Membrane separation and Ionexchange
SRM University
Internal circulation only

1. What is membrane?

A membrane may be defined as "an interphase separating two phases and selectively controlling the transport of materials between those phases". A membrane is an interphase rather than an interface because it occupies a finite, though normally small, element of space.

2.What is mean by membrane separation?

The use of thin barriers (membranes) between miscible fluids for separating a mixture; a suitable driving force across the membrane, for example concentration or pressure differential, leads to preferential transport of one or more feed components.

Separations of liquids and gases are commonly accomplished using membrane separation methods which include dialysis, reverse osmosis, and ultrafiltration Hybrid and more exotic membrane methods that have also proven effective are electrodialysis, helium separation through glass, hydrogen separation through Palladium and alloy membranes, immobilized solvent and liquid-surfactant membranes.

Permeation of liquids and gases through polymeric membranes occurs where a constituent passes through the membrane by diffusion and sorption by the fluid on the other side of the membrane. The driving force is achieve either by pressure or concentration difference across the membrane.

3.Give some advantage of membrane over other process

(a) A higher overall liquid removal rate is achieved by prevention of the formation of an extensive filter cake.
(b) The process feed remains in the form of a mobile slurry suitable for further processing.
(c) The solids content of the product slurry may be varied over a wide range.
(d) It may be possible to fractionate particles of different sizes.

4.What is the limitation of membrane processes?

The specification and the characteristics of the feed is important in membrane process, cleaning of membranes at regular interval is necessary, concentration polarization, membrane fouling are the two usual phenomena in membranes

5.Give some example for membrane separation process

Some of the membrane process are dialysis, reverse osmosis, ultrafiltration, and electrodialysis,

6.Distinguish between osmosis & reverse osmosis

When two solutions of differing concentrations of dissolved materials are separated by a semi-permeable membrane, the liquid component will tend to flow from the lower to the more highly concentrated side. In a sense, the concentration difference will tend to equilibrate across the membrane. This process is called **osmosis**.

If the liquid on the more concentrated side is maintained at a higher pressure, however, this process can be reversed: the solvent will flow from the concentrated side to the less concentrated side. Since the membrane blocks the passage of the dissolved waste constituents, the concentrated solution becomes even more concentrated. This process is called **reverse osmosis**.

7. What are the membrane module?

The membrane modules are Tubular, flat sheet, spiral wound, hollow fibre.

8. Define electro dialysis

A ionic mobility under the influence of an electric field through the anionic and cationic membranes is known as electrodialysis. Charged ions can be removed from a solution by synthetic polymer membranes containing ion exchange groups. Anion exchange membranes carry cationic groups which repel cations and are permeable to anions, and cation exchange membranes contain anionic groups and are permeable only to cations. Electrodialysis membranes are comprised of polymer chains - styrene-divinyl benzene made anionic with quaternary ammonium groups and made cationic with sulphonic groups. 1-2V is then applied across each pair of membranes.

9. What are the various membrane plant configuration?

a) feed and bleed
b) continuous single pass
c) multiple stage feed and bleed

10. Define thermal diffusion

It involves the formation of a concentration difference within a single liquid or gaseous phase by imposition of a temperature gradient upon the fluid, thus making a separation of the components of the solution possible. Example: – Helium-3 separation from Helium-4

11.Write some industrial application for electrodialysis

- Cheese whey demineralization
- Brackish water desalination
- Nitrate removal for drinking water
- Food/sugar products desalting
- Tartaric wine stabilization
- NaCl removal from amino acid salts
- Acid removal from organic product
- Conversion of organic salts into acid and base (bipolar membrane ED)
- Desalting of amines.
- De-acidification of fruit juices
- Metals removal from ethylene glycol

12.Write some membrane materials for various application

Initially most of the membranes were cellulosic in nature. These are now being replaced by polyamide, polysulphone, polycarbonate and a number of other advanced polymers. These synthetic polymers have improved chemical stability and better resistance to microbial degradation. Membranes have most commonly been produced by a form of phase inversion known as immersion precipitation.

13.List out uses of membrane separation

In general, membrane separation techniques are especially useful in separating:

- Mixtures of similar chemical compounds,
- Mixtures of thermally unstable components (since no heating is needed), and In conjunction with conventional separation methods (such as using membranes to break azeotropic mixtures before feeding them)
- proteins can be separated in whey for the production of whey protein concentrate (WPC)
- milk can be concentrated prior to cheese making at the farm level apple juice and wine can be clarified
- waste treatment and product recovery is possible in edible oil, fat, potato, and fish processing
- fermentation broths can be clarified and separated
- whole egg and egg white ultrafiltration as a pre concentration prior to spray

Use of membrane separation to dry gas streams containing water vapor

14.Define sweep diffusion

If a condensable vapor (steam) is allowed to diffuse through a gas mixture, it carries one of the components along with it, thus making a separation by the operation known as Sweep diffusion.

15. Write short notes on Thermal diffusion

Diffusion is the movement, under the influence of a physical stimulus, of an individual component through a mixture. The term thermal itself denotes that the diffusion is caused due to temperature gradient. Molecular diffusion which is induced by temperature is referred to as Thermal Diffusion.

16. What is ultra filtration?

Ultrafiltration (UF) is a membrane separation process, driven by a pressure gradient, in which the membrane fractionates components of a liquid as a function of their solvated size and structure

17.Ion exchange – Explain.

The ion exchange is the exchange of equivalent numbers of similarly charged ions, between an immobile phase, which may be a crystal lattice or a gel, and a liquid surrounding the immobile phase. If the exchanging ions are positively charged, the ion exchanger is termed cationic,and anionic if they are negatively charged. The rate at which ions diffuse between an exchanger and the liquid is determined, not only by the concentration differences in the two phases, but also by the necessity to maintain electroneutrality in both phases.

18.Define resin capacity

Various measures of the capacity of a resin for ion exchange are in common use. The maximum capacity measures the total number of exchangeable ions per unit mass of resin,commonly expressed in milliequivalents per gram (meq/g). It is the number of fixed ionic groups which determines the maximum exchange capacity of a resin although the extent to which that capacity may be exploited depends also on the chemical nature of those groups.

PART-B

1.Explain ion exchange process and industrial application of ion exchange membrane

Ion exchange is not a membrane process but it is used for product of protein isolates of higher concentration than obtainable by membrane concentration.
Fractionation may also be accomplished using ion exchange processing. It relies on inert resins (cellulose or silica based) that can adsorb charged particles at either end of the pH scale. The design can be a batch type, stirred tank or continuous column. The column is more suitable for selective fractionation. Whey protein isolate (WPI), with a 95% protein content, can be produced by this method. Following adsorption and draining of the deproteined whey, the pH or charge properties are altered and proteins are eluted. Protein is recovered from the dilute stream through UF and drying. Selective resins may be used for fractionated protein products or enriched in fraction allow tailoring of ingredients.

Application examples of ion exchange membrane

* Production of High Purity Chemicals
* Production of Ultra Pure Water
* Battery Diaphragm
* Recovered developing solution

Food and pharmaceutical

* Demineralization of Cheese Whey
* Demineralization of Organic Acids and Amino Acids
* Desalination of Soy-Sauce
* Stabilization of Wine
* Demineralization, Deacidification of Fruit Juice
* Demineralization of Natural Extract

* Demineralization of Poly-saccharide
* Demineralization of Betaine
* Demineralization and Purification of Pharmaceutical Intermediate
* Molasses

Environmental conservation

* Desalination of Leachate
* Removal of Nitrate from Under-Ground Water

Others

* Production of Salt from Sea water
* Production of Drinking Water from Brackish Water
* Desalination of Deep Sea Water
* Acid Recovery from Waste Acid
* Recovery of Valuable Metals
* Recovery of Acid from Pickling Waste

2. Write about ion exchange resins

Ion-exchange operations are essentially metathetical chemical reactions between an electrolyte in solution and an insoluble electrolyte with which the solution is contacted. The mechanisms of these reactions and the techniques used to bring them about resemble those of adsorption so closely that for most engineering purposes ion exchange may be simply considered as a special case of adsorption.

Principles of ion exchange

The ion-exchange solids first used were porous, natural or synthetic minerals containing silica, the zeolites, such as the mineral Na20.AI20s.4Si02.2H20, for example. Positively charged ions (cations) of a solution which are capable of diffusing through 'the pores will exchange with the Na+ ions of such a mineral, and the latter is therefore called a cation exchanger. For example,

$$Ca^{++} + Na_2R \rightarrow CaR + 2Na^{+}$$

where R represents the residual material of the zeolite. In this manner "hard" water containing Ca^{++} may be softened by contact with the zeolite, the less objectionable Na+ replacing the C^{++} in solution and the latter becoming immobilized in the solid. The reaction is reversible, and after saturation with Ca^{++} the zeolite may be regenerated by contact with a solution of salt,

$$CaR + 2NaCl \rightarrow Na_2R + CaCl_2$$

Later certain carbonaceous cation exchangers were manufactured by treating substances such as coal with reagents such as fuming sulfuric acid, and the like. The resulting exchangers can be regenerated to a hydrogen form, HR, by treatment with acid rather than salt. Thus, hard water containing $Ca(HCO_3)_2$ would contain H_2CO_s after removal of the Ca^{++} by exchange, and since the carbonic acid is readily removed by degasification procedures, the total solids content of the water may be reduced in this manner. Early applications of ion exchangers using these principles were largely limited to water-softening problems.

. In 1935, synthetic resinous ion exchangers were introduced. For example, certain synthetic, insoluble polymeric resins containing sulfonic, carboxylic, .or phenolic groups can be considered as consisting of an exceedingly large anion and a replaceable or exchangeable cation. These make exchanges of the following type possible,

$$Na^{+} + HR \leftrightarrow NaR + H^{+}$$

and different cations will exchange with the resin with different relative ease. The Na^{+} immobilized in the resin may be exchanged with other cations or with H+, for example, much as one solute may replace another adsorbed upon a conventional adsorbent. Similarly synthetic, insoluble polymeric resins containing amine groups and anions may be used to exchange anions in solution. The mechanism of this action is evidently not so simple as in the case of the cation exchangers, but for present purposes it may be considered simply as an ion exchange. For example,

$$RNH_3OH + Cl^{-} \leftrightarrow RNH_3CI + OH^{-}$$

$$H^{+} + OH^{-} \rightarrow H_20$$

where RNH_3 represents the immobile cationic portion of the resin. Such resins may be regenerated by contact with solutions of sodium carbonate or hydroxide. The synthetic ion-exchange resins are available in a variety of formulations of different exchange abilities, usually in the form of fine, granular solids or beads,]6 to 325 mesh. The individual beads are frequently nearly perfect spheres.

Ion exchange resins

There are two general types of ion exchange resins: those that exchange positive ions, called cation resins, and those that exchange negative ions, called anion resins. A cation is an ion with a positive charge. Common cations include Ca , Mg , Fe , and H . A cation resin is one that exchanges positive ions. An anion is an ion with a negative charge. Common anions include Cl , SO , and OH . An anion resin is one that exchanges negative ions. Chemically, both types are similar and belong to a group of compounds called polymers, which are extremely large molecules that are formed by the combination of many molecules of one or two compounds in a repeating structure that produces long chains. A mixed-bed demineralizer is a vessel, usually with a volume of several cubic feet, that contains the resin. Physically, ion exchange resins are formed in the shape of very small beads, called resin beads, with an average diameter of about 0.005 millimeters. Wet resin has the appearance of damp, transparent, amber sand and is insoluble in water, acids, and bases. Retention elements or other suitable devices in the top and bottom have openings smaller than the diameter of the resin beads. The resin itself is a uniform mixture of cation and anion resins in a specific volume ratio depending on their specific gravities. The ratio is normally 2 parts cation resin to 3 parts anion resin. In some cases, there may be chemical bonds formed between individual chain molecules at various points along the chain. Such polymers are said to be cross-linked. This type of polymer constitutes the basic structure of ion exchange resins. In particular, cross-linked polystyrene is the polymer commonly used in ion exchange resins. However, chemical treatment of polystyrene is required to give it ion exchange capability, and this treatment varies depending on whether the final product is to be an anion resin or a cation resin. All of the resin, except the exchangeable ion, is inert in the exchange process. Thus, it is customary to use a notation such as R-Cl or H-R for ion exchange resins. R indicates the inert polymeric base structure and the part of the substituted radical that does not participate in exchange reactions. The term R is inexact because it is used to represent the inert portion of both cation and anion resins, which are slightly different. Also, the structure represented by R contains many sites of exchange, although only one is shown by the notation, such as R-Cl. Despite these drawbacks, the term R is used for simplicity.

3.Discuss various membrane configuration with neat diagram

OR

What are the different ways by which the membrane modules can be configured to produce a plant of required separation capability?

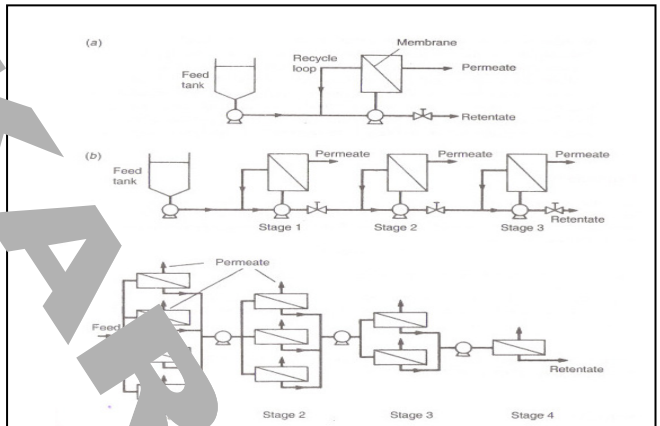

Figure 8.13. ...atic flow-di...ams of (a) Single-stage "feed and bleed", (b) Multiple-stage "feed and bl... (c) Continuous single-pass membrane plants

Membranes modules can be configured in three ways

1. single stage feed and bleed
2. multistage feed and bleed
3. continuous single pass as shown in figures

These three configurations can be explained with reference to the above figure.

4.Explain the following procerss

(a) Osmosis

(b) Reverse osmosis

Principle of Operation

When a solution and water are separated by a semi-permeable membrane, the water will move into the solution to equilibrate the system. This is known as osmotic pressure If a mechanical force is applied to exceed the osmotic pressure (up to 700 psi), the water is forced to move down the concentration gradient i.e. from low to high concentration. Permeate designates the liquid passing through the membrane, and retentate (concentrate) designates the fraction not passing through the membrane.

When two solutions of differing concentrations of dissolved materials are separated by a semi-permeable membrane, the liquid component will tend to flow from the lower to the more highly concentrated side. In a sense, the concentration difference will tend to equilibrate across the membrane. This process is called **osmosis**.

If the liquid on the more concentrated side is maintained at a higher pressure, however, this process can be reversed: the solvent will flow from the concentrated side to the less concentrated side. Since the membrane blocks the passage of the dissolved waste constituents, the concentrated solution becomes even more concentrated. This process is called **reverse osmosis**.

Reverse osmosis (RO) designates a membrane separation process, driven by a pressure gradient, in which the membrane separates the solvent (generally water) from other components of a solution. The membrane configuration is usually cross-flow. With reverse osmosis, the membrane pore size is very small allowing only small amounts of very low molecular weight solutes to pass through the membranes. It is a concentration process using a 100 MW cutoff, 700 psig, temperatures less than 40°C with cellulose acetate membranes and 70-80°C with composite membranes.
Reverse osmosis is often used to remove dissolved organics and metals where concentrations are less than 300 parts per million. However, special care and testing must be performed to assure that the wastes don't dissolve or clog the membrane. Low solubility salts are also prone to precipitate on the membrane surface.

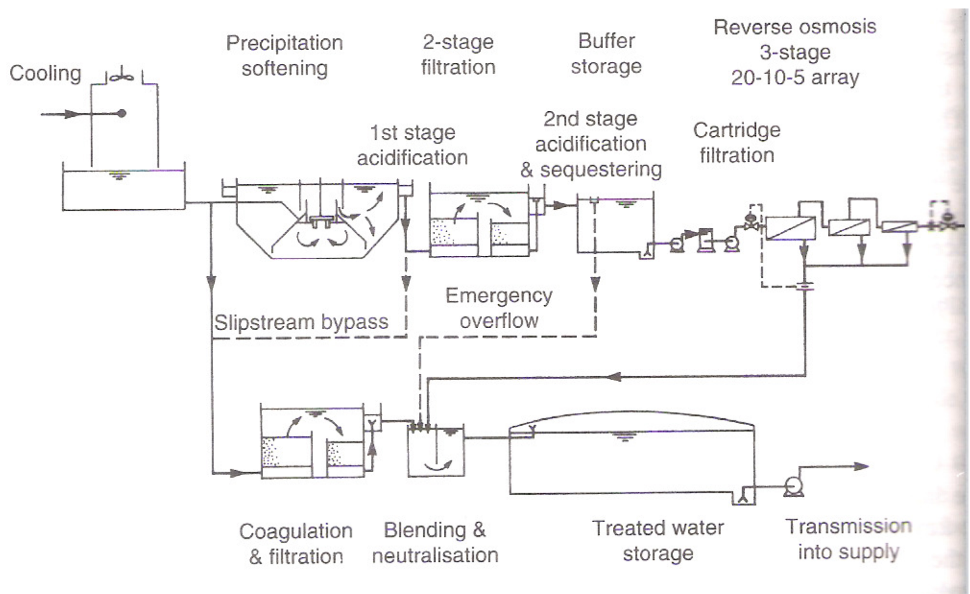

Figure Large scale RO plant for the demineralization of blackish water

5.Discuss electrodialysis process with industrial application

Electrodialysis

Ions in aqueous solution can be separated using a direct current electrical driving force on an ion-selective membrane. Electrodialysis usually uses many thin compartments of solution separated by membranes that permit passage of either positive ions (cations) or negative ions (anions) and block passage of the oppositely charged ion.

Cation-exchange membranes are alternatively stacked with anion-exchange membranes placed between two electrodes. The solution to be treated is circulated through the compartments and a direct current power source is applied. All cations gravitate toward the cathode (negatively terminal) and transfer through one membrane, while anions move in the opposite direction, thereby concentrating in alternative compartments.

Electrodialysis is commonly used to recover spent acid and metal salts from plating rinse. It obviously is not effective for non-polar solutions. Electrodialysis is used for demineralization of milk products and whey for infant formula and special dietary products. Also used for desalination of water.

Principles of operation:

Under the influence of an electric field, ions move in an aqueous solution. The ionic mobility is directly proportioned to specific conductivity and inversely proportioned to number of molecules in solution. ~3-6 x 10^2 mm/sec.Charged ions can be removed from a solution by synthetic polymer membranes containing ion exchange groups. Anion exchange membranes carry cationic groups which repel cations and are permeable to anions, and cation exchange membranes contain anionic groups and are permeable only to cations.Electrodialysis membranes are comprised of polymer chains - styrene-divinyl benzene made anionic with quaternary ammonium groups and made cationic with sulphonic groups. 1-2V is then applied across each pair of membranes.

Electrodialysis process:

Amion and cation exchange membranes are arranged alternately in parallel between an anode and a cathode (see schematic diagram). The distance between the membranes is 1mm or less.

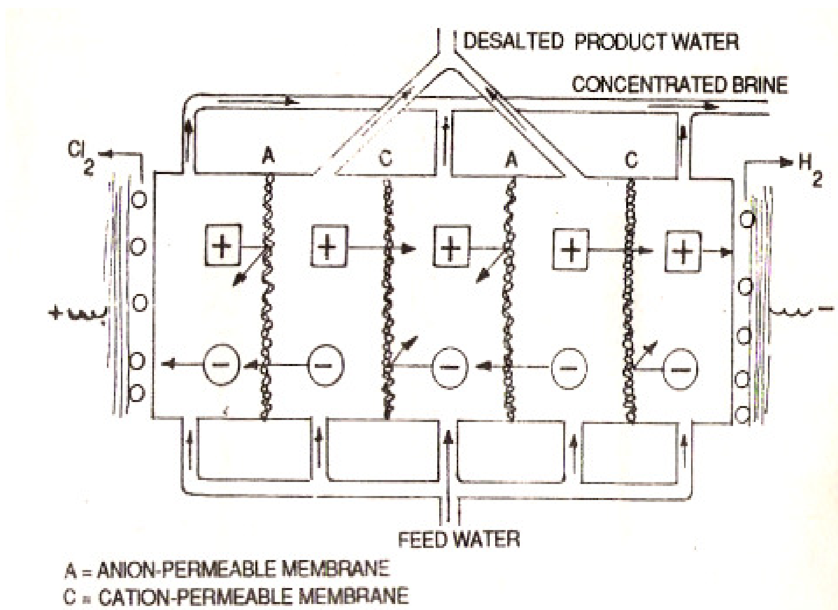

Figure: Schematic flow diagram for an electrodialysis stack

A plate and frame arrangement similar to a plate heat exchanger or a plate filter is used. The solution to be demineralized flows through gaps between the two types of membranes. Each type of membrane is permeable to only one type of ion. Thus, the anions leave the gap in the direction of the anode and cations leave in the direction of the cathode. Both are then taken up by a concentrating stream.

APPLICATIONS OF ELECTRODIALYSIS:

- Cheese whey demineralization
- Brackish water desalination
- Nitrate removal for drinking water
- Food/sugar products desalting
- Tartaric wine stabilization
- NaCl removal from amino acid salts
- Acid removal from organic product
- Conversion of organic salts into acid and base (bipolar membrane ED)
- Desalting of amines.
- De-acidification of fruit juices
- Metals removal from ethylene glycol

6.Miscellaneous uses of membrane separation -Discuss

The use of thin barriers (membranes) between miscible fluids for separating a mixture; a suitable driving force across the membrane, for example concentration or pressure differential, leads to preferential transport of one or more feed components.

Separations of liquids and gases are commonly accomplished using membrane separation methods which include dialysis, reverse osmosis, and ultrafiltration Hybrid and more exotic membrane methods that have also proven effective are electrodialysis, helium separation through glass, hydrogen separation through Palladium and alloy membranes, immobilized solvent and liquid-surfactant membranes. Permeation of liquids and gases through polymeric membranes occurs where a constituent passes through the membrane by diffusion and sorption by the fluid on the other side of the membrane. The driving force is achieve either by pressure or concentration difference across the membrane.

Uses of Membrane separation

In general, membrane separation techniques are especially useful in separating:

- Mixtures of similar chemical compounds,
- Mixtures of thermally unstable components (since no heating is needed), and In conjunction with conventional separation methods (such as using membranes to break azeotropic mixtures before feeding them)
- proteins can be separated in whey for the production of whey protein concentrate (WPC)

- milk can be concentrated prior to cheesemaking at the farm level

apple juice and wine can be clarified

- waste treatment and product recovery is possible in edible oil, fat, potato, and fish processing

- fermentation broths can be clarified and separated

whole egg and egg white ultrafiltration as a preconcentration prior to spray

Use of membrane separation to dry gas streams containing water vapor

Categories of membrane separation

Membrane separation processes are classified under different categories depending on the materials to be separated and the driving force applied:

(1) In ultrafiltration, liquids and low-molecular-weight dissolved species pass through porous membranes while colloidal particles and macromolecules are rejected. The driving force is a pressure difference.

(2) In dialysis, low-molecular-weight solutes and ions pass through while colloidal particles and solutes with molecular weights greater than 1000 are rejected under the conditions of a concentration difference across the membrane.

(3) In electrodialysis, ions pass through the membrane in preference to all other species, due to a voltage difference.

(4) In reverse osmosis, virtually all dissolved and suspended materials are rejected and the permeate is a liquid, typically water.

(5) For gas and liquid separations, unequal rates of transport can be obtained through nonporous membranes by means of a solution and diffusion mechanism. Pervaporation is a special case of this separation where the feed is in the liquid phase while the permeate, typically drawn under subatmospheric conditions, is in the vapor phase.

(6) In facilitated transport, separation is achieved by reversible chemical reaction in the membrane. High selectivity and permeation rate may be obtained because of the reaction scheme. Liquid membranes are used for this type of separation.

Ultrafiltration

Suspended materials and macromolecules can be separated from a waste stream using a membrane and pressure differential, called Ultrafiltration. This method uses a lower pressure differential than reverse osmosis and doesn't rely on overcoming osmotic effects. It is useful for dilute solutions of large polymerized macromolecules where the separation is roughly proportional to the pore size in the membrane selected. Ultrafiltration membranes are commercially fabricated in sheet, capillary and tubular forms. The liquid to be filtered is forced into the assemblage and dilute permeate passes perpendicularly through the membrane while concentrate passes out the end of the media. This may prove useful for the recovery and recycle of suspended solids and macromolecules.

Ultrafiltration (UF) designates a membrane separation process, driven by a pressure gradient, in which the membrane fractionates components of a liquid as a function of their solvated size and structure. The membrane configuration is usually cross-flow. In UF, the membrane pore size is larger allowing some components to pass through the pores with the water. It is a separation/ fractionation process using a 10,000

MW cutoff, 40 psig, and temperatures of 50-60°C with polysulfone membranes. In UF milk, lactose and minerals pass in a 50% separation ratio; for example, in the retentate would be 100% of fat, 100% of protein, 50% of lactose, and 50% of free minerals.

Excellent results have been achieved in textile finishing applications and other situations where neither entrained solids that could clog the filter nor dissolved ions that would pass through are present. Membrane life can also be affected by temperature, pH, and fouling.

Microfiltration

Microfiltration (MF) designates a membrane separation process similar to UF but with even larger membrane pore size allowing particles in the range of 0.2 to 2 micrometers to pass through. The pressure used is generally lower than that of UF process. The membrane configuration is usually cross-flow. MF is used in the dairy industry for making low-heat sterile milk as proteins may pass through but bacteria do not. Please click above link for a schematic diagram of these membrane processes.

7. Write about membrane fouling?

A limitation to the more widespread use of membrane separation processes is membrane fouling, as would be expected in the industrial application of very finely porous materials.

Fouling results in a continuous decline in membrane permeation rate, an increased rejection of low molecular weight solutes and eventually blocking of flow channels. On start-up of a process, a reduction in membrane permeation rate to 30–10 per cent of the pure water permeation rate after a few minutes of operation is common for ultrafiltration. Such a rapid decrease may be even more extreme for microfiltration. This is often followed by a more gradual decrease throughout processing. Fouling is partly due to blocking or reduction in effective diameter of membrane pores, and partly due to the formation of a slowly thickening layer on the membrane surface.

The extent of membrane fouling depends on the nature of the membrane used and on the properties of the process feed. The first means of control is therefore careful choice of membrane type. Secondly, a module design which provides suitable hydrodynamic conditions for the particular application should be chosen. Process feed pretreatment is also important. The type of pretreatment used in reverse osmosis for desalination applications . In biotechnological applications pretreatment might include prefiltration, pasteurisation to destroy bacteria, or adjustment of pH or ionic strength to prevent protein precipitation. When membrane fouling has occurred, backflushing of the membrane may substantially restore the permeation rate. This is seldom totally effective however, so that chemical cleaning is eventually required. This involves interruption of the separation process, and consequently time losses due to the extensive nature of cleaning required. Thus, a typical cleaning procedure might involve: flushing with filtered water at 35–50 .C to displace residual retentate; recirculation or back-flushing with a cleaning agent, possibly at elevated temperature; rinsing with water to remove the cleaning agent; sterilisation by recirculation of a solution of 50–100 ppm of chlorine for 10–30 minutes (600–1800s) at (293–303 K) (20–30 .C); and flushing with water to remove sterilising solution. More recent approaches to the control of membrane fouling include the use of more sophisticated hydrodynamic control effected by pulsated feed flows or non-planar membrane surfaces, and the application of further perturbations at the membrane surface, such as continuous or pulsated electric fields.