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MEMBRANE OPERATIONS

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ABSTRACT

The success of any industrial pretreatment program is dependent on correct choice of technology and management. The rapid growth in the industrial sector has increased the mass of toxic and hazardous pollutants to the municipal wastewater treatment works. This may again inhibit the conventional biological treatment processes. Membrane separation is in this context a physical pretreatment process which splits the flow of water in two; a less toxic permeate and a more concentrated retentate. Typically, the volume reduction is one order of magnitude from the feedflow to the retentate.

Engineering contractors in general do not possess proper knowledge of membrane technology to convincingly include membranes as a viable process option in design of pre-treatment systems. Attractive features of membranes are low weight and space requirements without use of chemicals. Moreover, the equipment is modular and can be scaled up or operated at partial capacity.

The paper documents examples of accumulated field experiences with the intention to prove that membrane separation is a mature technology for the industry to utilize and for the engineering contractor to master. Also, the paper conveys information pertinent to advances in membrane separation to better enable academia to adjust curricula to meet industrial demands for separation engineers. The challenge is to pick the right membrane for a specific wastewater and couple the membrane to compatable auxiliary equipment such as pumps, pipes, valves and meters. © 1997 IAWQ. Published by Elsevier Science Ltd

KEYWORDS

Flux; fouling; membrane separation; microfiltration; reverse osmosis; ultrafiltration; volume reduction.

INTRODUCTION

Traditional membrane separation techniques involve microfiltration (MF), ultrafiltration (UF), reverse osmosis (RO) as well as electrodialysis (ED). MF and UF separate molecules according to their size and molecular mass. These membranes are generally defined by their cut-off threshold; i.e., the maximum molecular weight (MW) which is capable of passing through the membranes (Figure 1).

Microfiltration allows macromolecules to flow through the membrane. Bacteria, however, all of which are larger than 100 nm, are prevented from passing through the membrane wall. The diameter of the micromembrane wall-pores varies generally from 100 to 1000 nm. Microfiltration is considered a sterile filtration technique and has been used for many years in a dead-end filtration mode. Today crossflow microfiltration (CMF) or tangential filtration is the usual mode of operation. CMF has considerably increased performance and reduced problems associated with clogging and pressure losses so very common with classical dead-end operations.

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reverse osmosis (RO)                          microfiltration (MF)
                         ultrafiltration (UF)
<--------------------->                     <--------------------->
            <------------------------------------------------>
_I____________I____________I____________I____________I____ (nm)
0.1           1            10           100          1000
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Figure 1. Membrane processes and pore sizes (nm).

For ultrafiltration the MW cut-off threshold ranges between 1,000 and 100,000 daltons. This roughly corresponds to membrane pore sizes from 1 to 100 nm.

The principle of reverse osmosis is quite different from MF and UF. This solubilization-diffusion technique makes use of a semipermeable membrane which acts as a barrier to all dissolved salts and inorganic molecules, as well as organic molecules with molecular weights greater than 100 daltons. RO membranes have no true pores as such.

Electrodialysis and pervaporation (PV) are also membrane processes. In electrodialysis (Figure 2) electrically charged membranes are used. An elementary cell consists of two compartments separated by a cationic membrane and bordered at their extremities by two anionic membranes. The cations migrate in the direction of the electric current and are able to leave the first compartment by flowing through the cationic membrane, while remaining in the second compartment because they run up against the anionic membrane. The anions, which travel in the opposite direction, are also trapped in this same compartment which therefore is enriched in salts. The first compartment gives off a desalinated solution. An electrodialysis unit consists of a series of concentration cells.

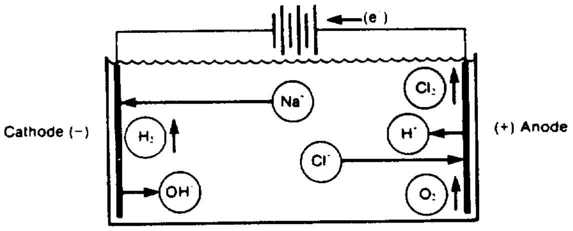

Figure 2. Principles of electrodialysis.

Pervaporation is a procedure whereby fluid mixtures can be separated by partially evaporating them through a dense membrane placed on their surface. The lower face of the membrane is maintained under low pressure to ensure the transport of material. This procedure requires first the intervention of selective adsorption on the upper interface, then membrane diffusion and, finally, lower interface desorption.

In the chemical industry, separation processes are as important as chemical reactions. It is not uncommon to find that more than one-third of the processing cost can be attributed to separation operations. Synthetic membranes can achieve separations in a wide variety of industrial processes, often with substantial energy savings over more traditional separation techniques. The membrane efficiency is critically dependent on permeability and selectivity, and the membrane manufacturer has the potential to tailor membranes to specific processing needs.

Currently, practical industrial membrane applications vary from small scale batch separations in the biotechnology and pharmaceutical industries, to very large systems, such as gas separations in the petrochemical industry.

Membrane separation is a pressure driven process with no moving parts and without use of chemicals. The required process equipment is simple, compact and easy to control. Moreover, the equipment is modular and can therefore be scaled up or operated at partial capacity.

Potential applications are growing as the performance of the membranes improve. The main applications of membrane separation include (1) concentration of solutions, (2) separation of solids, (3) recovery of materials from waste streams and (4) purification of highly polluted water.

METHODS

A wide variety of materials are used in membrane production. The first membranes used commercially were uniform in structure and had very low flow rates. In the late 1950s Loeb and Sourirajan (1962) developed a method of phase inversion for the preparation of cellulose acetate (CA) membranes which involved dissolving the ester in a solvent to make a viscous solution which was poured in a thin film onto glass. The ester was then precipitated by contacting the upper surface of the film with cold water. The addition of various pore-formers and conditioning agents was later found to improve the product and it was found possible to achieve a large variety of pore sizes. In the early 1960s Michaels (1968) made an asymmetric polyionic membrane and now a wide variety of polymers have been formed into membranes. Recently rather coarse membranes have also been made from sintered ceramics, from stainless steel and from alumina using an anodizing process. Other membranes are produced by biaxially stretching a polymeric sheet; in the first stretch the pores are created, and then they are opened by stretching at right angles to the first stretch. At least one type of membrane is made from polycarbonate by irradiating the membrane and then etching out along the tracks taken by the radiation.

All membrane separations rely on a driving force across the membrane to induce the flow or flux and a separation factor which prevents some materials from crossing. The driving force for flow differs from one system to the next.

Pressure is the most common driving force and accounts for separations in such systems as pervaporation, ultrafiltration, reverse osmosis and microfiltration. Although RO and PV are partially pressure and partially concentration driven, UF and MF are totally pressure driven. The driving force overcomes osmotic pressure effects, drag of solvent through the membrane and the resistance of fouling layers and deposits on the membrane surfaces. In many pressure driven separations there is an effective limit to the fluxes which can be achieved owing to osmotic pressure resistances building up at the membrane surface, as the rejection of the retained solute causes its concentration to build up in the region of the membrane surface. Compressibility of the deposits present on the membrane can also limit the flux. There are a number of theories which discuss the relationship between a flux limit with increasing pressure and the concentration polarization occurring on the membrane. Notable is one by Aimar and Sanchez (1985) which shows that as the concentration at the membrane surface builds up so does the viscosity of the solution. This makes the solutions non-Newtonian. As these characteristics become more pronounced, the mass-transfer coefficient for removal of built-up solute back to the bulk flow changes significantly.

Electrodialysis is used to separate charged species. Membranes of ion-exchange material will reject either cations or anions. If a stack of such membranes suitably arranged is placed in an electric field, the anions and cations will migrate until they come to a selectively impermeable barrier. They will then be discharged from the cell. Desalting of cheese whey is a popular application. New bilayer membranes are used to produce acids and alkalis from waste dilute salts, thus introducing a recycling technology.

Membranes are produced in a variety of shapes (Figures 3, 4 and 5) which are further formed into modules. Membrane processes require large areas of membranes. These must be geometrically such arranged as to minimize the total volume of hardware and yet allow the passage of fluids past the membrane at sufficient velocity to prevent excessive deposits on the membrane.

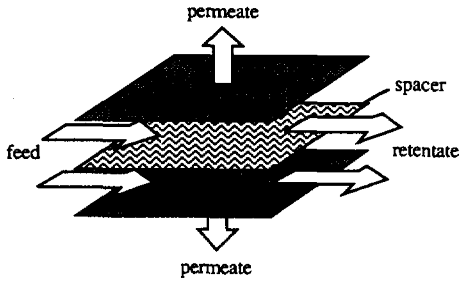

Figure 3. Schematic drawing of a plate-and-frame module.

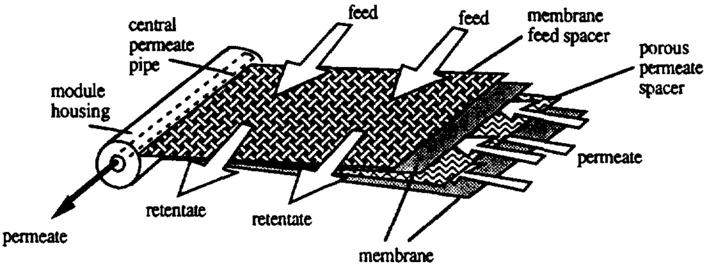

Figure 4. Schematic drawing of a spiral-wound module.

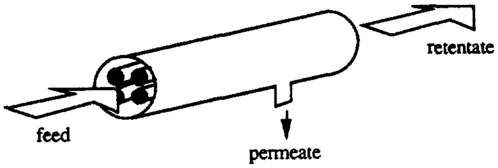

Figure 5. Schematic drawing of a tubular module.

The simplest approach is the use of flat sheets of membrane mounted between support plates. The support plates contain molded grooves to channel the fluid past the membrane and sometimes several sheets of membrane and backing are bonded together in a cartridge. Membranes are sometimes separated by turbulence promoters (a mesh) placed in the feed stream to give better mass transfer at low fluid velocities.

The spiral membrane is a pair of sheets bonded around three sides with the opening, as the fourth side, connected to a porous tube. This envelope can then be wound around the central tube with a suitable separator to provide a spirally wound membrane. This is a convenient way of packing a large flat sheet of membrane into a small volume and the technique is used in a wide variety of commercial installations.

Another method of packing a large surface area of membrane into a small volume is to provide the membrane surface in the form of hollow fibers packed into bundles. In ultrafiltration and microfiltration the fibers are about 1 mm in diameter and the feedflow is in the inside of the fibers. For RO and gas separation the fibers are much finer and often the separating surface and the associated feedflow is on the outer membrane surface. Plants with 8 000 m^2 of membrane per m^3 of separator volume are available for gas separation (Howel, 1990).

In microfiltration it is found that high crossflow velocities are desirable and, with very viscous pastes being produced, tubes of about 5 mm diameter are often used. Tubular membranes are also used for ultrafiltration and reverse osmosis.

The simplest method of arranging a membrane concentration system is to place the membrane in a circuit containing the storage tank V_0 (Figure 6). The feed solution enters the membrane through a high pressure pump and then spilled back to the storage tank through a pressure control valve. In larger systems a second pump is used to recirculate the solution around a high pressure loop with only a partial spill-back to the storage tank. Some spill-back is essential because otherwise there would be excessive concentration in the loop and the system would operate at lower fluxes than necessary. There would also be the risk of solidification in the loop. V_p and V_r represent permeate and retentate, respectively.

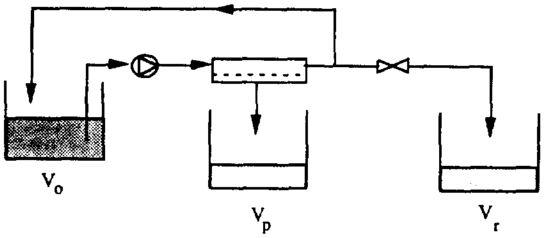

Figure 6. Schematic diagram of a batch system.

A continuous system may be operated in which the loop operates at the desired product concentration. As new feed arrives, product is bled from the retentate side and not spilling back to the feed tank (Figure 7).

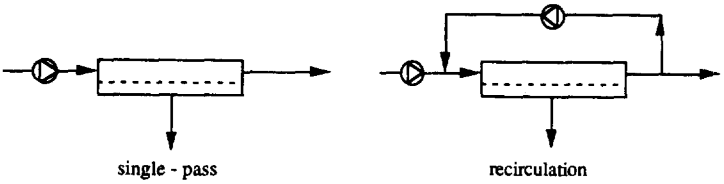

Figure 7. Schematic diagram of a single pass and a recirculation system.

An improvement on the feed and bleed systems is to have several stages each operating at a constant concentration and feeding its product to the next stage (Figures 8 and 9). The system operates effectively at a steady state except for a slow decline in flux due to fouling over the day's operation (corrected for by system pressure increase). Cleaning of the membrane by specific detergent solutions takes place at regular intervals so that fluxes are maintained.

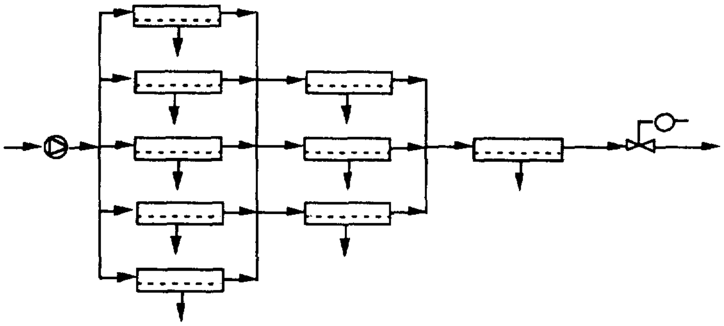

Figure 8. Single-pass system (tapered cascade or "christmas tree").

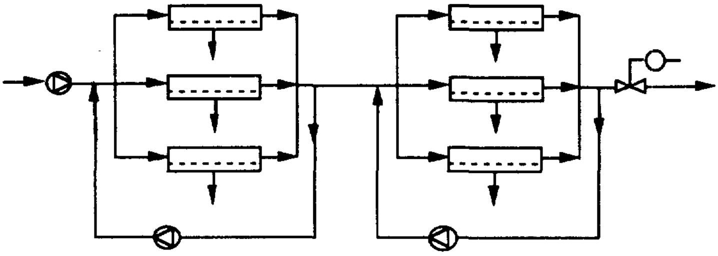

Figure 9. Recirculation systems.

EXAMPLES OF PRETREATMENT BY MEMBRANES

Dewatering of manure makes it easier to store and transport nutrients. A tubular RO membrane plant separates 95% of the total nitrogen from the liquid fraction of pig manure (Bilstad *et al.*, 1992). The particle-free permeate meets the effluent criteria for direct discharge to a neighboring fjord. The domestic sewer is an alternative point of discharge for the membrane treated pig manure.

Leachates from chemical and domestic landfills are defined as hazardous wastewater. Quantitative and qualitative control of leachate is performed by membrane separation of the total produced leachate volume. Dissolved and suspended solids in the leachate are removed by reverse osmosis from the major portion of the water phase. The particle-free permeate meets the effluent requirements for direct discharge to virtually any watercourse, including the public sewer (Bilstad *et al.*, 1992).

Wastewater from washing wool has a high organic content; 100,000 mg/l COD. A tubular UF membrane separation plant reduces the COD in the permeate by 80%. The volume reduction factor is 10, meaning the feed is split into one part retentate and nine parts permeate. The permeate is piped to the public sewer and further treated at the city's domestic wastewater treatment works (Bilstad *et al.*, 1994).

Water treatment also means recovery of solids from water. The production of china and porcelain results in effluents rich in clay and glaze particles. Traditionally, clay is difficult to separate without space consuming and chemical intensive processes such as coagulation, flocculation and sedimentation. After installing a microfiltration plant, a china producer in Norway has nearly eliminated clay in the effluent. Also, the membrane plant effectively concentrates and recovers the clay for reuse in the production of china (Bilstad, in preparation). There is no other sludge production from this separation process.

DISCUSSION

The permeability of the membrane is the most important primary consideration. High permeabilities lead to the potential for higher product fluxes.

Fouling of the membrane surface during processing is especially a problem with liquid processing. Electrodialysis, reverse osmosis, ultrafiltration and microfiltration are all affected. A secondary membrane or fouling layer may form across the original membrane and totally control the flux properties of the system. High original flux membranes can in fact foul more rapidly than lower flux membranes.

In the case of solution diffusion mechanisms for RO, the solubility of the permeant in the membrane material is vital. Often one permeant plasticizes the membrane and makes the second permeant more soluble, thereby reducing selectivity.

The necessity for compact and in some cases light plants places a premium on high packing densities. The advantage of the very fine hollow fibre systems is the high volumetric packing densities that can be achieved. With liquid systems the channel widths must be larger than for gas separation. Where solids are present or very highly viscous retentates are produced, large diameter tubes are necessary even though it yields lower packing densities.

Selectivity is of vital importance for gas separation and pervaporation. With ultrafiltration, current selectivity between macromolecules is low. Higher selectivity in the process would introduce a large new market currently satisfied by adsorptive separations.

Early membranes suffered durability problems and some quality control difficulties. These have largely been overcome. As long as the membranes are properly selected for each application, the cleaning processes are adhered to and process water is correctly pretreated, long lifetimes can be expected. Ultrafiltration plants normally expect a minimum of two years of membrane life, whereas reverse osmosis plants in desalination expect at least five years without replacing of membrane elements. Remembraning is expensive and constitutes a major item of plant cost. Mistreatment of membranes can still cause rapid failure, although automation has minimized the problem.

Analyses of plant costs show that membrane replacement is a major element of the total annualized cost of a plant, amounting to over 20 % in many systems. This cost has priced the technology out of some bulk applications where the quality of the product would be desirable. If bulk membranes can be provided more economically or alternatively higher fluxes obtained, then large new markets in wastewater treatment are likely to develop in addition to other markets.

CONCLUSIONS

Membranes are used in a great variety of applications and come in a great variety of configurations. Current estimates of membrane applications which are growing at 20 % per year, suggest that membranes will be used even more widely in the future. In 1986 an estimated US Dollar 1.1 billion worth of modules was sold. This figure was expected to triple within 1996 according to ICI; Imperial Chemicals International.

Several of the leaders in membrane technology are in Europe, although the US and Japan have the largest share of the market. Membrane manufacturers in the UK, The Netherlands, Germany and France are adding ideas and investment to the technology.

Mineral membranes are mainly used in the treatment of products with high added value. Although mineral membranes have longer lives than organic membranes and perhaps a lower operating cost, the fact remains that they entail a higher investment cost.

Other factors of a technical nature also means that organic membranes have a good future. One of the greatest advantages of certain polymers is that their high degree of flexibility enables them to be adapted for almost any kind of use.

Challenges in treating liquids in industries are certainly many, complex and severe. The variation of contamination problems include heavy metals, oily wastes, chlorinated hydrocarbons and sludges which defy description. Membrane separation offers many advantages which can be realized through careful and deliberate integration into the total treatment system. Membrane separation is "ideal" for small and intermittent water flows such as pretreatment of industrial wastewater.

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