Characterization of Thin-Film Polyamide Nanofiltration Membranes

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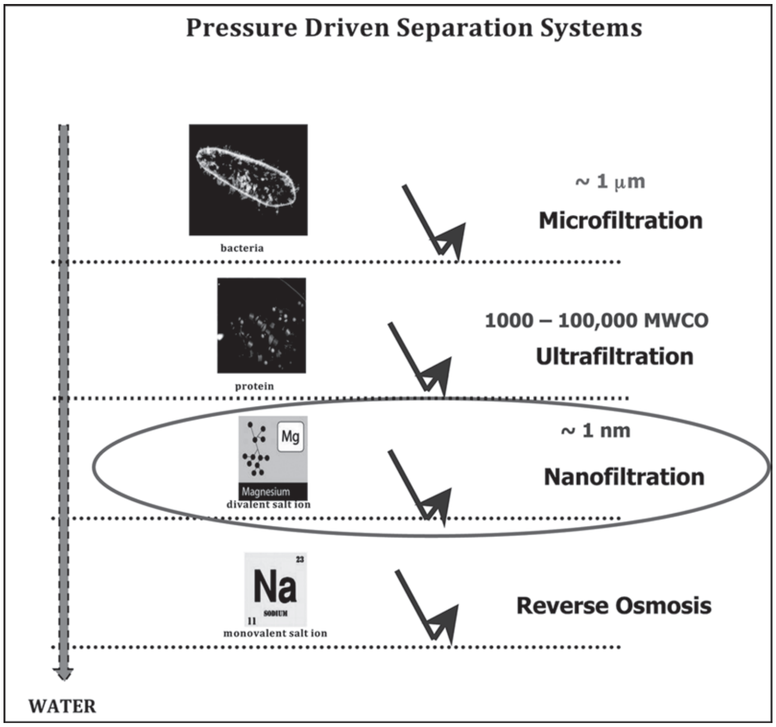

Figure 1: Pressure driven membrane separation systems and the specific particles they can successfully separate from aqueous solutions.

Background:

Nanotechnology describes the study of matter, usually measuring less than 100 nanometers (nm), on the atomic and molecular scale. The applications of nanotechnology are numerous and far-reaching, ranging from electrical engineering and biology to environmental engineering. An important application of nanotechnology in the field of environmental engineering is water treatment and purification. Thin film polymer composites can be fabricated into membranes that, when modified, have impressive separation qualities/characteristics. Nanofiltration (NF) membranes have a mean pore size of 1 nm. Their separation characteristics lie between ultrafiltration (UF) membranes, which separate suspended solids and solutes with high molecular weight from water and low molecular weight solutes, and reverse osmosis (RO) membranes which reject all ions. Figure 1 depicts pressure driven membrane separation systems and the specific particles they can successfully separate from aqueous solutions. NF membranes are chemically modified using various techniques to increase flux and rejection while decreasing membrane fouling. Figure 2 illustrates electrostatic deposition, a common membrane modification technique which involves placing bilayers of charged polymers on the membrane's active surface. These charged layers can decrease membrane fouling while increasing monovalent ion rejection. Nanofiltration membranes can filter multivalent salts without any modification, but the purpose of this project is to improve the separation qualities of NF membranes to the level of RO membranes. To assess the success of membrane modification in improving NF membrane filtration, the membranes were characterized using several different techniques: atomic force microscopy, electrokinetic analysis, scanning electron microscopy, and goniometry (contact angle analysis). Characterization of unmodified and modified membranes helps determine which membrane surface features enhance or detract from their membrane separation qualities.

Methodology:

The membranes used in this experiment were NF270 membranes from Filmtec Corporation. Each membrane was soaked in water for 24 hours, then characterized using several different techniques. The polyamide thin-film composite that composed the NF membrane was negatively charged, but the polyanions and polycations deposited on the membrane surface during the modification process changed the charge of the membrane surface. An electro-kinetic analyzer (EKA) machine was utilized to monitor the surface charge of the membrane before, during, and after the membrane modification process.

As an electrolyte solution was pumped through the fluid cell containing a membrane, the streaming potential of the surface was measured using electrodes clamped on both sides of the sample. The EKA machine used the streaming potential measurements to calculate the zeta potential of the membrane's active surface, which was directly proportional to the magnitude of the surface charge. The machine simultaneously measured the temperature, pH, and conductivity of the membrane's active surface, and presented these values in graphic or tabular format.

Another method used to characterize membrane surfaces was atomic force microscopy, commonly referred to as AFM. AFM

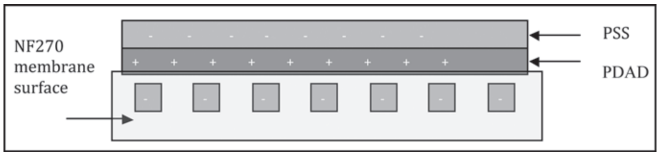

Figure 2: Electrostatic deposition.

uses a high-resolution scanning probe with a resolution 1000x greater than the optical diffraction limit and can magnify matter more than one million times its actual size. Data is gathered when a fine probe attached to cantilever "feels" the sample surface for changes in force along the x-y plane. Different types of probes serve different purposes. Most AFM imaging of NF membranes is performed using sharp silicon probes, but colloid probes can be used for specialized tests such as measuring particle adhesion and other surface characteristics. The NF270 membranes were imaged in several different modes: the cut pieces of membrane were imaged in contact and non-contact mode, and in both air and liquid media.

AFM and EKA testing provide useful information, but a test is needed to determine the hydrophilicity of a membrane's active surface. Membranes used for water treatment purposes need to be hydrophilic in nature, because water continuously flows around and through these membranes. Hydrophilic membrane surfaces help maintain a high flux and decrease particle adhesion. Goniometry, also known as contact angle analysis, was used to study the interactions between water and membrane surfaces. Static contact angle measurements were taken when the membrane surface was in a fixed position and water was dropped onto it in a controlled manner. A camera and specialized software captured and analyzed the exact angle the water droplet made with the sample surface.

The final mode of characterization used was scanning electron microscopy (SEM). Electron-sample interactions produce electrostatic images that can be read to analyze morphological features of the membrane surface.

Results:

The various tests performed on the NF270 membranes' surface provided a great deal of useful information about NF membranes. Electrokinetic analysis showed the charged bilayers of PDAD-MAC and PSS changed the magnitude of the surface charge upon deposition. When PDAD-MAC was deposited on the surface, the negatively charged surface became positively charged. When PSS, a polyanion, was deposited, the magnitude of the membrane's surface charge was reversed again. AFM proved that as the surface roughness of membranes increases, particle adhesion to the surfaces also increase. Humic particles tend to adhere to rough membrane surfaces more than their smoother counterparts. Goniometric analysis demonstrated the hydrophilic nature of the membrane's surface. The contact angle measurements of membrane surfaces were all near or less than 30 degrees, which is extremely hydrophilic in nature. Figure 3 shows some results of goniometric analysis. SEM data was inconclusive

Unmodified NF270 Membrane	
Contact Angle (˚)	**Left Angle (˚)**
23.31	23.31
22.35	22.35
28.861	28.861
37.825	37.825

Figure 3: Results of goniometric analysis.

because the membrane's morphological features were too small to be imaged using this technique. Field emission SEM is more commonly used to image NF membranes because the technique is better with imaging objects in the nanoscale range.

Conclusions:

The purpose of testing and characterizing the NF270 membranes was to compare the separation qualities of modified and unmodified membranes. Modified membranes should have separation characteristics similar to RO membranes which can reject all ions in aqueous solutions. Characterization using AFM, EKA and goniometry showed that the modified NF270 membrane surfaces were less rough and more hydrophilic than the unmodified membranes, indicating that the modified membranes should exhibit increased rejection and decreased fouling when compared to the unmodified membranes.

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