

# ADVANCED TECHNOLOGIES FOR AQUEOUS CLEANER WASTEWATER TREATMENT

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For the last two or three decades, protection of the environment has steadily been moving up on the priority list of the American public. Concern over issues such as the ozone hole, the greenhouse effect, overflowing landfills, acid rain, destruction of the rain forests and over population have created an attitude of conservation and environmental responsibility throughout the country.

The United States Congress has passed the Pollution Prevention Act of 1990, which emphasizes "point-of-source" reduction, recycle or recovery.

The phase-out of CFCs has led to a sharp increase in the utilization of aqueous cleaning technologies for degreasing and precision cleaning applications.

The pressure driven membrane processes of crossflow microfiltration, ultrafiltration, nanofiltration and reverse osmosis show outstanding promise for aqueous cleaner wastewater treatment, including the isolation, concentration and possible recycling of certain cleaning components, as well as recovery and reuse of the water stream.

In particular, membrane technologies possess certain properties which make them unique when compared to other separation operations. These include:

- Continuous process, resulting in automatic and uninterrupted operation
- Low energy utilization involving neither phase nor temperature changes
- Modular design - no significant size limitations
- Minimum of moving parts with low maintenance requirements
- Discrete membrane barrier to ensure physical separation of contaminants
- No chemical addition requirements

Other, specific treatment technologies can be utilized to create a total integrated system to meet the demands of a particular application. Such technologies include electrodialysis, deionization, carbon adsorption, biological treatment and ozonation.

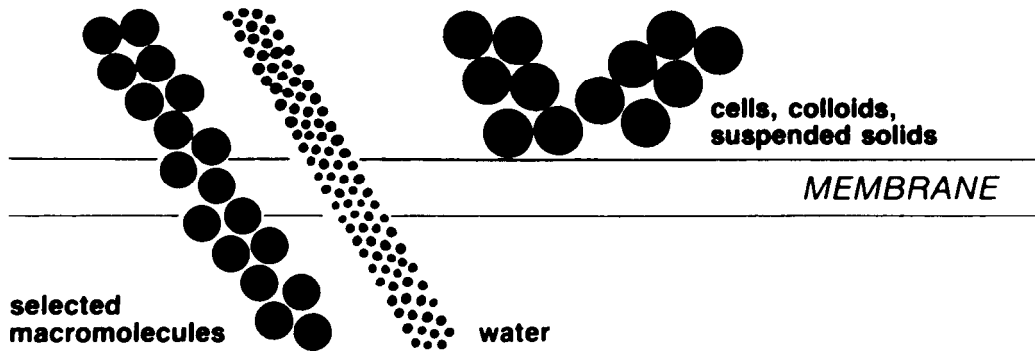


Figure 2: Microfiltration

Ultrafiltration

Figure 3 depicts ultrafiltration, which is used to separate materials in the 0.001 to 0.1 micron range (10-1000 angstroms). Basically, ultrafiltration is used to remove dissolved materials, whereas suspended solids are removed by microfiltration.

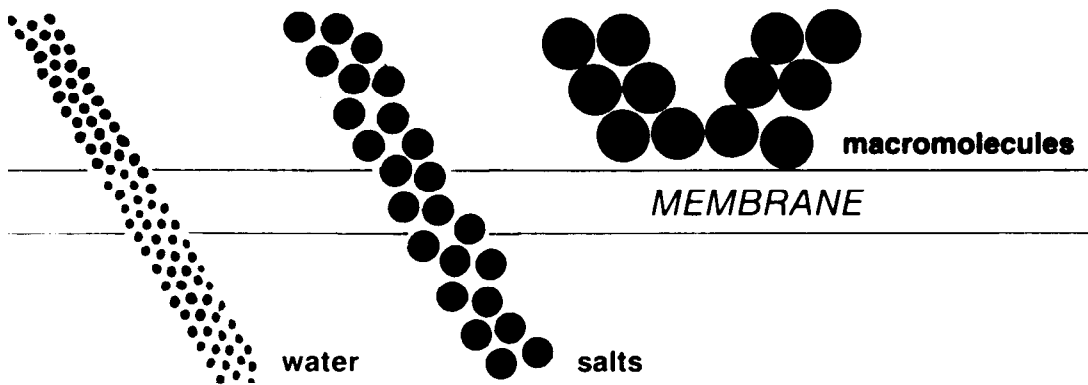


Figure 3: Ultrafiltration

Nanofiltration

This is an intermediate process between ultrafiltration and reverse osmosis. The molecular weight cut-off (MWCO) properties of nanofiltration membranes are in the range of 400 to 800 daltons. Ionic rejections vary widely depending upon the valence of the salts: multivalent salts such as magnesium sulfate ( $MgSO_4$ ) are rejected as much as 99%, while monovalent salts such as

## FUNDAMENTALS

A recent development in filtration technology known as "crossflow" or "tangential flow" filtration allows for continuous processing of liquid streams. In the process, the bulk solution flows over and parallel to the filtration surface, and because the system is pressurized, water is forced through the filter. The turbulent flow of the bulk solution over the surface minimizes the accumulation of particulate matter on the filter and facilitates continuous operation of the system.

Figure 1 illustrates both the conventional and crossflow mechanisms.

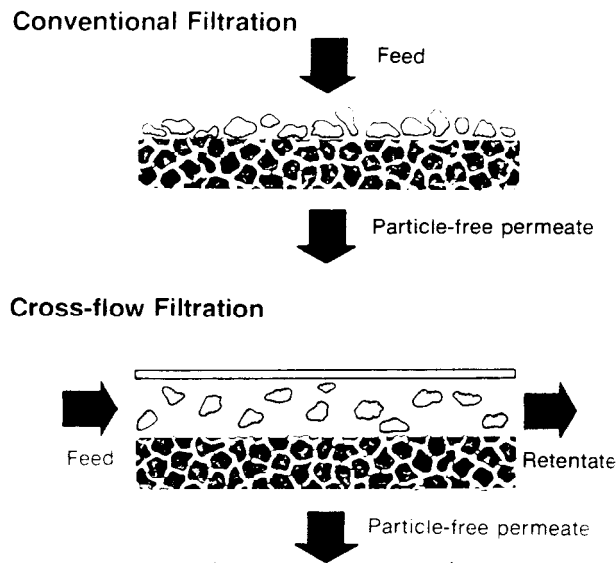


Figure 1: Conventional and Crossflow Filtration

### Microfiltration

Figure 2 depicts the mechanism of crossflow microfiltration. Microfiltration involves the removal of insoluble particulate materials ranging in size from 0.1 to 1.0 microns (1000-10,000 angstroms).

## Membrane Element Configurations

To be usable, these membrane materials must be packaged into a device, known as a "membrane element" or "module".

The particular way that the membrane polymer is configured in an element design has a direct bearing on the resistance of the membrane to fouling. It is economically desirable to pack as much membrane area into the device as possible without it becoming too large or heavy. Unfortunately, the element designs that provide the greatest "packing density" (surface area per unit volume) also have the lowest resistance to fouling as a result of the close spacing required to accomplish the high packing density.

The available membrane element configurations are described below and illustrated in Figure 5:

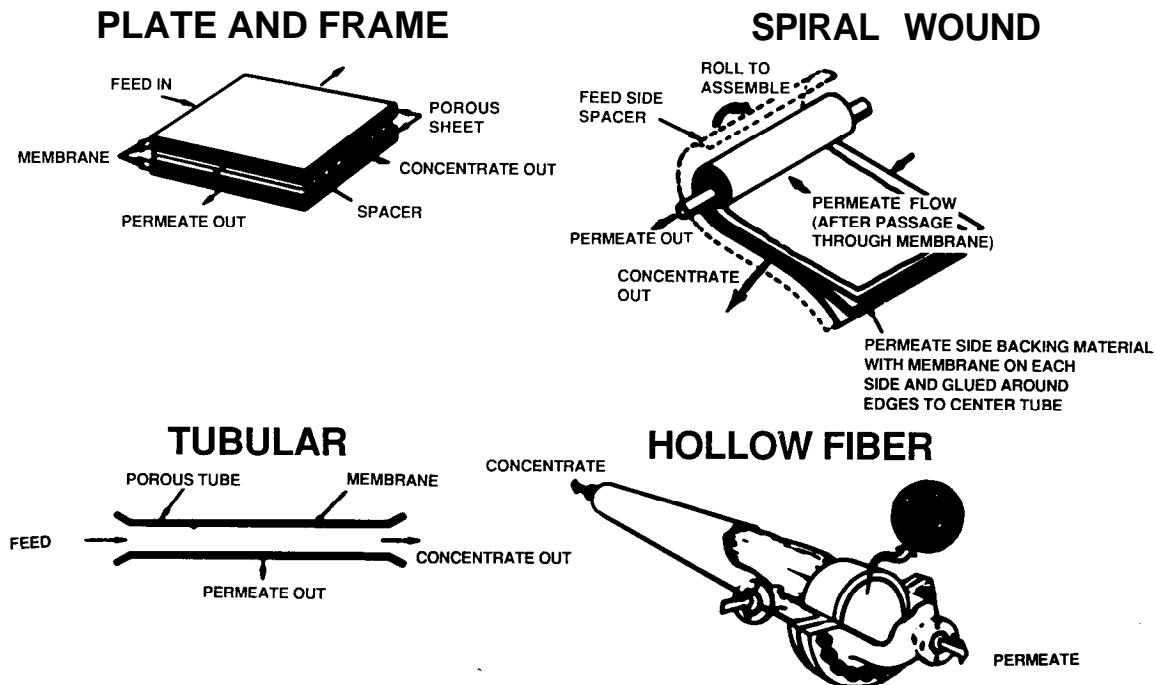


Figure 5, Membrane element configurations

### Tubular

Manufactured from ceramic, carbon, stainless steel, or a number of porous plastics, these tubes have inside diameters ranging from 3/8 inch up to approximately 1 inch (10 to 25 mm). The membrane is typically coated on the inside of the tube and the feed solution flows through the interior (lumen) from one end to the other, with the permeate passing through the wall to be collected on the outside of the tube. Packing density is low, but resistance to fouling is very high.

sodium chloride (NaCl) may have rejections as low as 20%, depending on the particular polymer design.

### Reverse Osmosis

This process will remove all dissolved organic (non-ionic) solids with molecular weights above approximately 100 daltons, as well as a high percentage of ionic materials. Because reverse osmosis membranes are not perfect (they will typically remove 90-99% of the ionic contaminants), for ultrapure water production, they are usually used as pretreatment to a final "polishing" deionization unit.

Figure 4 illustrates the reverse osmosis mechanism.

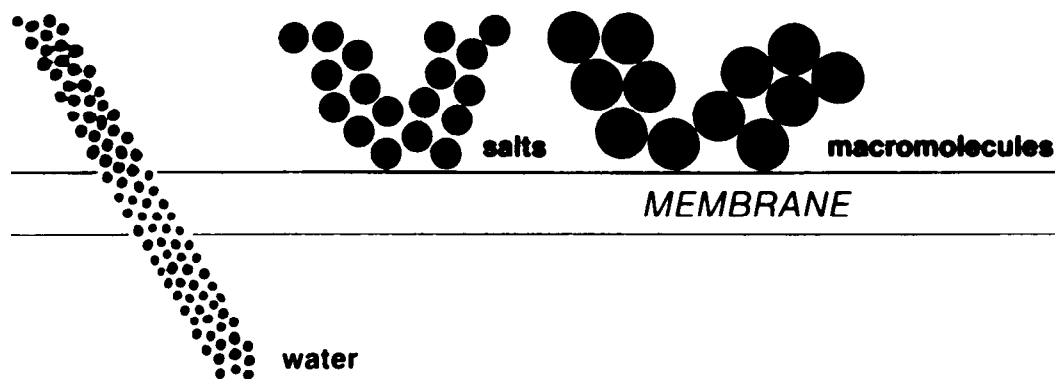


Figure 4, Reverse osmosis

### Membrane Materials

All of the above membrane processes utilize thermoplastic polymers or certain inorganic materials in their construction which have been optimized for a specific range of applications.

Microfiltration membrane polymers include such thermoplastic films as Nylon, cellulose, PVDF (Kynar), Teflon and polysulfone. Ceramic and metallic materials are also constructed with porosities in the microfiltration range.

Most ultrafiltration membrane polymers are manufactured from polysulfone, polyacrylonitrile or a cellulosic derivative. Nanofiltration and reverse osmosis polymers are typically either cellulosic (cellulose acetate, cellulose triacetate or a mixture thereof) or a thin film composite ("TFC") construction. The latter usually consists of a layer of polysulfone membrane on which is deposited a thin film of a proprietary polymer related to the polyamide family.

the case of the other membrane processes, electrodialysis utilizes membranes which selectively allow either the cation or anionic solute to pass through in response to the electrical charges imposed by the anode and cathode. Electrodialysis is represented in Figure 6.

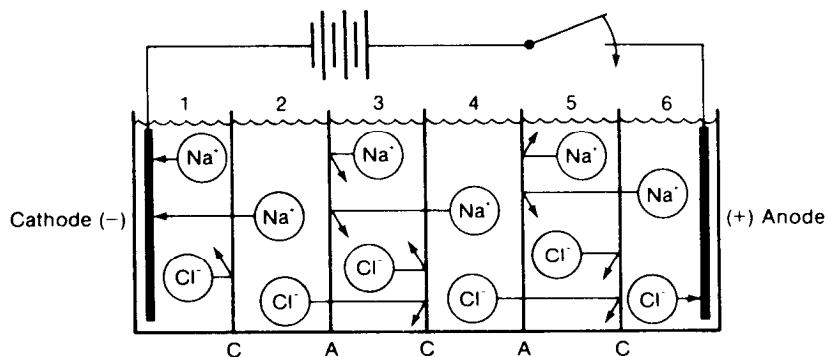


Figure 6, Electrodialysis

### Ion Exchange

For inorganic contaminant recovery, ion exchange offers significant potential for recycling. Utilizing the ability of certain resins to adsorb ionic solute, ion exchange can be effective in treating contaminated streams containing up to approximately 30,000 mg/L of inorganic salts. Figure 7 illustrates this process. Suspended solids in excess of 50 mg/L and certain organic contaminants may foul the resin. Also, it is a batch process in that it must be taken offline during regeneration. It offers excellent potential in those applications requiring that the reverse osmosis permeate be polished to achieve very high purity.

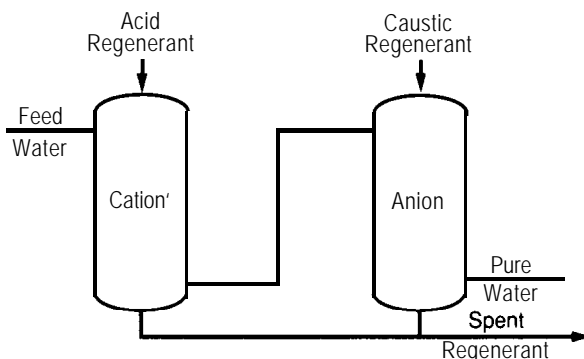


Figure 7, Ion Exchange

### Ozonation

Ozone, a colorless gas with a pungent odor, is created when oxygen is exposed to either a high voltage electrical discharge (lightning, electrical "short") or ultraviolet radiation. Ozone is very unstable and reverts back to oxygen in minutes. When dissolved in water, ozone is a powerful oxidizing agent and is very effective at destroying organic compounds, particularly in

## Hollow Fiber (Capillary)

These elements are similar to the tubular element in design, but smaller in diameter and require rigid support such as is obtained from the epoxy "potting" of a bundle inside a cylinder. Feed flow is either down the interior of the fiber or around the outside of the fiber. Packing density is medium and fouling resistance is high.

## Fine Hollow Fiber

This element was once widely used in a variety of water purification applications. It consists of a bundle of thousands of hair-like hollow fibers. The flow is "outside-in" with the permeate exiting from the interior (lumen) of each fiber. The fibers are extremely fragile and so easily fouled that these elements only find special application today in seawater desalting markets, particularly in the Middle East.

## Spiral-Wound

This element is constructed from an envelope of sheet membrane wound around a permeate tube that is perforated to allow collection of the permeate. Water is purified by passing through one layer of the membrane and flowing into the permeate tube. Packing density is low and resistance to fouling is fair.

## Plate and Frame

This element incorporates sheet membrane stretched over a frame to separate the layers and facilitate collection of the permeate. Packing density is low and resistance to fouling quite high.

The following table lists the important physical characteristics of the various membrane element device configurations available today:

<u>Element Configuration</u>	<u>Packing Density*</u>	<u>Suspended Solids Tolerance **</u>
Tubular	Low	High
Hollow fiber	Medium	High
Fine hollow fiber	High	Low
Spiral-wound	Medium-Low	Fair
Plate and Frame	Low	High

\* Membrane area per unit volume of space required.

\*\* Fouling resistance

## Electrodialysis

Electrodialysis utilizes permeable membranes as well as an anode and cathode to effect separation. Instead of driving pure water through the membrane and leaving contaminants behind, as in

fouling problems - the bane of all membrane systems. Certainly, suspended solids of any kind represent a potential problem, and as indicated above, the configuration of the membrane element plays a major role in its ability to resist fouling.

In reverse osmosis applications (and to a lesser extent ultrafiltration), osmotic pressure considerations can have a significant effect on the system design. Osmotic pressure ( $\Delta\pi$ ) is loosely defined as the resistance of a particular solution to becoming concentrated by the membrane process. It is a function of both the solute itself and its concentration.

Membrane Polymer - The polymers from which the various membrane elements are constructed have been previously addressed. Obviously, the choice of membrane polymer is a key component with regard to effecting the separation and each polymer has its particular strong and weak points; none is perfect. It is essential that the design engineer understand the particular characteristics of each polymer well enough to select the one most appropriate for the specific application.

Membrane Area - The larger the membrane area in a system, the greater the permeate rate, everything else being equal.

Membrane Element Configuration - This factor is addressed above.

Temperature - Because of its lower viscosity, warm water will flow more readily through membrane pores than cold water: hence, as temperature is increased, permeate rate increases. Because most membrane polymers are thermoplastic, they become softer and more compressible when warmed. The combination of temperature and pressure can cause irreversible compaction in some polymers (e.g. cellulosic), resulting in premature failure. Certain plastic polymers as well as most non-plastic membranes exhibit excellent thermal stability and offer significant promise in those applications where it is considered desirable to process a stream at elevated temperatures. Each membrane element manufacturer provides data on the relationship of temperature to permeate rate for its products.

Applied Pressure - In general, the permeate rate of a membrane element is directly proportional to the net driving pressure. Net driving pressure is defined as the total pump pressure minus the osmotic pressure minus any back pressure in the permeate line. Net driving pressures range from as low as 30 psi (2 bar) for microfiltration systems to approximately 1000 psi (68 bar), considered to be the practical limit for available reverse osmosis systems.

Osmotic pressure deserves more discussion at this point because of its effect in many reverse osmosis applications. Osmotic pressure increases as the concentration of the solute increases. Because osmotic pressure is related to ionic concentration, such factors as pH and temperature may also have

ppm concentrations.

Figure 8 illustrates the production of ozone gas by the corona discharge method.

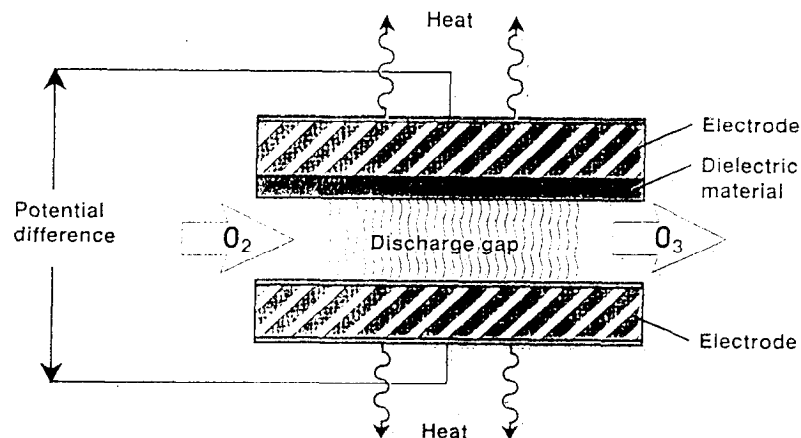


Figure 8, Corona Discharge Production of Ozone Gas

### B i o l o g i c a l

Utilizing either aerobic or anerobic bacteria, these processes have recently expanded from municipal wastewater treatment into the pollution control arena. Most effectively used for dissolved organic contaminants, the mechanism involves destruction of the contaminant by microbial catabolism. The resulting products may be as basic as carbon dioxide, methane, and water. Limitations include a maximum BOD concentration of approximately 10,000 mg/L as well as sensitivity to heavy metals and certain organic chemicals.

### DESIGN CONSIDERATIONS

In general, the following factors affect performance and efficiency in any membrane based treatment system:

- Water Analysis
- Membrane Polymer
- Membrane Area
- Membrane Element Configuration
- Temperature
- Applied Pressure
- Recovery
- Flow Conditions
- Membrane Element Array

Water Analysis - The chemical composition of the feed stream can affect the membrane element in a number of ways. The polymer itself can be degraded by certain chemicals. For example, cellulosic membrane polymers are subject to hydrolysis by high pH and polyamide and most TFC polymers are degraded by oxidizing agents such as chlorine. Water chemistry can also contribute to

## Effect of Recovery on Increase in Solute Concentration in Concentrate Stream

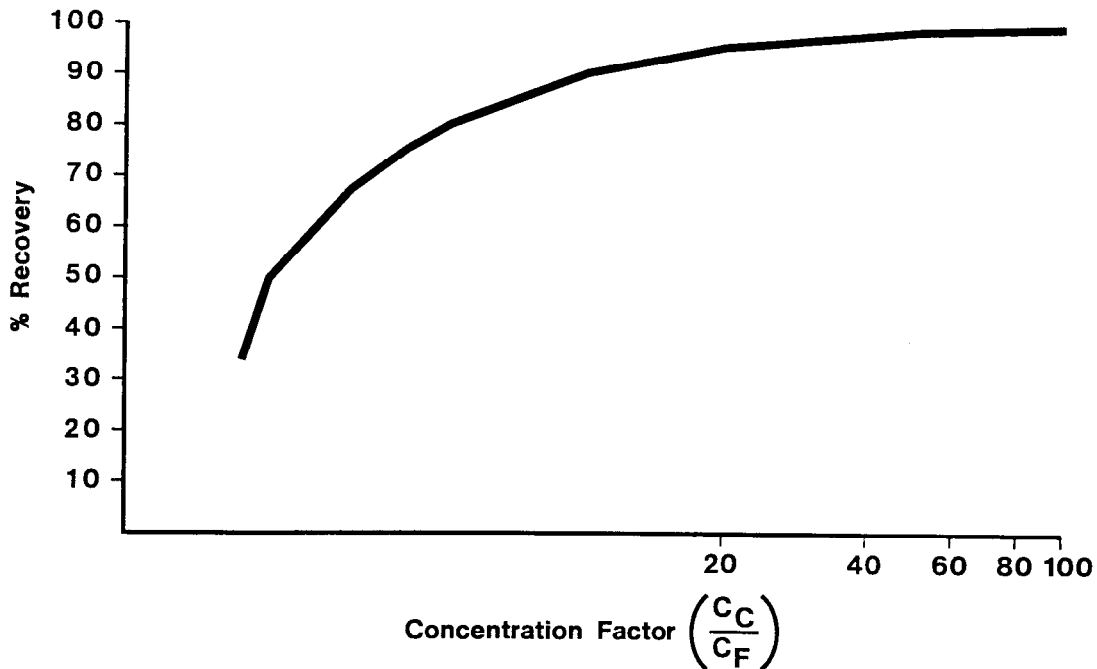


Figure 10: Plot of recovery vs. concentration factor

Each membrane element manufacturer will indicate the maximum recommended recovery for its products. If this figure is exceeded in the system design, there is danger that flows through the element will no longer be turbulent, thereby resulting in increased concentration polarization and fouling.

Concentration polarization is a phenomenon associated with reverse osmosis. When a fouling layer (dirt, scale, biofilm, etc.) builds up on a membrane surface, it prevents normal mixing of rejected ionic contaminants (salts) throughout the flowing stream. This buildup of salts can produce additional scaling and further fouling. Additionally, because the rejection of salts is always a percentage of the concentration at the membrane surface, concentration polarization produces lower permeate quality (higher TDS). In many cases, this drop in permeate quality will indicate a fouling condition prior to a drop in permeate flow - the traditional fouling indicator.

Flow Conditions - It has been shown that membrane elements are much less susceptible to fouling from suspended or precipitated solids if all of the flows through the element are turbulent. This is indicated by the term "Reynolds number", which is a dimensionless number expressed as:

$$\frac{\text{diameter} \times \text{mass velocity}}{\text{viscosity}}$$

an effect with certain solutes. In most water purification applications, the total dissolved solids (TDS) concentration of the feed water is sufficiently low so that osmotic pressure is not significant. Exceptions to this are brackish water supplies (TDS > 10,000 ppm) and seawater (TDS > 35,000 ppm).

In waste treatment and processing applications, osmotic pressure considerations become increasingly important. These applications typically involve high recoveries, described in the waste treatment section.

Recovery

Figures 9 and 10 illustrate the relationship of system recovery to solute concentration, expressed as "concentration factor," defined as 1.

$$C_C \approx \frac{C_F}{1-\text{Recovery}} = X C_F$$

**X ≡ Concentration Factor**

<b>Recovery</b>	<b>X</b>
<b>33%</b>	<b>1.5</b>
<b>50%</b>	<b>2</b>
<b>67%</b>	<b>3</b>
<b>75%</b>	<b>4</b>
<b>80%</b>	<b>5</b>
<b>90%</b>	<b>10</b>
<b>95%</b>	<b>20</b>
<b>97 1/2%</b>	<b>40</b>
<b>98%</b>	<b>50</b>
<b>99%</b>	<b>100</b>

Figure 9: Concentration factor vs recovery

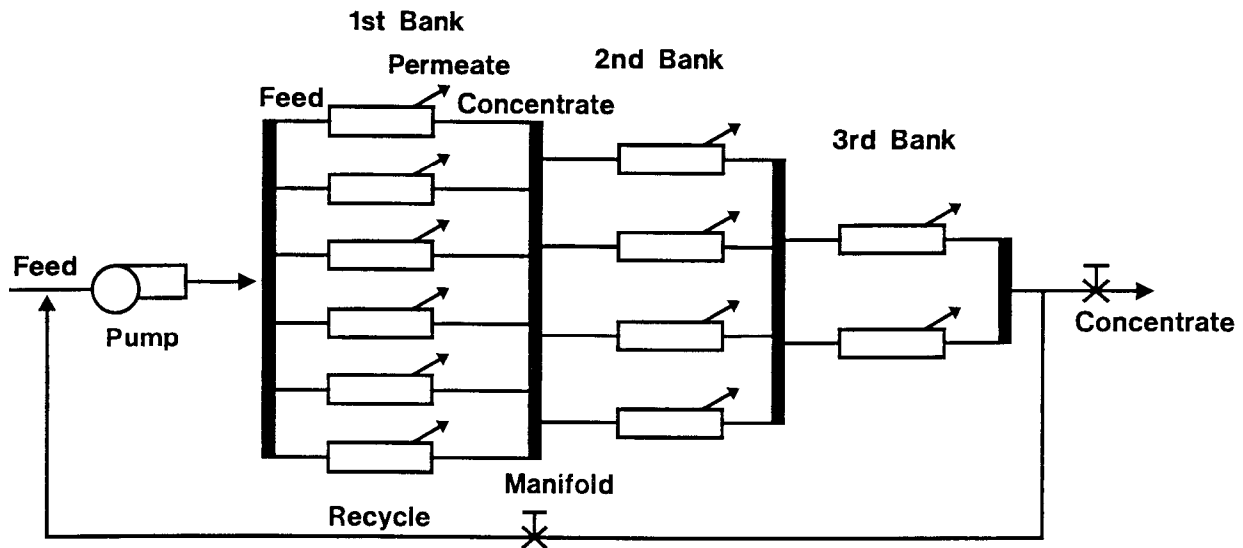


Figure 12: Schematic of membrane element array

Each membrane element manufacturer provides detailed information, and in most cases computer programs, to assist the engineer in designing systems utilizing its membrane elements.

Figure 13 is a general schematic of a membrane system. In membrane technologies, an important engineering design consideration is "recovery," which is defined as the permeate flow divided by the feed flow: in other words, that percentage of the feed flow which is pumped through the membrane. Typically, for water purification applications, recovery of the system ranges from 25% to 80%. For effluent treatment applications, the recovery figure is at least 90%.

The recovery of the system is controlled by restricting the quantity of flow in the concentrate stream, normally through the use of a concentrate valve. As recovery is increased, with the resulting decrease in concentrate stream flow (quantity), the concentration of salts and other contaminants increases which results in an increased osmotic pressure. Osmotic pressure is discussed in detail later in this document.

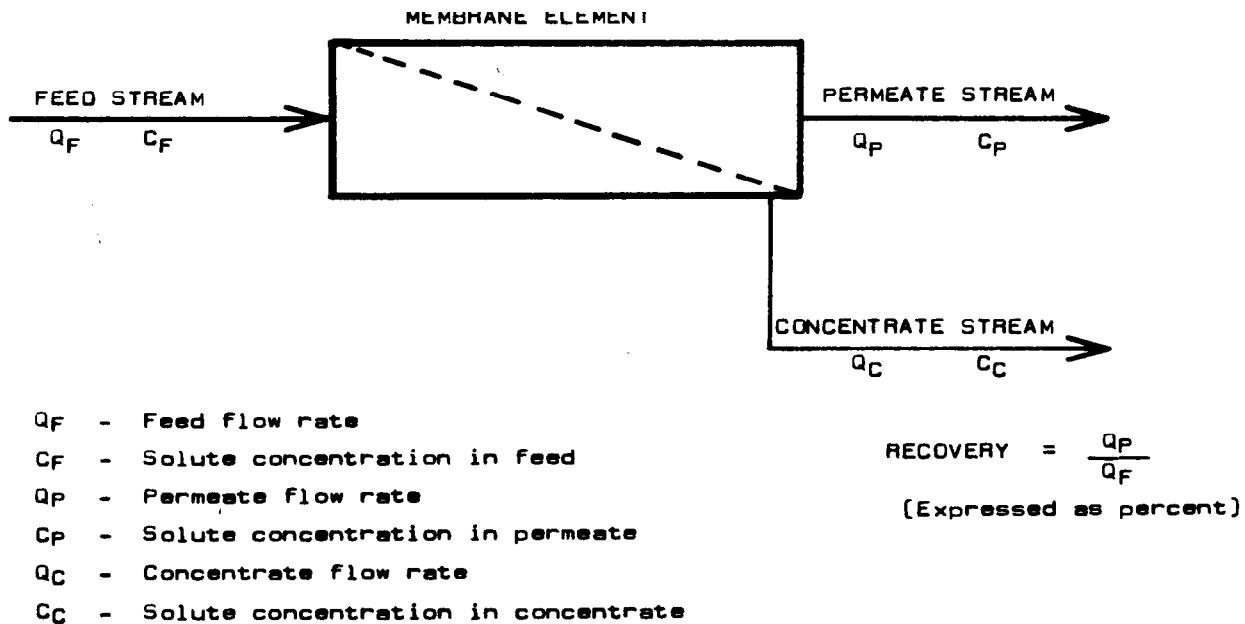


Figure 13: Membrane system schematic

### APPLICATIONS

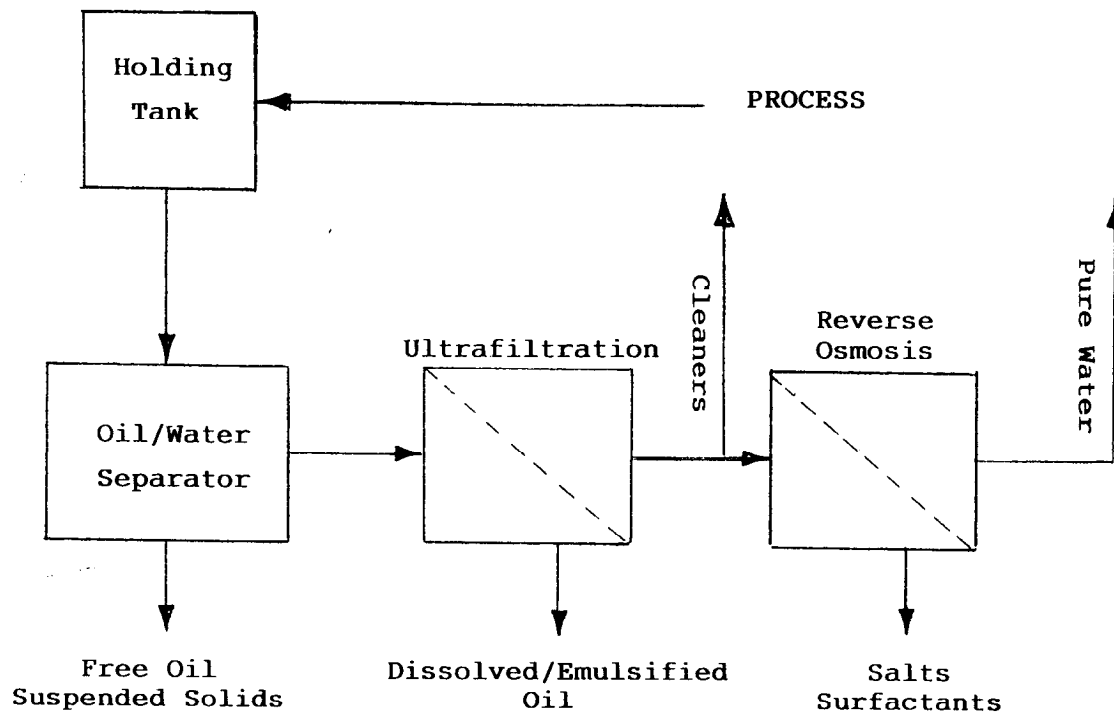
Aqueous cleaners can be divided into three subgroups: alkaline, detergent and emulsion cleaners, as described below.

Alakline cleaners are aqueous cleaners containing phosphates, borates and silicates. They generally also contain surfactants.

Detergent cleaners are simply solutions of detergents in water.

Emulsion cleaners contain emulsified solids. Because these solutions are only semi-aqueous, may have flammability problems and leave only residues, they are used only in special applications.

Membrane separation technologies can be used to separate emulsified and dissolved oils from the rest of the solution; however, particulate materials and free oils are often present in these applications and can create fouling problems. If the concentration of these contaminants is high enough to cause a potential problem, they can be reduced utilizing such technologies as filtration, dissolved air flotation, and coalescing.



**Figure 14**

Figure 14 illustrates the application of membrane technologies to contaminated rinse waters from aqueous cleaning processes. In applications where the cleaning chemistries can be separated from the oily contaminants, ultrafiltration can be utilized to effect this separation and the cleaners can be recovered for reuse.

In those cases where the water is to be discharged to the local POTW (Publicly Owned Treatment Works) or to a surface water source, reverse osmosis technology may be required to remove excessive concentrations of ionic contaminants. In certain applications where the purified water must meet specific high quality requirements, ion exchange can be utilized to "polish" the reverse osmosis permeate.

In those cases where there is a need to further reduce the volume of the reverse osmosis concentrate stream, electrodialysis technology can be used to concentrate ionic contaminants, and, if necessary, evaporation can be used to remove the last traces of water.

For oily wastes in the concentrate stream, it may be possible to utilize biological treatment to break down the BOD/COD components.

#### CONCLUSIONS

Membrane technologies combined with more traditional technologies, offer significant opportunities in waste treatment applications associated with precision cleaning industries. Hopefully, this presentation has provided insight and a better understanding of these technologies.