and serve as a methodology for membrane characterization in the growing area of loose nanofiltration.

2. Experimental section

2.1. NF membranes and chemicals

All reagents and chemicals in this study were analytical grade and were used as received without any further purification, unless otherwise specified. Ultrapure water (electrical resistance of 18.2 MOhm cm, Millipore water system) was used throughout this work.

Two NF membranes, Sepro NF 6 and NF 2A (Ultura, USA), were investigated in this study. The properties of these two membranes are shown in Table 1.

2.2. Membrane characterization

2.2.1. Fourier-transform infrared spectroscopy (FTIR) measurement

Aiming at exploring the surface chemical functionality of the clean loose NF membranes, FTIR measurement was performed through an ATR-FTIR spectrometer (Perkin-Elmer Spectrum 100, Germany), which is equipped with a platinum diamond for single reflection. The spectra were taken in the range of 400–4000 cm^{-1} at a resolution of 1.43 cm^{-1}.

2.2.2. X-ray photoelectron spectroscopy (XPS) analysis

XPS spectroscopic measurement can provide important chemical and element information for the surface of NF membranes. XPS spectroscopy was performed on virgin NF membrane using a Kratos Axis Ultra DLD spectrometer (Japan) with an Al Kα (1486.6 eV) anode mono X-ray source operating at 45 W (3 mA × 15 kV). For each survey measurement, the NF membranes were scanned over a range from 0 to 1400 eV with a resolution of 1 eV and a surface area of $300 \times 700\ \mu m^2$. High-resolution scans for C (1s) peak were obtained with a resolution of 0.1 eV. The high-resolution XPS spectra were subtracted by the Shirley-type background, and Gaussian–Lorentz peak deconvolution was conducted to determine the binding energy shift of C (1s). All binding energies were referenced with the C (1s) hydrocarbon peak at 284.8 eV.

2.2.3. Scanning electron microscopy (SEM) observation

The morphology of loose NF membranes was visualized by SEM measurement with a Philips Scanning Electron Microscope XL30 FEG (Netherlands). The samples were dried prior to analysis in a vacuum chamber, then sputter-coated with gold nanoparticles. The SEM images were taken in high vacuum condition at different magnifications. For SEM observation of membrane sections, membrane samples were fractured in liquid nitrogen.

2.2.4. Atomic force microscopy (AFM) analysis

In order to investigate the surface topographies of loose NF membranes, AFM measurement was performed at ambient conditions using an Agilent Technologies 5500 Scanning Probe

Table 1
Properties of NF membranes used in this study.

Membrane	Sepro NF 6	Sepro NF 2A
L_p (L m^{-2} h^{-1} bar^{-1}) at 25 °C[a]	16.7	10.1
Max. temperature (°C)	50	50
Process pH limitation[b]	3.0–10.0	3.0–10.0
Salt rejection (NaCl, %)[c]	8.4	24.8

[a] Pure water flux at 10 bar and 25 °C, obtained experimentally in this work.
[b] Data provided from membrane manufacturer.
[c] Salt rejection of 2000 ppm NaCl solution at 10 bar and 25 °C, obtained experimentally in this work.