LECTURE NOTES OF
NOBEL SEPARATION TECHNOLOGY
Branch: Chemical
Sem: 6th
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CHAPTER 1 : INTRODUCTION

Separation is an indispensable part of downstream operation in chemical, petrochemical, biochemical, food and several other allied process industries. It is needed to achieve the goals of enrichment, concentration, purification, refining and isolation of any desired product from a mixture. Efficient separation processes are also required to obtain high-value products in the food and pharmaceutical industries, to supply communities and industry with high quality water, and to remove and recover toxic or valuable components from industrial effluents.

Equilibrium and rate governed separation:

In general, separation processes of fluid mixtures can be divided into two categories: equilibrium separation and rate governed separation. Conventional separation processes such as evaporation, distillation, extraction, adsorption and absorption.

if separation is based on differences in transport rate through some medium under the influence of a driving force resulting from a gradient in pressure, concentration, temperature, or electrical field, it is termed as rate governed separation.

Membrane:

The membrane can be defined essentially as a barrier which separates two phases and restricts transport of various chemicals in a selective manner.

The membrane can be a selective or a contacting barrier. In the former case, it controls the exchange between the two regions

adjacent to it in a very specific manner, whereas in the latter case, its function is mainly to contact the two regions between which the transport occurs. Contrary to the conventional mass transfer operations, the two phases between which transfer of one or more species occurs are not in direct contact in membrane separation.

A membrane can be homogenous or heterogeneous, symmetric or asymmetric in structure, solid or liquid, can carry a positive or negative charge, or can 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. Membranes can also physically or chemically modify the permeating species (as with ion exchange or biofunctional membranes), prevent permeation (e.g. in packaging or coating applications) or regulate the rate of permeation (as in controlled drug delivery). Thus membranes may be either

passive or active, depending upon the membrane's ability to alter the chemical nature of the permeating species. The membrane thickness may vary from as small as 100 micron to several millimetres. Another characteristic property of membrane is its permselectivity, which is determined by differences in the transport rates of various components in the membrane matrix.

Basic principe of membrane separation:

Porous membranes discriminate according to the size of particles or molecules. Non porous membranes discriminate according to the chemical affinities between components and membrane materials.

The thinner the membrane, the higher will be the flux.

From the thermodynamic point of view, there may be three types of transport through membrane. These are active transport, passive transport and facilitated or carrier mediated transport.

In a system characterised by a single force and a single flow, the flow must be directed from a region of higher electrochemical potential to one of lower electrochemical potential.

The term 'active transport' should be applied to flows that are directed against their conjugate driving forces and conversely the passive transport' are those where flows are directed in the direction of conjugate driving force.

In facilitated or carrier mediated transport, the carrier molecules which reside in the membrane, can interact with a given permeant.

Classification of membrane processes:

Membranes for industrial separation can be broadly classified into the following four groups according to the driving force that causes the flow of the permeant through the membranes:

1. Pressure driven membrane process:

- Reverse osmosis (RO)
- Nanofiltration (NF)
- Ultrafiltration (UF)
- Microfiltration (MF)
- Pervaporation (PV)
- Membrane gas separation

2. Concentration gradient driven membrane process:

- Dialysis
- Membrane extraction

3. Electrical potential driven membrane process:

- Electrodialysis (ED)

Advantages of membrane processes:

Membrane processes provide a highly flexible separation technique for selective solute separation/concentration, and permeate recycling and reuse. The special features for membrane processes that make them attractive for industrial applications are their compactness, ease of fabrication, operation and modular design.

Appreciable energy savings: An advantage of membrane technology as compared to conventional processes is that it permits concentration and separation without the use of heat. Since membrane separations do not require a change in the state of the solvent (except for pervaporation) to effect a dewatering, this should result in considerable savings in energy.

Clean technology with operational ease: No complicated heat transfer or heat generating equipment is needed in membrane operations. These processes can be operated at ambient temperatures. A further advantage over evaporators is that no condenser is needed; thus avoiding related problems like thermal pollution and sewage water.

Replaces the conventional processes: Existing non-membrane based equilibrium driven separation technologies (e.g. adsorption, absorption, extraction, distillation and stripping) may have significant shortcomings:

inherent operational difficulties (emulsification, foaming, entrainment, weeping, etc.), lack of flexibility (flooding, loading and need for density difference), slower rate, lack of modularity, and the need for large space. These shortcomings are mitigated by membrane processes.

Recovery of high value products: As technology develops, more and more situations arise where substance of high unit value are formed in very low concentration. In conventional separation processes, the separation efficiency drops rapidly as the concentration of the desired component falls. Membrane separation techniques, on the contrary, can give better answer to these problems.

Greater flexibility in designing systems: With the development of new membranes with improved transport properties and better chemical and thermal stability in recent years, a large number of new potential applications are identified.

Hybrid process development: It is more advantageous to use both distillation and membrane unit operations in series. The hybrid can successfully increase capacity of existing plants and improve product quality. A hybrid process is successful if its overall cost and performance is an improvement over the individual alternatives.

Disadvantages of membrane separation processes:

Membrane separation processes do suffer from certain disadvantages which lead to its application constraints. Some of the disadvantages are stated below:

Membrane fouling: Membrane fouling is a pertinent problem in membrane separation process. Contaminated feed increases the rate of membrane fouling, especially for hollow fibre modules.

Upper solid limits: In fact, membrane processes are quite limited in their upper solid limit. In RO, it is frequently the osmotic pressure of the

concentrated solutes that limits the process. In the case of UF and MF, it is rarely the osmotic pressure of the retained macromolecules, but rather the low mass transfer rates and high viscosity that makes the pumping of the retentate difficult.

Expensive: In general membrane processes are expensive compared to other processes. It is due to the fabrication method, occasional replacement, fouling & poor cleanability of the membrane.

Major areas of application:

Membrane processes are no longer bound in the domains of laboratory but processes have achieved impressive industrial in many applications.

Chemical Industry:

Membrane separation has emerged as the most important and practically useful 'modern separation technique' in chemical process industries. Some of the major applications are:

- Production of process water for industrial use.
- Waste water treatment.
- Desalting of food, acid and reactive dyes.
- Concentration of all types of dyes

Pharmaceutical Industry:

In pharmaceutical and cosmetic manufacturing, membrane technology assumes importance in the success of many new products and processes, while traditional processes have been changed over to membranes with dramatic cost savings and improved yields. Due to the macromolecular nature of most bioengineered products, Membrane processes are already playing a key role in the following processes:

- Concentration and purification of soluble macromolecules such as plasma proteins, vaccines, enzymes and yeasts
- Process water as per USP standards
- Endotoxin free water

Food and Dairy Industry:

Though the applications have been few, yet the potential is very large and will provide energy saving, processing without phase change and higher recovery of quality products. Following are the various membrane processes used in milk processing industries:

- Lactose and protein concentration
- Concentration of whole and skim milk
- Lactose protein separation
- Fractionation and concentration of egg albumin and animal and fish oils and proteins
- Concentration of extracts of vanilla, lemon peel, malt, etc.

Biotechnology Industry:

Some major areas of membrane application in biotechnology are as follows:

- Enzyme concentration
- Fermentation broth clarification
- Separation of microsolutes like antibiotics and vitamins
- Purification and concentration of vitamins
- Tissue culture reactor systems

Future prospects:

- Developing new membrane materials.
- Identification of new ways of using permselective membranes.
- Combining conventional unit operations and membrane separation processes, which often results in separation processes that offer significant advantages over individual processes.

CHAPTER 2: MEMBRANE TYPE, MODULE & FLOW PATTERN

The choice for a certain kind of membrane depends on number of factors as:
- Good permeability.
- Chemical stability and compatibility.
- Mechanical strength.
- Resistance to fouling.
- Ability to cast into a thin film.
- Pore characteristics.

Classification of membranes:
On the basis of nature of the membrane:
- Natural
- Synthetic

On the basis of structure of the membrane:
- Porous
- Nonporous

On the basis of Pore geometry:
- Cylindrical
- Spongelike
- Modular

On the basis of Final morphology:
- Woven

- Sintered
- Cast and extruded
- Irradiated

Microporous membranes:

- A microporous membrane is very similar in structure and function to a conventional filter. It has a rigid, highly voided structure with randomly distributed, and interconnected pores.
- However, these pores differ from those in a conventional filter by being extremely small, on the order of 0.01 to 10 μm in diameter.

- All particles larger than the largest pores are completely rejected by virtue of a sieving effect.

The microporous membranes are further classified as:

- •Isotropic: Here the pores are of uniform size throughout the membrane; and
- •Anisotropic: Here the pores change in size from one surface of the membrane to the other.

Microporous membranes are designed to retain all particles above its rating. For example, a 0.45 µm membrane implies that it will not allow particles larger than 0.45 um to pass through it. However, this does not mean that the size of the pores is 0.45 µm or less.

Asymmetric membrane:

- Also known as skinned membrane.
- These are characterised by a thin(0.1 to 1 micron) skin on the surface of membrane.
- There is one porous sub-layer underneath which acts as a support for the thin, fragile

skin and has little effect on the separation characteristics.
- It's separation characteristics are determined by the nature of membrane or pore size and mass transfer rate is determined mainly by the skin thickness.

Asymmetric membranes are again of two types:
- •Integrally skinned: skin layer resulting from phase inversion process which are porous.
- •Non-intergrally skinned: skin layer that are deposited from the solution and are homogeneous in nature.

Thin film composite membrane(thin layer composite):
- Also known as second generation membrane.
- These membranes are primarily designed for RO and NF applications.
- Thin film composite have a thin dense polymer skin formed over a microporous support.
- These are available in spiral, plate & frame and tubular module configurations.

- These membrane requires a very finely porous substrate to which the film can adhere well.
- For adequate film support, the pores in the substrate must be smaller in diameter than the thickness of the film to be applied.

Electrically charged membrane:

- These are necessarily ion exchange membrane membranes consisting of highly swollen gel carrying fixed positive or negative charge.
  - Electrically charged membranes can be dense or microporous , but are most commonly very finely microporous with the pore walls carrying fixed positively or negatively charged ions.
  - A membrane with fixed positively charged ion is referred as anion exchange membrane because it binds anions in the surrounding fluid. Similarly a membrane containing fixed negatively charged ions is called cation exchange membrane.

- Here separation is achieved mainly by the exclusion of ions of ions of the same charge and to a much lesser extent by the pore size.
- These are mainly used in electrodialysis.

Inorganic membrane(Ceramic membrane):
- They are versatile and can be operated at elevated temperature.
- Metal membranes are stable at temperatures ranging from 500-800°C and many ceramic membranes are usable at over 1000°C.
- They are also much more resistant to chemical attack.
- Because of the wide variety of materials that may be used in the fabrication of the inorganic membranes, they are also resistant to corrosive liquid and gases.
- Ceramic membranes normally have an asymmetrical structure composed of at least two, but mostly three, different porosity levels.

Membrane module:

The device in which the membranes are installed is known as membrane module.

(or)

Membrane module is the smallest unit into which the membrane are is packed.

The membranes can be cast as flat sheets, tubes and fine hollow fibres. For accommodating such shapes and structures, different types of membrane modules are available. There are basically four different designs of membrane

modules which are most commonly used. These are:

(a) Plate and frame
(b) Tubular
(c) Spiral wound
(d) Hollow fibre

The choice of module configuration as well as the arrangement of modules in a system depends on:
- Economic considerations.
- Type of separation problem.
- Ease of cleaning.
- Ease of maintenance and operation.
- Ease of compactness of the system.
- Scale and possibility of membrane replacement.

Plate and frame:
- This is also known as flat sheet Tangential Flow(TF) module.
- These are similar to plate and frame filter press with a series of flat membrane sheets.

- Here sets of two membranes are placed in a sandwich like manner with their feed sides facing each other.
- In each feed and permeate compartment, a suitable spacer(support screen) is placed.
- The units may have square, rectangular or oval cross-section.
- Sometimes to reduce channelling(i.e. the tendency to flow along a fixed pathway) and to establish uniform flow distribution, so called 'stop discs'(baffles) can be introduced.

Advantages:
- Sheets can be quite close to one another to reduce concentration polarisation.
- Can be easily disassembled for cleaning and replacement of defective membranes.
- Provides good flow control on both permeate and feed side of the membrane.
- They have the ability to accommodate low levels of suspended solids ad viscous fluids.

Disadvantages:

- Large number of spacer plates and seals are required.
- Leakage through gaskets.
- Low packing density.
- Flow pattern and pressure drop distribution are difficult to characterise.
- High module cost/expensive units.

Spiral wound:
- The spiral wound module is the next logical step from a flat membrane.
- It is in fact a plate and frame system wrapped around a central collection pipe.
- A permeate spacer is sandwiched between two membranes.
- Feed flows through the feed spacer parallel to the central tube, where as the permeate flows through the permeate spacer, spirally perpendicular to the feed flow direction.

- Spiral wound elements are most commonly manufactured with flat sheet membrane of either a cellulose diacetate and triacetate blend or a thin film composite.
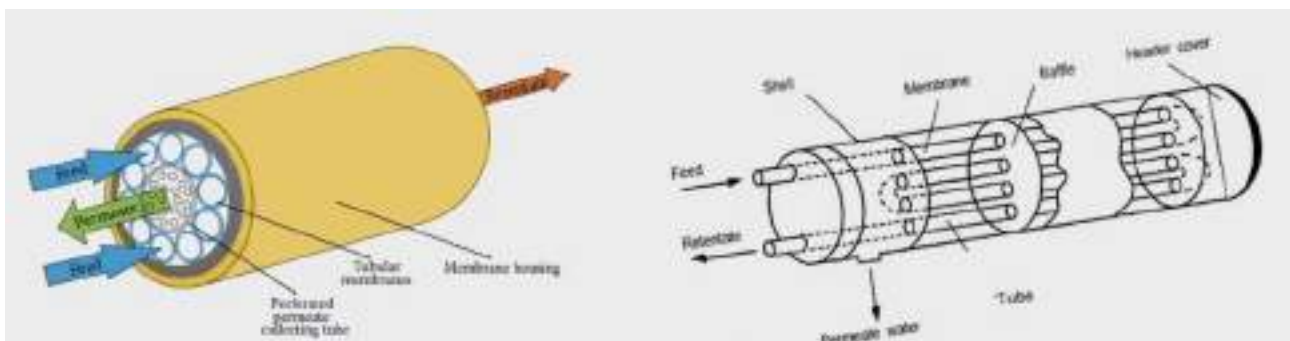
Advantages:
- They are compact; high membrane packing density results in more efficient utilisation of floor space.
- High pressure spiral elements can withstand pressures in excess of 1000 psi.
- Low pressure drop and membrane contamination .
- Minimum concentration polarisation.

Disadvantages:
- Difficult to disassemble and clean.
- Problems in handling suspended solids.
- It is not useful in high temperature applications.

Tubular:

- Tubular module resembles a shell and tube heat exchanger, but feed flows through the tubes.
- Permeate passes through the wall of the tubes into the shell side of the module and retentate passes out through the other end of the tubes.
- Tubular module consists of parallel bundles of rigid walled, porous or perforated tubes.
- Tubular membranes unlike hollow fibres are not self supporting. Therefore these membranes are kept inside a porous metallic,

ceramic or polymeric tube.

Advantages:

- Turbulent flow(providing good membrane-feed contact and removing retentate film build up)
- Relatively easy cleaning.

- Easy in handling suspended solids and viscous fluids.
- Ability to replace or plug a failed tube while the rest of the system runs.
- The feed flow pattern is easy to characterise and therefore design and analysis based on fluid dynamics principles is possible.

Disadvantages:
- Low packing density.
- High capital cost and pumping cost.
- Limited achievable concentration.

Hollow fibre:
- A perforated pipe is located in the centre of the module through which the feed solution enters.
- Here we have two different flow patterns i.e. inside-out and outside-in.
- In inside-out, the feed solution is more uniformly distributed throughout the module

so that the whole surface area is more effectively used.

- In gas separation, the module will be of outside-in type to avoid high pressure losses inside the fibre and to attain a high membrane area.

Advantages:

- Very high packing density.(4.5×10^6 fibres inside a 25.4 cm diameter cartridge)
- Ease of cleaning using back flushing.
- Ability to achieve high concentration.
- Hollow fibre membranes can be designed for recirculation and single pass operation.

Disadvantages:

- Fragility of fibre.
- Inability to handle suspended solids well.
- Channelling may occur in outside-in type arrangement.
- The hollow fibre module could be used only when the feed stream is relatively clean.

Flow pattern:

Ideally there are four different flow patterns for membrane separation processes:
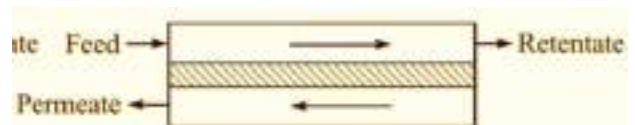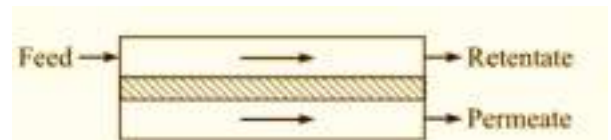
1) Perfect mixing/complete mixing:

- Both the feed and permeate sides of the membrane are well mixed.
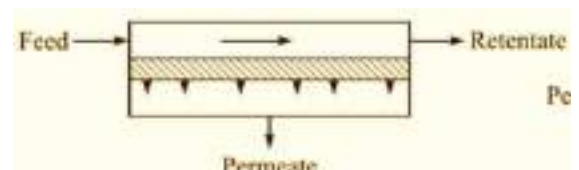- It is similar to a continuous stirred-tank reactor(CSTR).
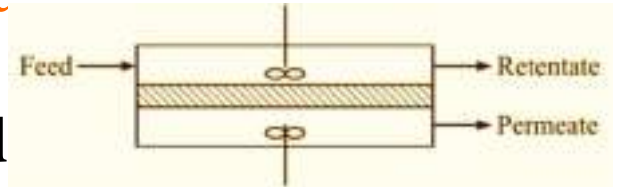
2) Co-current flow:

- Here fluid on the feed or retentate side flows along and parallel to the upstream surface of the membrane and permeate side fluid flows on the downside parallel to the retentate.

3) Countercurrent flow:

- Both the feed stream and permeate stream are plug flow countercurrent to each other.

4) cross flow:

- Feed stream is in plug flow and permeate flows in a normal direction away from the membrane.

Membrane materials:

There are large varieties of polymers which are extensively used for

preparation of membranes. In general these can be classified into three major

groups as follows:

1. Rubbery polymer:

When the polymer operates at a temperature above the glass transition temperature (T_g), it is called rubbery polymer. Their behaviour is essentially that of a viscous liquid. In rubbery polymers segmental motion of polymeric molecules are rapid like liquid molecules. These polymers have high fluxes of organics and low flux of water. Silicone rubber, Polydimethyl siloxane, polyvinylammonium thiocyanate, etc. are the examples of rubbery polymers.

2.Glassy polymer:

When the polymer operates at a temperature lower than the glass transition temperature (T), it is known as glassy polymer. These polymers

are either amorphous or crystalline. Segmental motion or rotation of polymeric molecules is restricted leading to heterogeneity of polymer structure. Polycarbonate, cellulose acetate, polysulphone, etc. are the examples of glassy polymers.

3. Lon exchange polymer:

Ion exchange membranes are essentially ion exchange resins made in membrane form. These are having ionic charges on the polymeric segment. A negatively charged membrane is permeable only to cations, and therefore, is called a cationic membrane. Similarly, when the membrane is positively charged, it is permeable to anions and is called an anionic membrane. Ion exchange membranes are very selective for water.

Some of the polymers that are widely used as potential membrane materials are discussed in the following:

Cellulose derivatives:

The high structural regularity and intermolecular hydrogen bonding of its hydroxyl groups make cellulose difficult to dissolve. They show pronounced hydrophilicity, which is very useful in minimizing fouling of the membrane. One of the important advantages of CA membrane is that these are available with wide range of pore sizes with reasonably high fluxes. However, CA membrane suffers from certain disadvantages also. These include narrow temperature range (30°C to 40°C), low pH range (pH 3 to pH 6) and poor resistance to chlorine. Another limitation of cellulose derivatives is borderline glass transition temperature (68.6°C) which limits its utility at elevated temperatures and pressures.

Aromatic polyamides:

Aromatic polyamides (also called aramides) are highly melting (275°C) crystalline polymers with better thermal stability. They are prepared either by the self condensation of aromatic amino acids or by the polycondensation between aromatic diacid

chlorides and aromatic diamines. These are characterised by having an amide (-CONH-) bond in its structure. Polyamide (PA) membranes can overcome some of the drawback of CA membrane. These have higher pH tolerance. However, PA membranes are worse than CA in terms of chlorine tolerance due to electrophilic substitution of aromatic rings by chlorine which disrupt intermolecular hydrogen bonding resulting in increased permeability and reduced selectivity.

Polysulphone:

Polysulphone is a condensation product of bisphenol-A and dichlorodiphenyl sulfone. Polysulphones (PS) and polyether sulphones (PES) are having high degree of molecular immobility, high rigidity, creep resistance and dimensional stability. Their salient features include wide range of operating temperature (up to 75°C for PS and up to 125°C for PES), wide pH tolerance (pH 1 to pH 10), and fairly good chlorine resistance.

Polyimides:

Polyimides are extensively investigated as candidate polymer for reverse osmosis membranes. Polyimides are obtained by reaction of diamines with dianhydrides and subsequent condensation of the resultant polyamic acid. Because of the supposed absence of-NH-groups in their backbones, it was initially felt that polyimides would be resistant to oxidation by chlorine. However, the chlorine resistance of polyimides has proven, in the long run, to be inadequate and the interest in polyimide reverse osmosis membranes has subsided. Present activity in polyimide membrane polymers centres around their use in gas separation membranes.

Interfacially synthesized polymers:

The high melting temperatures of aromatic polyamides and related polymers required their synthesis by interfacial or low temperature polycondensation techniques. Interfacial polycondensation is unusual in that neither monomer purity nor exact stoichiometry of reagents is required and can

be adopted for direct synthesis of the films in situ over a microporous support. This technique is utilized commercially for the preparation of polyurea, polyamide (PA 300) and crosslinked aromatic polyamide (FT 30) membranes. In each case, a microporous polysulphone membrane with surface pores of < 0.1 um size was first wetted with a dilute aqueous solution of the water soluble component like polyethyleneimine (PEI) or meta-phenylenediamine and interfacially reacted with hexane solutions of toluene diisocyanate (TDI), isophthaloyl chloride or trimesoyl chloride. As compared to asymmetric membranes, interfacially synthesized membranes provide high permeability rates without sacrificing selectivity.

Polytetrafluoroethylene (PTFE):

Polytetrafluoroethylene (PTFE), also known as Teflon, in trade, may be visualized as polyethylene with all its hydrogen atoms substituted by fluorine. The monomer tetrafluoroethylene (TFE) is produced by dechlorination of dichloro tetrafluoroethane or by the decarboxylation of sodium perfluoro-

propionate. PTFE is a straight chain, highly crystalline polymer with a very high degree of polymerization of the order of 100,000, which gives it considerable strength. It is also very stable to strong acids, alkalis and solvents and can be used at a wide range of temperature from -100°C to 260°C. It is made by a combination of heating and stretching melted films. It is extremely hydrophobic and finds many uses in the treatment of organic feed solutions vapours and gases.

Polycarbonate:

The commercial aromatic polycarbonates (PC) are a class polyesters derived from carbonic acid and bisphenol-A. Polycarbonates are characterised by the presence of the -OCOO- group in the chain. They are mainly amorphous in structure. Thin dense films (~ 10 um) of high molecular weight PC are the most common substrate for the preparation of microporous radiation track membranes. The non planner configuration of the polycarbonates provides a large average interchain displacement in the membrane with the result that gas permeability

is much higher through PC films. Polycarbonates differ from most other amorphous polymers in that they possess ductility and toughness below T. Since polycarbonates are thermoplastic, they can be extruded into various shapes, including films and sheets. Polycarbonates are often investigated for preparing block copolymers with polyethylene glycols (PEG) and silicones. Copolymers of PC and PEG are known to be suitable for making hemodialysis membranes. Block copolymers of PC with silicone combine the excellent film forming properties of PC and gas separation properties of silicone. Both flat sheet and hollow fibre membranes of silicone polycarbonate copolymers are investigated for use in membrane blood oxygenators.

Polypropylene:

Polypropylene is produced by the polymerization of propylene using the famous Ziegler-Natta catalysts. The typical polymerization catalysts are Al(iso-C,H,), and TiCl,, or Al(C,H,), and TiCl: Polypropylene can be made by thermal inversion process and also by

the melt-extruding and stretching. It is usually available in the form of hollow fibres. They are hydrophobic, relatively inert, and can withstand moderately high temperatures.

Inorganic membrane materials:

The application of polymer membranes is generally limited to temperatures below about 200°C and to the separation of mixtures that are chemically inert. Most inorganic membrane materials have much better selectivity and permeability (at high temperatures) than polymeric membranes (at low temperature), with data points falling beyond the Robeson boundary lime" for most gas pairs. A large number of materials (from alpha alumina to zircon) are available for the manufacture of ceramic membranes. The most common membranes are made of Al, Si, Ti or Zr oxides, with Ti and Si being more stable than Al or Si oxides. In some less frequent cases, Sn or Hf are used as base elements. Each oxide has a different surface charge in solution. Other membranes can be composed of mixed oxides of two of the previous elements, or are

established by some additional compounds present in minor concentration. Ceramic membranes are available form several manufacturers in different shapes, mainly round and hexagonal, and with various channel diameters.

CHAPTER 3: REVERSE OSMOSIS

Reverse osmosis (RO), less commonly known as hyperfiltration, is a high pressure, energy efficient technique for de watering process streams, concentrating low molecular weight substances in solution, or purifying wastewater. It has. the ability to concentrate dissolved as well as suspended solids. RO is widely used in the desalination of brackish water. To desalinate water, it is required to create a flow through a membrane, causing the water to leave the salty side of the membrane, passing into the unsalted side. To achieve this, pressure must be created upon the water column on the salt side of the membrane; firstly, to remove the natural osmotic pressure and secondly, to create extra pressure on the water column in order to push the water through the membrane. As the name suggests, reverse osmosis is osmosis in reverse. Therefore, to describe reverse osmosis, it is first necessary to understand the phenomenon of osmosis.

Concept of osmosis:

The word 'osmosis' is originated from the Greek word osmos which means "to push'. Osmosis is a natural phenomenon, most commonly observed in plants. If we do not water our plants they wilt. A plant cell is a semipermeable (water flows through the membrane but salts do not) membrane with the living stuff inside in a salt solution. Water is drawn into the cell from outside because pure water moves across a semipermeable membrane to dilute the higher concentration of salt inside. This is how water is drawn in from the ground when we water our plants. On the other hand, if we add salt to plants (over fertilise or spill some salt on the grass), the plant wilts because the salt concentration outside of the cell becomes higher than inside and then water moves across the membrane from inside to outside.

Osmosis may be defined as the physical movement of a solvent through a semipermeable membrane based on a difference in chemical potential between two

solutions separated by that semipermeable membrane. Let us take a simple example to demonstrate osmosis. A beaker of water as shown in Figure 3.1 is divided through the centre by a semipermeable membrane. The thick dotted line represents the semipermeable membrane. We will define this semipermeable membrane as lacking the capacity to diffuse anything other than the solvent, in this case water molecules. Now, if we add a small amount of common salt (NaCI) to the solution on one side of the membrane, the salt water solution will be having a higher chemical potential than the water solution on the other side of the membrane. Therefore, in an effort to equilibrate the difference in chemical potential, water begins to diffuse through the membrane from the water side to the salt water side. This movement is osmosis. The pressure exerted by this mass transfer is known as osmotic pressure.

The diffusion of water will continue until one of the two constraints is met. One constraint would be that the solutions essentially equilibrate, at least to the extent that the remaining difference in chemical potential is offset by the resistance or pressure loss of diffusion through the membrane. The other constraint is that the rising column of salt water exerts sufficient hydrostatic pressure to limit further diffusion. By observation, then, we can measure the osmotic pressure of a solution by

noting the point at which the head pressure impedes further diffusion.

Determination of Osmotic Pressure:

The thermal movement of a solute molecule within a solvent is overdampened by the solvent molecules that surround it. The solute movement is wholly determined by fluctuations of thermal collisions with nearby solvent molecules. However, the average thermal velocity of the solute molecule is the same had it been free in a gas phase, without nearby solvent molecules. Whenever a solute movement is blocked by the membrane it will transfer momentum to it and, therefore, generate pressure on it. Since the velocity is the same as that of a free molecule, the pressure will be the same as the pressure of an ideal gas of the same molecular concentration. Hence, the osmotic pressure I, is given by the Van't Hoff formula, which is identical to the pressure formula of an ideal gas:

where n is the number of kg mol of solute, I the molar volume of pure solvent water in m' associated with n kg mol of solute, R is the gas constant (82.057×10^a m' atm/kg mol K, and T is the absolute temperature in K. The osmotic pressure does not depend on the solute type, or its molecular size, but only on its molar concentration, as the formula states. Figure 3.3 shows connected vessels separated by a semipermeable membrane. If there is only water in the device, the level will be the same at both arms. When solute molecules are added to one arm. water will start to flow into it, so that its level will rise at this arm, and fall at the other arm. Figure 3.3

The system will stabilise when the osmotic pressure is balanced by the hydrostatic pressure generated by the difference h in the water levels. This can be given by the following expression: $cRT = ph$

where p is the specific gravity of water. The physical significance of osmotic pressure is well known in biological and clinical situations. Germination of seeds to burst open their

protective layer, transportation of water from the soil to the root system in plants and activation of dormant cells in a solution of lower osmotic pressure are all due to the difference of osmotic pressure. Even relatively small concentrations of dissolved solutes can develop fairly large osmotic pressures. Table 3.1 shows osmotic pressure of various dilute aqueous solutions of NaCl at 25°C.