



Probing flow activity in polyamide layer of reverse osmosis membrane with nanoparticle tracers



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ABSTRACT

We investigate the flow activity of the nanostructured polyamide layer in reverse osmosis (RO) membrane, using gold nanoparticle (NP) tracers of 1–40 nm diameter. Following a detailed structural examination of a commercial SW30RH membrane selected for this study, NP solutions were infiltrated from either the polyamide front or the polysulfone support side. The permeate was then analyzed spectroscopically while the entrapment of NPs within the membrane was mapped by high resolution electron microscopy. Results show that back-filtered NPs exhibited a fractionated distribution according to size: 1 nm nanoparticles permeate across the polyamide-polysulfone interface reaching the interior of the polyamide corrugations, while the larger ones (> 10 nm) are retained within the polysulfone and gradually arrested at approximately 100 nm below the polyamide-polysulfone interface. Intermediate-sized 5 nm nanoparticles reached the undulating folds just below the polyamide layer. Permeation pathways across polyamide layer appear to exclude all tracers above 1 nm, which become selectively distributed across the polyamide layer: positively charged NPs label the outer surface of the polyamide film (expected to be carboxylate-rich), while negatively charged particles are uniformly distributed within the layer. Diafiltration measurements quantify the transient kinetics of NP retention and permeation. Overall, our results establish the flow activity of the polyamide nodular surface and provide estimates for the dimensions of permeation pathways.

1. Introduction

Reverse Osmosis (RO) is widely recognized for its low energy usage and reduced environmental footprint, and is thus employed in sea water desalination and industrial water purification [1,2]. Within the oil and gas industry, low-salinity water obtained by RO is extensively used in offshore drilling to increase oil recovery from sandstone reservoirs [3,4]. A typical RO membrane is a composite structure comprising a layer of fully cross-linked aromatic polyamide (PA) nanofilm, a porous polysulfone (PSf) support layer and a polyester (PET) fabric backing layer. The PA layer has an overall thickness of approximately 200–500 nm [2], depending on spatial variations and membrane type, and the PSf layer is 50–100 μm thick. The PET layer provides the mechanical support for membrane handling and operation. The full RO membrane is referred to as a thin film composite (TFC) membrane because of the layered PA-PSf-PET structure.

The PA thin film is generally fabricated onto the phase-inverted PSf support layer by an interfacial polymerization reaction between m-

phenylenediamine (MPD) and trimesoylchloride (TMC) [5,6,7]. This results in a highly heterogeneous, rough surface with many protruding, nodular features. It has recently been reported from cross-sectional transmission electron microscopy (TEM) and atomic force microscopy (AFM) [5,6] that the PA membrane layer comprises ‘crumpled’ films, whose individual thickness is approximately 10 nm. Crumpling results in the large roughness, heterogeneity, and surface contour, yielding the overall 200–500 nm PA thickness [2]. These contrast to nanofiltration (NF) membranes prepared from piperazine and TMC which generally yield smooth, flat surfaces [8]. RO membranes are therefore distinct in both morphology and salt rejection performance.

However, a clear link between active layer nanostructure, support layer, and water and salt transport remains, so far, elusive. Transport through thin film composite (TFC) membranes has been reported to depend on both the permeability and selectivity of the PA layer, and the pore morphology of the underlying PSf support [9,10,11]. However, the role of the surface crumpling, heterogeneity, and voids within the PA layer, as well as the nature of the PA/PSf interface, in terms of flow

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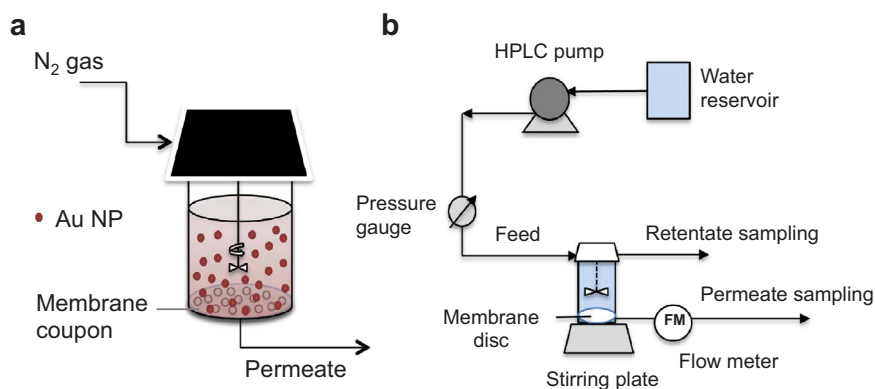


Fig. 1. (a) Pressurized dead-end (batch) filtration cell set-up, and (b) diafiltration cell and schematic of NP solution concentration measurement.

activity and nanoporosity are yet to be understood. Cross-sectional structures of many synthetic polymeric membranes have been recently reported [12,13,14,15]. Wong et al. provided evidence of the existence of voids in SW30HR and XLE membranes using TEM, whose overall volume was estimated to be approximately 30% [12]. Lin et al. applied a combination of TEM, quartz crystal microbalance (QCM) and spectroscopic ellipsometry to estimate the void fraction in a range of membranes from NF (NF90) to RO (SW30HR, XLE, ESPA3, SWC4+) [13]. Recently, Pacheco et al. employed TEM tomography to resolve the 3D structure of the voids within the PA layer in ESPA3 and SWC3 membranes [14], reconstructing the spatial distribution of void volumes down to a lengthscale of approximately 15 nm. A positive correlation between the presence of nanometer scale voids and surface undulations of the PA active layer, has been found to be consistent with a higher water permeance [13,14].

A number of characterization techniques are routinely used to investigate the morphology, roughness and porosity of such RO membranes [5,16,17,18]. Given the amorphous structure of the polymers, direct imaging of permeation pathways by electron microscopy is challenging due to the low electron contrast in the membrane and the non-rigid and non-linear structure of the pathways [16]. Techniques such as (energy variable) positron annihilation lifetime spectroscopy (PALS) [19,20], and neutron or X-ray reflectometry [21,22,23] provide depth-averaged free-volume estimates (electron or scattering length) of density with angstrom to nanometer (\AA -nm) resolution, but cannot resolve actual permeation pathways or free volume connectivity. Further, polymeric materials exhibit rich, dynamic processes [24] (from the atomic to segmental and cooperative reorganization) that are likely coupled with solute transport, but are inaccessible to these structural probes. Visualization at the nanoscale in the hydrated state has thus not been reported.

Nanoparticles (NPs) and stains can effectively aid visualization by enhancing contrast in membrane imaging, and enabling the study of particle-membrane interactions [25]. Rizwan et al. showed that NPs preferentially accumulate near the “peaks” and not the “valleys” of the rough NF membrane surface [25]. A method for determining the skin thickness of ultrafiltration (UF) membranes was developed by Cuperus et al. [26] in which poly (2,6-dimethyl-1,4-phenylene oxide) (PPO) and PSf membranes were investigated using colloidal gold NPs of 6 nm and 50 nm average sizes. SEM was then used to image the cross-sectional areas of the membranes, and revealed a well-defined skin layer where even the smallest gold NPs failed to penetrate. Similarly, Stawikowska et al. used osmium dioxide NPs, adsorbed with polystyrene, and filtered into integrally skinned asymmetric organic solvent nanofiltration (OSN) membranes, which have larger pores than RO membranes and are not TFCs [27,28]. However, significant questions remained relating to particle geometry, its polydispersity and interpretation of the contrast in relatively thick TEM sections.

In this paper, we extend these studies by considering the flow

through a model, high salt rejection RO membrane SW30HR using NP tracers (gold 1–40 nm diameter, of positive and negative charge) with are infiltrated from either the front or back side of the membrane. We then track their spatial distribution, seeking to resolve transport active pathways through the PSf and PA layers under relevant operating conditions. This approach provides thus a proxy for *in operando* visualization, since the NP tracers are infiltrated during filtration, and resulting NP distribution is then mapped at the nanoscale by electron microscopy. Diafiltration measurements provide further insight into the transient behavior during NP infiltration, and elucidate the asymptotic distribution of NP within the membrane structure.

2. Experimental section

2.1. RO membrane and nanoparticle imaging agents

The membrane selected for this work is the commercial, high rejection seawater flat sheet membrane, SW30-HR[®] (FilmTech™ FT-30 series), purchased from Sterlitech Co. Gold (Au) NPs of diameters 5, 10, 20, 40 nm (negatively charged) suspended in H₂O were purchased from BBI[®] Solutions, and 1 nm, both positively and negatively charged, from Undecagold[®] Nanoprobes. The 1 nm NPs were received as a dry powder and were dissolved in deionized H₂O to form the solution. The size and distribution of the nanoparticles were characterized by Dynamic Light Scattering (DLS, Malvern Zetasizer Nano series) and by UV-Vis spectroscopy (Shimadzu), as shown in SI Fig. S1 and Table S1.

2.2. Batch Filtration

Batch dead-end filtration experiments, using a stirred ultrafiltration cell (Millipore), were used to investigate transport of particles through the membrane and measure salt rejection, as illustrated in Fig. 1a. A volume of 3 mL of NP solution (5×10^{12} particles/mL for the 5–40 nm particles and 3×10^{15} particles/mL for the 1 nm particles) was filtered through a membrane coupon of 25 mm diameter under a pressure of 3 bar at the front, and a pressure of 1 bar in the back. Filtration experiments were run at room temperature until completion. For each NP size, and filtration experiment (at least 3 repeats per NP size), a separate membrane coupon was employed. Nanoparticle rejection was measured when the initial feed volume had halved. The concentration of particles in the permeate and retentate were quantified by UV-vis spectroscopy. Uncertainties were computed from maximum deviation between measurements.

2.3. Diafiltration

Diafiltration was used to measure NP transport over a time period corresponding to 10 diavolumes, for the smallest NPs, 1 nm (+) and 1 nm (–) in back-filtration, illustrated in Fig. 1b. The pH conditions

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