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Tuning the nanofiltration performance of thin film strong polyelectrolyte hydrogel composite membranes by photo-grafting conditions

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ABSTRACT

Polyethersulfone ultrafiltration membranes were converted into charged nanofiltration membranes having a strong polyelectrolyte hydrogel as selective barrier layer through the UV-photo initiated graft polymerization technique. This was accomplished by using vinyl sulfonic acid as the functional monomer and N,N′-methylenbisacrylamide as a cross linker monomer (Bernstein et al., ACS Applied Materials & Interfaces, 4 (2012) 3438–3446). In this research the resulting composite membranes were further characterized using different methods (ATR-FTIR spectroscopy, zeta potential, contact angle, scanning electron microscopy). ATR-FTIR data were used to quantify the degree of grafting. The composite membranes' zeta potential was negative throughout the pH range and as high as -70 mV. The hydrogel composite membranes were also very hydrophilic with a contact angle of 11°. The membrane performance—salt rejection and water permeability—obtained at varied functionalization conditions—molecular weight cut-off of the base membrane, monomer concentration, cross linker fraction, UV irradiation intensity and time—was systematically investigated and the results were correlated to the membrane characterization data. Separation performance was also tested using mixed salt solutions. Larger composite membrane samples were prepared and long-term stability of nanofiltration (NF) performance was evaluated in cross-flow experiments. The performance of the best of the newly fabricated composite membranes was comparable to other polyelectrolyte-based NF membranes as well as to some commercial NF membranes presented in the literature.

1. Introduction

The separation properties of nanofiltration (NF) membranes are between those for materials used for reverse osmosis (RO) and ultrafiltration (UF). These membranes are characterized by high rejection of multivalent ions and uncharged solutes (above 300 g/mol), high flux at a relatively low pressure and low operational and maintenance costs [1].

NF membranes are used today in many applications, including water softening [2], and removal of dissolved organic matter from natural [3], municipal [4], and industrial [5] water sources. Because of their advantages, the use of such membranes for other applications is also being explored [6–8]. Yet, the current commercial NF membranes have some shortcomings [1], therefore, new NF membranes are being developed.

NF membranes are usually made from polymeric materials, though ceramic membranes are also available [9]. The most common commercial polymeric NF membrane is a composite structure with a thin selective barrier layer made of a slightly negatively charged polyamide fabricated by interfacial polymerization. These membranes have a high salt rejection but they have a poor resistance to chlorine and similar oxidative disinfectants [10], and a high fouling and biofouling propensity [11], because of their relatively high hydrophobicity. This type of membrane is also sensitive to temperatures higher than 40 °C, to extreme pH values ($pH < 2$ or $pH > 12$), and to organic solvents. Other commercially available NF membranes are made from positively charged polyamide and negatively charged sulfonated polyethersulfone. The latter membranes have better stability, but usually a lower separation performance.

For the past years many attempts have been made to fabricate NF membranes that will overcome the aforementioned drawbacks. These include the improvement of the current NF membranes [12,13], the synthesis of NF membranes from new materials [14–16] and the use of new fabrication techniques [17–19].

NF membranes having a polyelectrolyte as a selective barrier layer presented promising results, especially thin-film composite membranes which were fabricated using the 'layer by layer' (LBL) deposition technique [17,20–22]. However, this method is still complicated and difficult to up-scale for commercial usage [23,24]. Another appealing and easy method for obtaining a

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polyelectrolyte-based membrane is by surface graft copolymerization of a thin film of a suited charged polymer on a UF base membrane, most preferably using the UV-photo irradiation method. This method was successfully applied for modification of UF to NF membranes [25–29]. Yet, many of these membranes had either low rejection or low permeability. Another way which might result in an improved polyelectrolyte NF membrane while still using the relatively simple photo-initiated graft copolymerization method is the fabrication of a hydrogel as a selective barrier layer. This can be realized by copolymerization of a functional monomer and a cross linker monomer on a UF support membrane. Functionalization of UF membranes with hydrogel layers by UV-photo initiated graft copolymerization was already performed for other applications such as pervaporation [30], the improvement of protein separation [31] and the reduction of fouling and biofouling propensity for UF and RO membranes [32–34].

In a previous paper, we had explored the possibility of broadening this approach and functionalizing an UF membrane with a polyelectrolyte hydrogel, thus converting it into a NF membrane [35]. It was shown that a negatively charged strong polyelectrolyte hydrogel can be successfully fabricated on a polyethersulfone (PES) UF membrane by means of UV-photo initiated graft polymerization using vinyl sulfonic acid (VSA) as functional monomer and N,N′-methylenebisacrylamide (MBAA) as a cross linker monomer. In addition, it was demonstrated that the fabricated membrane had significant advantages over other NF membranes: a very low surface roughness, a stable salt rejection with increased salt concentration which only slightly reduced at high concentration (up to 8 g/L Na_2SO_4), and a stable performance at low and high pH values (pH 1.5 and pH 10). While the focus of the previous work had been onto the functionalization and its mechanism and the application potential, in the current study, the polyelectrolyte hydrogel composite NF membranes were further characterized and their separation performance as function of different fabrication conditions was investigated in detail. Ultimately, correlations between preparation conditions, surface and barrier structure and separation performance were established, and the membranes were compared with other NF membranes reported in the literature.

2. Experimental

2.1. Materials

The polyethersulfone (PES) membranes were supplied by Sartorius Stedim Biotech S.A. (Göttingen, Germany) with nominal molecular weight cut off (MWCO) in the range from 10 kDa to 300 kDa. It is noted that in a previous report the MWCO of these membranes measured using dextrans as probes was found higher for all membranes [36]. Prior to the modification the membranes were cut with a 56 mm diameter punch hole and washed in methanol for 1 h, then thoroughly washed with Milli-Q water and left in Milli-Q water until used.

Vinylsulfonic acid sodium salt (VSA; 25% in water), N,N′-methylenbisacrylamide (MBAA), $MgSO_4$, NaCl, Na_2SO_4 and $CaCl_2$ and glucose were purchased from Aldrich and used without purification. Sucrose was purchased from Acros, Geel, Belgium. As reference substance for the ATR-FTIR spectra polyvinylsulfonic acid (PVSA; 25%, Sigma-Aldrich) was used and air dried before the measurement.

In order to obtain a monomer solution with 40% VSA, the 25% VSA solution was concentrated under reduced pressure at 37 mbar and 45 °C. The monomer concentration was 40% when the solution density was 1.32 g/L.

All experiments were done with purified water from a Milli-Q system from Millipore.

2.2. Modification procedure

The modification was carried out as described in our previous report [35]. Briefly, 5 mL monomer/ cross linker solution (which had been deaerated with nitrogen for 10 min) was placed on the surface of a PES membrane (56 mm). The membrane was covered with a special glass filter to narrow the UV wavelength to $\lambda = 315–400$ nm, was put inside the UV photo reactor (UVA Cube 2000, Hönle AG, Germany; equipped with a 20 cm long mercury lamp, allowing a homogenous irradiation of 0.1 m^2 area via reflecting walls) and was immediately irradiated for various times (4.5–35 min) and at 16 or at 50 mW/cm^2 irradiation intensity. Thereafter, the membrane was washed with Milli-Q water for 24 h at room temperature and stored in Milli-Q water until further used.

For the long term NF experiment a 30 kDa PES membrane having an effective area of 84 cm^2 was covered with a filter paper to attain a homogenous distribution of the monomer solution over the membrane. The monomer/ cross linker mixture (25% VSA and 1.5% MBAA, in water) was poured over the filter paper soaking it up completely and the membrane was UV-irradiated at 50 mW/cm^2 for 18 min.

2.3. Degree of grafting

The degree of grafting (DG_s) was determined by attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy (Varian 3100, USA equipped with a one reflection KRS-5 crystal, 45°; sixty-four scans were taken for each spectrum at a resolution of 4 cm^{-1}) and defined as follows:

$$DG_s = I_{mon}/I_{mem}, \qquad (1)$$

where I_{mon} is the intensity of the 1040 cm^{-1} band assigned to the symmetric stretching of the VSA sulfonate group and I_{mem} is the intensity of the 1577 cm^{-1} band, a C-H peak from the aromatic ring in the base PES membrane which does not appear in the functional monomer or the cross linker IR spectra.

2.4. Membrane characterization

Zeta potential was measured using a SurPASS streaming current analyzer (Anton Paar GmbH, Graz, Austria) with an adjustable gap cell that was set to 100 μm and at pressure differentials of 0–400 mbar. Prior to measurement the membranes were soaked for few hours in 1 mM KCl solution. Three distinct samples were measured; each sample was measured in two cycles at each direction and was rinsed 10 minutes at each new pH value. The background solution used was 1 mM KCl and the pH was adjusted using HCl (0.1 M) and NaOH (0.1 M). The zeta potential was calculated using the Fairbrother-Mastin equation.

Contact angle was determined using the captive bubble method with an optical measurement system (OCA 15 Plus, Dataphysics GmbH, Filderstadt, Germany). An air bubble of 5 μL was released from a stainless steel needle onto the inverted sample with its separation layer surface immersed into Milli-Q water. The reported values are the average of at least 2 distinct membrane samples and 5 measurements on each sample.

Scanning electron microscopy (SEM) images of the modified membranes surface and cross section were examined with a ESEM Quanta 400 FEG instrument (FEI) at standard high-vacuum conditions. A K 550 sputter coater (Emitech, U.K.) was used to coat the outer surface of the sample with gold. The cross section images were obtained by cutting the membrane in liquid nitrogen.