New York State Pollution Prevention Institute

MEMBRANE TOOLKIT

Introduction

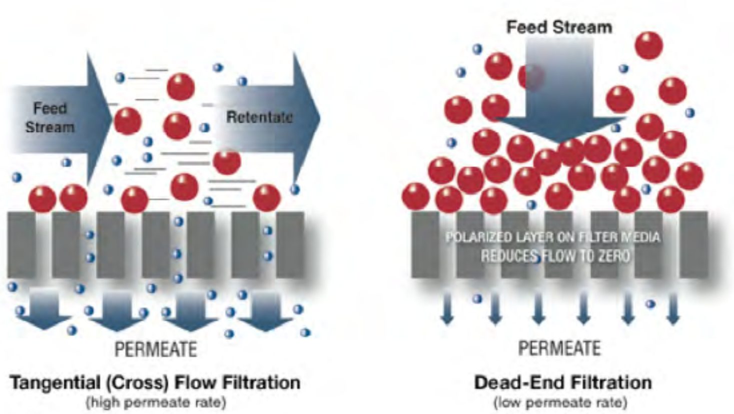
Pollution prevention (P2) focuses on the reduction or elimination of waste at the source, as opposed to treatment of waste after it has been created. P2 can mitigate toxics use and reduce waste in manufacturing companies. While various approaches can be used to reduce a company's environmental footprint, effective programs include process modification and in-process recycling, where potential wastes are immediately recycled back into the process. Membrane filtration is an effective P2 methodology that can separate and purify materials for reuse and product manufacturing, or used to produce environmentally acceptable water for discharge when upstream process modification is not possible. The advantages of using membrane technology include the following features:

- primarily a mechanical separation process that does not require use of toxic chemicals
- often less energy intensive than comparable technologies for a given application

Some industries that utilize membranes include metal finishing, food & beverage, biotechnology, pharmaceuticals, and optics manufacturing.

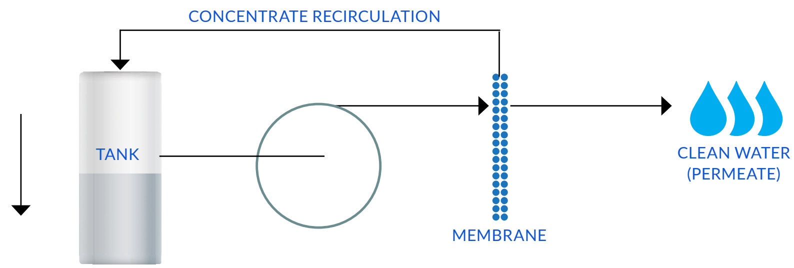
What are Membranes?

Membranes are special filters that are designed to separate smaller particles, metals and various chemical species. Through the use of pressure or concentration differential, separation can be achieved without the use of additional chemicals or major energy costs. Unlike typical dead-end flow which filtration is usually thought of, the solution to be filtered flows tangentially to the membrane filter surface:

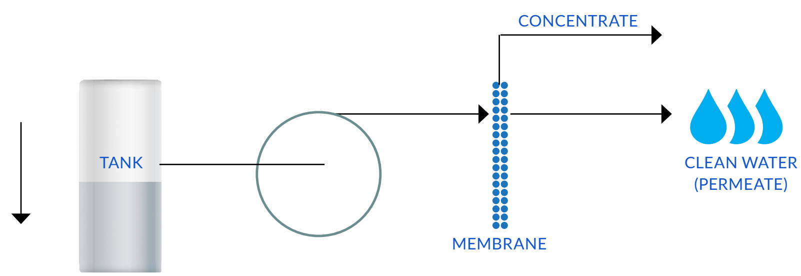


Source - (http://www.spectrumlabs.com)

As can be seen in the graphic, if the solution to be filtered is forced through perpendicularly (dead-end filtration), the contaminants or solutes will quickly build up on the surface, clog the filter, and reduce the filtrate flow (also called permeate). In most membrane applications, cross-flow filtration involves parallel, tangential flow that, under sufficient turbulence, keeps the filter surface relatively clean of material and allows more continuous filtration. The back pressure applied on the solution forces permeate through the membrane pores. However, unlike dead-end filtration where 100% of the fluid would permeate the filter, only a fraction of the feed solution ends up being filtered in a single pass. As a result, systems need to be designed to take into account this flow scheme. Cross-flow membrane systems can be set up as either batch recirculation or single-pass:



Batch Concentration Mode

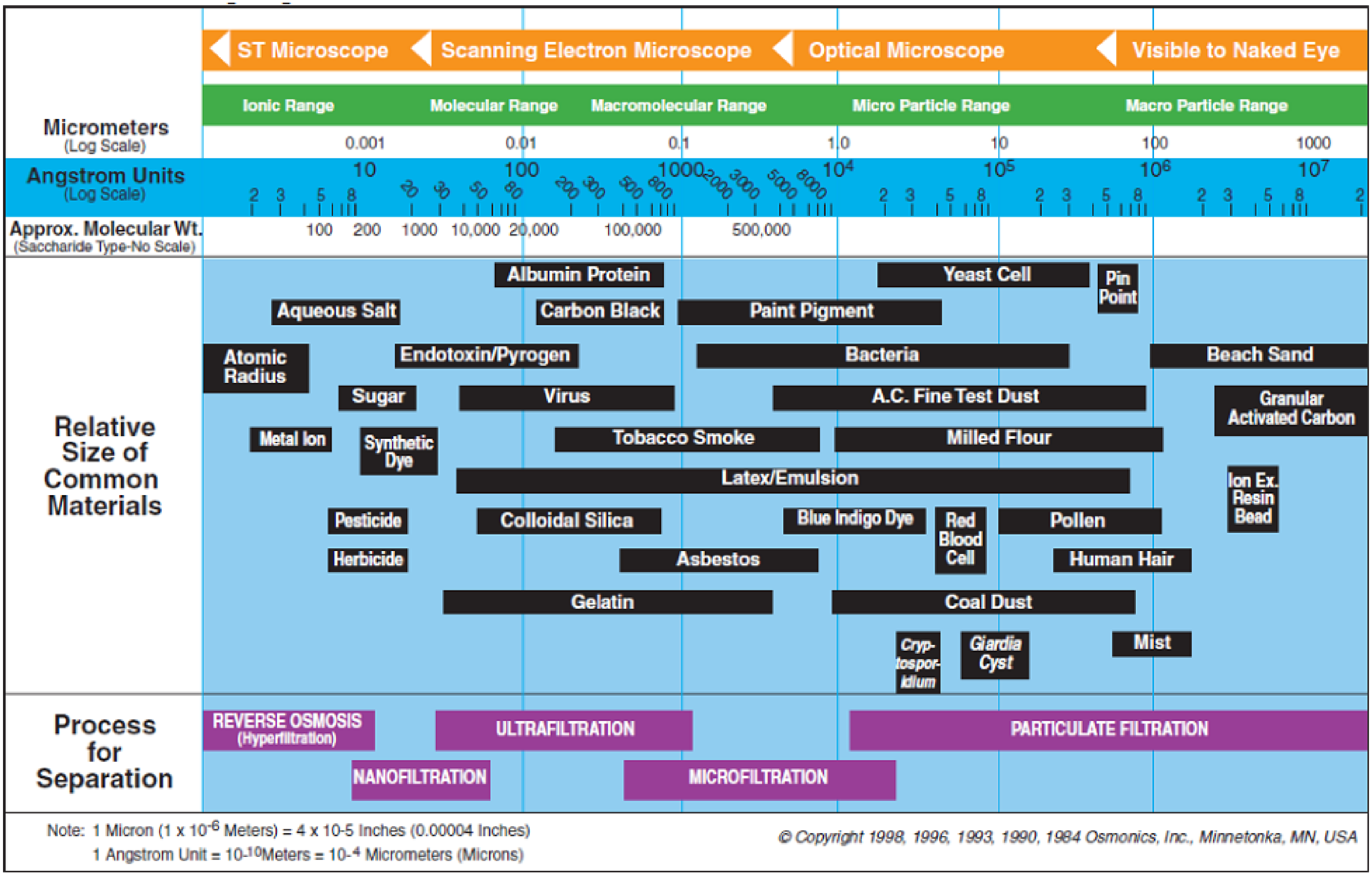


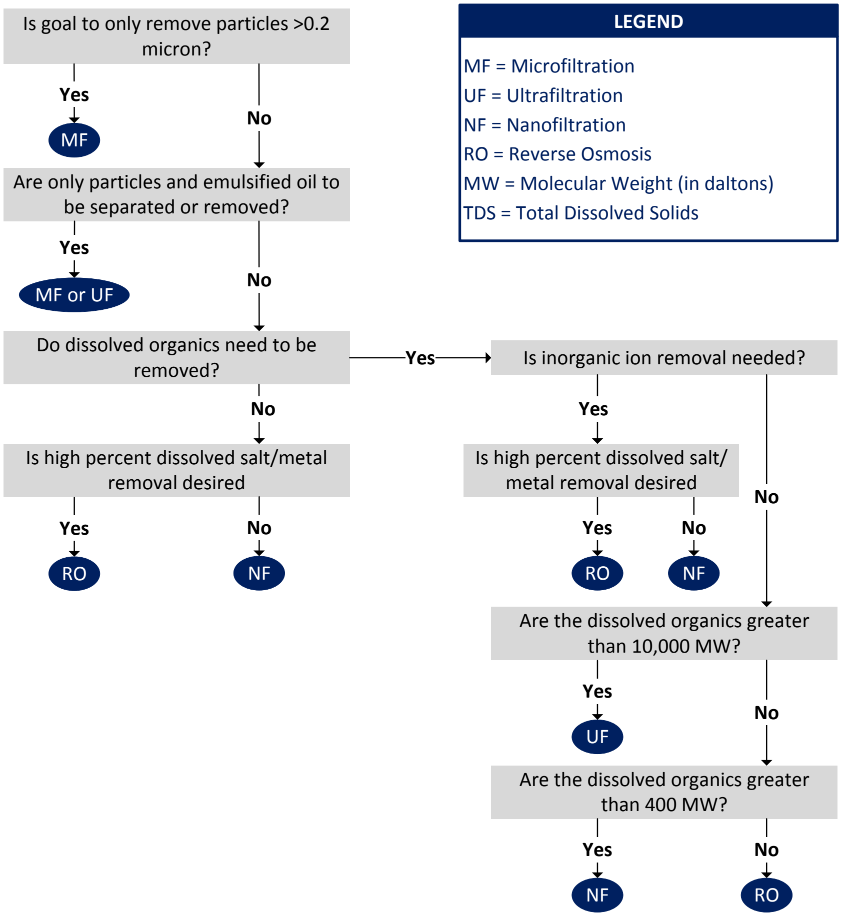
Single Pass Mode

Depending on the application, one mode may be preferred over the other.

The filtrations spectrum is shown below:

Source - (http://www.sswm.info/content/membrane-filtration)





NOTE: This simplified chart is based on common assumptions and should not be applied to every situation without more detailed analysis

ASSUMPTIONS

A. Relative Cost

- MF<UF<NF<RO

B. Removals

- MF – particles > 0.2 Micron
- UF – organics > 10,000 MW, virus, and colloids
- NF – organics > 400 MW and hardness ions
- RO – salts and low MW organics
- Particles include *Giardia*, *Cryptosporidium*, bacteria, and turbidity

Portions of diagram credited to National Drinking Water Clearinghouse (http://www.nesc.wvu.edu/pdf/dw/publications/ontap/2009_tb/membrane_DWFSOM43.pdf)

For the most part, particulate membranes are used when separation greater than 1-2 microns is desired. Microfiltration (MF) is the coarsest membrane type and typically separates out contaminants that are 0.05-2 microns in size. Ultrafiltration (UF) is tighter than MF, separating particles smaller than 0.1 microns and is also able to separate large molecular weight (MW) species ranging from 5,000-100,000 MW. UF is typically used to remove or concentrate emulsified oil, bacteria, large molecules like proteins, and many suspended solids from solution that can pass through a MF membrane. Nanofiltration (NF) is tighter than UF and can achieve separation of smaller size organic molecules as well as a portion of ionic species like salts, similar to reverse osmosis. NF was actually known as a “loose” reverse osmosis (RO) membrane to soften water but has developed into a useful filter for many different industrial applications. RO is the tightest membrane filter traditionally used to produce very clean water and is also used to concentrate and recover valuable process chemicals like plating solutions in metal finishing operations.

The decision flow chart to the left can be used to decide which membrane is best for a given application.

Membrane Configurations

The membrane itself is made of polymeric or inorganic materials (e.g., ceramic) and is usually supported on porous substrate materials for stability and strength. Different physical configurations are available and are designed for different applications. In cross-flow filtration schemes, the most common configurations are spiral wound, tubular, and hollow fiber. Commercially available inorganic membranes (ceramic, sintered metal) are typically in the MF/UF range. Factors that need to be considered when selecting the right membrane configuration include extent of separation desired (how clean the permeate needs to be), flow rates, solids loadings, temperature, and pH of the fluid.

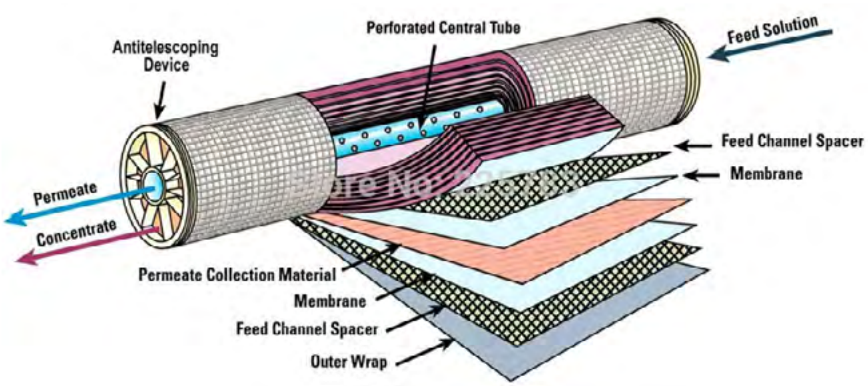
Spiral Membranes

- Contains high amount of surface area per unit volume since membrane sheets are tightly packed in specially-designed envelopes around a center tube that collects the permeate
- Best for low suspended solids applications because of tight flow channels, which do allow for smaller pumps (lower flow) to maintain sufficient crossflow velocity; coarse prefiltration stage usually required to prevent channel plugging
- UF, NF and RO membranes typical for spiral configuration
- Applications include process water purification, desalination, oil/water separation, wastewater treatment/recycle
- **Drawbacks:** reduced flux (flow per area membrane, compared to other configurations), requires prefiltration step

Spiral Membranes, cont

Source - (http://spectrumlabs.com/filtration/Edge.html)

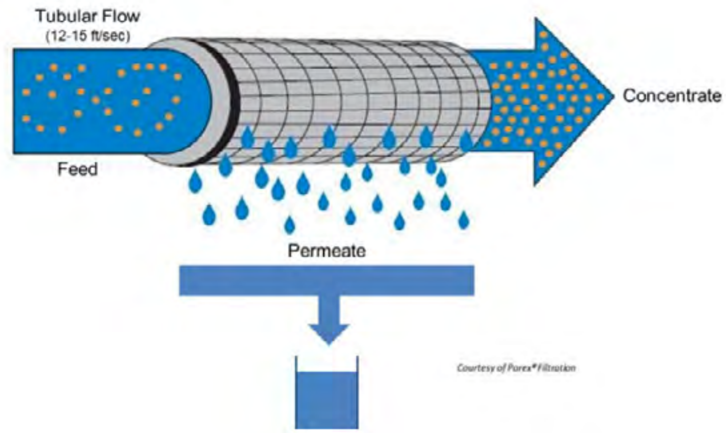
(Applied Membranes Inc. http://www.appliedmembranes.com)



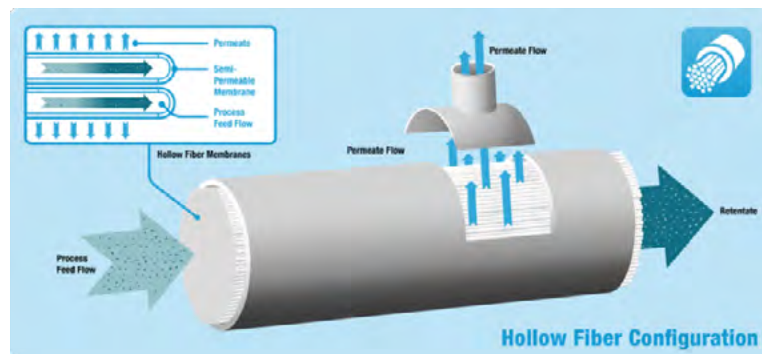
(aliexpress.com)

Tubular Membranes

- Feed flow enters tube, diameter from 5 to 25 mm (1 inch)
- Can handle higher suspended solids applications, less prefiltration required
- MF and UF membranes typical for tubular configuration
- Applications include solids/liquid separation for wastewater treatment or materials recovery and oil/water separation
- **Drawbacks:** larger size system footprint needed to produce given amount of permeate because less membrane surface area per unit volume, larger pump needed to achieve sufficient cross-flow velocity



(Porex Filtration, http://www.porexfiltration.com)



(Koch Membrane Systems, http://www.kochmembrane.com)

Hollow Fiber Membranes

- Hollow fibers are bundled inside housing
- Feed flow enters bundled fibers, inner diameter from 0.5 to 5 mm
- Similar to spiral wound membranes, best for lower suspended solids applications because of tighter flow channels; coarse prefiltration stage usually required
- MF, UF membranes typically used
- Applications include process water purification, oil/water separation, wastewater treatment/recycle, protein separation
- Fouled membranes can be backwashed
- **Drawbacks:** requires prefiltration step, rupture of any single fiber requires removal of entire module for repair

(Encyclopedia of Membranes (Editors: Enrico Drioli, Lidietta Giorno), “Hollow Fiber”, Khayet Mohamed, 2014)

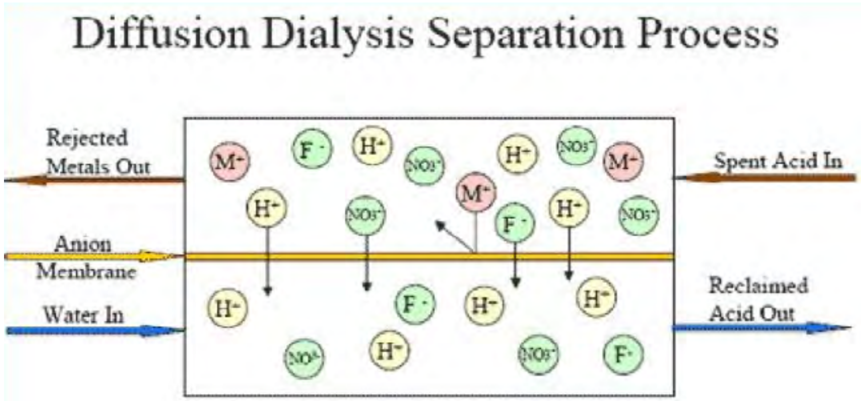
Other Types of Membrane Filtration

Other membrane separation processes worth mentioning are diffusion dialysis, electrodialysis, and pervaporation. These membrane processes do not involve cross-flow filtration or pressure-driven mechanisms. Electrical charge, concentration differences or chemical permeability is more important in these types of membrane separation.

Diffusion Dialysis

Diffusion dialysis is a membrane process where separation is achieved solely due to concentration differences, namely a concentration gradient across the membrane barrier. Diffusion dialysis can be used to recover acids and bases from process solutions and can thus reduce chemical purchase costs and hazardous waste generation. For example, sulfuric, hydrochloric, and combinations of hydrofluoric and nitric acids can be recovered from metal etching, stripping, refining, and smelting processes. Diffusion dialysis is also used to remove carboxylic acids from fermentation tanks in the brewing and winery sectors. The limiting factor of diffusion dialysis is the amount of solution that can be processed per day, making it a poor choice for large-scale operations but ideal for small and medium scale processes.

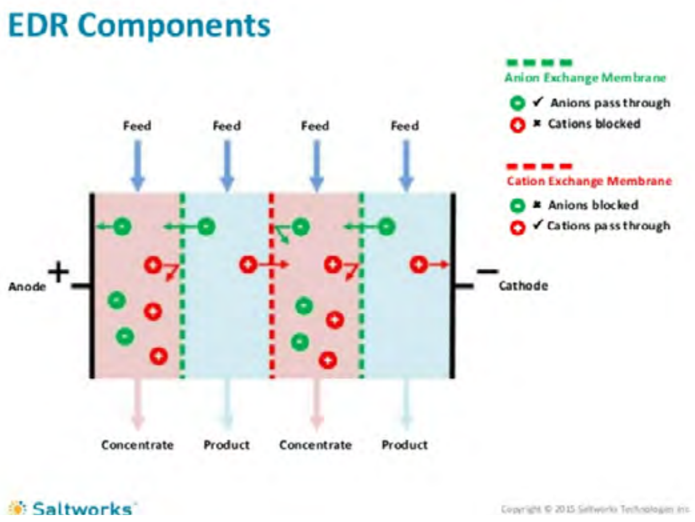
Source (http://www.acidrecovery.com/news/recycling-of-nitric-hydrofluric-acid-with-diffusion-dialysis)



Electrodialysis

Electrodialysis (ED) or electrodialysis reversal (EDR) is an electrochemical charge-driven separation process where dissolved ions are separated through permeable membranes under the influence of an electrical potential gradient. Ion exchange membranes have the ability to selectively transport ions with a positive or negative charge and reject ions of the opposite charge. An ED stack consists of a series of anion exchange membranes and cation-exchange membranes arranged in an alternating mode between an anode and a cathode. The positively-charged cations migrate toward the cathode, pass through the cation-exchange membrane and are rejected by the anion-exchange membrane; the opposite occurs for negatively charged anions that migrate to the anode. The result is an enriched ion concentration in one compartment (concentrate) and depleted concentration in the other (diluate). EDR is similar to ED, except that it also uses reversal of polarity to help reduce membrane scaling and fouling, thus allowing the system to operate at relatively higher water recoveries. ED can achieve only low removal of neutrally charged species (e.g., many organic compounds, boron, silica). ED and EDR have been utilized for municipal water and wastewater treatment plants and for desalination of brackish water and reclaimed water. In wineries, ED has shown to remove tartrates from wine solution, an energy-saving alternative to the traditional cold stabilization (tartrate precipitation) method.

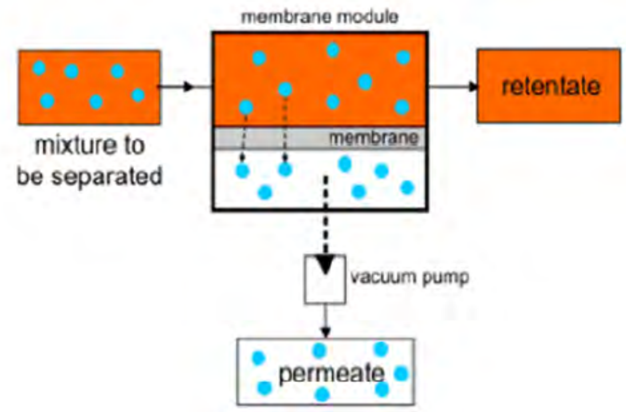
Source - (http://www.saltworkstech.com/)



Source - (http://www.saltworkstech.com/)

Pervaporation

Pervaporation is a membrane-based process for separating mixtures of organic fluids. The pervaporation membrane is non-porous and dense, made of polymeric or ceramic materials that exhibit different permeabilities for different components, resulting in the desired separation of the components. The feed is first heated up to the operating temperature and then brought into contact with the active (feed) side of the pervaporation membrane. The component with the higher permeability passes through the membrane and is continuously removed as vapor from the back (permeate) side of the membrane. The continuous removal of the vaporous permeate creates a concentration gradient across both sides of the pervaporation membrane. This concentration gradient acts as a driving force for the process. Solvent dehydration is a common application where pervaporation is used. Pervaporation has also been used in conjunction with distillation to achieve high purity solvent recovery.



Source (https://www.omicsonline.org/open-access/membranes-with-favorable-chemical-materials-for-pervaporation-process-areview-2155-9589-1000164.php?aid=83520)

Industries Where Membrane Technologies are Used

Industry	Application
High Purity Water Production (Pharmaceutical, Electronics)	• Membrane treatment (RO) before ion exchange to extend life of resins before regeneration is required
Beverage	• Process treatment of wine, beer, and juice (concentration, clarification, alcohol and color adjustments, etc.) • Acid and caustic recovery from CIP streams (oil, dirt removal).
Biotechnology	• Fermentation broth clarification • Amino acid concentration and clarification • Product concentration
Chemical Industry	• Concentration of latex, colloidal silica, photoresist development, flexographic ink, etc. • Pervaporation to separate and recover solvent(s) from mixtures
Pulp and Paper	• Black liquor concentration • Lignin and caustic recovery
Textile	• PVA and caustic recovery
Automotive & Appliance	• Electrophoretic coating recovery via ultrafiltration • Bath pH control • Wastewater degreasing • Alkaline cleaner and zinc phosphate recovery
Pharmaceuticals	• Concentration and purification of active ingredients
Food/Dairy	• Milk protein and whey protein concentrate • Reduce mineral content in whey • Removal of calcium phosphate and fat • Cheese brine clarification • Acid and caustic chemical recovery from CIP streams
Semiconductor Industry	• Recycling of process and ultrapure water used in wafer manufacturing processes
Metal Finishing	• Recovery of plating chemicals and rinsewater • Cleaning and reusing mass finishing solution • Diffusion dialysis to recover acid • Treatment of wastewater streams containing heavy metals
Lens Manufacturing	• Recovery of polishing compounds while producing clean water
Metal Working/Machining	• Oil removal from machining coolants

About NYSP2I

The New York State Pollution Prevention Institute (NYSP2I) is a statewide research and technology transfer center funded by the Environmental Protection Fund as administered by the New York State Department of Environmental Conservation (NYSDEC), located at Rochester Institute of Technology (RIT) and partnered with three additional universities. The purpose of our goals is to provide full geographic coverage of pollution prevention programs and services to manufacturers across New York State.

Areas of Technical Expertise:

- Improving efficiency and reducing the environmental "footprint" of a manufacturing process or facility
- Independent product technology assessments, validation and effectiveness studies, new product commercialization acceleration
- Supply chain sustainability assessments, strategy, and implementation (i.e., ISO 14001)
- Food waste reduction and diversion

In addition, NYSP2I focuses on the development and support of pollution prevention programs within our communities. Community organizations, academic institutions and municipalities that seek to improve health, the environment, and the economy through pollution prevention are funded by NYSP2I.

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