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Understanding the oxidative cleaning of UF membranes

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ABSTRACT

Increased protein fouling of polyether sulphone membranes after NaOCl cleaning was previously reported but not explained. Here we show that the cleaning increases the hydrophilicity, and the degree of increase linearly correlates with the amount of adsorbed protein. The high initial flux through the cleaned membrane is a result of the hydrophilization of the membrane surface and a promise for the enhanced fouling. We propose that the proper oxidative cleaning should target the restoration of the initial flux and not its increase over initial values. The previously reported pore size changes are subjective as higher hydrophilicity of the membrane surface increases water permeability and adsorption of size test solutes.

1. Introduction

Chemical separations are a major cost component of most pharmaceutical and biotechnological industrial applications. Low-pressure polymer nanoporous membranes with a low cost/area ratio, good flux, low energy consumption, range of pore sizes, rich surface chemistry, simple up-scaling and continuous separation ability [1] are the attractive separation technology. The most persistent problem associated with the low-pressure micro- and ultra-filtration (MF/UF) membranes is the problem of organic fouling. The problem has been of interest of more than 1200 papers [2]. The solution to the fouling problem, the periodical chemical cleaning applied to relieve "foulants" [3,4], has received significantly less attention. Only 50 papers had been published, and all of the papers point on the immediate and long-term effects of cleaning on membrane performance.

The cleaning is a sequence of 4–6 steps that include transport of the cleaning agents through fouling layers and membrane surface reactions to detach the foulants from the membrane surface. To overcome mass transfer barrier and to maintain reasonable reaction rate the cleaning is usually performed with concentrated solutions. One of the most popular cleaning agents, sodium hypochlorite [5], is very successful in restoration and sometimes even growth of the permeate flux [6]. A more detailed investigation revealed that the increase comes on the expenses of the polymer chain breakage [7–12]. The breakage is held responsible for the expansion of the membrane pore size [7,13], changes in membrane hydrophilicity [13], increased streaming potential [14], and deteriorated mechanical strength [15,16]. The oxidative cleaning also results in profound fouling [17] and enhanced protein retention [17,18] of post-cleaned membrane, the two phenomena that were previously observed but not explained.

Our study confirms the previous reports on chlorine-induced changes in hydrophilicity, initial flux, degree of fouling and protein retention. However, the pore size changes were minor and did not influence post-cleaned performance. Experiments with intensity of chlorine cleaning of polyethersulphone (PES) and polyvinyldifluoride (PVDF) membranes proved that the key change that affects the membrane performance is the increased hydrophilicity. The hydrophilization of the membrane surface improves adsorption of polyethylene glycols (PEGs) [19] and dextrans [20] conventionally used for pore size estimation. The higher water permeability of post-cleaned membrane [6] is related to higher hydrophilicity and increased surface charge [7]. The boosting protein fouling [17] of intensively cleaned membranes is governed by hydrophilic nature of proteins. On the operational level, the NaOCl cleaning with aggregate free chlorine doses of 5 g/(l h) and higher increases surface charge [21,22] and affects the membrane hydrophilicity. An increase in the permeate flux over the initial values can be viewed as a worrying sign that points on changes in membrane structure and increased fouling potential.

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2. Materials and methods

2.1. Membranes—preparation and characterization

The new 30 kDa PES and PVDF membranes (Sterlitech Corporation, Kent, WA, USA) were used. Before the filtration the membranes were soaked in NaOH solution (pH 9) and vibrated at 55 °C for 2 h. The cleaning resulted in similar feed and permeate TOC levels in filtration of deionized water DIW (RO quality).

Membrane contact angle was measured with OCA 20 (DataPhysics Instruments GmbH) contact angle meter using the sessile 10 μL DIW drops. Eight to ten measurements with separate membrane pieces per sample were performed.

Pore size distribution was evaluated by water permeability and solute transport tests. The water permeability test determines the geometric mean pore diameter d_{50} (nm) with Hagen–Poiseuille equation [23]:

$$d_{50} = 2\sqrt{\frac{8\mu\,\Delta x M}{A_k}} \quad (1)$$

where μ is the water viscosity (kg/(m s)), Δx is the membrane thickness (100 ± 50 nm), A_k is the membrane porosity determined by weighing the dry and wet samples (0.16 and 0.18 for PES-30 and PVDF-30, respectively), and M is the membrane permeability (l/(m^2 h bar)).

The solute transport tests were performed with 0.3 g/l solutions of PEGs, polyethylene oxides (PEOs) and dextrans (Sigma–Aldrich). The 0.6, 3.4, 6.0, 10.0, 20.0, 35.0 kDa PEG; 100, 200, 600 kDa PEO; 6, 40, 70, 100 kDa dextran polymers were used unmodified. The tests were performed at 1 bar transmembrane pressure (TMP) and ambient temperature. The polymer concentration was measured with Apollo 9000 total organic carbon (TOC) analyzer (Tekmar Company). The polymer rejection percentage R was calculated using the relation:

$$R = \left(1 - \frac{C_p}{C_0}\right) \times 100\% \quad (2)$$

where C_p and C_0 are the polymer concentrations (g/l) in the permeate and in the feed, respectively. The MW_{50} (Da) of a polymer that was rejected by 50% was converted into d_{50} (nm) using the correction [24]:

$$d_{50} = 0.156(MW_{50})^{0.33} \quad (3)$$

Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) spectra were recorded on a Nicolet spectrometer (model 5PC, Thermo Electron, Waltham, MA, U.S.A.). The ATR accessory contained a ZnSe crystal (25 mm × 5 mm × 2 mm) at a nominal incident angle of 45° yielding about 12 internal reflections at the membrane surface. All spectra (100 scans at 4.0 cm^{-1} resolution and rated to the appropriate background spectra) were recorded at ambient temperature. The instrument was purged with dry nitrogen to prevent interference of atmospheric moisture. The membrane samples were kept in closed Petri dishes filled with water and blotted dry before the analysis. The excess water was removed by drying in a desiccator over P_2O_5 for 2 h.

AFM 512 × 512 pixel images were obtained in tapping mode with a Digital Instrument Dimension 3100 (Digital Instruments) mounted on an active anti-vibration table. The scan size was 1 μm and a scan rate was 1 Hz. The root mean square (rms) membrane surface roughness was calculated as:

$$\mathrm{rms} = \sqrt{\frac{\sum (Z_i - Z_{av})^2}{N}} \quad (4)$$

where Z_i is the height value for a particular point on the image, Z_{av} is the mean height of all the pixels in the image and N is the total number of pixels within the image.

2.2. Filtration experiments

Filtration experiments were performed in 150 ml autoclaved stirred cell (magnetic stirring, 400 rpm) equipped with a back-pressure TMP controller [17]. The TMP was set with precision regulator IR2000-FO2, equipped with digital pressure display ISE40 (SMC Corporation). The membranes were first compacted with 30 min transmembrane flux of DIW (pH 5.5) at 2 bar N_2 (99.99% purity). The 30 min filtration cycles were performed with 0.3 g/l bovine serum albumin (BSA) [25] (Sigma–Aldrich) in DIW at 1 bar TMP. The BSA 4 nm × 14 nm dimensions [26,27] were confirmed with Transition electron microscope JEM-1230 (JEOL Ltd.) equipped with TemCam-F214 (TVIPS Company) camera. The point of zero charge at pH 4.2 [28] was confirmed with ZetaPlus analyzer (Brookhaven Instruments Corporation) equipped with a 30 mW 657 nm laser (Hamamatsu Photonics K.K.).

The BSA concentration in permeate was detected in triplicates with Bradford assay after 5.5, 12.5 and 27.5 min filtration. The absorption peak at 595 nm was monitored with Synergy HT Multi-Mode Microplate Reader (BioTek Instruments). The BSA retention R_{BSA} was calculated as [29]:

$$R_{BSA} = 1 - 2(1-\lambda)^2 + (1-\lambda)^4 \quad \text{for } \lambda \le 1 \quad (5)$$

$$R_{BSA} = 1 \quad \text{for } \lambda > 1 \quad (6)$$

where λ is the ratio of BSA hydrodynamic diameter d_{BSA} to the mean pore diameter d_{50}. Membrane flux was calculated gravimetrically at 10 run intervals (0.5, 0.5, 0.5, 1.0, 1.0, 2.0, 3.0, 4.0, 5.0, 10.0 min) as

$$J = \frac{\Delta m}{\rho S\ \Delta t} \quad (7)$$

where Δm is the permeate weight difference (kg) measured with Kern PLS 2100-2 (Germany), Δt is the frequency interval (h), S is the active membrane surface area (0.0025 m^2), and ρ is the permeate density (~1000 kg/m^3).

2.3. Membrane cleaning

Membrane cleaning was performed with 0.5 g/l sodium hypochlorite (Unilever Best Foods Israel, 30% free chlorine) in DIW at pH 10.0 in closed Petri dishes. The membrane soaked in 50 ml cleaning solution was fixed on a vibration table for the time periods of 10, 20, 30, 40, 100, 140 and 240 h. The cleaned membrane was washed with DIW. The cleaning intensity was displayed as Ct value, a product of free chlorine concentration C and contact time t. The hydraulic cleaning efficiency was evaluated as:

$$CE_h = \frac{J_{0,clean}}{J_{0,virgin}} \quad (8)$$

where $J_{0,clean}$ is the flux through chemically cleaned membrane, and $J_{0,virgin}$ is the flux through virgin membrane. Cleaning efficiency was determined as a ratio of aggregate DIW flux through cleaned and virgin membranes after 12.5 min filter run.

3. Results

The typical experiment included the stages of BSA fouling, NaOCl cleaning and another BSA fouling, all carried with PES-30 and PVDF-30 membranes. The fouling stage was conducted with 0.3 g/l BSA for 30 min at 1 bar TMP. The cleaning was performed with 0.5 g/l NaOCl at different times to achieve the cleaning intensities Ct between 5