

Novel Technologies for Food Processing and Shelf Life Extension
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Lecture – 13
Membrane Technology - Part 1

In this lecture, membrane technology and its application in food processing will be introduced.

Membrane technology


- A recent development in food processing industry.
- Main criterion is size of molecules. Sometimes, surface charge may have some effect.
- Driving force is 'pressure differential'.

Shelf life extension ← Purpose → Processing or value addition

Membrane technology is a comparatively recent development in food processing industry. Major criterion of this technology is separation on the basis of size of the molecules. Sometimes even surface charge may also have some effect. The driving force is generally the pressure differential. There are two main purposes of this technology; processing or value addition and shelf life extension.


Membrane

- Basic unit of membrane technology is 'membrane'.
- Acts as a barrier - separates two phases.
- Acts as filtering medium – very effective as filters in separation and purification processes.
- Selective in nature (Semipermeable) – allows some materials to permit through while restricting the transport of various molecules in a selective manner.
- Permits separation of particles and molecules over a very wide range of size and molecular weights.
- Performs separation by a combination of sieving and diffusion mechanisms.




Of any membrane process, the basic unit or the heart of the process is the membrane. The membrane acts as a filtering medium and a barrier that separates the solution into two phases. It is semi permeable in nature; it allows some substances to pass through while restricting the transport of various molecules in a selective manner. It is very effective as filter in separation and purification processes. The membrane permits separation of particles of wide ranging size and molecular weights, and performs the separation by a combination of sieving and diffusion mechanisms.

Membrane separation process



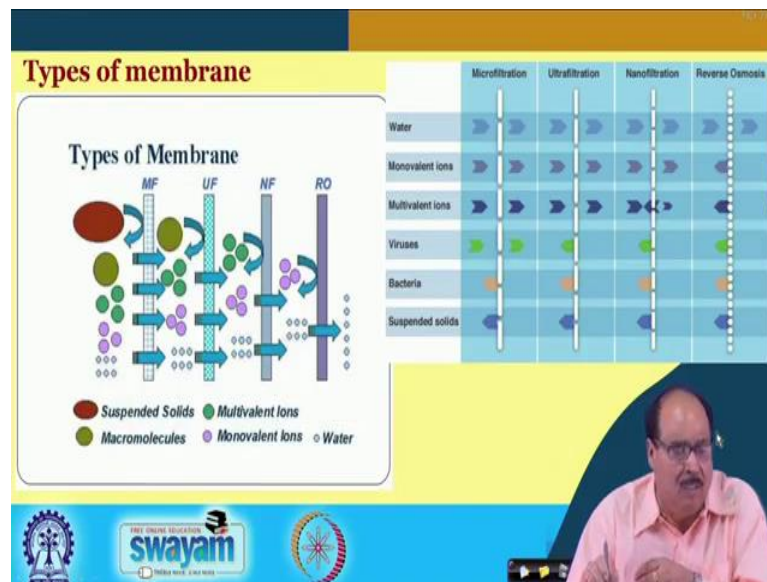
- Feed stream is divided into two streams
 - (i) Retentate
 - (ii) Permeate
- Either the concentrate (retentate) or filtrate (permeate) is the product of interest of any membrane filtration process.



The membrane separation process is shown in this figure, where it can be seen that, on one side of the membrane there is the feed material comprising of different solutes. The feed solution is forced with some pressure; a pressure differential between the upstream

and downstream is created that becomes the driving force for the passage of materials through the membrane. Here, mostly the solvent particles and some solutes have come in the permeate and major portion of the solutes are retained on the other side.

The component which is retained on the surface of the membrane is generally known as retentate whereas the solute or other components which are allowed to pass through by the membrane are normally known as permeate. So, the feed stream can be divided into two streams viz., retentate stream and permeate stream. So, it depends upon the process; either the concentrate (retentate) or the filtrate (permeate) is the product of interest of any membrane filtration process, sometimes even both the permeate and retentate may be of use. So, it is decided on the basis of the product and process that whether to collect retentate or permeate or whatever the case may be.



Depending upon the nature of the molecules or atoms which are to be separated by these processes there are different types of membranes:

- (1) Microfiltration membrane; it allows the passage of multivalent ions, macromolecule, monovalent ion, water, etc., but retain bacteria and all other suspended solids.
- (2) Ultrafiltration; viruses, bacteria, and other macromolecules are retained; multivalent ion and monovalent ions, water, etc. are allowed to pass through.
- (3) Nanofiltration; it allows the passage of only the monovalent ion and water
- (4) Reverse osmosis, it simply allows the passage of water and almost all the components are retained on the other side.

	Microfiltration (MF)	Ultrafiltration (UF)	Nanofiltration (NF)	Reverse Osmosis (RO)	Categories of pressure driven membrane processes
Pore size (μ)	$10^2 - 10^4$	$1 - 10^2$	$1 - 10$	$10^{-1} - 1$	
Operating Pressure (bar)	< 1	1 - 10	20 - 40	30 - 60	
Basis of rejection	Absolute size of particles (0.02-10 μ m)	MWCO ($10^3 - 10^5$ Da)	MWCO (200-1000 Da)	MWCO	
Solutes to be separated	Clay, paint, oil droplets, suspended matters, microorganisms	Pectins, proteins, high mol. wt. polyphenols, enzymes	Sugars, low mol. wt. polyphenols, dyes	Salts, electrolytes	
Purpose	Clarification or turbidity removal	Decolourization and purity increase	Concentration and desalination		

This is the table showing categories of the pressure driven membrane processes where the normal size spectrum, operating pressures, purpose, and basis of the rejection of each process has been reported.

In case of microfiltration (MF), the particles of size 10^2 to 10^4 μ are retained, whereas in ultrafiltration (UF), 1 to 10^2 μ , nanofiltration (NF) further is smaller 1 to 10 μ and reverse osmosis (RO) even further smaller pore size 10^{-1} to 1 μ . The operating pressure required in MF is less, may be less than 1 bar whereas in UF, 1 to 10 bar. NF may require more pressure may be 20 to 40 bar and RO processes need maximum pressure among all these membrane technology processes i.e. may be 30 to 60 bar or even 70 bar.

In MF process which is based on a sieving mechanism, the basis of the rejection is basically the absolute size of the particle. In other processes viz., UF, NF, and RO, the separation takes place on the basis of the molecular weight cut off (MWCO). Solutes like clay, paint, oil droplets, suspended matters, microorganisms etc. are retained by the MF membrane. In addition to these, pectin, proteins, high molecular weights substances, polyphenol, enzymes, etc. are separated in UF process. NF separates sugar, and other low molecular weight substances, polyphenol, dyes, etc. while salt and electrolytes are retained in case of RO.

The purpose of MF and UF processes are used for clarification or turbidity removal in general, whereas NF is used for decolourization and purity increase and the RO process is used for concentration and desalination processes.

Reverse osmosis (RO) or Hyperfiltration

Fig. 2: Principles of (a) osmosis (b) Reverse osmosis

- The contribution of any species to the total osmotic pressure (Π) is inversely proportional to its molecular weight .
- Small molecules such as salts & sugars contribute much more to the Π than do large molecules like proteins, etc.

Liquid	Average TS (%)	Osmotic pressure (bar)
Milk	11	6.7
Whey	6	6.7
Orange juice	11	15.3
Sea water	3.5	14.1
Casein solution	3.5	0.03
Apple juice	14	20.9

Suppose in a system, there are solution and solvent and if they are separated by a semi permeable membrane. The membrane is selective to solvent that it will allow the passage of the solvent, but not the solutes, then the flow will take place in a direction from the solvent to solution and the gradient for this flow obviously is the osmotic pressure exerted by the various solute particles. If a pressure higher than the osmotic pressure exerted by different solutes present in the solution is applied, then the direction of the flow can be reversed. So, this is known as reverse osmosis. Earlier case it was osmosis.

Any food material like water, orange juice or sea water, they contain different types of solutes. The solutes vary in their nature, in their size, and other characteristics. They all contribute towards the osmotic pressure of the system. In general, the contribution of any species to the total osmotic pressure is inversely proportional to its molecular weight. Smaller molecules such as salt and sugars contribute much more to the total osmotic pressure of the system than do the large molecules or macromolecules like protein, etc. For example, sea water and casein solution with the same amount of total solids (3.5%), there is a huge difference in the osmotic pressure of both, the sea water exerts 14.1 bar osmotic pressure whereas, the casein solution gives only 0.03 bar pressure. Similarly, milk and whey both exert same osmotic pressure of 6.7 bar approximately but the average total solids of milk is almost double than that of whey. So, the nature of the macromolecule particularly the molecular weight and size of the macromolecule majorly contribute to this.

Solvent transport through membranes


- Membrane performance can be described by two quantities: permeate flux rate and rejection rate (R)

$$R = \frac{C_f - C_p}{C_f}$$

- Solvent flux (J_p) is calculated by volume of filtrate collected per unit effective membrane surface area per unit time. Unit of permeate flux is m³/m²s

$$J_p = \frac{Q}{A \times \Delta t}$$

- Membrane permeability (L_p) is determined by permeate flux divided by applied transmembrane pressure (ΔP).

$$L_p = \frac{J_p}{\Delta P}$$


In solvent transport phenomena through membranes, two important properties should be considered. One is permeate flux and another is the rejection rate i.e. what is the amount of the permeate that is allowed to pass through the membrane and what are the components that are rejected by the membrane.

Rejection rate, R is equal to concentration of feed minus concentration of solutes in the product divided by concentration of solutes in the feed.

$$R = \frac{C_f - C_p}{C_f}$$

Solvent flux, J_p is calculated by the volume of filtrate collected per unit effective membrane surface area per unit time.

$$J_p = \frac{Q}{A \times \Delta t}$$

Membrane permeability, L_p is determined by the permeate flux that is J_p divided by applied trans-membrane pressure.

$$L_p = \frac{J_p}{\Delta P}$$

Factors	Change	Effect on flux	Factors controlling membrane processing
Membrane properties			
Pore size	Increase	Increase	
Thickness	Increase	Decrease	
Porosity	Increase	Increase	
Tortuosity	Increase	Decrease	
Compaction	Increase	Decrease	
Feed properties			
Concentration	Increase	Decrease	
Viscosity	Increase	Decrease	
Temperature	Increase	Increase	
Hydrostatic effect			
Trans-membrane pressure	Increase	Increase	
Cross flow velocity	Increase	Increase	

There are certain factors which govern the membrane separation process. Three major factors which influence the flux are membrane properties, feed properties, and hydrostatic effect. So, increasing membrane properties like pore size and porosity increases the flux, while the flux decreases by increasing thickness, tortuosity, and compaction. Regarding the feed properties, increase in concentration and viscosity of the feed, results in decrease in flux, whereas increase in temperature causes increase in the flux. Hydrostatic effects like trans-membrane pressure and cross flow velocity have a direct effect on flux.

Other flux expressions

- **Solvent flux** is proportional to pressure difference (applied pressure - osmotic pressure).

$$J_w = L_p \times A \times (\Delta P - \Delta \pi)$$
- **Hazen-Poiseuille equation**

$$J_w = \frac{d^2 \times \Delta \pi}{32 \times \mu \times L}$$

Where, d is capillary or pore diameter, μ is dynamic viscosity, and L is capillary length.
- **Model equation for flux**

$$J = \frac{(\Delta P - \Delta \pi)}{\mu (R_m + R_f + R_p)}$$

Where, R_m is membrane resistance, R_f is fouling resistance, and R_p is resistance of concentration polarization layer.

There are few other calculations which need to be taken into consideration for better process efficiency. Solvent flux is proportional to the pressure difference i.e. applied pressure minus osmotic pressure.

$$J_w = L_p \times A \times (\Delta P - \Delta \Pi)$$

From Hazen-Poiseuille equation, the solvent flux can be calculated by,

$$J_w = \frac{d^2 \times \Delta \pi}{32 \times \mu \times L}$$

Where, d is the capillary or pore diameter, μ is the dynamic viscosity and L is the capillary length.

Another model equation developed for the flux is:

$$J = \frac{(\Delta P - \Delta \pi)}{\mu (R_m + R_f + R_p)}$$

Where, R_m is membrane resistance, R_f is fouling resistance and R_p is resistance of concentration polarization layer.

Fouling and concentration polarization are the other important factors which influence the membrane separation process will be discussed separately in the next slides.

Types of membrane

1) **Based on material composition**

- **Inorganic membranes**
 - ✓ Can resist high temperature process streams.
 - ✓ Lowest pore size attainable is micron range.
 - ✓ **Examples:** Ceramic, alumina, zirconia, etc.
- **Polymeric membranes**
 - ✓ Temperature limitation, maximum 90 °C.
 - ✓ Can control the pore size, tune up to angstrom level.
 - ✓ **Examples:** Cellulose acetate (CA), polysulphone (PS), polyethersulphone (PES), polyacrylonitrile (PAN), polyvinylidene fluoride (PVDF).

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The membranes which are normally used in this membrane separation processes are categorized into two ways. One way is on the basis of the material of composition, by which the membranes are classified as inorganic membranes or polymeric membranes. Inorganic membranes can resist high temperature in the process streams. The lowest particle size attainable in this case is micron range. Examples of inorganic membranes include ceramic membrane, alumina, zirconium etc. Polymeric membranes have some sort of temperature limitation i.e. maximum temperature they can tolerate is 90 °C. Its pore size can be tuned up to the angstrom level. Examples of polymeric membranes include cellulose acetate membrane, polysulfone membrane, PS or PES, PAN, PVDF, etc.



2) In terms of developmental stage

- **1st generation membranes**
 - ✓ 1st membrane used in commercial scale was cellulose acetate (CA) membrane.
 - ✓ These are prepared as 0.1 - 1 μ thick skin; are held with thicker porous supports.
 - ✓ They are pH (2-8) dependent and limited to temperature (<40 °C).
 - ✓ Require very frequent cleaning due to problem of clogging.
- **2nd generation membranes**
 - ✓ Polymeric membranes which are made of polyamide (PA), PS, PAN, PVDF, etc.
 - ✓ These are much resistant to pH variations and higher temperature than CA membranes.
- **3rd generation membranes**
 - ✓ Development of inorganic materials like glass, metal, Al, Ti coated on a solid support.
 - ✓ They are tough, highly resistant to mechanical pressure, pH, temperature, etc.

The slide also features logos for 'THE INDIAN EDUCATION swayam' and 'INDIAN INSTITUTE OF TECHNOLOGY' at the bottom left, and a small video inset of a man in a pink shirt in the bottom right corner.

Another way of classifying these membranes is in terms of their developmental stage and by this way, the membranes are classified as 1st generation, 2nd generation and 3rd generation membranes.

First generation membranes used in the commercial scale was the cellulose acetate membrane. These are prepared as 0.1 to 1 μ thick skin held with a thick porous support. They are however pH dependent (2 – 8) and limited to temperature (up to 40 °C) Also, they require very frequent cleaning due to problems of clogging.

In 2nd generation membranes, most of the limitations of the 1st generation membranes are taken care of. These membranes are mostly the polymeric membrane which are made

of polyamide, PS, PAN, PVDF etc. These are much resistant to pH variations as well as higher temperature as compared to the CA membrane.

The 3rd generation membranes include inorganic membranes like glass, metal, aluminum, titanium coated on a solid support. They are tough, highly resistant to mechanical pressure, pH and temperature. So, they are very rough and they have the versatile applications.

Membrane configuration and modules

- A module is the simplest membrane element that provides support to the membrane.
- Module design must deal with the following issues.
 - Economy of manufacture
 - Minimum waste of energy
 - Membrane integrity against leaks and damages
 - Easy egress of permeate
 - Permit easy membrane cleaning

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A module is the simplest membrane element that provides the necessary support for keeping the membrane in normal place. Of course module design must deal with the aspects like economy of the manufacture. There should be minimum waste of energy, membrane integrity against leaks and damages, easy egress of the permeate and it should permit easy membrane cleaning. So, the membrane module should have these characteristics.

Modes of membrane filtration

Dead end

- Feed flow is perpendicular to the membrane surface.

Causes a large reduction in flux

Cross flow

- Flow of solution is parallel to the membrane surface.

Flow causes turbulence and produces shear

PERPENDICULAR VS. CROSS FLOW FILTRATION

There are basically two types of flow: one is the dead end flow; another is the cross flow. In the dead end flow, the feed flows perpendicular to the membrane surface. This type of flow normally is used in batch processes and it has some problems particularly regarding fouling and concentration polarization as the solute particles tend to get deposited on the surface of the membrane, causing a large reduction in flux.

These problems are reduced to a greater extent in the cross flow where the feed flows parallel to the membrane surface. Here flow causes turbulence and produces shear and thereby, making the surface resistant to pore blocking or concentration polarization.

Machinery & system

(a) Batch System

(b) Feed and bleed system

(c) Multistage Plant

CP = circulation pump

(a) Batch system

(b) Feed & bleed system

(c) Multistage plant

Handwritten notes:

Amount of permeate to be removed (19g)

$$Q_p = \left[\frac{177 - 171}{121 - 171} \right] \times Q_f$$

Let Q_p be the initial quantity of permeate

$171 = 3.71 \times \text{feed}$

$121 = 3.71 \times \text{retentate (total amount)}$

$171 = 3.71 \times \text{permeate}$ (48-49)

It was the invent of the cross flow system which facilitated the application of membrane technology in the industrial or commercial processes.

There are three types of systems batch system, feed and bleed system and multistage system. In the Batch system, with the help of a pump, the material is allowed to flow over the membrane module. There are pressure valves, necessary instrumentations for the temperature control, pressure control, pressure indicator, etc.

For example, suppose 100 kg tomato juice with 5 % total solids is to be concentrated up to 20 % total solids. In the batch process, one can calculate the amount of permeate to be removed using the formula,

$$Q_P = \frac{RTS - FTS}{RTS - PTS} \times Q_F$$

Where, FTS, RTS and PTS are the percentages of total solids in feed, in retentate, and in the permeate respectively and Q_F is the initial quantity of juice in kg. So, one can calculate the amount of water that can be removed from the juice and accordingly, the amount of desired concentrate can also be obtained.

In case of Feed and Bleed system, the materials are allowed to flow through the membrane module with the help of a circulation pump for some time. When this process system is stabilized, concentrate is allowed to flow at the same rate at which the feed is pumped in. So, a balance between concentrate going out and feed coming in is maintained.

In the multistage plant, several feed and bleed systems are put in series or in parallel. So, this improves the efficiency of the processes. They can be either continuous or batch systems.

Advantages of membrane technology

Pressure driven

Operate at low or ambient temperature

Membrane filtration

No phase change

Cost-effective

Provide specific separations

Membrane

Feed

Permeate

Particle or Solute Molecule

Solvent

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As the food industry is getting wide scope, the membrane technology has a great potential. The membrane filtration process provides specific separations like amino acids, fatty acids or any selective compound can be separated using this process. It is a pressure driven process that does not involve heat or temperature or any phase change. It is a non-thermal processes; the problems associated with the thermal processes are avoided here. This even operates at a low temperature or ambient temperature. It results in minimal destruction of the components or bioactives etc. that helps in preserving nutritional and sensorial qualities intact. So, again it is beneficial from the product quality or functionality point of view and it is a cost effective technology.

In the next lecture, further details of this, particularly types of the different modules and its application in food industry will be taken up.