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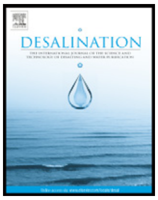

Improved membrane structures for seawater desalination by studying the influence of sublayers

Arcadio Sotto [a,b], Ali Rashed [a], Rui-Xin Zhang [a], Ana Martínez [c], Leen Braken [a], Patricia Luis [a], Bart Van der Bruggen [a,*]

[a] Department of Chemical Engineering K.U.Leuven, Leuven, Belgium
[b] Department of Chemical and Energy Technology, Rey Juan Carlos University, Madrid, Spain
[c] Department of Basic Sciences Applied to Engineering, Technical University of Madrid, Madrid, Spain

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ABSTRACT

This study describes the influence of polyethersulfone (PES) sublayers on the performance of polyamide (PA) reverse osmosis membranes. Asymmetric polymeric sublayers were synthesized by using the DIPS technique (Diffusion Induced Phase Separation). Sublayers are optimized mainly with respect to hydrophilicity, permeability and rejection potential by adjusting synthesis procedures. Parameters that were found to have an influence are the type of solvent (DMF and NMP were used), the air humidity, processing time, and concentrations of polymer. By carefully controlling these parameters, it was possible to prepare a range of sublayers with different characteristics, in the ultrafiltration–nanofiltration area. To visualize membrane surface characteristics, both scanning electron microscopy (SEM) and atomic force microscopy (AFM) measurements were performed. In addition, titanium (TiO_2) nanoparticles were assembled with polyethersulfone (PES) membranes at ultralow concentrations of nanoparticles to characterize TiO_2/PES composite membranes and evaluate their permeate flux and solute rejection.

Subsequently, a polyamide top layer was added by interfacial polymerization using typical reagents both in the aqueous and in the organic phase. The membrane performance was evaluated in terms of flux and salt rejection. Experimental design was performed in order to obtain the importance of some experimental variables during the polymerisation process. It was found that depending on the type of sublayer used in the procedure, a different membrane performance could be obtained.

1. Introduction

Membrane fouling is one of the main remaining drawbacks for the use of reverse osmosis for desalination [1]. Causes of fouling comprise supersaturation of salts such as $CaCO_3$ and $CaSO_4$, particle deposition, interactions with micro-organisms leading to growth of bacterial colonies, and adsorption of organic compounds on the membrane surface. The main consequences of fouling are a decrease of the membrane lifetime due to the need for chemical cleaning, a possible change in the membrane's rejection capacity [2], and a significant loss of feed water in the concentrate stream [3]. Legal limitations on concentrate discharge may apply; the risk of fouling imposes working at relatively low recovery rates. Avoiding membrane fouling and solving the concentrate problem are therefore (indirectly) related challenges [3].

Strategies to minimize the effect of fouling are based on either avoiding fouling or remediation of fouling [4]. Remediation by chemical cleaning is necessary for all membrane processes in nearly all applications, but can be minimized by optimizing process conditions and the choice of membrane materials. Various methods for cleaning have been developed, aimed at a posteriori impact on reverse osmosis membranes. All of these are mainly based on chemical interactions using alkaline, acid or oxidizing solutions in the presence of surfactants [5]. Since the polymers used in reverse osmosis membranes have only a limited chemical resistance (a typical example is polyamide, one of the most used materials for reverse osmosis membranes), it can be easily understood that in each cleaning cycle, the membrane material will be partly damaged. After a number of cycles, the membrane has to be replaced because of leakages or reduced permeate quality. Early detection systems may improve this by allowing to take action before fouling takes place, or at the very beginning of the process [6].

Making the membranes more chemically resistant therefore helps in handling fouling, because more cleaning cycles can be applied or a harsher environment can be used [7]. Nevertheless, this strategy does not reduce the need for cleaning, and even increases the impact of cleaning on the environment. Various other materials for top layers have been proposed [8]. Impact on the chemical resistance of the

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[*] Corresponding author. Tel.: +32 16 32 23 40; fax: +32 16 32 29 91.
E-mail address: bart.vanderbruggen@cit.kuleuven.be (B. Van der Bruggen).

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membrane can be obtained by using other polymers in the top layer, or by strengthening the structure underneath, i.e., the sublayers.

Avoiding fouling is possible by using adequate take-in procedures, pretreatment methods and operation modes. Hydrodynamics can be optimized in view of reducing concentration polarization; the increase of solute concentrations at the membrane surface, which is inherent to membrane separations, is minimized in this way [9]. This is not a solution to fouling, but avoids the situation to become worse.

Pretreatment is generally considered indispensable for a stable operation in RO. In addition to classical processes such as coagulation/ precipitation or slow sand filtration, micro- and ultrafiltration have been studied [10], and were considered the best choice applications which are thought to be especially problematic; for beach well intake it might be too expensive. Vedavyasan [11] also indicates that ultrafiltration is probably the 'safest' method. Nanofiltration has been studied as an advanced pretreatment method in view of hardness removal [12,13], with the additional possibility of operating reverse osmosis at higher recovery. However, Vedavyasan [11] also points out that the advances in pretreatment methods have not kept pace with the advances in membrane development, e.g., fouling resistant (FR), extra low energy (XLE) membranes.

This strategy involves the membrane material itself; the aim is to modify membrane surfaces in view of obtaining a membrane less susceptible to fouling. The surface roughness was found to play a major role for low pressure reverse osmosis and nanofiltration membranes: a more rough surface is more prone to fouling than a 'smoother' surface [14,15]. Hydrophilicity also plays a role: more hydrophobic membranes are clearly more susceptible to membrane fouling than hydrophilic membranes [16]. A careful control of surface roughness, hydrophilicity and charge may result in an improvement of the fouling resistance due to a better repulsion of the membrane surface [17]. Surface modifications can be done by UV-irradiation [18,19], or by plasma treatment [20]. This would give the membrane a more hydrophilic character and intrinsically avoid fouling. Yu et al. [21] showed that an increased surface hydrophilicity due to the deposition of P(NIPAM-co-Am) coating layer increases the reverse osmosis performance. The membrane surface modification conducted under certain conditions tended to increase both the water permeability and the salt rejection. The water permeability was enhanced significantly by 12%, while the salt rejection increased slightly from 98.5% to 98.9%. Rana et al. [22] prepared membranes by incorporating in-situ hydrophilic surface modifying macromolecules (iLSMM) into the TFC membranes, rendering the surface of the TFC membranes significantly more hydrophilic. A slight improvement in NaCl rejection was observed for all the membranes. Kang et al. [23] observed that the NaCl rejection of RO membranes had no significant change after surface modification, which was also reported by other researchers [24–26]. For example, the NaCl rejection of one RO membrane changed from 98.5% to 98.0% [25], and from $99.0 \pm 0.3\%$ to $99.3 \pm 0.5\%$ for another membrane [26] after surface modification using triglyme and PEGDA, respectively.

All methods involving membrane modifications and optimization of membrane materials are based on the top layer. Direct interaction between foulants and the membrane indeed occurs through the thin top layer; therefore, the characteristics of the top layer determine the performance of the membrane structure, including fouling rate and resistance against fouling. Nevertheless, by evaluating the overall membrane structure, it is obvious that the sublayers will also play a role during transport through the membrane. Tang et al. [27] compared coated and uncoated reverse osmosis membranes and visualized the polyethersulfone sublayer by using TEM. It was shown by using XPS that the surface characteristics were significantly different from the structure underneath. The sublayers are microporous materials that have their own characteristics: pore size, mass transfer resistance, hydrophobicity. Poly(ether)sulfone is commonly used for the support layers; this polymer is suitable because the pore size obtained by phase inversion synthesis methods is in the range of ultrafiltration–nanofiltration membranes [28]. In a recent study [29], it was found that these membranes have a poor reproducibility and may suffer from large variations in molecular weight cut-off (MWCO), water flux and surface roughness. In addition, it is not clear to what extent the morphology of the sublayer influences the eventual reverse osmosis membrane. Currently used approaches can be based on a single sublayer or a sequence of up to three sublayers on a porous support. The sublayers have to make a compromise between high pore size, high flux for avoiding additional resistance to mass transport, and low pore size, low flux for providing a smooth transition to the top layer. This has also implications for membrane fouling, on two levels. The first one is related to the top layer itself: properties of the top layer, including membrane thickness and surface roughness, are influenced by the nature of the sublayers. Therefore, an optimized sublayer structure should directly lead to a better fouling resistance, on condition that the sublayer is evaluated with respect to the overall fouling resistance; this has never been done before.

The second implication is that even though the sublayer is shielded from the feed solution due to the presence of the top layer, it may still be accessible for small foulants permeating through the membrane material and clogging the sublayers. This is not to be expected for relatively porous sublayers with large pore sizes available, but may be an overlooked problem when multilayer membranes are manufactured in view of obtaining a gradually finer structure without any residual defects. This is particularly important for reverse osmosis membranes, of which the performance is limited by defects in the top layer.

This work was focused on improving the performance of the membrane in terms of water affinity and permeation, taking into account the requirements for flux and salt rejection.

2. Materials and methods

2.1. Materials

Polyethersulfone (PES) supplied by Radel, Solvay was employed as the base polymer. 1-Methyl-2-pyrrolidone (NMP, 99.5%) and N,N-Dimethylformamide (DMF, 99.5%) purchased from Sigma Aldrich (St. Louis, MO) were used as the polymer solvents. The support layer (Viledon FO2471) used for the PES membrane manufacturing was obtained from Freudenberg (Weinheim, Germany).

Amine monomer piperazine (PIP, 99%) was purchased from Across Organics (Geel, Belgium). Distilled water was used as solvent for amine monomers. Acid chloride monomers trimesoyl chloride (TMC, 98%) was also purchased from Across Organics. The solvent used for acid chlorides, hexane, was purchased from NYSSENS GRAPHICS, Belgium.

Sigma–Aldrich Humic acid (St. Louis, MO) was selected as a model organic foulant in this study. Sodium chloride (NaCl) and magnesium sulfate ($MgSO_4$) supplied by Sigma–Aldrich were used as model monovalent and divalent salts, respectively.

Polyethylene glycols (PEGs) with increasing molar mass (400, 600, 800, 1500, 4000, 6000 and 8000) purchased from Scharlab, S.L were chosen to estimate the molecular weight cut-off (MWCO) of manufactured membranes. Their feed solutions were made by dissolving the appropriate chemical in pure particle-free Milli-Q water to achieve initial concentrations of 200 mg L^{-1}. The selected dyes were neutral-red (288.77 Da) and methylene-blue (319.85 Da).

The detailed synthesis procedure for TiO_2 nanoparticles was described elsewhere [29]; the nanoparticles were found to be anatase with 25 nm particle diameter. It should be noted that after membrane synthesis, aggregates were observed with a size in the order of 1 μm [29].