Membrane Separation Processes - Technology and Business

Membrane Separation Processes - Technology and Business Opportunities G. Srikanth The development of ion exchange membrane some forty years ago paved the way for the membrane separation technology. Since then due to a whole lot of technological innovations, especially in the area of new materials, membrane technologies have been established as very effective and commercially attractive options for separation and purification processes.

What is a Membrane?

The membrane can be defined essentially as a barrier, which separates two phases and restricts transport of various chemicals in a selective manner. A membrane can he homogenous or heterogeneous, symmetric or asymmetric in structure, solid or liquid, can carry a positive or negative charge or be neutral or bipolar. Transport through a membrane can be effected by convection or by diffusion of individual molecules, induced by an electric field or concentration, pressure or temperature gradient. The membrane thickness may vary from as small as 100 rnicron to several mms.

Membrane Separation Technology

A membrane separation system separates an influent stream into two effluent streams known as the permeate and the concentrate. The permeate is the portion of the fluid that has passed through the semi-permeable membrane. Whereas the concentrate stream contains the constituents that have been rejected by the membrane. Membrane separation process enjoys numerous industrial applications with the following advantages: Appreciable energy savings Environmentally benign Clean technology with operational ease Replaces the conventional processes like filtration, distillation, ion-exchange and chemical treatment systems Produces high quality products Greater flexibility in designing systems.

Types of Membranes

The proper choice of a membrane should he determined by the specific application objective: particulate or dissolved solids removal, hardness reduction or ultra pure water production, removal of specific gases/chemicals etc. The end-use may also dictate selection of membranes for industries such as potable water, effluent treatment, desalination or water supply for electronics or pharmaceutical manufacturing. The following section explains the types of membranes commonly used.

Microporous Membranes

The membrane behaves almost like a fibre filter and separates by a sieving mechanism determined by the pore diameter and particle size. Materials such as ceramics, graphite, metal oxides, polymers etc. are used in making such membranes. The pores in the membrane may vary between 1 nm-20 microns.

Homogeneous Membranes
This is a dense film through which a mixture of molecules is transported by pressure, concentration or electrical potential gradient. Using these membranes, chemical species of similar size and diffusivity can be separated efficiently when their concentrations differ significantly.

Asymmetric Membranes
An asymmetric membrane comprises a very thin (0.1-1.0 micron) skin layer on a highly porous (100-200 microns) thick substructure. The thin skin acts as the selective membrane. Its separation characteristics are determined by the nature of membrane material or pore size, and the mass transport rate is determined mainly by the skin thickness. Porous sub-layer acts as a support for the thin, fragile skin and has little effect on the separation characteristics.

Electrically Charged Membranes
These are necessarily ion-exchange membranes consisting of highly swollen gels carrying fixed positive or negative charges. These are mainly used in the electrodialysis.
Liquid Membranes A liquid membrane utilizes a carrier to selectively transport components such as metal ions at relatively high rate across the membrane interface.

Membrane Modules
The membranes can he cast as flat sheets, tubes and fine hollow fibres. For accommodating such shapes and structures, different types of membrane modules are available. The last decade of membrane and module development has lessened the effects of physical compaction and has brought forth spiral membrane modules capable of operating at pressures in excess of 800 psig (55.2 bar). The techno-economic factors for the selection, design and operation of membrane modules include cost of supporting materials and enclosure (pressure vessels), power consumption in pumping and ease of replaceability. The following membrane modules are largely used for industrial applications: Plate and frame module Spiral wound module Tubular membrane module Capillary membrane module Hollow fibre membrane module.

Membrane Separation Processes
Various types of membrane separation have been developed for specific industrial applications. Some of the widely used processes are discussed hereunder: Schematic diagrams of plate and frame membrane module and spiral-wound membrane module

Reverse Osmosis (RO)

Unlike water filtration, that can only remove some suspended materials larger than 1 micron, the process of reverse osmosis (RO) will eliminate the dissolved solids, bacteria, viruses and other germs contained in the water. RO is essentially a pressure driven membrane diffusion process for separating dissolved solutes. The RO is generally used for desalination seawater for its conversion into potable water. The salient features of the process are that it involves no phase change and it is relatively a low energy process. Almost all RO membranes are made polymers, cellulosic acetate and matic polyamide types rated at 96%-99+% NaCl rejection. RO membranes are generally of two types , asymmetric or skinned membranes and thin film composite (TFC) membranes. The support material is commonly polysulfones while the thin film is made from various types of polyamines, polyureas etc. RO membranes have the smallest pore structure, with pore diameter ranging from approximately 5-15 A0 (0.5 nm - 1.5 nm). The extremely small size of RO pores allows only the smallest organic molecules and unchanged solutes to pass through the semipermeable membrane along with the water. Greater than 95-99% of inorganic salts and charged organics will also be rejected by the membrane due to charge repulsion established at the membrane surface. RO finds extensive applications in the following: Potable water from sea or brackish water Ultrapure water for food processing and electronic industries Pharmaceutical grade water Water for chemical, pulp & paper industry Waste treatment etc.

Future Directions for RO Applications

Municipal and industrial waste treatment Process water for boilers De-watering of feedstreams Processing high-temperature feed- streams etc. In the last six to eight years the technology has gained industry acceptance as a viable water treatment option for many different fluid separation applications. Low operating costs and the ability to remove organic contaminants and 95-99% of inorganic salts with minimal chemical requirements make RO an attractive technology for many industrial applications. A complete RO equipment comprising pre-treatment system, membrane modules etc. is estimated to cost around US $ 450 per m3 of flow per day.

Nanofiltration (NF)

Nanofiltration is a form of filtration that uses membranes to separate different fluids or ions. NF is typically referred to as "loose" RO due to its larger membrane pore structure as compared to the membranes used in RO, and allows more salt passage through the membrane. Because it can operate at much lower pressures, and passes some of the inorganic salts, NF is used in applications where high organic removal and moderate inorganic removals are desired. NF is capable of concentrating sugars, divalent salts, bacteria, proteins, particles, dyes and other constituents that have a molecular weight greater than 1000 daltons. Membranes used for NF are of cellulosic acetate and aromatic polyamide type having characteristics as salt rejections from 95% for divalent salts to 40% for monovalent salts and an approximate 300 molecular weight cut-off (MWCO) for organics. An advantage of NF over RO is that NF can typically operate at higher recoveries, thereby conserving total water usage due to a lower concentrate stream flow rate. NF is not effective on small molecular weight organics, such as methanol.

Ultrafiltration (UF)

Ultrafiltration is most commonly used to separate a solution that has a mixture of some desirable components and some that are not desirable. UF is somewhat dependent on charge of the particle, and is much more concerned with the size of the particle. Typical rejected species include sugars, bio-molecules, polymers and colloidal particles. The driving force for transport across the membrane is a pressure differential. UF processes operate at 2-10 bars though in some cases up to 25-30 bars have been used. UF processes perform feed clarification, concentration of rejected solutes and fractionation of solutes. UF is typically not effective at separating organic streams. UF membranes are capable of retaining species in the range of 300-500,000 daltons of molecular weight, with pore sizes ranging from 10-1000 Angstroms (103-0.1 microns). These are mostly described by their nominal molecular weight cut-off (1000-100,000 MWCO), which means, the smallest molecular weight species for which the membranes have more than 90% rejection. UF usually implies separation of macromolecules such as protein from low molecular weight solvents. Pores in the support layer of the membrane are relatively larger than those of the surface layer. Material passing into fine pores can readily be transported through the open-celled, sponge-like structure of the support layer. For example, in electrodeposition paint recovery, the paint, composed of resin, a pigment and water are separated into two streams that can he reused. The first stream includes the water and a small amount of paint resin, which can be used to rinse the parts later in the process. The paint pigment is separated from that stream and can be re-used in the paint bath, allowing the bath to be concentrated to a useable level. Schematic diagrams of tubular membrane module and capillary membrane module It is found that, whenever the solvent of a mixture flows through the membrane, retained species are locally concentrated at the membrane surface, thereby resisting the flow. In the case of processing solution, this localized concentration of solute normally results in precipitation of a solute gel over the membrane. When processing a suspension, the solids collect as a porous layer over the membrane surface. In view of the above, it is clear that the permeate rate can be effectively controlled by the rate of transport through the polarization layer rather than by membrane properties. Hence, UF throughput depends on physical properties of the membrane, such as permeability, thickness, process and system variables like feed consumption, feed concentration, system pressure, velocity and temperature. UF has a wide range of applications as shown below: Oil emulsion waste treatment Treatment of whey in dairy industries Concentration of biological macromolecules Electrocoat paint recovery Concentration of textile sizing Concentration of heat sensitive proteins for food additives ' Concentration of gelatin Enzyme & pharmaceutical preparations Pulp mill waste treatment Production of ultrapure water for electronics industry Macromolecular separations replacing the conventional change of phase methods. The important characteristics for membrane materials are porosity, morphology, surface properties, mechanical strength and chemical resistance. Polymeric materials, viz., polysulfone, polypropylene, nylon 6, Polytetrafluoroethylene (PTFE), PVC, acrylic copolymer etc. have been used successfully as UF membranes. Inorganic materials such as ceramics, carbon based membranes, zirconia etc. have been commercialized by several vendors. UF may find wide range of applications in the near future and some of those processes important from the separation and energy savings point of view are mentioned below: Ultraflitration of milk Bioprocessing: Separation and concentration of biologically active components Protein harvesting, useful for grass proteins, algal / plankton proteins In food areas based on the ability to change protein and starch/ sugar, salt and water ratios Refining of oils.

Microfiltration (MF)
This is by far the most widely used membrane process with total sales greater than the combined sales of all other membrane processes. Microfiltration has numerous small applications. It is essentially a sterile filtration with pores (0.1-10.0 microns) so small that micro-organisms cannot pass through them. Microfiltration is a process of separating material of colloidal size and larger than true solutions. A MF membrane is generally porous enough to pass molecules of true solutions, even if they are large. Microfilters can also he used to sterilize solutions, as they are prepared with pores smaller than 0.3 microns, the diameter of the smallest bacterium, *pseudomonas diminuta*. While the mechanism for conventional depth filtration is mainly adsorption and entrapment, MF membranes uses *sieving mechanism* with distinct pore sizes for retaining larger size particles than the pore diameter. Hence, this technology offers membranes with absolute rating, which is highly desirable for critical operations such as sterile filtration of parental fluids, sterile filtration of air and preparation of particulate free-water for the electronics industry. The MF membranes are made from natural or synthetic polymers such as cellulose nitrate or acetate, polyvinylidene difluoride (PVDF), polyamides, polysulfone, polycarbonate, polypropylene, PTFE etc. The inorganic materials such as metal oxides (alumina), glass, zirconia coated carbon etc. are also used for manufacturing the MF membranes. The properties of membrane materials are directly reflected in their end applications. Some criteria for their selection are mechanical strength, temperature resistance, chemical compatibility, hydrophobility, hydrophilicity, permeability permselectivity and the cost of membrane material as well as manufacturing process. MF has a wide array of applications as mentioned below: Preparation of parenterals and sterile water for pharmaceutical industry Food & beverages (concentration of fruit juices and alcoholic beverages Chemical industry Microelectronics industry Fermentation Laboratory/analytical uses etc. The following are the likely applications of MF in the near future: In biotechnology for concentration of biomass, separations of soluble products In diatomaceous earth displacement In non-sewage waste treatment for removing intractable particles in oily fluids, aqueous wastes which contain particulate toxics and stack gas In paints for separating solvents from pigments etc