Kirk-Othmer Encyclopedia of Chemical Technology.

ULTRAFILTRATION

Ultrafiltration is a pressure-driven filtration separation occurring on a molecular scale (see Dialysis; Filtration; Hollow-fiber membranes; Membrane technology; Reverse osmosis). Typically, a liquid including small dissolved molecules is forced through a porous membrane. Large dissolved molecules, colloids, and suspended solids that cannot pass through the pores are retained.

Ultrafiltration separations range from ca 1 to 100 nm. Above ca 50 nm, the process is often known as microfiltration. Transport through ultrafiltration and microfiltration membranes is described by pore-flow models. Below ca 2 nm, interactions between the membrane material and the solute and solvent become significant. That process, called reverse osmosis or hyperfiltration, is best described by solution–diffusion mechanisms.

Membrane-retained components are collectively called concentrate or retentate. Materials permeating the membrane are called filtrate, ultrafiltrate, or permeate. It is the objective of ultrafiltration to recover or concentrate particular species in the retentate (eg, latex concentration, pigment recovery, protein recovery from cheese and casein wheys, and concentration of proteins for biopharmaceuticals) or to produce a purified permeate (eg, sewage treatment, production of sterile water or antibiotics, etc). Diafiltration is a specific ultrafiltration process in which the retentate is further purified or the permeable solids are extracted further by the addition of water or, in the case of proteins, buffer to the retentate.

Membrane filtration has been used in the laboratory for over a century. The earliest membranes were homogeneous structures of purified collagen or zein. The first synthetic membranes were nitrocellulose (collodion) cast from ether in the 1850s. By the early 1900s, standard graded nitrocellulose membranes were commercially available (1). Their utility was limited to laboratory research because of low transport rates and susceptibility to internal plugging. They did, however, serve a useful role in the separation and purification of colloids, proteins, blood sera, enzymes, toxins, bacteria, and viruses (2).

In the late 1950s and 1960s, a technique was developed that produced highly anisotropic or asymmetric structures, ie, membranes constructed of a very thin, tight surface skin having a porous substructure. The substructure provided the necessary mechanical support for the skin without the hydraulic resistance of previous isotropic structures. Flux rates improved by orders of magnitude, and inherent resistance to plugging increased. A molecule entering a pore through the skin traverses a channel of increasing diameter. Both high flux and plugging resistance are important for achieving an economical membrane performance in industrial applications.

The subsequent improvement of the physical and chemical characteristics of these membranes, their incorporation into machines, and the development of procedures to prevent or clean surface-fouling films were the principal areas of significant advancement. By 1990, the industrial ultrafiltration market had grown to an estimated $\$(90 - 100) \times 10^6$.

2 ULTRAFILTRATION

1. Media

Most ultrafiltration membranes are porous, asymmetric, polymeric structures produced by phase inversion, ie, the gelation or precipitation of a species from a soluble phase (see Membrane technology).

Typically, a polymer is first dissolved in a mixture of miscible solvents and nonsolvents. This mixture (lacquer solution) is frequently a better polymer solvent than any of the components (3, 4). The lacquer solution is dearated and spread as a thin film on a suitable support. The surface of the film is then placed in contact with a nonsolvent diluent (precipitant) miscible with the solvent. This precipitates or gels the surface almost instantaneously, forming a membrane skin.

Macroscopically, the solvent and precipitant are no longer discontinuous at the polymer surface, but diffuse through it. The polymer film is a continuum with a surface rich in precipitant and poor in solvent. Microscopically, as the precipitant concentration increases, the polymer solution separates into two interspersed liquid phases: one rich in polymer and the other poor. The polymer concentration must be high enough to allow a continuous polymer-rich phase but not so high as to preclude a continuous polymer-poor phase.

The skin is highly stressed because of the polymer consolidation. The surface tears at polymer-poor sites, forming cracks or pores that expose a more fluid internal polymer layer to the precipitant–solvent mixture (5). The pores propagate into so-called fingers by drawing the precipitating polymer from the bottom to the side of the pore (Fig. 1). Because this process proceeds along a moving boundary into the polymer film, additional pores do not form on the walls. The polymer solution behind these precipitated walls gels into an open-sponge structure (Fig. 2). The capillary stresses (surface activity) must be low enough to avoid collapsing the structure. Polymers with high elastic moduli and solvents that do not plasticize the polymer are preferred.

Membrane structure is a function of the materials used (polymer composition, molecular weight distribution, solvent system, etc) and the mode of preparation (solution viscosity, evaporation time, humidity, etc). Commonly used polymers include cellulose acetates, polyamides, polysulfones, dynels (vinyl chloride–acrylonitrile copolymers) and poly(vinylidene fluoride).

Modification of the membranes affects the properties. Cross-linking improves mechanical properties and chemical resistivity. Fixed-charge membranes are formed by incorporating polyelectrolytes into polymer solution and cross-linking after the membrane is precipitated (6), or by substituting ionic species onto the polymer chain (eg, sulfonation). Polymer grafting alters surface properties (7). Enzymes are added to react with permeable species (8–11) and reduce fouling (12, 13).

Polyelectrolyte complex membranes are phase-inversion membranes where polymeric anions and cations react during the gelation. The reaction is suppressed before gelation by incorporating low molecular weight electrolytes or counterions in the solvent system. Both neutral and charged membranes are formed in this manner (14, 15). These membranes have not been exploited commercially because of their lack of resistance to chemicals.

Inorganic ultrafiltration membranes are formed by depositing particles on a porous substrate (16, 17). In one form, inorganic particles (alumina, Zr_2SiO_2) of two discrete sizes are deposited. The smaller size can pass through the porous support whereas the larger size cannot. The mixture forms a controlled porosity film at the entrance of the support's pores. These membranes can be removed and regenerated *in situ*. Alternatively, inorganic or organic binders can be added as stabilizers. Inorganic membranes exhibit good thermal and chemical stability.

Dynamic membranes are concentration–polarization layers formed *in situ* from the ultrafiltration of colloidal material analogous to a precoat in conventional filter operations. Hydrous zirconia has been thoroughly investigated; other materials include bentonite, poly(acrylic acid), and films deposited from the materials to be separated (18).

Track-etched membranes are made by exposing thin films (mica, polycarbonate, etc) to fission fragments from a radiation source. The high energy particles chemically alter material in their path. The material is then dissolved by suitable reagents, leaving nearly cylindrical holes (19).

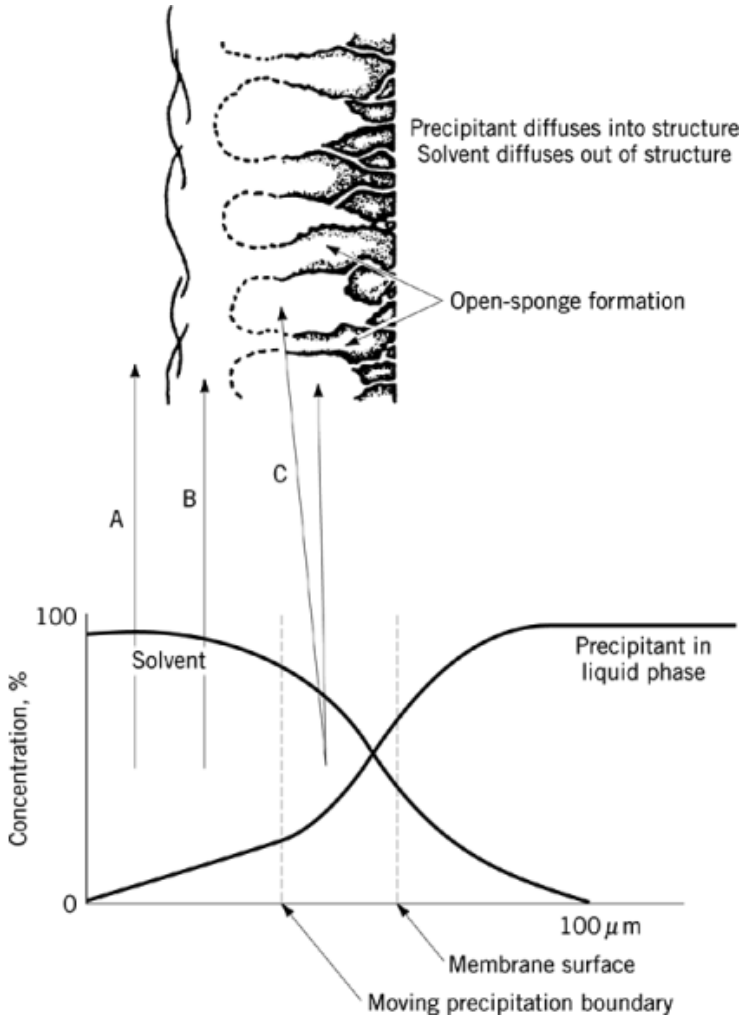

Fig. 1. Formation of an ultrafiltration membrane: A, unprecipitated polymer solution; B, polymer solution separating into two phases; C, pore fingers with precipitant–solvent mixture.

2. Process

Pore-flow models most accurately describe ultrafiltration processes. Other membrane transport mechanisms, which may occur simultaneously although generally at a much lower rate, include dialysis (diffusion), osmosis (solvent by osmotic gradient), anomalous osmosis (osmosis with a charged membrane), reverse osmosis (solvent by pressure gradient larger and opposite to osmotic gradient), electrodialysis (solute ions by electric field), piezodialysis (solute by pressure gradient), electroosmosis (solvent in electric field), Donnan effects, Knudsen flow, thermal effects, chemical reactions (including facilitated diffusion), and active transport.

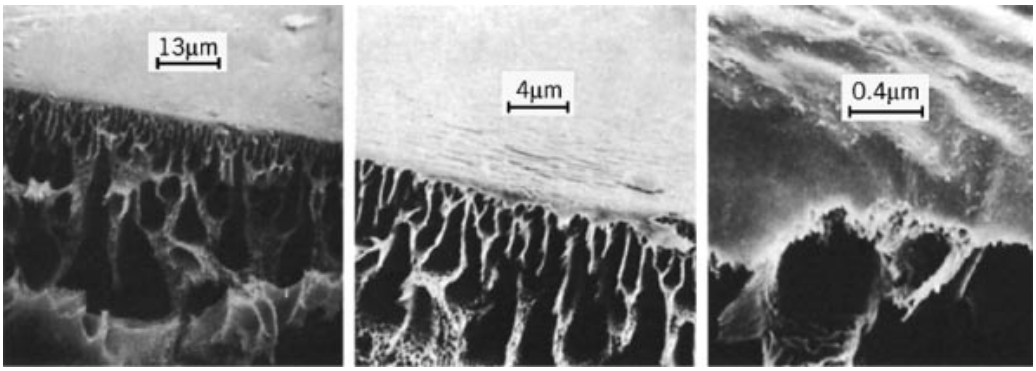

Fig. 2. A series of progressively closer (scanning electron microscope) SEM photographs of the same membrane cross section, clearly showing skin and substructure.

When pure water is forced through a porous ultrafiltration membrane, Darcy's law states that the flow rate is directly proportional to the pressure gradient:

$$J = \frac{V}{A \cdot t} = \frac{K_m \Delta P}{\mu} \qquad (1)$$

where J is permeate flux in units of volume V per membrane area A, at time t, K_m is the membrane hydraulic permeability, μ is the fluid viscosity, and ΔP is the membrane pressure drop between the retentate and permeate.

The membrane hydraulic permeability K_m is a function of the pore size, tortuosity, and length, and any resistance in the substructure. Because ultrafiltration membranes are plastic and can yield (compact) or creep under pressure, K_m is also a function of the pressure history. Dynamic pressure drops from flow through a membrane and static pressure drops from a force applied on a membrane surface (eg, across a fouling film) can both cause compaction. Initial compaction occurs rapidly during startup, whereas long-term compaction occurs slowly over the operating life of the membrane. Swelling agents can sometimes (partially) reverse compaction.

Initial membrane compaction is illustrated by Figure 3. Equation 1 predicts a straight-line response of J to ΔP, or J_3 at P_1. Owing to the compaction, a lower flux J_2 is observed. Once a membrane has been subjected to some pressure (P_1), equation 1 is valid for predicting flux up to that pressure (Fig. 3, curve B). If the membrane is subsequently subjected to higher pressure (P_2), the hydraulic permeability constant is changed (Fig. 3, curve D).

The addition of small membrane-permeable solutes to the water affects permeate transport in the following ways. (*1*) Solute–solvent interactions change the permeating fluid viscosity. (*2*) Solute adsorption reduces the apparent membrane-pore diameter (20). Because of high interfacial tension between water and certain materials, the water phase in the pores can be replaced. Dynel and polysulfone membranes, for example, preferentially extract partially soluble alcohols from water. Surfactants suppress hydrophobic adsorption. Adsorption of permeate species is characterized by a lag in permeate concentration as a function of time. (*3*) The interfacial charge between the membrane-pore wall and the liquid affects permeate transport when the Debye screening length approaches (ca 10%) the membrane-pore size. Flux declines, rejection increases, and electrolyte is retained. Other electrokinetic phenomena become pronounced and may influence fouling (21). (*4*) High surface tension on hydrophobic membranes forces water molecules to form large clusters in the pores. Water-structuring ions (eg, Na^+, Mg^{2+}, and OH^-) tend to decrease permeability and increase rejection; destructuring ions (eg, Cl^-, NO^-_3, and ClO^-_4) have the opposite effect (22). (*5*) Solvents, swelling agents, and

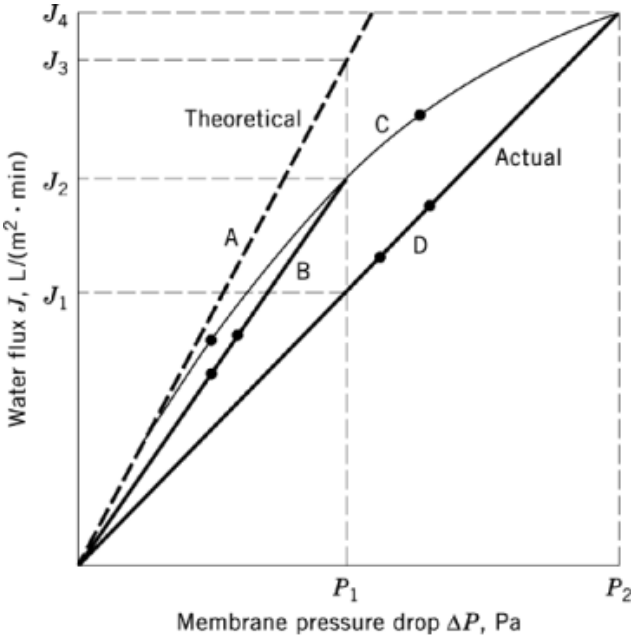

Fig. 3. Water flux versus pressure. Equation 1 predicts the line (– – –) having flux J_3 at P_1. Actual initial water flux follows curve C to flux J_2 at P_1. Subsequent operation at pressure drops less than P_1 follows curve B (eq. 1). If pressure is increased above P_1, flux follows curve C (additional compaction) to P_2. A new value of K_m is used in equation 1. Operation at pressure drops less than P_2 follows curve D. Flux at P_1 is lowered to J_1.

plasticizers that diffuse into the polymer structure can change the apparent pore size (K_m in eq. 1) or increase the rate of long-term compaction. The rejection R of a solute is defined as:

$$R = 1 - \frac{C_{pi}}{C_{bi}} \qquad (2)$$

where C_p is the permeate concentration of species i and C_b is the concentration of that species in the retentate. There are two components of rejection. Observed rejection, R_o, is based on the concentration of the solute in the bulk solution, C_b. The intrinsic rejection, R_i, is based on the concentration of the solute on the surface of the membrane, C_w.

$$R_o = 1 - \frac{C_p}{C_b} \qquad R_i = 1 - \frac{C_p}{C_w}$$

If the solute size is approximately the (apparent) membrane-pore size, it interferes with the pore dimensions. The solute concentration in the permeate first increases, then decreases with time. The point of maximum interference is further characterized as a minimum flux. Figure 4 is a plot of retention and flux versus molecular weight. It shows the minimum flux at ca 60–90% retention.

If the solute size is greater than the pore dimensions, the solute is retained by mechanical sieving.

Membrane pores are not of uniform size (23). They are not cylindrical, but rather resemble fissures (24) or cracks (5). Similarly, molecules are not spherical. A long chain of 100,000 mol wt (eg, dextran) may readily pass through a pore which retains a globular protein of 20,000 mol wt. Branching chains may block or plug pores. Frequently, macromolecules change shape as a function of solution pH or ionic strength. The transition

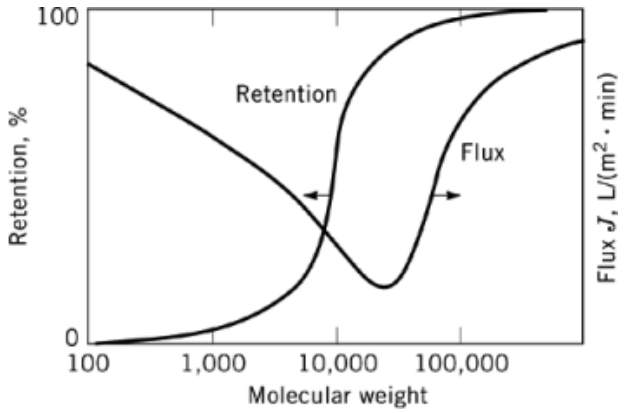

Fig. 4. Retention and flux versus molecular weight.

between solute molecular weight and rejection is therefore gradual and involves conformational considerations (25, 26). The slope of the retention curve of Figure 4 is a measure of the interaction between the pore-size and the solute-size distributions.

Retained species are transported to the membrane surface at the rate:

$$J_i = JC_{bi} \qquad (3)$$

where J is the permeate flux and C_{bi} is the bulk concentration of the retained species i. They accumulate in a boundary layer at the membrane surface (Fig. 5). This deposit is composed of suspended particles similar to conventional filter cakes, and more importantly, a slime that forms as retained solutes exceed their solubility. The gel concentration C_g is a function of the feed composition and the membrane-pore size. The gel usually has a much lower hydraulic permeability and smaller apparent pore size than the underlying membrane (27). The gel layer and the concentration gradient between the gel layer and the bulk concentration are called the gel-polarization layer.

The concentration boundary layer forms because of the convective transport of solutes toward the membrane due to the viscous drag exerted by the flux. A diffusive back-transport is produced by the concentration gradient between the membranes surface and the bulk. At equilibrium the two transport mechanisms are equal to each other. Solving the equations leads to an expression of the flux:

$$J = K\ln\left(\frac{C_w}{C_b}\right)$$

where K is the mass-transfer coefficient, C_{w} is the concentration of the solute at the surface of the membrane, and C_{b} is the solute concentration at the bulk. The concentration boundary layer can form a resistance to the flux owing to the formation of a gel, or to the osmotic pressure created by the layer.

Feed–constituent interactions further affect retention (28, 29). Dispersing agents and emulsifiers are partially retained because they attach to the dispersed phase. Small molecules may similarly adsorb onto larger particles.

The gel-layer thickness is limited by mass transport back into the solution bulk at the rate:

$$J_i = K\frac{dC_i}{dX} \qquad (4)$$

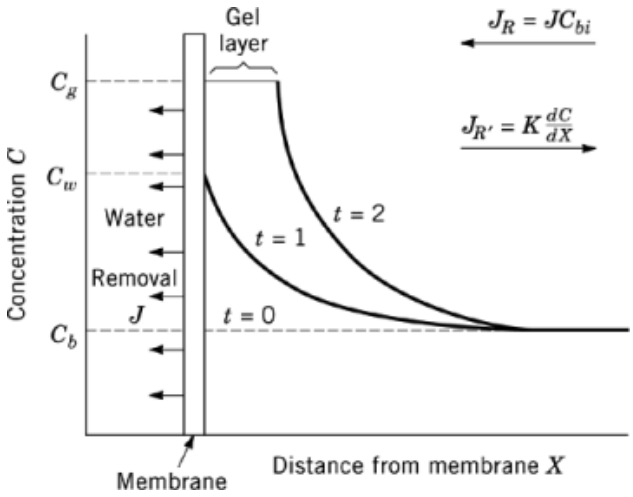

Fig. 5. Concentration polarization: C_w=concentration at membrane wall, C_b=bulk concentration, C_{bi}=bulk concentration of species i, J=flux, and C_g=gel concentration.

where the mass-transfer coefficient K is multiplied by the concentration gradient.

At steady state,

$$JC_b = K\frac{dC}{dX} \qquad (5)$$

where C_b is the bulk concentration of all retained species. Integration gives

$$J = K \cdot \ln\frac{C_g}{C_b} \qquad (6)$$

In a static system, the gel-layer thickness rapidly increases and flux drops to uneconomically low values. In equation 6, however, K is a function of the system hydrodynamics. Typically, high flux is sustained by moving the solution bulk tangentially to the membrane surface. This action decreases the gel thickness and increases the overall hydraulic permeability. For any given channel dimension, there is an optimum velocity which maximizes productivity (flux per energy input).

A number of analytical solutions have been derived for K as a function of channel dimensions and fluid velocity (30). In practice, the fit between theory and data for K is poor except in idealized cases. Most processes exhibit either higher fluxes, presumably caused by physical disruption of the gel layer from the nonideal hydrodynamic conditions, or lower fluxes caused by fouling (31). In addition, K is a function of the fluid composition.

Ultrafiltration equipment suppliers derive K empirically for their equipment on specific process fluids. Flux J is plotted versus log C_b for a set of operation conditions in Figure 6; K is the slope, and C_w is found by extrapolating to zero flux. Operating at different hydrodynamic conditions yields differently sloped curves through C_w.

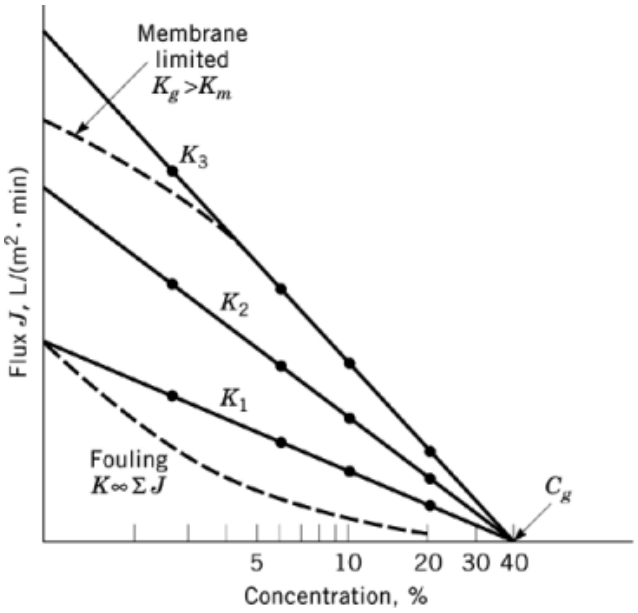

Fig. 6. Flux versus concentration, illustrating the effect of operating conditions on K and deviations from equation 6.

The gel-polarization layer has an hydraulic permeability of K_g. Equation 6 states that flux is independent of pressure, and K_g must therefore decrease with increasing pressure. Equation 1 becomes

$$J = \frac{\Delta P}{\mu\left(\frac{1}{K_m} + \frac{1}{K_g}\right)} = \frac{\Delta P}{\mu\left(R_m + R_g\right)} \qquad (7)$$

where R_m and R_g are the hydraulic resistances of the membrane gel.

Flux is independent of pressure when the process flux is much less than the water flux ($K_g \ll K_m$). If $K_g > K_m$, the process is limited by the membrane water flux and flux would flatten out at low concentrations of solids (see Fig. 6).

For very small ΔP, flux is linear with pressure. Figure 7 shows a graph of flux versus pressure. Curve A is the pure water flux from equation 1, curve B is the theoretical permeate flux (TPE) for a typical process. As the gel layer forms, the flux deviates from the TPF following equation 7 and curve D results. Changing the hydrodynamic conditions changes K_g and results in a different operating curve, curve C.

2.1. Fouling

If the gel-polarization layer is not in hydrodynamic equilibrium with the fluid bulk, the membrane may be fouled. Fouling is caused either by adsorption of species on the membrane or on the surface of the pores, or by deposition of particles on the membrane or within the pores. Fouled systems are characterized as follows: flux is a function of total permeate production when hydrodynamic conditions are constant (see Fig. 6); if hydrodynamic conditions are changed, hydraulic permeability response of the gel layer is not reversible; and theoretical permeate flux (TPF) changes with time. A sensitive test for predicting fouling or process instability is to measure change in TPF after subjecting the system to process extremes (eg. high pressure with no flow).

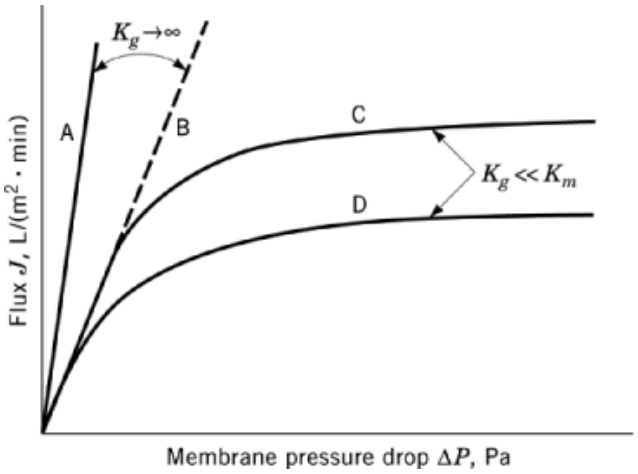

Fig. 7. Flux versus membrane ΔP.

Fouling is controlled by selection of proper membrane materials, pretreatment of feed and membrane, and operating conditions. Control and removal of fouling films is essential for industrial ultrafiltration processes.

Suspensions of oil in water (32), such as lanolin in wool (qv) scouring effluents, are stabilized with emulsifiers to prevent the oil phase from adsorbing onto the membrane. Polymer latices and electrophoretic paint dispersions are stabilized using surface-active agents to reduce particle agglomeration in the gel-polarization layer.

Dairy wheys containing complex mixtures of proteins, salts, and microorganisms rapidly foul membranes. Heat treatment and pH adjustment accelerate the aggregation of β-lactoglobulin with other whey components (33, 34). Otherwise, they would interact within the polarization layer (35, 36), forming sheet-like fouling gels. These methods also reduce microbial fouling and the formation of apatite gels. Other whey pretreatment methods include demineralization, clarification, and centrifugation (37, 38).

Pretreatment of membranes with dynamically formed polarization layers and enzyme precoats have been effective (12, 13, 39). Pretreatment with synthetic permeates prevents startup instability with some feed dispersions.

When fouling is present or possible, ultrafiltration is usually operated at high liquid shear rates and low pressure to minimize the thickness of the gel polarization layer.

2.2. Cleaning

Fouling films are removed from the membrane surface by chemical and mechanical methods. Chemicals and procedures vary with the process, membrane type, system configuration, and materials of construction. The equipment manufacturer recommends cleaning methods for specific applications. A system is considered clean when it has returned to $>75\%$ of its original water flux.

In order to develop an effective cleaning method, it is essential to know the fouling constituents and whether the cleaning agents solubilize or disperse the foulants. Detergents emulsify oils, fats, and grease (40), whereas protein films are dispersed by proteolytic enzymes and alkaline detergents (38). Acids or alkalies solubilize inorganic salts; sodium hypochlorite is used as a cleaning agent for organics. If the feed contains a mixture of different components, several cleaners may be needed. Depending on the process, cleaning agents may be used in combination or sequentially, separated by rinses.

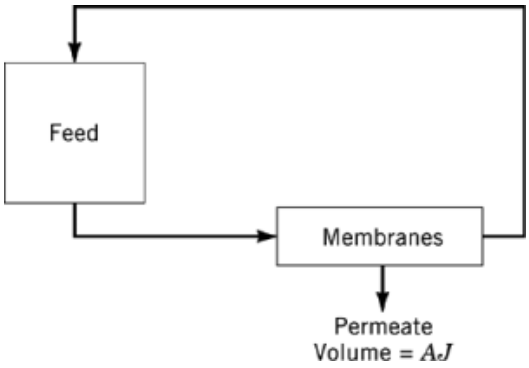

Fig. 8. Open-loop system.

Dissolved fouling material may pass into the membrane pores. Reprecipitation upon rinsing must be avoided. Membrane-swelling agents, such as hypochlorites, flushout material which may be lodged in the pores.

Cleaning is frequently aided mechanically. Foam balls scour the center of tubes, and hollow-filter systems can be back-flushed. Hollow fibers and membranes attached to rigid supports can be back-pressured, thereby eliminating the pressure drop that holds redispersed films on the membrane surface.

Unless redispersed foulants are completely flushed away before using membrane swelling agents (for sanitizing), they may become entrapped in the membrane structure. Water flux does not recover and the subsequent process fouls faster than usual. This phenomenon is discontinuous and differs from a steady reduction in water flux over many cleaning cycles, which indicates a gradual buildup of a fouling component not attacked by the cleaning composition.

Certain applications require that the equipment meet FDA and USDA sanitary requirements. These requirements ensure that the products are not contaminated by extractables or microorganisms from the equipment. Special considerations are given to the design of such equipment (41–44) (see Sterilization techniques).

3. Practical Aspects

The theoretical models cannot predict flux rates. Plant-design parameters must be obtained from laboratory testing, pilot-plant data, or in the case of established applications, performance of operating plants.

Flux response to concentration, cross flow or shear rate, pressure, and temperature should be determined for the allowable plant excursions. Fouling must be quantified and cleaning procedures proven. The final design flux should reflect long-range variables such as feed-composition changes, reduction of membrane performance, long-term compaction, new foulants, and viscosity shifts.

Flux is maximized when the upstream concentration is minimized. For any specific task, therefore, the most efficient (minimum membrane area) configuration is an open-loop system where retentate is returned to the feed tank (Fig. 8). When the objective is concentration (eg, enzyme), a batch system is employed. If the object is to produce a constant stream of uniform-quality permeate, the system may be operated continuously (eg, electrocoating).

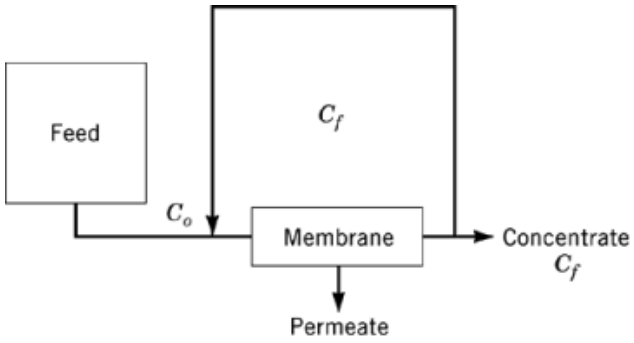

Fig. 9. Closed-loop system (feed bleed).

Table 1. Flux Comparisons Between Batch and Staged Systems Operating on Cheese Whey

Configuration	Relative flux, %
batch open loop	100
single-stage feed bleed	67
two-stage cascade	82
three-stage cascade	87
four-stage cascade	89

The upstream concentration C_b starts at C_o and ends at C_f, as described by the following relationship:

$$C_b = C_o \frac{(V_o)^R}{V_b} \qquad (8)$$

$$V_b = V_o - AJt \qquad (9)$$

where V_o is the original volume, R is rejection, A is the membrane area, and t is time. Because J is a function of C_b (eq. 6), the solution can only be approximated.

Open-loop systems have inherently long residence times which may be detrimental if the retentate is susceptible to degradation by shear or microbiological contamination. A feed-bleed or closed-loop configuration is a one-stage continuous membrane system. At steady state, the upstream concentration is constant at C_f (Fig. 9). For concentration, a single-stage continuous system is the least efficient (maximum membrane area).

The single-pass system and the staged cascade (Figs. 10 and 11) have high flux at low residence time. Both trade the concentration dependence of the batch system on time for concentration dependence on position in the system. Thus, a uniform flux is maintained (assuming no fouling) allowing continuous process integration. In practice, the single-pass system is difficult to implement, and therefore most commercial systems are multistaged cascade. The more stages used, the closer the average flux approaches the batch flux. Table 1 compares the flux for batch and staged systems operating on cheese whey.

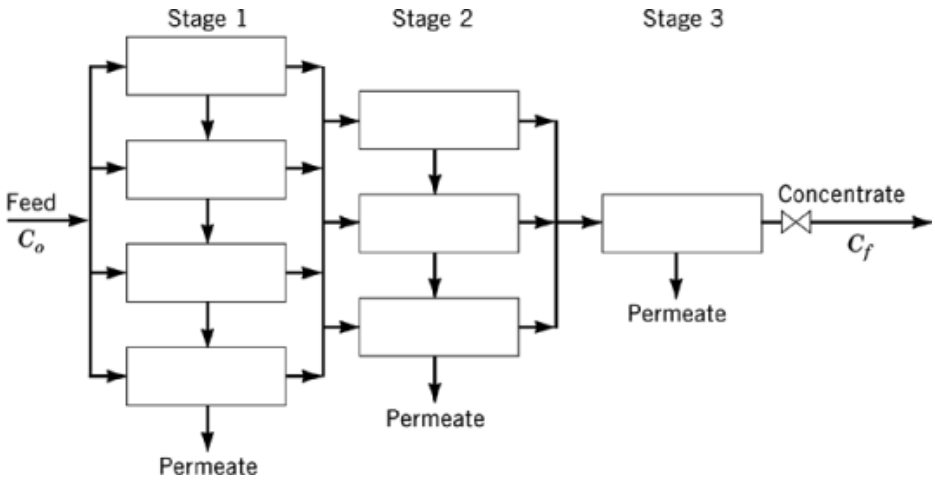

Fig. 10. Single-pass system.

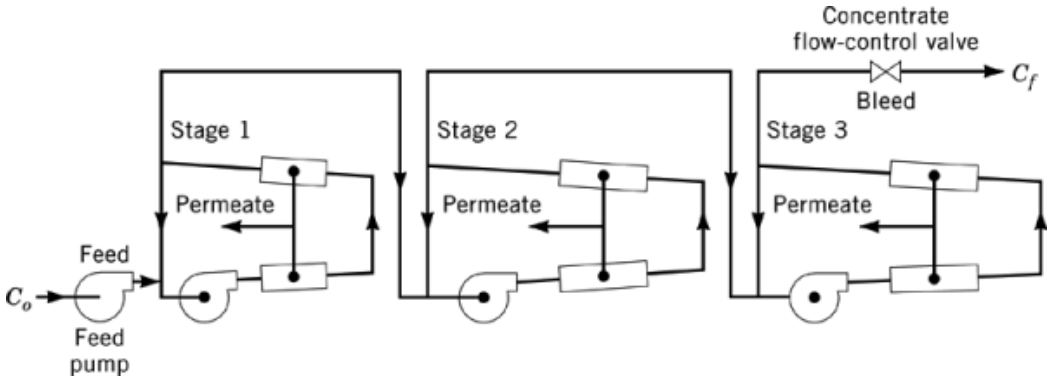

Fig. 11. Continuous multistage (cascade system).

4. Electroultrafiltration

Electroultrafiltration (EUF) combines forced-flow electrophoresis (see Electroseparations, electrophoresis) with ultrafiltration to control or eliminate the gel-polarization layer (45–47). Suspended colloidal particles have electrophoretic mobilities measured by a zeta potential (see Colloids; Flotation). Most naturally occurring suspensoids (eg, clay, PVC latex, and biological systems), emulsions, and protein solutes are negatively charged. Placing an electric field across an ultrafiltration membrane facilitates transport of retained species away from the membrane surface. Thus, the retention of partially rejected solutes can be dramatically improved (see Electrodialysis).

Electroultrafiltration has been demonstrated on clay suspensions, electrophoretic paints, protein solutions, oil–water emulsions, and a variety of other materials. Flux improvement is proportional to the applied electric field E up to some field strength E_c, where particle movement away from the membrane is equal to the liquid flow toward the membrane. There is no gel-polarization layer and (in theory) flux equals the theoretical permeate flux. It follows, therefore, that E_c is proportional to ΔP.

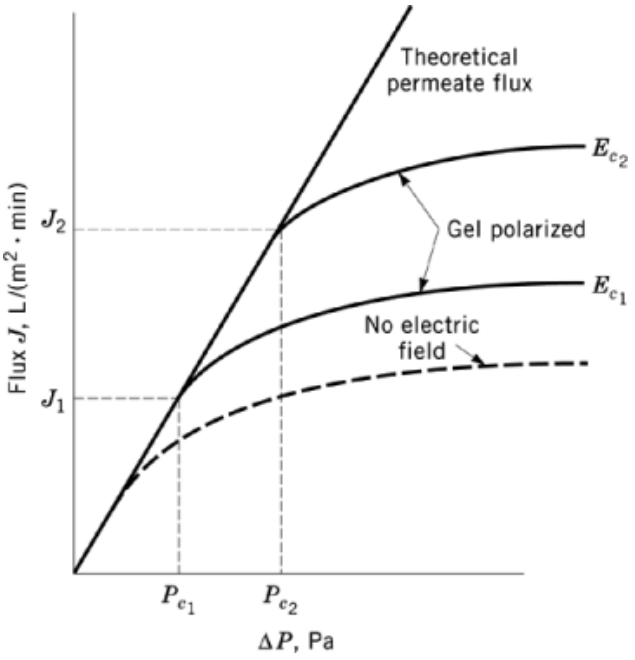

Fig. 12. Electroultrafiltration, flux versus ΔP.

At electric-field strengths greater than E_c, flux is proportional to ΔP up to the critical pressure P_c where E becomes E_c (Fig. 12).

Anodic deposition is controlled by either fluid shear (cross-flow filtration) (48), similar to gel-polarization control, or by continual anode replacement (electrodeposited paints) (46). High fluid shear rates can cause deviations from theory when $E > E_c$ (49). The EUF efficiency drops rapidly with increased fluid conductivity.

5. Diafiltration

Diafiltration is an ultrafiltration process where water or an aqueous buffer is added to the concentrate and permeate is removed (50). The two steps may be sequential or simultaneous. Diafiltration improves the degree of separation between retained and permeable species.

Constant-volume batch diafiltration is the most efficient process mode. For species that freely permeate the membrane,

$$\ln\left(\frac{C_o}{C_t}\right) = \frac{V_p}{V_o} = N \equiv \text{turnover ratio} \qquad (10)$$

where C_o is the permeate concentration at the start of diafiltration, C_t is the instantaneous permeate concentration at time t, V_o is the constant retentate volume, and V_p is the total permeate volume at t, which also equals the added water volume.

The fractional recovery of permeable solids in the retentate is

$$Y_r = \left(\frac{C_t}{C_o}\right) = \exp(-N) = 1 - Y_p \qquad (11)$$

where Y_p is the fractional recovery in the permeate.

For partially retained solutes, equation 10 becomes

$$\ln\left(\frac{C_o}{C_t}\right) = 1 - \delta\left(\frac{V_p}{V_o}\right) \qquad (12)$$

Area–time requirements for a specific diafiltration mission are defined as

$$A{\cdot}t = \frac{V_p}{J} = \frac{NV_o}{J} \qquad (13)$$

When flux is independent of C_p:

$$A{\cdot}t = \frac{K}{C_b \ln\left(\frac{C_g}{C_b}\right)} \qquad (14)$$

The optimum concentration for any diafiltration (minimum area time) is the minimum of the plot:

$$\frac{1}{J{\cdot}C_b} \text{ versus } C_b \qquad (15)$$

When fouling is absent, the optimum concentration is 0.37 C_g. If the permeate solids are of primary value, it is usually preferable to diafilter at the minimum retentate volume to minimize permeate dilution.

Sequential batch diafiltration is a series of dilution–concentration steps. The concentration of membrane-permeable species is

$$\frac{C_o}{C_t} = \left(1 + \frac{V_p}{V_o}\right)^{n(1-\delta)} \qquad (16)$$

where V_p is the permeate volume produced in each of n equal operations, and δ is the rejection of solids. As $n \longrightarrow \infty$, equation 16 approaches equation 10.

Continuous diafiltration practiced in one or more stages of a cascade system has the same volume turnover relationship for overall recoveries as sequential batch diafiltration. The residence time however is dramatically reduced. If recovery of permeable solids is of primary importance, the permeate from the last stage may be used as diafiltration fluid for the previous stage. This countercurrent diafiltration arrangement results in higher permeate solids at the expense of increased membrane area.

6. Membrane Equipment

Commercial industrial ultrafiltration equipment first became available in the late 1960s. Since that time, the industry has focused on five different configurations.

6.1. Parallel-Leaf Cartridge

A parallel-leaf cartridge consists of several flat plates, each having membrane sealed to both sides (Fig. 13). The plates have raised (2–3 mm) rails along the sides in such a way that, when they are stacked, the feed can flow between them. They are clamped between two stainless-steel plates with a central tie rod. Permeate from each leaf drains into an annular channel surrounding the tie rod (33).

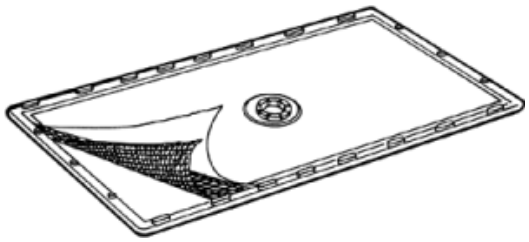

Fig. 13. Flat-plate membrane element.

Fig. 14. Flat plate cartridge and housing.

Another type has several flat plates manifolded into a plastic header. The surface of the laminate is suitable for dip-casting membranes, whereas the interior is several orders of magnitude more porous. Permeate collects in the center of the laminate and drains into the header.

Cartridges are inserted in series into plastic or stainless-steel tubular pressure housings of square cross section (Fig. 14). Feed flows parallel to the leaf surface. A permeate fitting secures each cartridge to the housing wall, which allows permeate egress and facilitates sealing between concentrate, atmosphere, and permeate channels.

6.2. Plate and Frame

Plate-and-frame systems consist of plates (Fig. 15) each with a membrane on both sides. The plates have a frame around their perimeter which forms flow channels ca 1 mm wide between the plates when they are stacked. The stack is clamped between two end plates, sealing the frames together.

At least one hole near the perimeter of each plate connects the flow channels from one side of the plate to the other. The membrane is sealed around the hole to isolate the permeate from the concentrate. Permeate collects in a drain grid behind the membrane and exits from a withdrawal port on the frame perimeter.

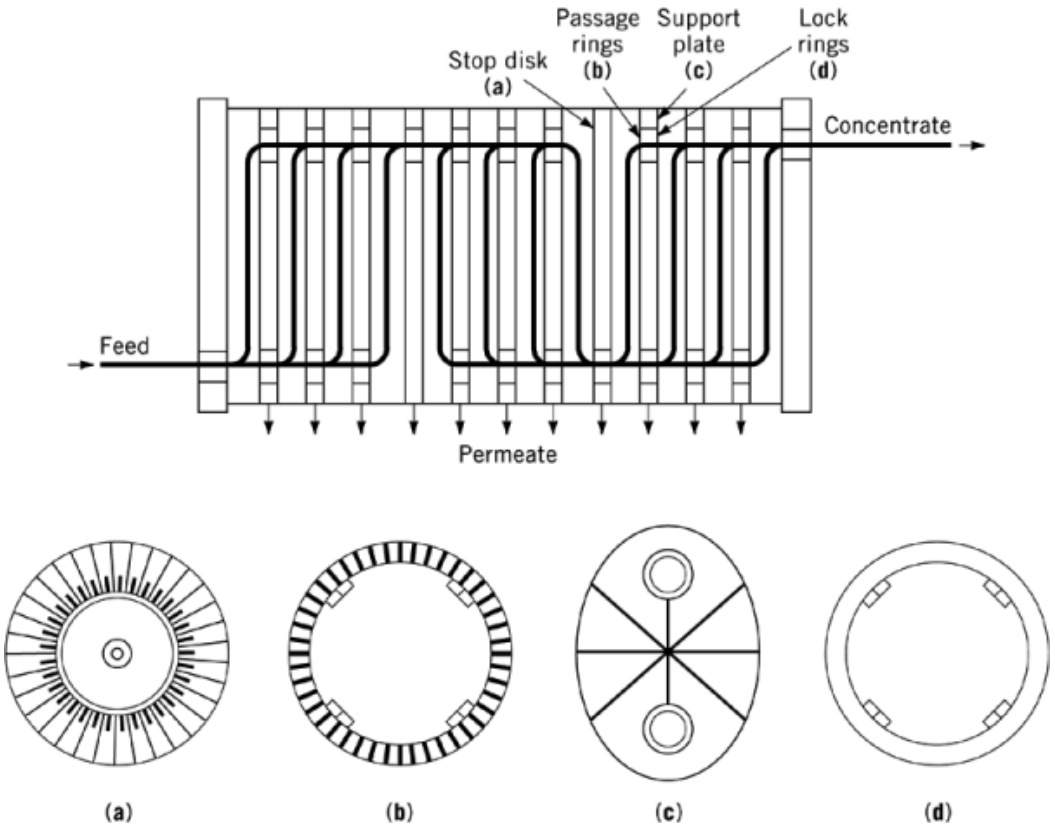

Fig. 15. Plate-and-frame ultrafiltration module.

6.3. Spiral Wound

A spiral-wound cartridge has two flat membrane sheets (skin side out) separated by a flexible, porous permeate drainage material. The membrane sandwich is adhesively sealed on three sides. The fourth side of one or more sandwiches is separately sealed to a porous or perforated permeate withdrawal tube. An open-mesh spacer is placed on top of the membrane, and both the mesh and the membrane are wrapped spirally around the tube (Fig. 16).

Spiral-wound cartridges are inserted in series into cylindrical pressure vessels. Feed flows parallel to the membrane surfaces in the channel defined by the mesh spacer which acts as a turbulence promoter. Permeate flows into the center permeate-withdrawal tube which is sealed through the housing end caps.

6.4. Supported Tube

There are three types of supported tubular membranes: cast in place (integral with the support tube), cast externally and inserted into the tube (disposable linings), and dynamically formed membranes.

The most common supported tubes are those with membranes cast in place (Fig. 17). These porous tubes are made of resin-impregnated fiber glass, sintered polyolefins, and similar materials. Typical inside diameters are ca 25 mm. The tubes are most often shrouded to aid in permeate collection and reduce airborne contamination.

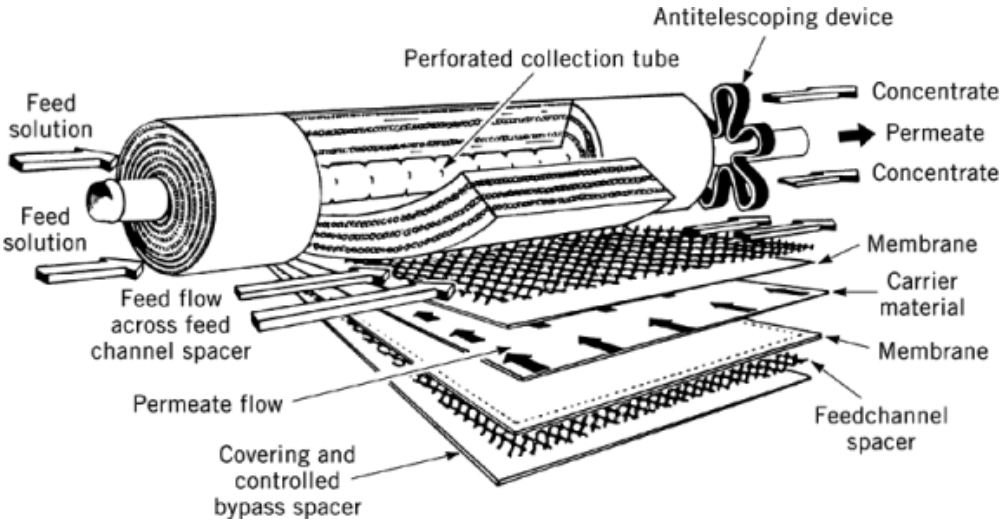

Fig. 16. Spiral-wound membrane configuration (51).

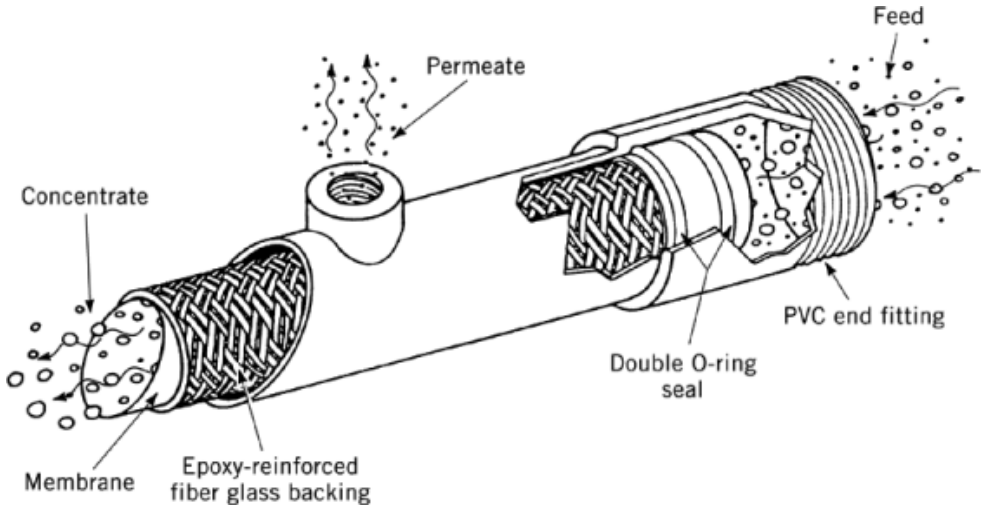

Fig. 17. Tubular membrane element with membrane cast in place.

Externally cast membranes are first formed on the inside of paper, polyester, or polyolefin tubes. These are then inserted into reusable porous stainless-steel support tubes; inside diameters are ca 12 mm. The tubes are generally shrouded in bundles to aid in permeate collection.

Tubes for dynamic membranes are usually smaller (ca 6-mm ID). Typically, the tubes are porous carbon or stainless steel with inorganic membranes (silica, zirconium oxide, etc) formed in place.

6.5. Self-Supporting Tubes

Depending on the membrane material and operating pressure, self-supporting tubes are less than 2-mm ID; inside diameters as small as 0.04 mm are commercially available. Hollow fibers with the skin on the inside

Table 2. Ultrafiltration Applications

Application	Process	Kirk-Othmer article	Refs.
electrophoretic paint	control of properties, recovery of solids from rinse systems	Paint	(52–56)
dairy wheys	protein recovery, concentration, purification, diafiltration	Milk and milk products	(33–38), (57–59)
milk	cheese and yogurt mfg, 15–20% yield improvement, standardization	Milk and milk products	(38, 60–68)
oil–water emulsions	concentration	Emulsions	(32, 40, 69, 70)
effluents of wool and yarn scouring	lanolin recovery, pollution abatement	Textiles; Wool	(71, 72)
enzymes	concentration, purification	Enzyme applications	(9–12, 73–78)
biological reactors	antibiotic mfg, alcohol fermentation, sewagetreatment	Antibiotics; Water, sewage	(74, 79–82)
vegetable proteins		Fermentation; Foods, nonconventional; Proteins	(75, 83–85)
latex concentration		Elastomers, synthetic; Latex technology	67
production of pure[a] water		Water	(51, 86)
pulp and paper	lignosulfonate separation from spent liquor	Paper; Pulp; Wood	
blood and blood products	fractionation, purification	Fractionation, blood	
vaccines	concentration, purification	Vaccine technology	
biotechnology products	concentration, purification	Genetic engineering; Hormones; Insulin and other antidiabetic drugs	

[a]Virus-free.

are extruded from a set of concentric nozzles. Membrane casting solution is forced through the outer annulus while diluent nonsolvent is pumped through the center (52).

A large number of fibers are cut to length, and potted in epoxy resin at each end (see Embedding). The fiber bundle is shrouded in a cylinder which aids in permeate collection, reduces airborne contamination, and allows back pressing of the membrane. Hollow-fiber membranes (qv) have also found use in ultrafiltration.

7. Systemization

Each of the membrane devices may be assembled by connecting the modules into combinations of series, parallel-flow paths, or both. These assemblies are connected to pumps, valves, tanks, heat exchangers, instrumentation, and controls to provide complete systems.

Because of the broad differences between ultrafiltration equipment, the performance of one device cannot be used to predict the performance of another. Comparisons can only be made on an economic basis and only when the performance of each is known.

8. Uses

Applications of ultrafiltration are summarized in Table 2.

Nomenclature Symbol	Definition
A	membrane area
C	concentration
C_b	bulk concentration of all retained species
C_{bi}	concentration of species i in retentate
C_{bR}	concentration of bulk of the retentate
C_f	final concentration
C_g	gel concentration
C_o	initial concentration
C_{pi}	concentration of species i in permeate
C_t	concentration at time t
C_w	concentration at membrane wall
E	electric field
E_c	critical field strength
i	species
J	permeate flux on membrane filtration rate
J_R	flux of retentate toward membrane surface
K	mass-transfer coefficient
K_g	gel hydraulic permeability coefficient
K_m	membrane hydraulic permeability coefficient
P_c	critical pressure
R,R_i,R_o	rejection
R_m,R_g	hydraulic resistances of membrane gel
t	time
V	volume
V_o	constant retentate volume
V_p	total permeate volume
X	distance from membrane
Y_p,Y_r	fractional recovery of permeable solids in permeate
μ	fluid viscosity
ΔP	membrane pressure drop
δ	rejection of solute

BIBLIOGRAPHY

"Ultrafiltration" in *ECT* 3rd ed., Vol. 23, pp. 439–461, by P. R. Klinkowski, Dorr-Oliver, Inc.

Cited Publications

1. M. C. Porter, *AIChE Symp. Ser.* **73**, 83 (1977).
2. R. E. Kesting, *Synthetic Polymeric Membranes*, McGraw-Hill, New York, 1971, 8–9.
3. C. M. Hansen, *I&EC Product Research and Development* **8**(1), (Mar. 1969).
4. J. D. Crowley, G. S. Teague, and J. W. Lowe, *J. Paint Technol.* **38**, 270 (May 1966).
5. H. Strathman, K. Kock, P. Amar, and R. W. Baker, *Desalination* **16**, 179 (1975).
6. H. P. Gregor, in E. Selegny, ed., *Charged Gels and Membranes*, D. Reidel Publishing Co., Holland, 1976.
7. R. E. Kesting in Ref. 2, p. 140.
8. Brit. Pat. 147,4594 (May 25, 1977), P. Klinkowski and E. Ondera (to Dorr-Oliver Inc.).
9. H. P. Gregor and P. W. Rauf, *Enzyme Coupled Ultrafiltration Membranes*, work supported by National Science Foundation Grant GI-32497.
10. R. A. Korus and A. C. Olson, *J. Food Sci.* **42**, 258 (1977).

11. U.S. Pat. 4,033,822 (July 5, 1977), H. P. Gregor.
12. O. Velicangil and J. A. Howell, *Biotechnology and Bioengineering*, Vol. **23**, John Wiley & Sons, Inc., New York, 1981, 843–854.
13. S. S. Wang, B. Davidson, C. Gillespie, L. R. Harris, and D. S. Lent, *J. Food Sci.* **45**, 700 (1980).
14. A. Michaels, H. Bixler, R. Hausslein, and S. Flemming, *OSW Research Development*, Report No. 149, U.S. Government Printing Office, Washington, D.C., Dec. 1965; *Ind. Eng. Chem.* **57**, 32 (1945).
15. A. Michaels, *Ind. Eng. Chem.* **57**(10), 32 (1965).
16. U.S. Pat. 3,977,967 (Aug. 31, 1976), O. C. Trulson and L. M. Litz (to Union Carbide Corp.).
17. U.S. Pat. 4,060,488 (Nov. 28, 1977), F. W. Hoover and R. K. Iler (to E. I. du Pont de Nemours & Co., Inc.).
18. H. Z. Friedlander and L. M. Litz in M. Bier, ed., *Membrane Processes in Industry and Biomedicine*, Plenum Press, New York, 1971.
19. R. Fleischer, P. B. Price, and E. Symes, *Science* **143**, 249 (1964).
20. C. R. Bennet, R. S. King, and P. J. Petersen, *Pressure Effects on Macromolecular—Water Interactions with Synthetic Membranes*, ACS 181st National Meeting, Atlanta, Ga., Mar. 1981.
21. G. B. Westermann-Clark, Ph.D. dissertation, Carnegie-Mellon University, Pittsburgh, Pa., 1981.
22. S. Sourirajan, *Ind. Eng. Chem. Fundam.* **2**(1), 51 (1963).
23. S. Jacobs, *Filtr. Sep.*, 525 (Sept.–Oct. 1972).
24. M. P. Freeman, *Colloid Interface Sci.* **5**, 133 (1976).
25. L. Zeman and M. Wales, in A. F. Turbak, ed., *Synthetic Membranes*, Vol. **2**, ACS Symposium Series 154, American Chemical Society, Washington, D.C., 1980.
26. A. S. Michaels, *Sep. Sci. Technol.* **15**, 1305 (1980).
27. P. Dejmek, "Permeability of the Concentration Polarization Layer in Ultrafiltration of Macro Molecules," *Proceedings of the International Symposium, Separation Processes by Membranes*, Paris, Mar. 13–14, 1975.
28. Q. T. Nguyen, P. Aptel, and J. Neel, *J. Membr. Sci.* **6**(1), 71 (1980).
29. P. S. Leung, in A. R. Cooper, ed., *Ultrafiltration Membranes and Applications*, Plenum Press, New York, 1980, 415–421.
30. W. F. Blatt, A. Dravid, A. S. Michaels, and L. Nelson, in J. E. Finn, ed., *Membrane Science and Technology*, Plenum Press, New York, 1970, 47–97.
31. R. F. Madsen and W. K. Nielsen, in Ref.29, 423–438.
32. Brit. Pat. 1,456,304 (Nov. 24, (1976) (to Abcor, Inc.).
33. A. C. Epstein and S. R. Korchin, paper presented at *91st National Meeting, AIChE*, Detroit, Mich., Aug. 1981.
34. M. W. Hickey, R. D. Hill, and B. R. Smith, *N.Z. J. Dairy Sci. Technol.* **15**(2), 109 (1980).
35. D. N. Lee and R. L. Merson, *J. Dairy Sci.* **58**, 1423 (1975).
36. D. N. Lee and R. L. Merson, *J. Food Sci.* **41**, 403 (1976); **41**, 778 (1976).
37. L. L. Muller and W. J. Harper, *J. Agric. Food Chem.* **27**, 662 (1979).
38. W. J. Harper, in Ref. 29, 321–347.
39. J. A. Howell and O. Velicangil, in Ref. 29, 217–229.
40. P. A. Bailey, *Filtr. Sep.* **14**(1), 53 (1977).
41. F. E. McDonough and R. E. Hargrove, *J. Milk Food Technol.* **35**(2), 102 (1972).
42. R. G. Semerad, "Sanitary Considerations Involved with Membrane Equipment," *Proceedings of the Whey Product Conference*, Atlantic City, N.J., 1976.
43. N. C. Beaton, *J. Food Protection*, **42**, 584 (July 1979).
44. B. S. Horton, *N. Z. J. Dairy Sci. Technol.* **14**(2), 93 (1979).
45. M. Bier, in Ref. 18.
46. U.S. Pat. 3,945,900 (Mar. 23, 1976), P. R. Klinkowski (to Dorr-Oliver, Inc.).
47. J. M. Radovich and R. E. Sparks, in Ref. 29, 249–268.
48. J. D. Henry, Jr., L. Lawler, and C. H. A. Kuo, *AIChE J.* **23**, 851 (1977).
49. J. D. Henry Jr., and C. H. A. Kuo, paper presented at *The Symposium on Recent Developments in Colloidal Phenomena*, AIChE National Meeting, New Orleans, La., Nov. 1981.
50. P. R. Klinkowski and N. C. Beaton, *J. Sep. Proc. Tech.* (1991).
51. *Abcor Sanitary Spiral-Wound Ultrafiltration Modules*, Product Bulletin, Abcor, Inc., Wilmington, Mass., 1981.
52. B. R. Breslau, A. J. Testa, B. A. Milnes, G. Medjanis, in Ref. 29, 109–127.
53. R. A. Scaddan, *Ind. Finish. Surf. Coat.* **27**, 326 (1975).

54. G. E. F. Brewer, paper presented at *Electrocoat 72*, Electrocoating Committee and the National Paint and Coatings Association, Chicago, Ill., Oct. 2–4, 1972.
55. B. J. Weissman, in Ref. 54.
56. U.S. Pat. 3,663,397 (May 16, 1972), L. R. LeBras and J. Ostrowski (to PPG Industries); U.S. Pats. 3,663,398 and 3,663,402–403 (May 16, 1972), R. Christenson and R. R. Twack (to PPG Industries); U.S. Pats. 3,663,399 and 3,663,404 (May 16, 1972), F. M. Loop (to PPG Industries); U.S. Pats. 3,663,400–401 and 3,663,405 (May 16, 1972), R. Christenson and L. R. LeBras (to PPG Industries); U.S. Pat. 3,633,406 (May 16, 1972), L. R. LeBras and R. R. Twack (to PPG Industries).
57. F. E. McDonough, W. A. Mattingly, and J. H. Vestal, *J. Dairy Sci.* **54**, 1406 (1971).
58. B. S. Horton, R. L. Goldsmith, and R. R. Zall, *Food Technol.* **26**(2) (1972).
59. M. E. Matthews, *N. Z. J. Dairy Sci. Tech.* **14**(2), 86 (1979).
60. F. Lang and A. Lang, *Milk Ind.* **78**(9), 16 (1976).
61. O. J. Olsen, in Ref. 6, Vol. **2**.
62. J. L. Maubois, "Application of Ultrafiltration to Milk Treatment for Cheese Making," in Ref. 27.
63. H. R. Covacevich and F. V. Kosikowski, *J. Food Sci.* **42**, 362 (1977).
64. J. E. Ford, F. A. Glover, and K. J. Scott, *Int. Dairy Congress*, 1068 (1978).
65. F. A. Glover, P. J. Skudder, P. H. Stuthart, and E. W. Evans, *J. Dairy Res.* **45**, 291 (1978).
66. S. Jepsen, *J. Cultured Dairy Products* **14**(1), 5 (1979).
67. J. L. Maubois, in Ref. 29, 305–318.
68. P. R. Poulsen, *J. Dairy Sci.* **61**(6), 807 (1978).
69. R. L. Goldsmith, D. A. Roberts, and D. L. Burre, *J. Water Pollut. Control Fed.* **46**, 2183 (1974).
70. I. K. Bansal, *Ind. Water Eng.* **13**, 6 (Oct.–Nov. 1976).
71. N. C. Beaton, *Textile Institute and Industry* **13**, 361 (Nov. 1975).
72. J. A. C. Pearson, C. A. Anderson, and G. F. Wood, *J. Water Pollut. Control Fed.* **48**, 945 (1976).
73. D. I. C. Wang, A. J. Sinskey, and T. A. Butterworth, in Ref. 30.
74. N. C. Beaton, in Ref. 29, 373–404.
75. H. S. Olsen and J. Adler-Nissen, in Ref. 25, Vol. **2**.
76. U.S. Pat. 3,720,583 (Mar. 13, 1973), E. E. Fisher (to A. E. Staley).
77. J. Hong, G. T. Tsao, P. C. Wankat, in Ref. 12, 1501–1516.
78. W. D. Deeslie and M. Cheryan, *J. Food Sci.* **46** 1035 (1981).
79. J. Gawel and F. V. Kosikowski, *J. Food Sci.* **43**, 1717 (1978).
80. U.S. Pat. 3,472,765 (Oct. 14, 1969), W. E. Budd and R. W. Okey (to Dorr-Oliver, Inc.).
81. A. G. Fane, C. J. D. Fell, and M. T. Nor, in Ref. 29, 631–658.
82. A. S. Michaels, C. R. Robertson, and S. N. Cohen, paper presented at *The 180th National Meeting ACS*, San Francisco, Calif., Aug. 1980.
83. G. Jackson, M. M. Stawiarski, E. T. Wilhelm, R. L. Goldsmith, and W. Eykamp, *AIChE Symp. Ser.* **70**, 514 (1974).
84. M. Cheryan, in Ref. 29, 343–325.
85. J. T. Lawhon, L. J. Manak, and W. E. Lusas, in Ref. 29.
86. G. Belfort, T. F. Baltutis, and W. F. Blatt, in Ref. 29, 439–474.

General References

87. Reference 30 is also a general reference.
88. N. C. Beaton, "Advances in Enzyme and Membrane Technology," *Institute of Chemical Engineers Symposium Series No. 51*, Institute of Chemical Engineers, London, 1977, 59–70.
89. N. C. Beaton and H. Steadly, in N. Li, ed., *Recent Developments in Separation Science*, Vol. **7**, CRC Press, Boca Raton, Fla., 1982, 2–25.
90. A. R. Cooper, ed., *Ultrafiltration Membranes and Applications, Proceedings of 178th National ACS Meeting*, Washington, D.C., 1979, Plenum Press, New York, 1980.
91. R. P. deFillipi and R. L. Goldsmith, in J. E. Flinn, ed., *Membrane Science and Technology*, Plenum Press, New York, 1970, 33–46.
92. R. J. Gross and J. F. Osterle, *J. Chem. Phys.* **49**, 228 (1968).

93. S. Hwang and K. Kammermeyer, *Membranes in Separations*, John Wiley & Sons, Inc., New York, 1975; good study of membrane transport phenomenon.
94. R. E. Kesting, *Synthetic Polymeric Membranes*, McGraw-Hill, New York, 1971; good bibliographies.
95. A. S. Michaels, L. Nelson, and M. C. Porter, in M. Bier, ed., *Membrane Processes in Industry and Biomedicine*, Plenum Press, New York, 1971, 197–232.
96. U.S. Pat. 3,615,024 (Oct. 26, 1971), A. S. Michaels (to Amicon Corp.).
97. A. S. Michaels, paper presented at *Clemson University Membrane Technology Conference*, Mar. 1979; OWRT Contract No. 14-34-0001-8548.
98. A. S. Michaels, *Chem. Technol.* **2**(1), 37 (Jan. 1981).
99. A. S. Michaels, *Desalination* **35**, 329 (1980).
100. L. Mir, W. Eykamp, and R. L. Goldsmith, *Ind. Water Eng.* **14**, (May–June 1977).
101. M. C. Porter and L. Nelson, in N. N. Li, ed., *Recent Developments in Separation Science*, Vol. **2**, CRC Press, Cleveland, Ohio, 1972, 227–267.
102. M. C. Porter, *Ind. Eng. Chem. Prod. Res. Dev.* **2**, 234 (1972).
103. M. C. Porter, in P. A. Schweitzer, ed., *Handbook of Separation Techniques for Chemical Engineers*, McGraw-Hill, New York, 1979.
104. R. N. Rickles, *Membranes, Technology and Economics*, Noyes Development Co., Park Ridge, N.J., 1967.
105. H. Strathman, K. Kock, P. Amar, and R. W. Baker, *Desalination* **16**, 179 (1975).
106. A. F. Turbak, ed., *Synthetic Membranes*, Vols. **1** and **2**, ACS Symposium Series 153 and 154, ACS, Washington, D.C., 1981.
107. *Equipment Available for Membrane Processes*, Bulletin No. 115, International Dairy Federation, Brussels, p. 1979 (available through Library of Congress or Harold Wainess and Associates, Northfield, Ill.).
108. L. J. Zeman and A. L. Sydney, *Microfiltration and Ultrafiltration*, Marcel Dekker, Inc., New York, 1996.

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