Membrane Chemistry Cellulose Acetate vs. Thin-Film Composite

Reverse osmosis and nanofiltration membranes are commercially available in either cellulose acetate or thin-film composite membrane chemistries. This bulletin explains the basics behind the two different membrane chemistries.

CELLULOSE ACETATE

Cellulose acetate (CA) membranes, originally developed in the early 1960s, were the first type of membrane used in commercial RO desalination plants. CA membranes are made from acetylated cellulose. Cellulose is a naturally occurring, asymmetric polymer; it is a linear, rod-like material that is relatively inflexible, which renders CA membranes their mechanically robust structure. Acetylation of cellulose occurs when in the presence of acetic anhydride and a catalyst (such as H_2SO_4) via the following reaction (Figure 1):

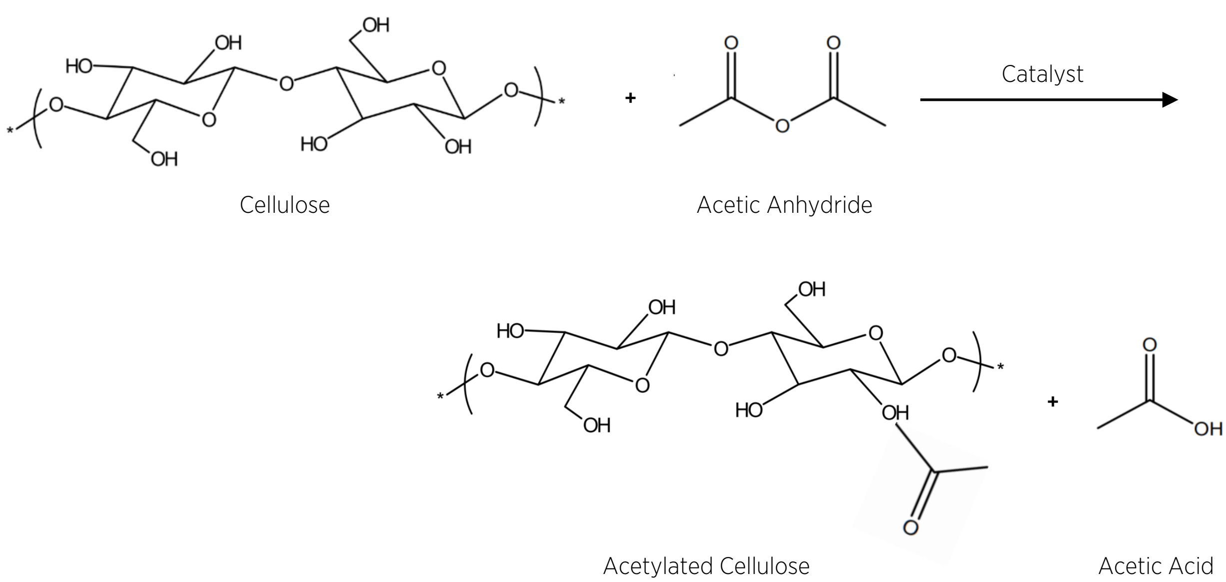

Figure 1. When cellulose reacts with acetic anhydride, acetylated cellulose and acetic acid are formed. Commercially available CA membranes are made from acetylated cellulose of varying degrees.

Acetylation describes the process where an acetyl functional group is transferred from one molecule to another. In this particular case, an acetyl group (-CH3COO) from the acetic anhydride is transferred to the cellulose, replacing the alcohol group (-OH). The degree of acetylation of cellulose describes the number of –OH groups on the cellulose that are replaced with -CH3COO groups.

The degree of acetylation can range from 0 to 3, where 0 represents unreacted cellulose and 3 corresponds to a completely substituted cellulose, also known as cellulose triacetate (CTA). The degree of acetylation has a large effect on how the membrane performs as a whole. A high degree of acetylation produces a membrane with high salt rejection, but low permeability. A lower degree yields membranes with lower rejection, but higher flux. Commercial membranes used for reverse osmosis typically have a degree of acetylation of about 2.7; providing a membrane with a good balance between salt rejection and permeate flux. TRISEP® CA membranes comprise of a blend of CA and CTA. Blending CA with CTA increases mechanical stability and resistance to hydrolysis but decreases the permeability slightly.

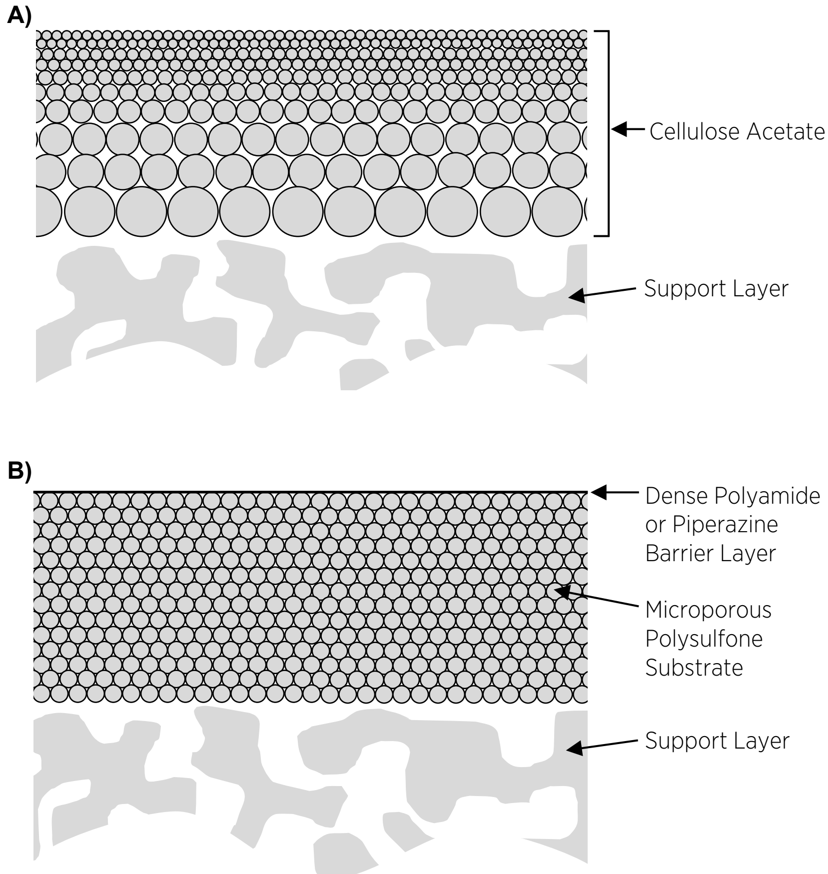

Figure 2. Cross sections of **A)** cellulose acetate membranes and **B)** thin-film composite membranes.

Cellulose acetate reverse osmosis and nanofiltration membranes comprise of two layers: a cellulose acetate layer and a support layer (Figure 2A). The cellulose acetate layer becomes denser farther away from the support layer, meaning the membrane surface is the densest part of the layer itself (creating a thin barrier layer much like that in thin-film composite membranes). The pores of this dense cellulose acetate layer dictate the permeability of particular dissolved solids and impurities. The support layer (commonly a non-woven polyester) provides a hard, smooth surface free of loose fibers allowing the membrane to withstand high operating pressures and resist mechanical stresses and chemical degradation.

CA membranes offer several advantages over other RO membranes on the market today. CA membranes are considered "uncharged" because their functional groups are not polar. Because CA membranes are non-polar, they do not attract foulants to the surface as easily. Additionally, less fouling is observed with CA membranes due to a smoother membrane surface. Another advantage of CA membranes is their relative tolerance to chlorine. TRISEP CA membranes can tolerate up to 0.5 ppm (nominal) and 1 ppm maximum of chlorine, which is much higher than the tolerance shown by other membranes. This is largely beneficial for systems to control biofouling, where free chlorine is used to maintain a sanitary environment or for systems that have feed streams containing trace amounts of chlorine.

CA membranes have some shortcomings. CA membranes are extremely sensitive to pH and are only stable in operating pH ranges of 4 to 7. These membranes also operate at higher pressures and should not treat feed water temperatures exceeding 35°C. CA membranes also tend to hydrolyze over time, which decreases their performance and operating life. Due to these characteristics, CA membranes are not recommended for process applications.

THIN-FILM COMPOSITE

Thin-film composite (also referred to as thin-film) membranes, developed in the late 1960s, proved to surpass the membrane fluxes and rejections of the CA membrane. Thin-film membranes are able to tolerate a wide operating pH range (1 – 12) as well as operate at a higher temperature (up to 80°C). They also operate at lower pressures and have greater hydrolytic resistance for improved membrane stability and membrane life. Although thin-film membranes have proven to address the disadvantages of CA membranes, thin-film membranes have limited tolerance to chlorine. Continuous chlorination causes attack on the polyamide barrier layer.

Thin-film reverse osmosis and nanofiltration membranes comprise of three layers: a thin, dense polyamide barrier layer (from which the term "thin-film composite" was derived), a microporous polysulfone substrate and a support layer (as illustrated in Figure 2B above).

The polyamide layer is responsible for the membrane's overall salt rejection and is selected for its permeability to water and relative impermeability to various dissolved salts and other impurities. MANN+HUMMEL Water & Fluid Solutions produces two general types of polyamide membrane chemistries. The first is an aromatic polyamide and is used in most TRISEP® thin-film RO membranes. The other is a mixed aromatic, aliphatic polyamide membrane (also referred to as polypiperazine membrane) used in most TRISEP thin-film NF membranes.

TRISEP® ACM™ membranes are made using 1,3 phenylene diamine and tri acid chloride of benzene (Figure 3). This resistant, long and stable polymer contains a carboxylic acid and free amines. Due to its high chemical stability, this membrane is very durable and easy to clean.

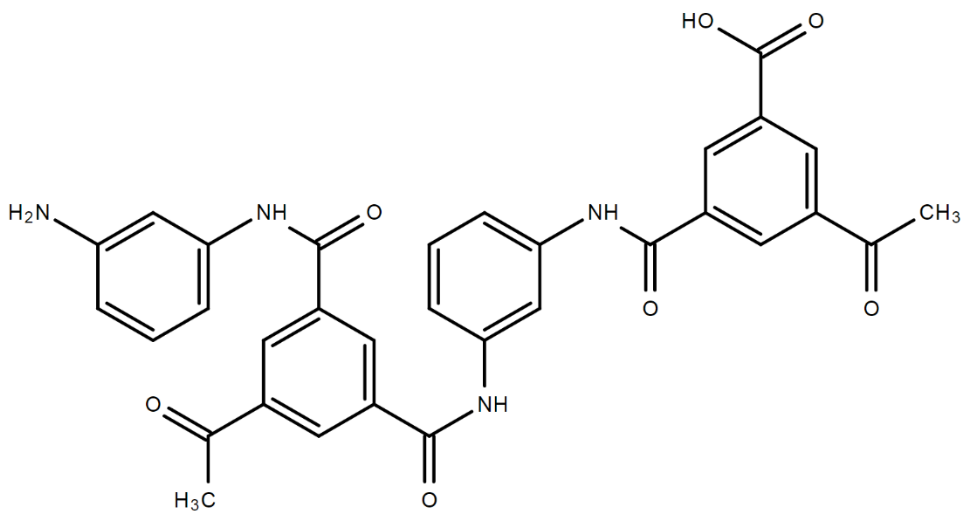

Figure 3. The approximate structure of the aromatic polyamide membrane.

The piperazine membrane used in most TRISEP thin-film NF membranes (Figure 4 below) contains trace additives within its chemistry, allowing for the development of a wide range of nanofiltration membranes with different monovalent and divalent salt transport characteristics. Piperazine NF membranes are typically used in divalent ion concentration, food and dairy, dextrose purification and process applications rather than aromatic polyamide NF membranes since the piperazine membrane allows for a greater passage of monovalent ions while still maintaining a high rejection of divalent ions.

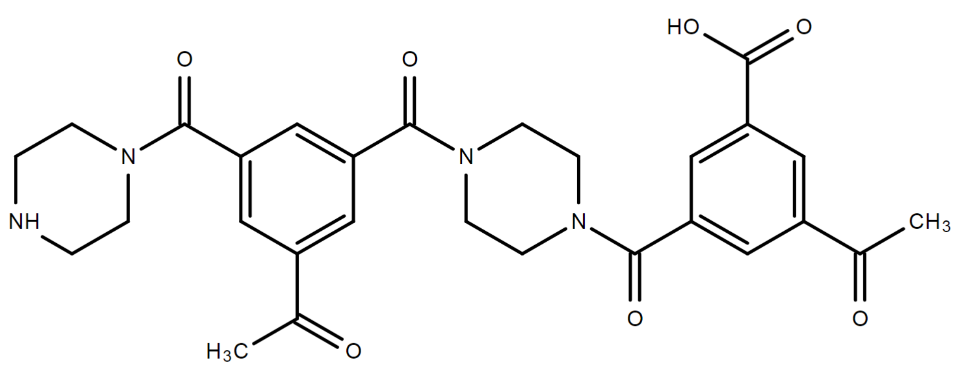

Figure 4. The approximate structure of the piperazine membrane.

Similar to the cellulose acetate membrane, thin-film membranes also incorporate a support layer (commonly a non-woven polyester) which provides a hard, smooth surface free of loose fibers (Figure 2B). However, since the web is too irregular and porous to provide a suitable substrate for the barrier layer, a microporous polysulfone substrate serves as an interlayer. The combination of the microporous polysulfone substrate and support layer allows the barrier layer to withstand high operating pressures for high water permeability. The supportive backing layers also allow the membrane as a whole to be highly resistant to mechanical stresses and chemical degradation.

MANN+HUMMEL WATER & FLUID SOLUTIONS RO & NF MEMBRANE PRODUCTS

MANN+HUMMEL Water & Fluid Solutions offers a line of cellulose acetate and thin-film composite RO and NF membrane chemistries that are available in flatsheet and a multitude of spiral-wound element designs. Please visit www.microdyn-nadir.com/en for specification sheets or contact MANN+HUMMEL Water & Fluid Solutions Technical Service for questions.

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