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Membrane Characterization and Autopsy and Water Quality Analysis:

Analytical Capabilities and Techniques

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Analytical Capabilities at AQWATEC

Water quality has tremendous effect on the health of human beings and the environment, but it also substantially affect the performance of engineered and natural processes that were designed to treat the water. Membrane fouling, for example, is a key impediment for successful application of membrane technologies; various organic and inorganic constituents in water can adsorb, accumulate, or precipitate on membrane surfaces or in membrane pores, leading to membrane fouling. Researchers in AQWATEC employ state-of-the-art analytical techniques for water analysis, membrane characterization, and membrane autopsy. Many analytical instruments are owned by the center and other instruments are owned by other academic departments on the Colorado School of Mines campus, and are available for use by AQWATEC researchers. These methods and instruments allow to accurately determine water quality and identify water constituents that can cause process upsets (e.g., membrane fouling and flux decline) and assist in developing strategies to improve process performance.

For additional process testing, including evaluation of permeability, rejection, cleaning efficiency, scale inhibition, optimization of pretreatment, and related questions please contact:

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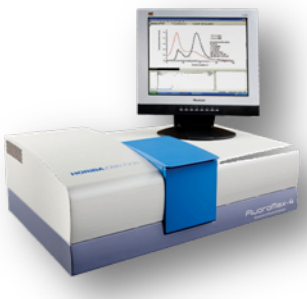
General Analytical Capabilities

Item	Analysis	Method
A	**Water Quality Analysis**	
A.1	Inorganic anions including F^-, Cl^-, Br^-, NO_3^-, PO_4^{3-}, SO_4^{2-}	Ion chromatography (IC)
A.2	Inorganic elements, including Ag, Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Se, Si, Sn, Sr, Ti, V, Zn, Mg, Sr, U	Inductive coupled plasma (ICP) spectrometry
A.3	Total organic carbon (TOC)	Carbon analyzer
A.4	UV absorbance	UV/Vis spectrophotometry
A.5	Characterization of protein, humic-like substances	3-D Fluorescence spectroscopy
A.6	Size distribution of organic and inorganic matter	Size-exclusion chromatography with dissolved organic carbon and UV absorbance detection (SEC-DOC/UVA)
B	**Membrane Characterization and Autopsy**	
B.1	Surface structure and morphology	Atomic force microscopy (AFM)
B.2		Scanning electron microscopy (SEM)
B.3	Surface potential	Electrokinetic analyzer (SurPASS, Anton-Paar)
B.4	Surface hydrophobicity	Wetting angle – sessile drop method
B.5		Contact angle – captive bubble method
B.6	Functional groups	Attenuated Total Reflection-Fourier Transform Infrared Spectroscopy (ATR-FTIR)
B.7	Elemental analysis	Inductive coupled plasma (ICP) spectrometer
B.8		Energy Dispersive Spectroscopy (EDS) with SEM surface imaging
B.9		Loss on ignition
B.10	Biological fouling	Optical microscopic observation
B.11		Phospholipids analysis
B.12	Chlorine damage	Fujiwara test



Aqualog® - Compact Spectrofluorometer

ADVANCED WATER QUALITY ANALYSIS

Water quality analysis is essential in determination of the constituents that affect membrane performance. Besides the standard analysis that determines concentrations of organic and inorganic constituents, we use state-of-art techniques to characterize different groups (or sizes) of constituents that may cause membrane fouling. These most commonly include proteins, humic-like substances, biopolymers, and inorganic colloids.

3-D Fluorescence Spectroscopy

Fluorescence excitation-emission matrix (EEM) spectroscopy is used to determine the presence of humic-like organic matter and protein-like organic matter in water. Fluorescence intensity for protein-like organic matter is quantified at an emission wavelength of 330 nm and an excitation wavelength of 270 nm. Humic matter (humic and fulvic acids) intensities are quantified at emission wavelengths of 420 and 450 nm and at excitation wavelengths of 350 and 250 nm, respectively. The specific fluorescence intensity is defined as the protein or humic fluorescence intensities (see wavelengths above) divided by DOC concentration. 3-D fluorescence spectra of microfiltration influent and effluent streams from a municipal wastewater treatment plant are illustrated in Figure 1.

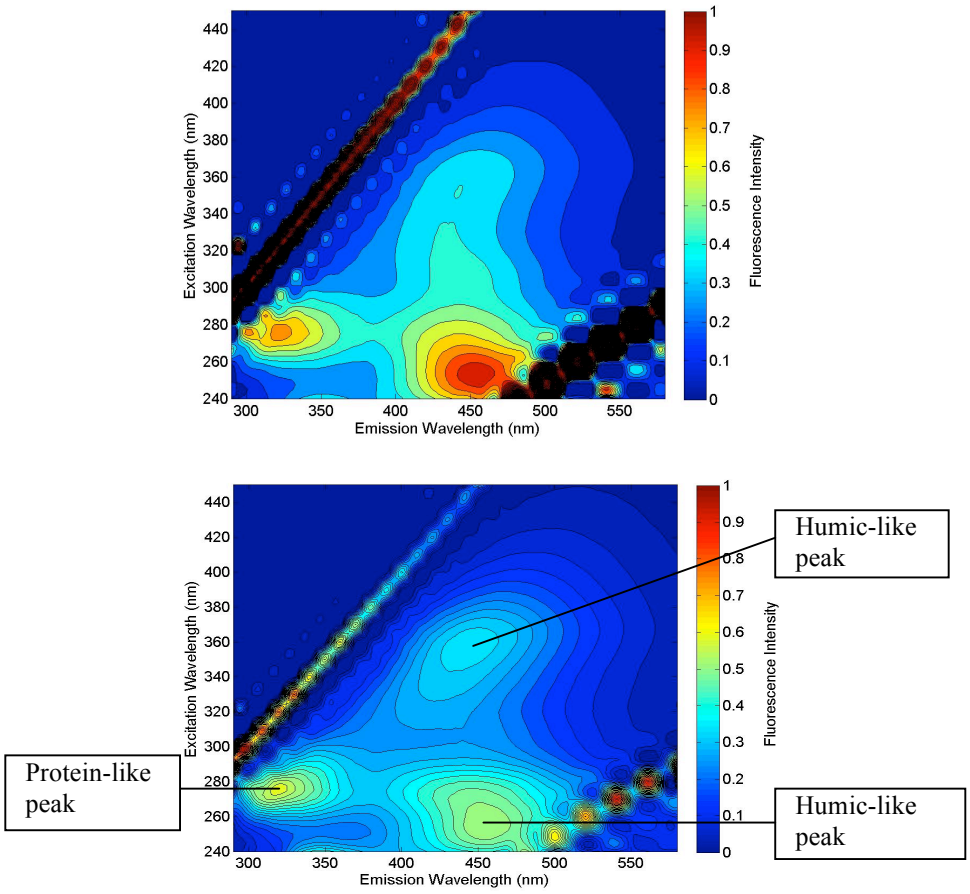


Figure 1. 3-D Fluorescence spectra of microfiltration influent (top) and effluent (bottom).

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Size-exclusion Chromatography (SEC)

Size-exclusion chromatography (SEC) is a chromatographic method in which molecules in solution are separated based on their size. It is applied to large molecules or macromolecular complexes such as proteins and industrial polymers. Size separation is achieved by differential pore permeation; larger molecules have shorter retention times in the pores of a packed column than smaller ones and are eluted from the column earlier. We use SEC with dissolved organic carbon and UV absorbance detection (SEC-DOC/UVA) to characterize the molecular weight distribution of organic carbon molecules in aqueous samples. SEC-DOC/UVA may also be used to detect inorganic complexes that have no DOC signal but UV absorbance peaks. The SEC-DOC/UVA chromatograms of a secondary effluent are illustrated in Figure 2.

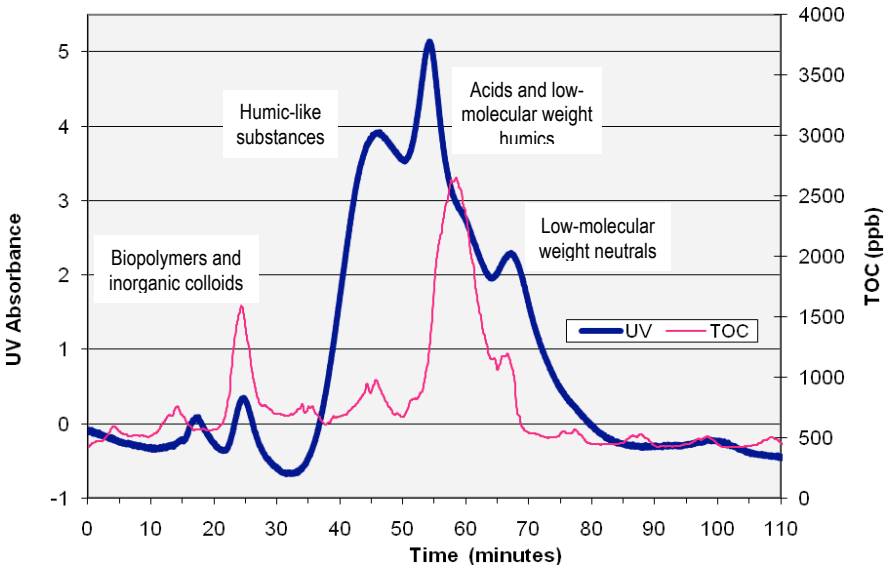
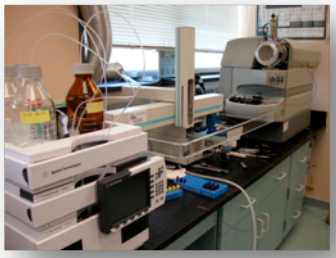


Figure 2. SEC-DOC/UVA chromatograms of a secondary effluent



Liquid Chromatography (LC-MS/MS)

Trace organic chemicals can be quantified using a liquid chromatography tandem mass spectrometry (LC-MS/MS) system composed of an Agilent 1200 high performance liquid chromatography (HPLC) system coupled to an HTS-PAL autosampler and an Applied Biosystems 3200 QTrap mass spectrometer. The system is capable of accurately quantifying and identifying very small quantities (< ng/L) of organic chemicals in water and solid samples. The sensitivity of the system is such that for many matrices (i.e., wastewater), no sample pre-concentration is required; samples can be directly analyzed (after filtration or centrifugation to remove suspended solids) and chemical concentrations accurately determined.

GENERAL WATER QUALITY ANALYSIS CAPABILITIES

In addition to the instruments described above, researchers at AQWATEC maintain many other analytical instruments for analysis of water quality. A list of available instruments and their capabilities is summarized in the table below.

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Analytical Equipment	Current/potential Application
GE, Sievers 900 TOC analyzer w/autosampler	TOC/DOC analysis
GE, Sievers 800 TOC analyzer w/autosampler	TOC/DOC analysis and TOC online monitoring for SEC
HACH 5000 UV/Vis spectrophotometer	Spectrophotometric analysis of multiple constituents
HACH 2500 spectrophotometer	Spectrophotometric analysis of multiple constituents
96-well plate reader	Enzyme-linked immunosorbent assays for multiple compounds, e.g. steroid hormones
HPLC Agilent HP1100 w/diode array, fluorescence, and refractometer index detector, autosampler	Analysis of pharmaceutical at ppb level Analysis of sugars and aliphatic amine
GC/MS Agilent HP5971 w/autosampler	Analysis of pharmaceutical and personal care product at ppt level
Two GC/MS Agilent HP5973 w/autosampler	Analysis of pharmaceutical and personal care product at ppt level
Large-volume rotary evaporator	Concentration of organic matter/ trace contaminants in water samples
XAD-8/4 Chromatographic columns (different sizes)	Bulk organic carbon fractionation
Dionex Ion chromatograph w/autosampler	Ion analysis

Shared analytical instruments	
HPLC Agilent 1100 w/diode array detector	Analysis of pharmaceutical at ppb level
Perkin Elmer atomic absorption spectroscopy/ICP	Metal and ion analysis
Fourier transform infrared (FTIR) spectrometry	Analysis of functional groups of contaminants

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MEMBRANE CHARACTERIZATION AND AUTOPSY

Surface Structure and Morphology

A number of microscopic techniques are typically employed for characterization of membrane roughness, microstructure, and morphology. These techniques provide important information for (1) understanding and improving membrane properties, and (2) characterizing and analyzing membrane fouling. The two most commonly used techniques for examining membrane fouling, surface structure and morphology, are atomic force microscopy (AFM) and scanning electron microscopy (SEM).

Atomic Force Microscopy (AFM)

AFM is used to measure membrane surface roughness and it provides morphological images by scanning a nanometer-scale sharp tip over a surface. It has become an important characterization tool of imaging the surface of materials at up to the atomic level resolution. Example of an AFM micrograph of ultra-low pressure RO membrane that was analyzed using the AFM tapping mode is illustrated in Figure 3.

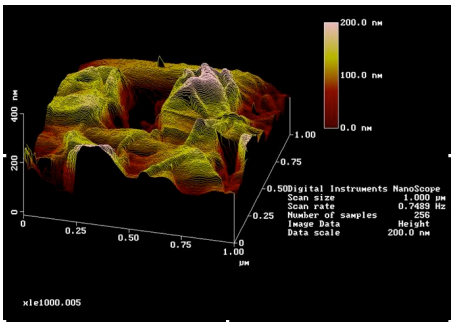

Figure 3. AFM micrograph of XLE membrane.

Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Spectroscope (EDS)

The SEM technique provides direct observation of a sample, including membrane morphology and fouling layer. Very high magnifications and high resolution can be obtained. The SEM can easily be combined with an energy-dispersive X-ray spectroscope (EDS), which enables analysis of elemental composition of the spot being imaged by the SEM. Another benefit of SEM is that the foulants do not have to be removed from the membrane in order to be analyzed. SEM-EDS is often used as a combined tool that can provide detailed information on the size, shape, structure, and chemical composition of membrane material and foulants. SEM-EDS may also be used to characterize very thin fouling layer, such as microbiological fouling, membrane scaling, or membrane degradation and defects.

Conventional SEM often requires sample preparation, such as coating with a thin layer of gold, carbon, or other material in order to reduce membrane surface charge. This may cause artifacts during membrane characterization when membrane samples are completely dried. The recently developed environmental scanning electron microscope (ESEM) is a special type of low-vacuum SEM. One of the technical advantages of ESEM is that nonconductive materials, such as RO membranes, can be

investigated without a need for coating with carbon or gold. SEM or ESEM can easily reach a magnification of 30,000 and observe membrane surface at the low micrometer range. ESEM micrographs of a biofouiled nanofiltration membrane and a virgin reverse osmosis membrane are illustrated in Figure 4. To achieve atomic-scale resolution such as in AFM, field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) can be used.

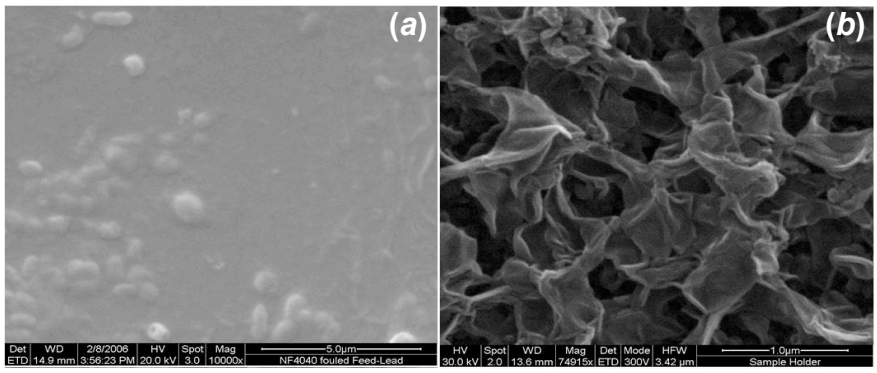

Figure 4. ESEM micrograph of (a) biofouled NF-4040 membrane used for reclaimed water treatment and (b) virgin XLE membrane.

Elemental Analysis

In addition to EDS that can characterize chemical composition of foulants on the membrane, foulants can be removed from membrane surface and ICP can be used to quantitatively identify the percentage of organic and inorganic constituents in foulants. ICP method can be used to quantify more than 33 elements, and loss on ignition test is used to determine the relative percentages by weight of the organic and inorganic fraction of the foulant. If the fouling layer is too thin to be removed from membrane surface, SEM/EDS can be used to analyze the scale or fouling layer. With SEM imaging, EDS can be performed on areas of interest on the membrane and spots such as specific grains and precipitates. An EDS spectrum of a fouled MF membrane used for municipal wastewater reclamation is illustrated in Figure 5.

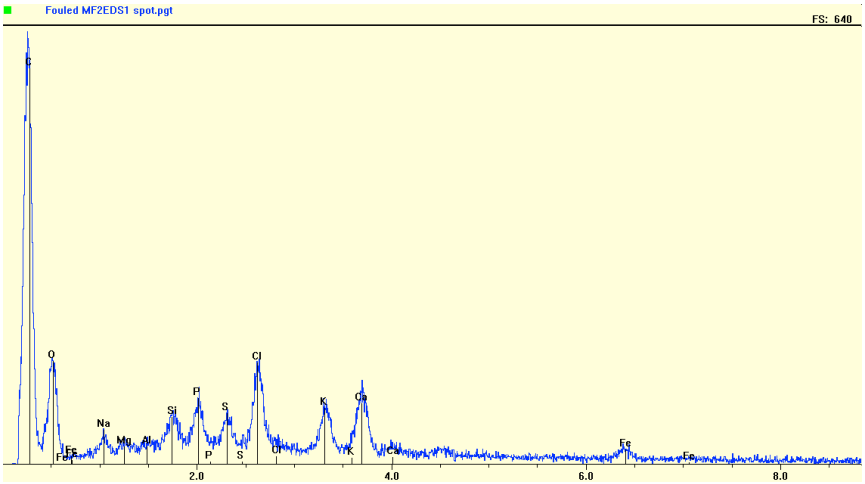

Figure 5. EDS spectrum of a fouled MF membrane

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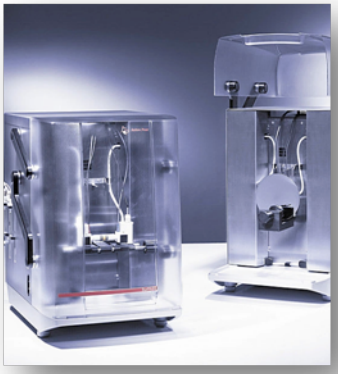

Surface Potential

The selectivity of a porous membrane is usually governed by both steric effects and electrostatic interactions occurring between charged solutes and the charged membrane surface. Most membranes acquire an electric surface charge when exposed to aqueous solutions to reject contaminants and reduce membrane fouling. Therefore, the characterization of membrane surface electrical properties appears to be a necessary step to understand and predict their filtration performances. Measurement of membrane surface potential can be performed by three available methods including streaming potential, electrophoresis, and titration. Results from streaming potential measurement of virgin and fouled hollow fiber MF membrane samples are illustrated in Figure 6.

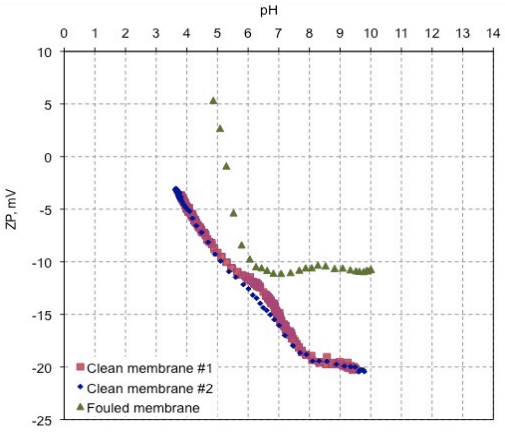

Figure 6. Streaming potential measurements of virgin and fouled hollow fiber MF membrane samples

Surface Hydrophobicity/Hydrophilicity

The wettability of solid surfaces is a very important property and is governed by both the chemical composition and geometrical microstructure of the surface. The polymers used to make membranes differ in their polarity and can yield either hydrophobic or hydrophilic membranes. Membrane hydrophobicity can be altered as a result of adsorption of organic matter and formation of biofilms.

The hydrophobicity of a surface is defined through the measurement of a contact angle between a surface and a droplet of a fluid. Contact angle can be measured in a number of different analytical methods, one of which is the captive bubble contact angle measurement that uses an air bubble immersed in a liquid (under the membrane) instead of a liquid droplet on top of the membrane. Yet, the most common method to measure contact angles is the sessile drop technique where the angle, contact radius, and the height of a sessile drop on a solid surface is viewed from its edge through an optical microscope. Computerized goniometer systems combining digital optics and shape recognition programs can more accurately measure the contact angle in both the captive bubble and sessile drop methods. A picture of contact angle measured using sessile drop method is shown in **Figure 7**.

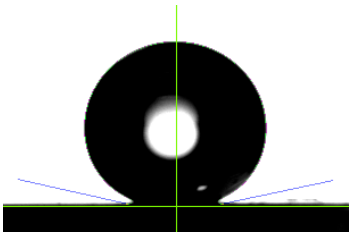

Figure 7. Contact angle measurement using sessile drop method.

Surface Functional Groups Identification

Functional group characteristics of membrane specimens can be characterized using a Fourier transform infrared (FTIR) spectrometer using the attenuated total reflection (ATR) method. FTIR spectrometry has been used to determine the functional chemistry of membrane fouling, such as inorganic colloids, proteins, and polysaccharides. Inorganic and organic compounds absorb the infrared radiation energy corresponding to the vibrational energy of atomic bonds. Based on the unique fingerprint of the absorption spectrum of a specific compound, the functional group can be identified through FTIR spectra. The ATR-FTIR spectra of new and fouled hollow fiber MF membranes and foulants are illustrated in Figure 8.

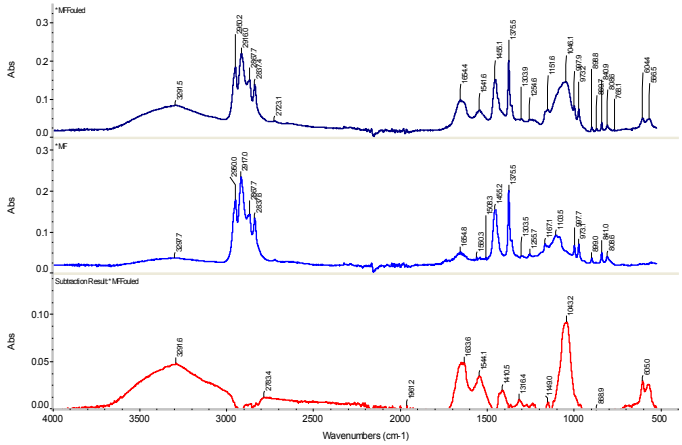

Figure 8. ATR-FTIR spectra of fouled (top), new (middle) hollow fiber MF membranes and the differential between the new and fouled fibers (foulants, bottom spectrum).

Biological Fouling

Optical microscopy can be used to observe the attachment of bacteria and growth of biofilms. Extraction of phospholipids (components of biological cell membranes) from membranes can be used to quantify viable biomass in fouling layer.

Chlorine Damage

Membrane damage by oxidizing halogens can be verified by the Fujiwara Test. The test analyzes qualitatively whether halogens have become part of a membrane polymer structure through oxidative attack. The test only detects alkyl halides.

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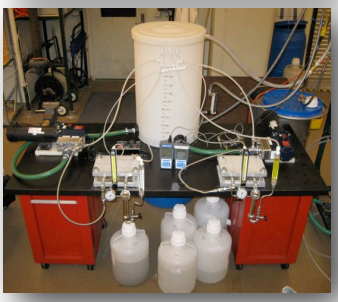

EXPERIMENTAL EQUIPMENT AT AQWATEC

Experimental Equipment	Current/potential Application
Membrane flat-sheet SEPA cells (5x) for ultrafiltration, nanofiltration and reverse osmosis membranes	Membrane flat-sheet rejection and fouling experiments
Membrane flat-sheet SEPA cells (2x) for forward osmosis and membrane distillation testing	Membrane flat-sheet flux, rejection, and fouling experiments
Laboratory-scale electrodialysis stack	Electrodialysis (ED) and electrodialysis reversal (EDR)
Laboratory-scale 2-stage NF/RO membrane skid w/SCADA system	Rejection tests of nanofiltration and reverse osmosis membrane with two 4040 spiral-wound elements in series
Laboratory-scale 1-stage NF/RO membrane skid	Rejection tests of nanofiltration and reverse osmosis membrane with two 2540 spiral-wound elements in series
Laboratory-scale 1-stage MF/UF membrane skid	Pre-treatment unit employing either microfiltration or ultrafiltration 4040 spiral-wound element
Laboratory-scale hybrid RO/FO membrane skid	Performance test of forward osmosis/reverse osmosis combined system with 5 2540 spiral wound RO elements and plate-and-frame FO membrane stack – under construction
Pilot-scale NF/RO membrane 4-stage skid w/SCADA system and clean-in-place skid	Performance test of nanofiltration and reverse osmosis membranes with 21 4040 spiral-wound elements and a feed capacity of 20 gpm. Trailer mounted.
Demonstration-scale, 7000 gpd membrane bioreactor (MBR)	Treatment of domestic wastewater, test system for both biological processes and submerged UF membranes
Amicon stir-cell membrane cell for rejection tests	Flat-sheet membrane experiments in dead-in filtration mode with feed solutions up to 400 mL
Diffusion cells (2x) for flat-sheet membrane specimens	Diffusion cells (half cell capacity 1.1 L) to study diffusion phenomena using flat-sheet membrane specimens
Electrodialysis cell for flat-sheet membrane specimens	Electrodialysis cell to hold individual ion-selective ED membranes
Soil-column set-ups, four 1-m columns in series (saturated, anoxic flow conditions)	To simulate subsurface systems such as soil-aquifer treatment or riverbank filtration
Soil-column set-ups, four 1-m columns in series (saturated, anoxic flow conditions)	To simulate subsurface systems such as soil-aquifer treatment or riverbank filtration
Soil-column set-ups, one 1-m columns in series (unsaturated, oxic flow conditions)	To simulate subsurface systems such as soil-aquifer treatment or riverbank filtration
Soil-column set-ups, four 1-m columns in series (unsaturated, abiotic flow conditions)	To simulate subsurface systems such as soil-aquifer treatment or riverbank filtration

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