Exploring The Future Of Membranes With QUA

The modern history of drinking water treatment can be traced through membranes. As our water expertise has grown over the last few decades, membranes have undergone a dramatic evolution, from straightforward filtration devices to complex systems that utilize nanotechnology.

To get a handle on the latest membranes, Water Online spoke with Fred Wiesler from QUA. We asked him about how membranes have come to replace conventional treatment solutions. We also asked him to talk about a new manufacturing process and where the technology is heading.

How have you seen membranes evolve over the span of your career?
Over the last 20 years, membrane use in water treatment has evolved significantly. Ultrafiltration (UF) membranes have really taken on a key role in water treatment and are now commonly used for the pretreatment of reverse osmosis (RO) feed water. UF membranes are used to remove suspended solids, colloidal matter, high-molecular-weight substances, bacteria, and viruses from various feed water sources. Their ability to produce a consistently high-quality feed to an RO membrane system allows the system to operate more efficiently with less membrane cleaning.

In addition, membrane bioreactor (MBR) technology has become universally accepted as a viable process for treating wastewater. The number of installed plants has grown significantly over the last 10 years.

Nanofiltration (NF) membranes have also become more widely adopted in water treatment applications. Their ability to soften water and remove trihalomethane (THM) precursors, like bromate and humic acid, will likely open new applications for membrane-based water treatment in the future.

These are just a few examples of membrane technology that have really started to expand and grow over the last 20 years.

Has the role of the membranes in water treatment changed? Or has it always been as central as it is now?
Membranes play a vital role in water treatment today. Membrane manufacturing developments have expanded their use in water treatment applications. If we look at the historical evolution of membrane use in water treatment, we can see membranes replacing conventional treatment technologies. For example, as RO replaced ion exchange, MBR technology is replacing conventional activated sludge processes. In both processes, the cost of water treatment has dropped, and the amount of space has been significantly reduced when adopting the membrane technology. These types of advances will continue to develop as new, innovative membranes and applications are developed.

How are polyethersulfone (PES) membranes typically manufactured?
PES is a commonly used polymer in UF membrane manufacturing for hollow fiber membranes. PES membranes are manufactured in a phase inversion process typically referred to as the solvent induced phase separation process (SIPS). In this process, a dope solution is made by dissolving the polymer into a solvent with some additional additives. The solvent is exchanged from the dope into a non-solvent solution. As the solvent is removed, it carries the additives out of the dope and forms a sponge-like structure. This process is used to manufacture a wide variety of membranes using polymeric materials.

How are hollow fiber membranes typically manufactured?
When manufacturing a hollow fiber membrane, the dope is extruded, or spun, into a hollow tube with a liquid inside the bore of the tube to retain its shape. The spun tube passes through the atmosphere and is then submersed into a coagulation bath where the solvent is removed from the dope and the membrane structure is formed.

In the formation of the membrane, a thin separation layer is formed, as well as a support structure and outer tube wall.

All of these characteristics are important properties of the hollow fiber membrane.

What are the challenges involved with manufacturing membranes of these types?

Hollow fiber membranes are more complex to manufacture than flat sheet membranes. Characteristics of the tube, like diameter, shape ratio, and wall thickness, must be controlled. In addition, membrane properties like pore size, porosity, and thickness must be carefully monitored and controlled as well.

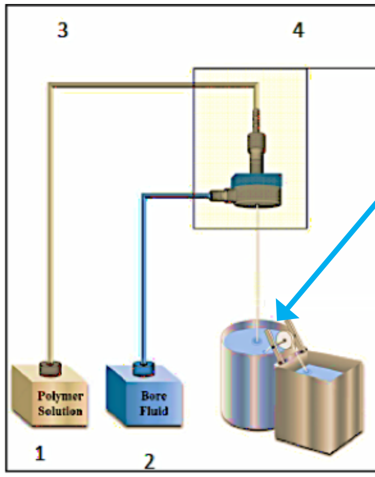
What is QUA's "cloud point precipitation" process for manufacturing membranes?

When we developed the cloud point precipitation process, we looked at ways to improve the current PES membranes that were available. We also looked at ways to better control the manufacturing process. When making a hollow fiber membrane module, thousands of fibers are used, so slight variations in the membrane formation can reduce the porosity, vary the pore size, or both.

The performance of the UF membrane module is based on the overall performance of the membrane inside the module. Sections of the membrane, will have higher porosity and larger pores that will increase the flux of the membrane, and sections will have smaller pores and lower porosity reducing the flux in these areas. When manufacturing the membrane, it is difficult to monitor and measure these characteristics over the entire membrane surface. One must take representative samples and evaluate and test the entire assembled device.

One of the most difficult steps in the phase inversion process is controlling the rate at which the solvent is exchanged from the dope. As the solvent moves through the dope, it is continually polymerizing and dissolving the polymer based on the relative concentration of the solvent in the dope. Once sufficient solvent is removed, the hollow fiber membrane is formed, and the hollow fiber membrane becomes a solid structure.

Control of this process is dependent on many variables. These include spinning speed (known as the dope extrusion rate), the distance between the extrusion head and coagulation bath, temperature, and humidity. Variations in these operating conditions impact the membrane formation. This varies the thickness, surface quality, pore-size distribution, and porosity of the membrane. Over the manufacturing batch, there is some known variability inherent in the process. Mathematical models for the actual membrane formation are difficult to construct, and manufacturers must go by experience to develop their unique membranes.

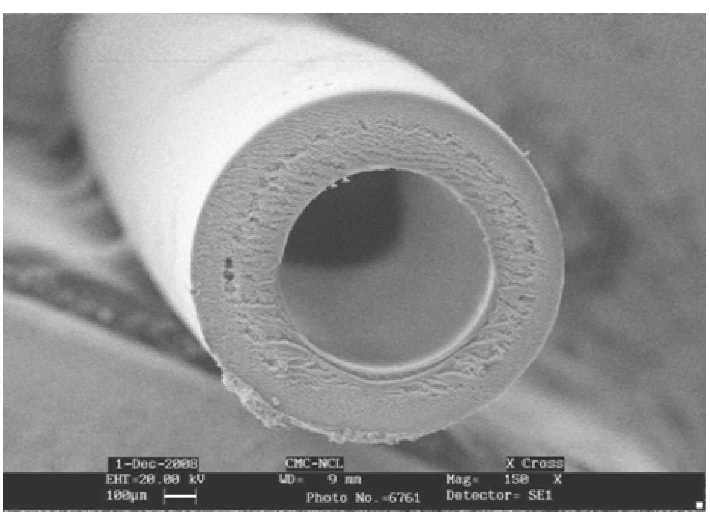


Membrane formation

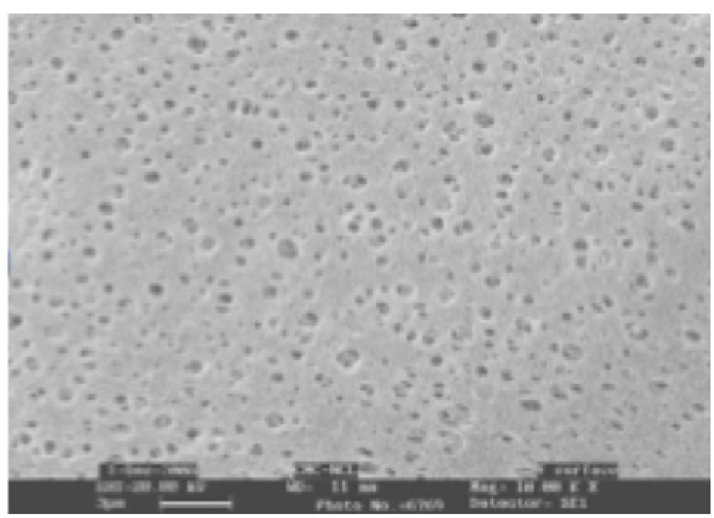
Starts in a precipitation bath when the polymer solution is submerged into the bath

- Precipitation occurs in the bath as the non-solvent in the bath is exchanged for the solvent in the polymer solution
- Polymer precipitation occurs, membrane layer thickness and porosity difficult to control

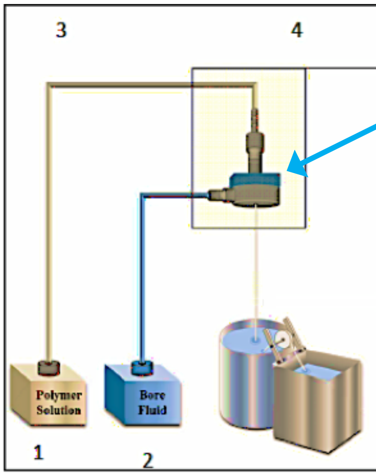
Conventional Phase Inversion Process for PES Hollow Fiber Membranes



Hollow fiber membrane with cloud point process



Outer surface of the membrane shows high porosity



In **cloud point precipitation**, membrane formation starts once the polymer solution contacts water

- Precipitation starts immediately when the polymer is in contact with the bore fluid
- Membrane is formed at tip of spinneret
- High level of control of precipitation process
- Forms a uniform membrane thickness with high porosity

Cloud Point Phase Inversion Process for PES Hollow Fiber

QUA's patented cloud point precipitation process utilizes a dope with three main components: polymer, solvent, and water. The dope is prepared in a traditional fashion with the polymer dissolved into the solvent. Water is then added to the dope to the cloud point of the solution. The cloud point is the point at which the addition of any additional water will start the polymer precipitation process.

How is it an improvement over the SIPS process?

The improvement eliminates one of the key steps in the process that is most difficult to control: the exchange of the solvent in the dope with a non-solvent. Transport of the solvent through the polymer dope creates inherent variability in the membrane formation. Portions of the hollow fiber membrane precipitate and are again dissolved as the solvent passes through the structure. This creates some inherent variability in the process. In the cloud point precipitation process, the membrane and support structure are instantaneously formed as water is added to the dope. This occurs at the extrusion head as the bore fluid, water, is introduced into the tube.

Why are membranes manufactured through the cloud point precipitation process better for treatment applications?

When you instantaneously form the membrane, the pore size and porosity can be more carefully controlled. This allows us to make a highly porous membrane with a very narrow pore size distribution. This process allows us to produce a UF membrane with a lower transmembrane pressure to start with, giving the user a wider operating range between cleanings. The membrane produced offers a very narrow pore size distribution with a high porosity. This increases the flux across the membrane while still removing viruses and bacteria. Additionally, the membrane separation layer formed is very thin, allowing the membrane to achieve a higher flux. The membrane surface is also highly hydrophilic and extremely smooth. This makes it more difficult for contaminants to stick to the membrane, reducing fouling potential and making the membrane easier to clean.

The, small, uniform pore size of each membrane fiber assures that the membrane will consistently deliver low SDI and turbidity values in the permeate stream, allowing the membrane to offer a higher quality of permeate water.

What do you see as the future of membrane technology?

Adoption of the membrane technology will really depend on two key points: lowering operating costs and improving permeate water quality. Operating costs will steadily decrease for complete water treatment systems as high-quality membranes are developed and adopted, as they will be able to consistently provide the water needed with less cleaning and maintenance required. As clean water becomes scarce, membranes will become more and more important in the quest to purify water and maintain a clean, sustainable source of water for future generations.

I see the capabilities of membrane treatment expanding as more research and development focuses on increasing the operating ranges and conditions that membranes can withstand. I also see membranes becoming more widespread as the technology enters into other markets, and new membrane materials and uses are identified.

Areas where severe droughts or water scarcity occur will likely be the pioneers of innovative membrane technologies and will likely drive and provide testing grounds for emerging membrane-based technologies. The membrane field is quickly evolving and innovating, and it will be exciting to be a part of it in the coming years. ■