Chapter 2

LITERATURE REVIEW

2.1 Natural rubber latex

The best-known plant latex, namely natural rubber latex, is a stable colloidal dispersion of *cis-1, 4-* polyisoprene. It has a high molecular mass in an aqueous medium with a specific gravity of 0.96 to 0.98 and a pH in the range of 6.5 and 7.0 [1]. Natural rubber latex is exuded from *Hevea brasilinesis* (Natural Rubber Tree) when the latex vessels found just outside the cambium are severed or tapped. It is a complex biological system. Apart from rubber hydrocarbon: the non-rubbers, which include sugar, proteins, lipids, carotenoids are all contained in an aqueous medium. Part of the protein and most of the lipids form a negatively charged protective layer, thus maintaining the stability of latex within the latex vessels. The composition of field latex (latex as obtained from trees) is given in Table 2.1.

Table 2.1 - Chemical composition of fresh latex

Constituent	Percentage by weight
Rubber	30 – 40
Proteins	1 – 1.5
Resins	1.5 – 3.0
Minerals	0.7 – 0.9
Carbohydrates	0.8 – 1.0
Water	55 – 60

Source: White and De, (2001) [1]

2.1.1 Rubber particle size and molecular weight distribution

The size of rubber particles in fresh natural latex varies from 20 to 5000 nm. Most of the volume of dispersed rubber in the latex is present in the form of a small minority of large particles. Thus less than 4% of the particles have diameter larger than 400nm. This minority of particle accounts for *ca.* 85% v/v of the total dispersed rubber and these large particles is formed by agglomeration and coalescence of small particles [2].

This large variation in particle size is evident from the molecular weight distribution study by Subramaniam [3]. Being a linear long chain polymer, natural rubber is composed of molecules of different sizes. The weight average molecular weight (M_w) of natural rubber ranges from 300,000 to about 10 million. A random blend would have an M_w of about 2×10^6 and a number average weight (M_n) of 5×10^5. A small portion of the rubber undergoes cross-linking even in the latex present within the latex vessels of the tree [1].

2.1.2 Natural rubber hydrocarbon

A typical composition for the rubber phase in fresh natural rubber latex is shown in Table 2.2 below. Trace metals, notably magnesium, potassium and copper, are also associated with the rubber particles to an aggregate extent of *ca.* 0.05% by weight. The density of the rubber particles is *ca.* 920 kg m^{-3}, this being determined principally by the density of the rubber hydrocarbon [1]. The rubber hydrocarbon in natural rubber latex is predominantly linear *cis*-1, 4-polyisoprene. The rubber hydrocarbon content is about 94%. The physical and chemical properties of the rubber are influenced by the presence of the non-rubber substances. The following provisos should be noted concerning this chemical description of the natural rubber hydrocarbon.

The description as a *polyisoprene* implies no more than that the structure is such as would be produced by the addition of polymerization of isoprene as shown in Figure 2.1, *n* being the number of repeating monomer (isoprene) unit to become a polymer (2-methyl, 1,3-butadiene) (CH_2: $C(CH_3)$. CH: CH_2) using an appropriate initiation system. There is no implication that the natural rubber hydrocarbon macromolecule is actually formed in this way [2, 3].

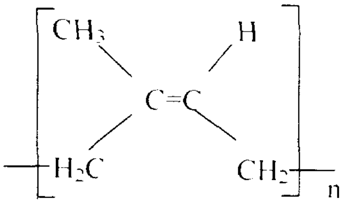

Figure 2.1 – Structure of NR Latex

The *1,4* refers to the mode in which the isoprene monomer units would have to combine by addition polymerization in order to produce a macromolecule like natural rubber hydrocarbon. The adjective *cis* implies that all carbon-carbon double bonds in the polyisoprene macromolecule have the *cis* configuration (as opposed to the *trans* configuration), i.e., that the disposition of the substituent group about each successive carbon-carbon double bonds is such that the polymeric chain substituent enters and leaves the double bond on the same side (as opposed to the opposite side) as that on which it entered.

Table 2.2 - Typical composition of rubber particles in fresh natural rubber latex

Constituent	**Proportion** (% by weight on whole latex)
Rubber hydrocarbon	86
Water (possibly dispersed in the rubber hydrocarbon)	10
Proteinaceous substances	1
Lipid substances	3

Source: White and De, 2001. [1]

2.2 Synthetic latex

Synthetic lattices (SL) are produced from the appropriate monomers by the chemical reaction known as emulsion polymerization. There are two types of SL namely: aqueous and non- aqueous. Non-aqueous SLs are also produced industrially by emulsion/dispersion polymerization in non-aqueous media. However, aqueous SL far exceeds non- aqueous SL as regards industrial importance [3]. The following aqueous synthetic lattices are industrially very important:

Styrene butadiene (SBR) copolymer lattices; Polychloroprene rubber lattices; Polyvinyl chloride lattices (PVC); Polyacrylonitrile lattices (PACN); Polystyrene lattices (PS). These lattices are formulated for specific use where the NRL becomes non-compatible.

2.3 The need to concentrate natural rubber latex

Natural rubber latex exudes from the *Hevea brasiliensis* tree having a rubber content of ca. 30 – 40% m/m, the average being ca. 33%. The remainder of the latex is mainly water. There are four principal reasons why it has become common practice to concentrate natural rubber latex before transportation [4, 7]:

It is uneconomical to transport preserved field natural rubber latex over large distances, because this would necessitate transporting a mass of water equal to approximately twice the mass of the dry rubber.

Several of the industrial processes, which use natural rubber latex, require it in a more concentrated form than *ca.* 33%. In particular, this is true of processes for the manufacture of latex foam rubber.

Natural rubber latex concentrates tend to be more uniform in quality than the field lattices from which they were obtained. This is mainly a consequence of the bulking and concomitant blending which precede and follow the concentration process. Differences between batches of field latex therefore tend to be mitigated.

The ratio of non-aqueous non-rubber substances to dry rubber is reduced in the course of some of the concentration process, because the non-rubber substances are preferentially eliminated. The product is, in consequence, a closer approximation to a colloidal dispersion of natural rubber in water than is preserved field natural rubber latex and closely approximates the characteristics required in several industrial processes. The normal practice is to concentrate the latex so that the dry rubber content is ca. 60% by weight or above.

2.3.1 Methods of concentrating natural rubber latex

Three methods of concentrations are currently used, namely, centrifugation, creaming and evaporation [4, 7]. Centrifugation is the preferred method and accounts for some 95% of the total concentrate produced in Malaysia. Creaming and evaporation produce the remaining 5%. In the centrifugation and creaming processes, about two-thirds of the water-soluble non-rubbers and some smaller particles present in field latex are removed. In the evaporation technique, only water is removed and therefore evaporated latex contains all the non-rubbers present in field latex and the particle size distribution is unaffected.

These three types of latex concentrates may be considered as general-purpose types. In addition, a range of special purpose NR lattices is available for special applications. This includes lattices concentrated by different techniques from those normally used and possesses lattices that are chemically modified. Some are available commercially, whilst others can be obtained by special arrangement with a latex producer. They include prevulcanised latex, twice or doubly centrifuged latex, freeze-thaw stable latex, methyl methacrylate grafted NR latex (Heveaplus MG latex), high dry rubber content centrifuged latex, and hydroxylamine-treated latex. Malaysia produces about three-quarters of the world's consumption of NR latex concentrate.

In the centrifugation process, ammonia-preserved blended field latex is fed into a centrifuge bowl rotating at a speed of about 7000 r.p.m. The design of the machine is such that under such condition an average centrifugal force equivalent to about 8000G is exerted on the latex particles and causes the latex to separate into two fractions: a rubber-rich less dense concentrate and denser skim latex. The settings on the centrifuge are adjusted so that the concentrate contains a minimum of 60% and the skim latex contains about 4% to 5% dry rubber content respectively.

In the creaming process, ammoniated field latex is treated with a creaming agent (ammonium alginate) and fatty acid soap and then clarified to remove sludge materials. The latex is heated to 40°C and then stored in bulk creaming tank. After a non-rubber constituents in the latex producing large amounts of acids. Under these conditions the protective protein/lipid layer gets disintegrated leading to the instability of latex: the latex thickens and coagulates with time. Thus, most of the naturally occurring changes in latex are attributed to the activities of bacteria [2.5.6].

It is common practice to add small quantities of preservatives to keep the latex fluid. If the latex is for concentrate production, the problem of keeping the latex fluid is even greater, as the build-up of volatile fatty acids (VFA) has to be arrested early. This is normally achieved by adding up to 1.0% (w/w) of ammonia. Ammonia, being a good biocide, has also several advantages: it controls the proliferation of acid-producing bacteria, neutralizes the free acid formed in the latex and helps in the precipitation of heavy metals such as magnesium, making the latex more stable. However, a high level of ammonia is undesirable, not only for economic reasons but also for practical difficulties involved in processing the resulting skim latex. It has further problems of smell and pollution.

Constituents of ammonia-preserved latex are proteins, higher fatty acid soaps (arising from hydrolysis of some lipids) and lipids (mainly neutral lipids). Under alkaline conditions, the higher fatty acids and proteins are ionized to yield negative charges: it is these electric charges on the surfaces of the rubber particles that are mainly responsible for the colloid stability of the latex. In simplified terms, electrostatic repulsion between two neighboring particles prevents them from coming into close approach (or contact) with each other. The detailed mechanism of repulsion is more complex than this and involves the ionic cloud of predominantly counter-ions (i.e. positive ions) surrounding each rubber particle (i.e. the electrical double layer). When two particles approach each other, the electrical double layers representative sample can be taken. This sample is referred to as laboratory sample and is used for coagulum content determination. For the other tests, it is necessary to filter the laboratory samples. The filtered samples are called test samples.

2.4.3 Dry rubber content (DRC)

The dry rubber content (DRC) is defined as the percentage by weight of latex, which is coagulated by acetic acid under closely, defined conditions. It is important to note that percentage DRC slightly exceeds the percentage rubber hydrocarbon content, as small quantities of various non-rubber constituents are co-precipitated with the rubber.

The standard method is as described in ISO 126:1982. The procedure involves dilution of a known weight of latex, coagulation of the latex by the addition of acetic acid, rolling of the coagulum into a thin sheet followed by drying of the rubber film in an oven until constant weight. This test is of great commercial significance as it determines the pricing of the latex concentrates.

2.4.4 Total solids content

The total solids content (TSC) is the percentage by weight of latex that is non-volatile at a definite temperature. The standard method is as described in ISO 124:1985. It involves heating a test sample to constant mass in an oven at 70°C or 100°C for 16 h or 2 h respectively at atmospheric pressure.

The difference between percentage TSC and percentage DRC gives a measure of the percentage non-rubber content. It is well known that the percentage TSC has a pronounced effect on mechanical stability. Lattices with high percentage of TSC have low mechanical stability time (MST) values and vice versa. This test also serves as a check for any possible slip-up by operators during compounding.

2.4.5 Alkalinity

Alkalinity means the free alkali content of latex, and is usually expressed as the percentage of ammonia in the latex. The method of determination is as described in ISO 125:1983. It involves the titration of latex to pH 6 in the presence of a stabilizer, either electrometrically or alternatively with methyl red as visual indicator, and calculation of its alkalinity from the quantity of acid which is required

2.4.6 Mechanical stability time

The MST of latex is defined as the time in seconds required for the coalescence of rubber particles to be initiated when the latex is subjected to high speed stirring under closely defined conditions.

The standard method is as described in ISO 35:1982. It involves dilution of a sample of latex to 55% TSC, equilibration of the latex at 35°C, stirring the diluted latex at 14 000 r.p.m. and finally recording the time in seconds required initiating visible flocculation.

MST gives a measure of the resistance of latex to destabilization by mechanical agitation or shear forces. Its value increases on storage and on addition of higher fatty acid soaps, the commonly used ones being ammonium or potassium laurate, or other stabilizing chemicals such as alkali (sodium or potassium hydroxides).

2.4.7 Volatile fatty acid number (VFA)

The volatile fatty acid number (VFA No.) is defined as the number of grams of potassium hydroxide equivalent to the volatile fatty acids in a latex containing 100 g of total solids.

The standard method is as described in ISO 506:1985. A test sample is first coagulated with ammonium sulphate. An aliquot of the resultant serum is separated and acidified with sulphuric acid. The acidified serum is steam distilled and the volatile acids, which are mainly acetic acid, are determined by titration of the distillate with a standard barium hydroxide solution. VFA No. gives a measure of the state of preservation of the latex. Low VFA numbers are indicative of good or adequate preservation and vice versa.

2.4.8 Potassium hydroxide number

The potassium hydroxide number (KOH No.) is the number of grams of potassium hydroxide equivalent to the ammonium forms of acid radicals in a latex containing 100 g of total solids. The standard method is as described in ISO 127:1984. It is based on the titration of the ammonium acid radicals in latex which has been partially de ammoniated with formaldehyde and diluted to 30% TSC with carbonate-free distilled water. The titration is carried out using 0.5M KOH solutions starting from about pH 9.5 to about pH 11. KOH No. gives the minimum quantity of KOH, which must be added to the latex in order to ensure virtual absence of ammonium ions and hence long-term latex stability in the presence of zinc oxide. No evidence, however, has been reported that relates KOH No. alone to processability or quality of latex.

2.4.9 Coagulum content

Coagulum content is defined as the percentage weight (on total solids) of the material, comprising pieces of coagulated rubber, latex skin and coarse foreign matter retained under the conditions of the test on a stainless steel wire cloth with an average width of 180 um or 85 mesh.

The standard method is as described in ISO 706:1985. The procedure involves dilution of 200 g of latex with an equal volume of 5% alkali soap solution followed by filtration of the diluted latex and drying to constant weight of the residue retained on the sieve. Formulation of coagulum in latex is an irreversible process. It is the result of destabilization influences e.g. overheating, poor latex stability, excessive agitation, etc.

2.4.10 Sludge content

Sludge content refers to the non-polymeric impurities in the latex, which tend to sediment under the influence of gravity. The standard method is as described in ISO 2005: 1985. It involves centrifugation of the latex followed by repeated washing of the resultant sludge with ammonia-alcohol solution and drying of the sludge to constant mass.

2.4.11 Determination of copper and manganese

The method used by the Rubber Research Institute of Malaysia (RRIM) is based on MS 3.35:1975. In this method, the latex is filmed, and digested in nitric acid. The absorbance of the solution at a selected wavelength, which is proportional to the concentration of the element of interest, is determined on an atomic absorption spectrophotometer.

Both copper and manganese in certain forms are known to catalyze the oxidative breakdown of NR. The mechanism by which degradation is brought about is not fully understood. It is recognized that other forms of copper or manganese can be present, even in relatively large amounts, without degradation taking place.

2.4.12 Viscosity

Although viscosity is not one of the specified properties of the ISO 2004:1979 specifications, it is a very important variable in the dipping process, as it has been correlated to film thickness.

The standard method is as described in ISO 1652:1985. It is based on the use of the Brookfield viscometer. As NR latex concentrates are pseudoplastic fluids, their viscosity decreases with increasing shear rate. To obtain a reliable estimate of the flow behaviour of the latex or its compound, it is necessary to measure viscosity values for at least two widely differing shear rates. All comparison of viscosity values must also be carried out at the same temperature, as viscosity is strongly temperature-dependent.

2.4.13 pH

Like viscosity, pH is not included in the ISO specifications. But it is a very important test from the standpoint of the dipping process. The pH values of the latex compound between batches are controlled to 9.5 ± 0.3 pH units as they have a significant influence on the stabilizing efficiency of all fatty acid soaps and the solubility of zinc oxide. These two factors, in turn, are correlated to latex stability. The standard method is as described in ISO976: 1986. Although it is a very simple test, round robin crosschecks among Malaysian laboratories showed very poor agreement and reproducibility of results. Accurate measurements of pH for NR latex require great care in maintenance, proper standardization and use of the pH meter.

2.5 Physico-chemical properties of latex concentrate

Natural rubber latex concentrates are very highly specified materials and a large measure of international agreement has been achieved regarding acceptable limits for their basic properties. The agreement is exemplified by the specifications published by the International Standards Organisation (ISO) [1, 7].

Full details of all these specifications and the summary of the ISO requirements and specifications for various types of natural latex concentrate are as shown in Table 2.3

The latex properties of chief significance to the user are dry rubber content (DRC), non-rubber solids (NRS) content, the mechanical stability time (MST), the volatile fatty acid number (VFA), the potassium hydroxide (KOH) number, and the alkalinity.

Table 2.3 The ISO 2004 requirements for centrifuged and creamed latex concentrates

	HA	LA	HA	LA
Total solids content (%) (min)	61.5	61.5	66.00	66.00
Dry rubber content (%) (min)	60.00	60.00	64.00	64.00
Non-rubber solids (%) (max)	2.00	2.00	2.00	2.00
Alkalinity (as NH_3) (on latex)	0.6 (min)	0.29 (min)	0.55 (min)	0.35 (min)
Mechanical stability (s) (min)	650	650	650	650
Coagulum content (%) (max)	0.05	0.05	0.05	0.05
Copper content (mg kg of solids) (max)	8	8	8	8
Manganese content (mg kg of solids) (max)	8	8	8	8
Sludge content (%) (max)	0.10	0.10	0.10	0.10
Volatile fatty acid number	>0.20	>0.20	>0.20	>10.20
Potassium hydroxide number	>1.0	>1.0	>1.0	>1.0
Colour on visual inspection		No pronounced blue or grey		
Odour after neutralization with boric acid		No pronounced odour of putrefaction		

Source: Gazeley, Gorton and Pendle, 1998 [7]

2.6 Natural rubber latex stability

Immediately on tapping and during collection, latex becomes contaminated by bacteria and yeasts, which mostly originate from the tapping panel, tree lace and tapping cup. They multiply rapidly under tropical conditions at the expense of the non-rubber constituents in the latex producing large amounts of acids. Under these conditions the protective protein/lipid layer gets disintegrated leading to the instability of latex: the latex thickens and coagulates with time. Thus, most of the naturally occurring changes in latex are attributed to the activities of bacteria [2.5,6].

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NR latex could be destabilized by physical or chemical means. The former include heating, freezing, mechanical agitation and removal of water by evaporation. Chemical means of destabilization include addition of acids, salts particularly multivalent ions such as calcium, magnesium, iron and aluminium, cationic surfactants and polymers, and water-miscible organic solvents [3].

2.7 Latex concentrate preservation system

2.7.1 Normal preservation system

NR latex concentrates need to be preserved with suitable preservatives to inhibit bacterial growth, [7, 8] which would destabilize the latex and ultimately result in spontaneous coagulation. Centrifuged or creamed latex concentrates are normally preserved with 0.7% ammonia on latex weight to give high ammonia (HA) latex or 0.2% ammonia to give low ammonia (LA) latex. For the latter type, a secondary preservative is required. Ammonia-free concentrates are usually preserved with a fixed alkali e.g. evaporated latex. Ammonia is the preferred preservative because it is volatile and leaves no residue in the produce.

2.7.2 Composite preservation system

Natural rubber latex as it emerges from the tree is sterile. Subsequent exposure to the environment and bacterial contamination results in acids being produced. This leads initially to putrefaction. When acids are produced in sufficient quantities, auto-coagulation takes place. The time lapse between tapping and the onset of thickening of latex is usually about 6 hours. This period is inadequate to allow for transportation of latex to factories and subsequent processing. It is essential therefore to preserve the field latex effectively especially if it is intended for latex concentrate production. Until recently, ammonia (NH_3) was exclusively used for preserving field latex intended for latex concentrate production. The volatile fatty acid (VFA) build-up in the latex is arrested by adding 0.4% - 1.0% ammonia. However, experience has revealed that even with the enforcement of strict hygiene both in the field and factory followed by early and adequate ammoniation and processing with minimum delay, the behavior of the latex concentrate is sometimes unpredictable. It has been shown that pretreatment of ammoniated field latex with a composite system consisting of TMTD and ZnO can maintain the latex for a considerable period with no rise in VFA number and ensure a good quality concentrate [5, 6]. This pretreatment has now been exploited commercially for both high ammonia (HA) and low ammonia (LA) concentrate production.

2.7.3 Preparation of the composite preservation system

Both TMTD and ZnO are from commercial sources that conformed to the specifications. In all the commercial trials TMTD in powder form was used. The formulation used for the preparation of the composite system to give a 25% solids content is as follows:

Table 2.4 Composition of composite preservation system

Constituents of composite preservation system	Composition
Water	75 parts
Sodium hydroxide (Analar grade)	0.013 parts
Dispersing agent (Dispersal LR grade, VULTAMOL, etc.)	0.025 parts
TMTD and ZnO	12.5 parts each

Source: Rama Rao, John and Ng, 1976 [5]

The water was first added and the chemicals were dispersed in the above order in a suitable plastic or stainless steel container (not aluminium). High-speed stirring (about 500 r.p.m.) for about 10 minutes gave a satisfactory dispersion. In some instances, manual stirring with a paddle was used for satisfactory results. Alternatively, a fine dispersion can be prepared by ball milling the ingredients for 10 hours and this can be stored for several weeks provided that it is agitated briefly before use to prevent settling.

Table 2.5 below gives various preservation system used for centrifuged latex concentrate and their market share in the world.

Table 2.5 Types of preservative systems used in centrifuged NR latex concentrate

Designation	Abbreviation	Market share (%)	Preservative system (% by weight)
High or Full ammonia	HA	66	0.7% ammonia
Low ammonia TZ	LA-TZ	17	0.2% ammonia, 0.025% zinc oxide, 0.025% tetramethylthiuram (TMTD) disulphide
Low ammonia pentachlorphenate	LA-SPP	6	0.2% ammonia, 0.2% sodium pentachlorphenate
Low ammonia boric acid	LA-BA	5	0.2% ammonia, 0.24% boric acid

Source: Gazeley, Gorton and Pendle, 1998 [7]

2.8 The need for alternative method of natural rubber latex concentration

2.8.1 Concentration by centrifugation is non-environment friendly

The widely used concentration by centrifugation produces skim latex as a by-product. Skim rubber processing involves the recovery of 4-5% of dry rubber by cheap grade sulphuric acid coagulation. The use of this acid makes the biological treatment of effluent difficult. Aerobic and anaerobic ponds situated next to the latex concentrate factory take the bulk of the effluent discharged. At the anaerobic pond the sulphate ion (SO_4^{2-}), which was derived from the sulphuric acid is converted to poisonous, hydrogen sulphide gas (H_2S), which has a pungent smell. This gas is released once a heavy downpour disturbs the scum top layer of the pond. This smell persists for a long period and affects the environment of the surrounding areas leading to a chain of events. The offensive odour has caused the relocation of some of the factories or ordered to close down by the Department of Environment. Throughout the country there are more than 100 latex concentrate factories and the combined effect would be quite disastrous, thus making natural rubber latex processing non-environmentally friendly [8, 9].

2.8.2 Pharmaceutical raw materials from latex

Scientists at Rubber Research of Malaysia (RRIM) had long known that the non-rubber portion of latex (5% w/w) contains numerous pharmaceutical raw materials. The largest single component of water-soluble substance is a carbohydrate family called Quebrachitol [10, 11], which is a chemical feedstock for the synthesis of a range of bioactive material. Researchers at the RRIM have developed an economically feasible method for extracting this product from the serum, which comprises about 23% by weight of the total non-rubbers. Kilogram quantities of pure Quebrachitol are now readily available. If all the serum from NRL processing could be tapped the income from biochemical extraction could be many folds [12-15].

8.3 Suitable processing technology to achieve zero discharge

A suitable processing technology needs to be developed to separate the aqueous phase from the hydrocarbon part of the latex, which is called serum. Thus the serum contains all the non-hydrocarbon component of latex, which accounts for about 5% of the total weight of the latex. The separation process should totally avoid producing im latex, which is a colloidal mixture of serum, and low dry rubber content (5%) ex. The processing technology should ideally be capable to separate serum from ex so that both products can be economically utilized i.e., latex concentrate used r latex product manufacturing and serum for biochemical extraction. This process uld eventually pave the way for zero discharge thus making latex processing more vironmentally friendly [16].

In this respect membrane separation technology, in particular ultrafiltration could come an alternative method of concentrating natural rubber latex and synthetic ex, which unlike centrifugation can produce concentrated latex and a clear serum. gineers in this field have long recognized ultrafiltration as a possible separation ethod. The major difficulties encountered in this endeavor are latex instability and itable membrane material [16-20].

.9 Membrane separation technology

A membrane is a selective barrier that permits the separation of certain species a fluid by a combination of sieving and sorption diffusion mechanisms. embrane separation processes are classified according to the driving force ministered, namely: pressure, electrical potential, concentration gradient and rtial pressure [21]. The scope of this study investigates pressure as the driving ce and evaluates the possibilities of using the pressure driven mechanism, such as crofiltration, ultrafiltration, and nanofiltration and reverse osmosis to concentrate tural rubber latex. The principal differences between each of the pressure driven ocesses are as shown in Table 2.6.

Membranes are usually made of a synthetic polymeric material as summarized in ble 2.7. They were formed from a liquid solution using a casting or spinning ocess. Microfiltration (MF) consists of membranes with pore sizes ranging from out five microns down to ca. 0.01 micron (µm). Ultrafiltration (UF) membranes the next finer type of membrane filter. The openings in an ultrafiltration embrane range from about 0.01 µm to 0.001 µm or less. In fact, it is customary to er to ultrafiltration membranes by a molecular weight cutoff size rather than a pore opening size. A molecular weight cutoff number designates the molecular weight the smallest molecules that would be rejected by the membrane. Such numbers approximations, as the actual rejection will be influenced by the size and shape of molecule as well as the weight. Typical molecular weight cutoffs for rafiltration membranes will range from 5,000 to 150,000. Thus, the membrane ll reject all macromolecules and suspended solids. Ultrafiltration membranes are o given "nominal" ratings that refer to the MW of a test solute that is 90% rejected the membrane under standard conditions. Dissolved salts will pass through the embrane. Nanofiltration (NF) membranes have pores between 0.0015 and 0.0025 n. NF separation process requires a lower transmembrane pressure and generally s a higher permeate flux compared to reverse osmosis (RO). Most multivalent ions l^{3+} and Cr^{3+}) can usually be retained by NF membranes. RO is a membrane (pore e < 0.001 µm) separation process that is even more selective than ultrafiltration. In erse osmosis, dissolved materials are rejected as well as the larger particles are o rated by the percent salt rejection. In all of the types of membrane filtration ntioned mentioned above pressure is the driving force, just as in conventional ration. The operating pressures for microfiltration and ultrafiltration generally are ween 0.5 and 15 bar. The operating pressure of reverse osmosis is generally ween 30 and 60 bar (Table 2.6) [22, 23].

ble 2.6 Principal differences between types of membrane separation, which use pressure as the driving force

o.	Parameters	Reverse Osmosis	Nano filtration	Ultra filtration	Micro filtration
1	Pressure (bar)	30-60	8-40	0.5-15	0.5-3
	Pressure (psi)	400-800	120-600	5-220	5-45
2	Cross flow (m/s)	2-3	2-3	3-4	3-8
	Cross flow (ft/s)	6-9	6-9	9-12	9-24
3	Flux (L/m2.hr)	5-40	20-80	3-200	50-500
4	Retention	>90% NaCl solution	>95% lactose solution <50% NaCl solution	0.01 to .001µm (>4kD size) particles <500 kD size particles	>0.01µm size particles <5µm size particles

urce: Zydney, 1996 [23]

10 Terminology in membrane separation process

The rate at which the molecules including solvent pass through the membrane ermed as flux. A rejection coefficient R (ratio no unit) is a measure of how well a mbrane retains or allows passage of a solute (Figure 2.2). When based on ncentrations in bulk of the permeate and retentate streams, it is the "apparent" ection. The "intrinsic" rejection is based on concentrations at the membrane face. Rejection coefficient R is given by:

$$R = \frac{Cf - Cp}{Cf} = 1 - \frac{Cp}{Cf} = 1 - \frac{Cp}{Cm} \qquad (2.1)$$

lectivity can be explained as the way in which a membrane can offer a barrier, ich is harder for some molecules to pass than others. Selectivity, S is given by:

$$S = \frac{Cp}{Cf} \qquad (2.2)$$

Where: Cp is the concentration of solute in the feed stream

Cf is the concentration of solute in the permeate.

Cm is the concentration of solute at the membrane

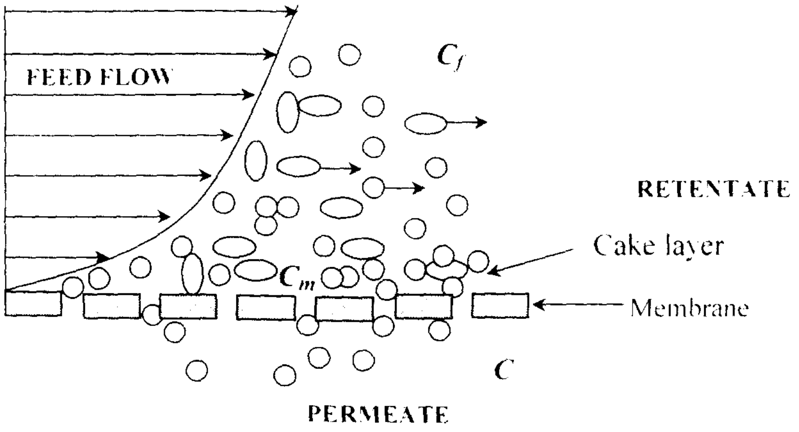


Figure 2.2. Schematic representation of membrane separation process

1 Cross-flow filtration system

The process of cross-flow pressure-driven membrane filtration requires only the mping of the feed-stream tangentially across the appropriate membrane, i.e., allel to the membrane surface (Figure 2.3). The membrane splits the feed stream o two streams: one stream is the permeate, consisting of components small enough pass through the membrane pores; the other stream is the concentrate (retentate) nsisting of components large enough to be retained by the membrane. The entate stream is usually recirculated through the membrane module because one ssage through the membrane may not deplete the feed significantly. Important erating variables are applied transmembrane pressure and cross-flow velocity ough the membrane module. Cross-flow velocity is the average rate at which the cess fluid flows parallel to the membrane surface. Velocity has a major effect on permeate flux. The permeate flux depends on the applied transmembrane ssure for a given surface area up to a threshold transmembrane pressure. Above s pressure, which has to be experimentally determined for each application, higher ssures have little or no effect. In fact, too high a pressure may aggravate fouling the membrane.

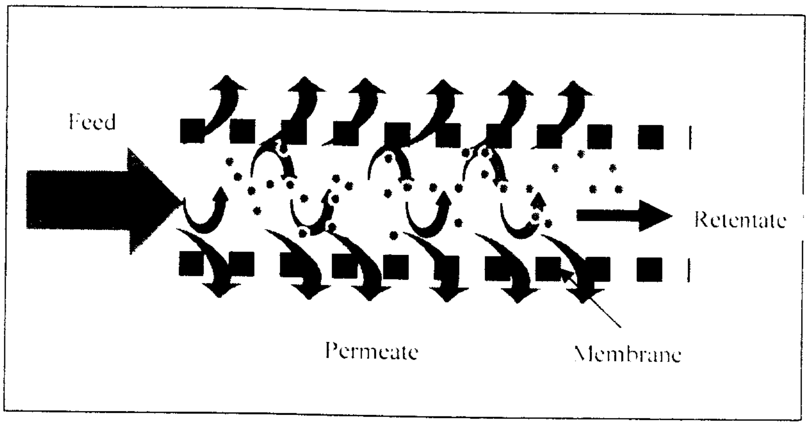


Figure 2.3 -The concept of tubular cross-flow ultrafiltration system

2 Membrane material

One of the earliest set-back of using membrane separation technology was ding suitable membrane material for specific applications. However the fast pace research development has resulted in finding various types of polymeric material signed for specific work. The choice of a particular membrane can be considered tical in order to achieve excellent performance. There are a number of criteria that st be satisfied on a particular choice of material or the polymer:

i) Must have suitable properties for the targeted applications
ii) Has to be compatible with the selected membrane formation technology
iii) Has to be available and affordable
iv) Has to be a good membrane former.

The early generation of membranes was made from cellulose acetate. However e to its limitation of usage in a narrow range of temperature and pH plus poor emical resistance character (especially to chlorine), other polymeric membranes re made. Membranes made from polyamide (PA), polysulfone (PS), polyether fone (PES) were developed to possess the following characteristics:

i) Work at wide range of temperature (25°C -125°C):

ii) Wide pH tolerances (1-13)

iii) Fairly good chlorine resistance (200ppm chorine for cleaning)

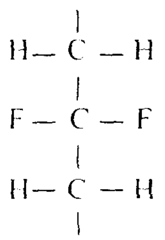
iv) Easy to fabricate membranes in a wide variety of configuration and modules

v) Good chemical resistance.

The main disadvantages of PS and PES are apparent low-pressure limits (7bar), drophobicity, which makes it prone to fouling, compared to CA. More recent mbranes include polyvinylidene flouride (PVDF), polytetrafluoroethylene FE), polypopylene(PP) and regenerated cellulose(RC). PVDF membrane has od chemical resistance (pH 1-13), although hydrophobic, it can be surface dified to be more hydrophilic so that its surface can be wetted and has better istance to chlorine than PS. PTFE membrane has good chemical resistance, can be ed for wide range of temperature (-100°C to 260°C), very hydrophobic and is well ted for the treatment of organic feed solutions. In order to develop tailor-made mbranes the properties of a material and of the membrane prepared from this terial must be studied in relation to the application [22, 23].

2.1 Surface modified membrane

The materials from which surface modified membranes are manufactured ve been selected on their ability to form a physically and chemically stable ucture with the requisite removal ability and good transmembrane flow/pressure op characteristics. The most common state-of-the-art materials are polyamides. lysulphones. PVDF and PTFE for microfiltration and ultrafiltration. Figures 2.4 d 2.5 show the structures of PVDF before and after modification [24].



ure 2.4 - Unmodified hydrophobic PVDF embrane

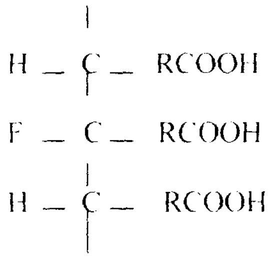


Figure 2.5- Modified hydrophilic (water wettable) PVDF membrane

e membrane market needs and awareness for membranes have become more manding, so membrane manufacturers have striven to produce more sophisticated oducts to meet specific requirements. In the area of critical microfiltration and rafiltration some of the most important developments have related to surface aracteristics in the form of: modified surface charge; low protein adsorption; drophobic/hydrophilic interaction. Table 2.7 is a summary of the most important lymeric membrane materials used today in pressure driven processes.

Table 2.7 - Materials for commercial polymer membranes

Material	Processes
Polypropylene (PP)	MF
Polytetrafluoroethylene (PTFE)	MF
Polyvinylidenefluoride (PVDF)	MF, UF
Cellulose nitrate (CN)	MF
Cellulose acetate (CA)	MF, UF, RO
Cellulose triacetate (CTA)	RO
Aliphatic polyamide (Nylon 6, Nylon 66)	MF, UF
Aromatic polyamide	MF, UF, RO
Polysulphone (PSp)	MF, UF
Polyethersulphone (PES)	MF, UF
Polyimide (PI)	MF, UF, RO
Polybenzimidazole (PBI)	RO
Polyetherimide (PEI)	MF, UF
Polyvinylalcohol (PVA)	MF, UF
Polyacrylonitrile (PAN)	UF
Polyacrylonitrile polyvinylchloridecopolymer (PAN/PVC)	MF, UF
Polycarbonate (PC)	MF
Polyetheretherketone (PEEK)	MF, UF

Source: Zydney, 1996) [23]

2.2 Suitable membrane material for NRL concentration

One of the early setbacks of using membrane separation to concentrate natural ber latex was finding a suitable membrane material. The membrane must be hly chemical resistant so that it could withstand a high pH of between11-12 when nstantly in contact with highly alkaline latex preservative: ammonia hydroxide of by volume. The membrane cleaning solution of 0.2% sodium hydroxide could ll reach a pH of 12. High solid content of NRL with NR hydrocarbon, and proteins varying molecular weight could easily foul any chemically resistant hydrophobic embranes. With the advent of robust polymeric membrane such as PVDF with its gh chemical resistance and its uniqueness which some fouling data may appear ntradictory this membrane appear to absorb or foul less with protein compared to S, PS and CA membrane [22, 23]. The main foulant for NRL appear to be the high olecular weight protein found as a component of rubber portion of the latex [22].

13 Concentration polarization

Concentration polarization (CP) is an additional complication that arises when acromolecules such as proteins and other relatively large solutes or particles are ered. These compounds, being largely rejected by the membrane, tend to form a er on the surface on the membrane. Depending on the type of solid, this layer uld be fairly viscous and gelatinous. Thus, a further resistance to the flow of rmeate is encountered, in addition to those of the membrane and the boundary er. This additional layer of solute is known by various terms such as the "gel er", "CP layer", "cake", or "polarization layer". This layer is different from the uling layer that occurs because of membrane-solute interactions [22].

Reduction in flux occurs by one of the two mechanisms: in one view, the reased solute concentration on the membrane surface results in a significantly gher osmotic pressure, causing a decrease in the driving force and flux. While this y be valid for reverse osmosis of small molecules in solution, osmotic pressures ring MF and UF are generally small because of the large molecular sizes of the ected solutes. However, osmotic pressure within the polarized layer could become portant if the local solute concentration is high enough, because of the importance the second and third virial coefficients in the osmotic pressure.

The alternate view is that the lower flux in polarization-limited systems is due to hydrodynamic resistance of the boundary layer. Initially, as a result of nvective transport of solute to the membrane solute buildup will cause a steep ncentration gradient within the boundary layer. This causes a back-transport of the ute into the bulk because of diffusion. Eventually, a steady state is reached where two phenomena balance each other. Solute concentration in the gel layer reaches naximum: i.e., no more solute molecules can be accommodated because of the ose-packed" arrangement and restricted mobility of solute molecules. This ncentration, if high enough could cause the solute to precipitate out and foul the mbrane. It is because of this consolidated particle or "gel" layer on the membrane it flux becomes independent of pressure. Increasing the transmembrane pressure rely results in a thicker or denser solute layer. After a momentary rise, the flux ll drop back to the previous valve. Initially, at low pressure, shear and lift forces re sufficient to minimize particle deposition, and the flux increased linearly with ssure. As soon as the particles started to deposit on the membrane (at 0.3 bar), the e of increase in flux decreased. Further increases in pressure increased the ckness of the particle layer without a corresponding increase [22, 23].

4 Module design and membrane configurations

The currently available commercial membrane modules can be classified into e distinct types: hollow fiber, tubular, flat plate (plate-and-frame), spiral wound, d vortex flow (e.g. rotating). There are also a number of different module designs

ed in dead-end filtration applications. Some of the important characteristics of the
ss-flow modules are summarized in Table 2.8. Hollow fiber and spiral wound
dules have the highest membrane packing densities since they have the thinnest
annels. However, this makes them more susceptible to particulate plugging, and it
n also make cleaning more difficult. Note that the values provided in Table 2.8 are
erages based on the available data for typical membrane processes. The modules
n be designed and operated well outside of the ranges listed in Table 2.8 for
ecialized applications [22, 23].

ble. 2.8 Comparison of different module configuration

odule nfiguration	Channel spacing (cm)	Packing density (m^2/m^3)	Energy costs (pumping)	Particulate plugging	Ease of cleaning
llow fiber	0.02 – 0.25	1200	Low	High	Fair
bular	1.0 – 2.5	60	High	Low	Excellent
t plate	0.03 – 0.25	300	Moderate	Moderate	Good
iral wound	0.03 – 0.1	600	Low	Very high	Poor – Fair
tating	0.05 – 0.1	10	*	Moderate	Fair

Energy costs in the rotating systems are determined largely by the rotation speed
stead of the pumping.
urce: Zeman and Zydney, 1996 [23]

4.1 Hollow fiber

Bundles of fibers (containing 50 – 10,000 fibers) are potted at the ends in an
oxy or polyurethane resin to form a tube sheet, which is machined to expose the
en bores (lumens) of the fibers. Most UF and MF devices use a parallel array of

›ers potted in separate tube sheets at each end of the unit [23]. This arrangement is alogous to that used in a shell-and-tube heat exchanger. An O-ring is placed ›und the epoxy tube sheets to form an effective seal within the cylindrical plastic using (the shell), thereby insuring complete separation of the feed and permeate eams. These modules are generally operated with the feed flow into the fiber nen, with the permeate moving radially outward through the fiber walls ("inside-t" filtration). This allows the devices to be operated at higher transmembrane essures since many UF and MF membranes have greater structural stability when flow is directed radially outward from the lumen. The cartridge is typically uipped with a single feed inlet, a process (retentate) outlet, and two permeate ports ne near each end of the unit). The feed and permeate can be designed to flow either - or counter-currently [22, 23].

14.2 Tubular devices

The tubular membranes are not self-supporting (with the exception of some ›rganic membranes). The membranes are usually kept in place within a porous pport tube made of fiberglass, ceramic, plastic, or stainless steel. The individual ›es can be placed inside a plastic or stainless steel sleeve to form a single tube rtridge or they can be packed together in small bundles, which are kept in place ing an appropriate end plate (Figure 2.6). The feed flows through the bore of the

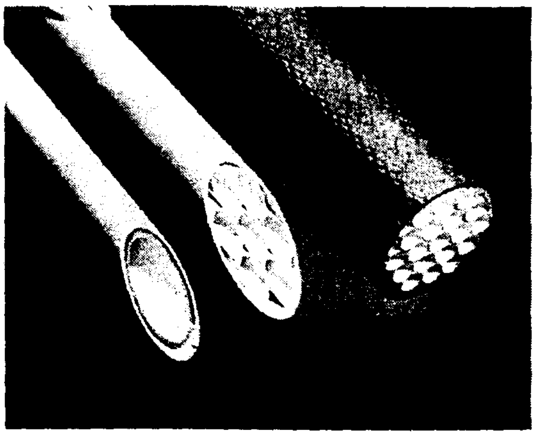
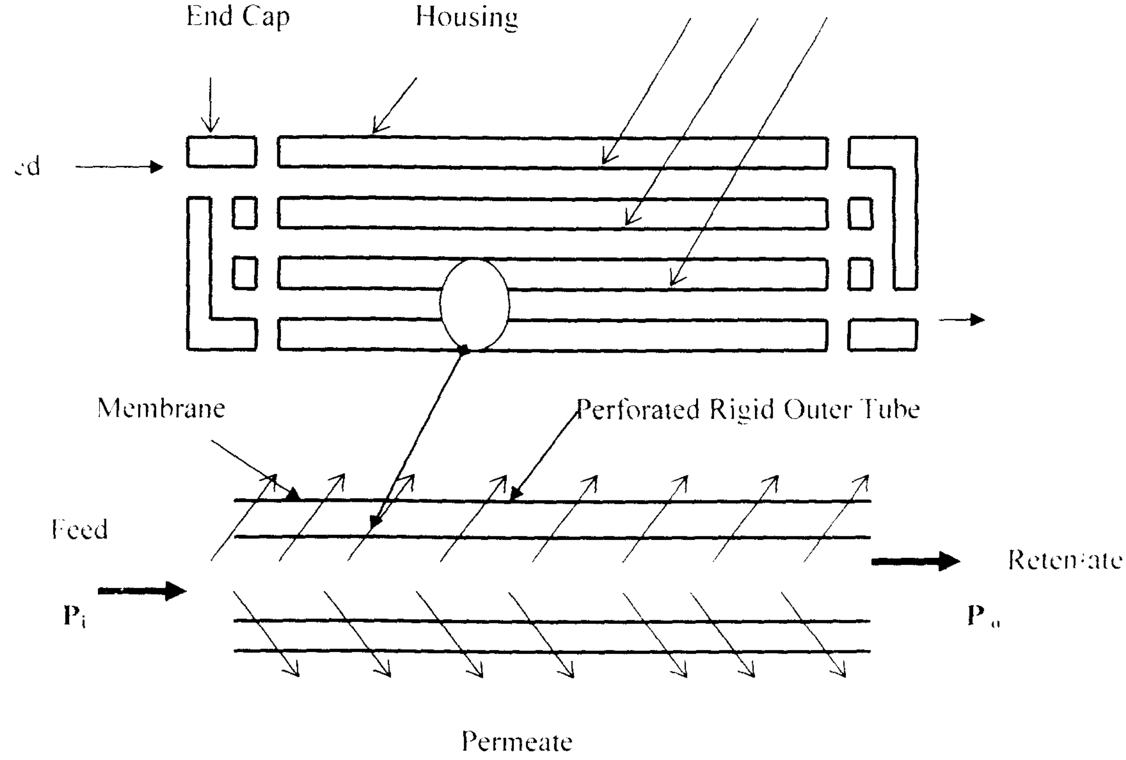


Figure 2.6 – Tubular UF/MF membranes enclosed in a module
Source: Cheryan, (1998)[22]



gure 2.7-Schematic of a tubular membrane designed for ultrafiltration applications
urce: Cheryan, 1998 [22]

bes, while the permeate flows radially outward across the membrane and the pport tube where it is collected from the permeate outlet ports (Figure 2.7). The o streams may flow either co- or counter-currently. The driving force through the annel is tangential to the membrane being the transmembrane pressure. Tubular vices are very similar in design to the hollow fiber modules described in the eceding section but employ much larger diameter tubes (typically 0.3 – 2.5 cm).

14.3 Plate-and-frame

The plate-and-frame modules (Figure 2.8) use multiple flat sheet membranes a sandwich arrangement consisting of the support plate (which also defines the rmeate flow path), the membrane, and the channel spacer or separator). The embranes can be sealed to the plates using gaskets, in which case the module ack) is hydraulically clamped to form a tight fit. Alternatively, the membranes can directly bonded or glued to the plates using heat sealing or an appropriate hesive to form an integral membrane element. Several of these membrane ements/plates are then stacked together and clamped to form a complete module. ie feed channel is typically 0.03 – 0.1 cm in height. The channel can either be fully en or it can employ an appropriate screen (typically a polypropylene mesh) to omote local mixing (flow turbulence) and improve the overall mass transfer aracteristics of the device. The permeate is manifolded within or outside of the odule, depending upon the particular device design [23].

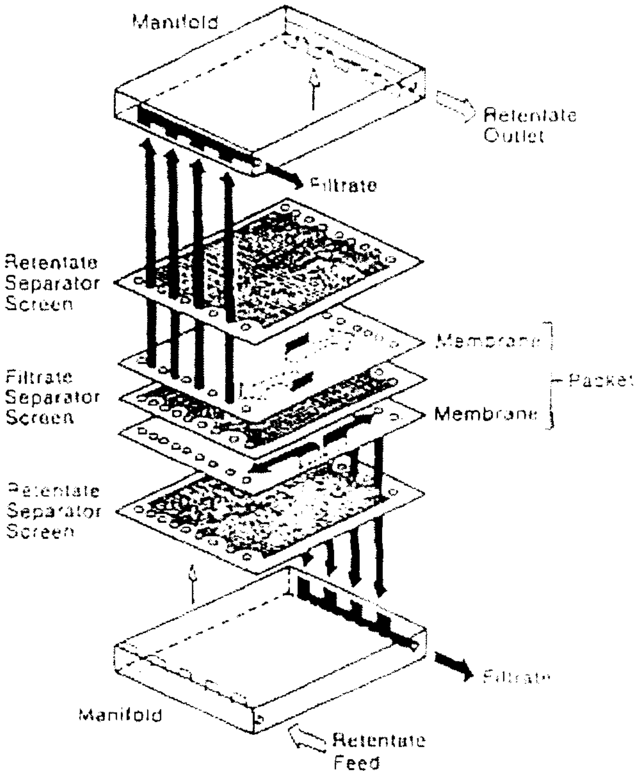


Figure 2.8 Schematic representation of the plate-and-frame module
Source: Zeman and Zydney, 1996 [23]

14.4 Spiral wound

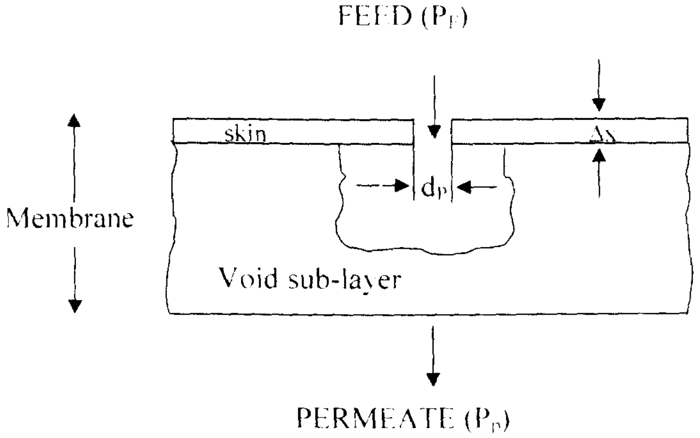
The spiral wound element is fitted into a tubular steel or plastic pressure ssel with an anti telescoping device placed at both ends of each element to prevent stortion of the spiral during operation (similar to the opening of a hand-held lescope). This also allows several spiral elements to be inserted into a single tube ith simple connectors placed between the permeate collection tubes from each unit. e pressurized feed solution is fed into one end of the pressure vessel so that it ows through the plastic screens along the surface of the membranes. The retentate then collected out the other end of the device. The permeate flows into the closed embrane pockets and spirals radially inward where it is collected through the ntral tube. The permeate-side spacer is designed to provide the necessary physical pport for the flat sheet membranes at the required operating pressures, while at the me time providing a sufficiently open flow path to minimize the hydraulic sistance to the permeate flow. The region between the outer edge of the spiral ement and the inside of the cylindrical housing is sealed to avoid fluid bypass. This eates a dead space in the device, which is difficult to clean and highly susceptible bacterial contamination. This is sometimes overcome by allowing a very limited ed bypass to continuously flush the annular space [22, 23].

.15 Models for predicting flux

Models for predicting flux can be divided into two regions namely: pressure ntrol region and pressure independent region. The variation between these two gions is a function of filtration time, nature of filtration sample and its ydrodynamic characteristics. At the beginning at low feed concentration, low essure and high feed velocity flux would be dependent on transmembrane pressure. his is known as pressure control region. As the filtration time increases new sistances originate from initial membrane resistance such as gel layer and embrane fouling resistances. A limiting value would be reached when the driving rce of transmembrane pressure has little or no effect at all and this is referred as the ressure independent region [22, 23, 35]. Models to predict both of these regions are iscussed below.

.15.1 Hagen-Poiseuille basic equation

Fluid flow through microporous membranes by the Hagen-Poiseuille basic quation for streamline flow is a function of pressure drop, viscosity, density and hannel dimensions (such as diameter or a tube) {Where J is the flux rate through the embrane.(volume/area/time): d_p is the channel diameter: P_T ($P_T = P_F - P_p$)is the pplied transmembrane pressure P_F is the applied pressure. P_p is back-pressure on the ermeate side (this is zero if the permeate side is open to atmosphere). subscripts F nd P refer to feed and permeate. respectively : μ is the viscosity of the fluid ermeating the membrane: Δ x is the length of the channel (the membrane "skin" ickness): and ε is the surface porosity of the membrane[22]}. The parameters are own schematically in Figure 2.9.



igure 2.9 Schematic representation of the cross section of typical asymmetric UF or IF Membrane. Source: Cherayan. (1998) [22]

$$J = \frac{\varepsilon d_p^2 P_T}{32 \Delta x \mu} \qquad (2.3)$$

Several assumptions have been made in deriving Equation 2.3 such as: the flow laminar (Re < 2100): density constant: steady state condition: Newtonian fluid:

nd effects are negligible. Increasing temperature and pressure will increase flux as iscosity decreases with temperature. This is true only at low feed concentration, low pressure and high feed velocity.

.15.2 Pressure dependent region

Darcy's law is an advancement of the Hagen-Poiseuille law basic equation. When a suspension contains particles which are too large to enter the membrane pores, then a sieving mechanism is dominant and a cake layer of rejected particles orms on the membrane surface. The cake layer provides an additional resistance to iltration, so the permeate flux declines with time. The cake layer and membrane may be considered as two resistances in series, and the permeate flux is then described by Darcy's law (see section 2.4) [35]:

This general membrane equation is an attempt to state the factors that may be mportant in determining the membrane permeation rate for pressure driven processes. This takes the form of:

$$J = \frac{1}{Am}\frac{dVp}{dt} = \frac{|\Delta P|}{(Rm + Rc)\mu} \tag{2.4}$$

f the membrane is only exposed to pure solvent, say water, the above equation educes to

$$J = \frac{|\Delta P|}{Rm\mu} \tag{2.5}$$

Where: J = permeation rate (flux)

Am = membrane filtration area

Vp = total volume of permeate

ΔP = transmembrane pressure

Rm = intrinsic membrane resistance

Rc = resistance of layers deposited on the membrane (filter cake)

μ = Viscosity of permeate

t = filtration time

2.15.2.1 Hydraulic resistance of the membrane, R_m

Hydraulic resistance is the property of a membrane to resist permeate flux. t is a characteristic property of membrane, which does not depend on the feed omposition or the applied pressure. It is dependent on the membrane material and ore-size distribution. The combined effect of these two factors is normally epresented as L_P, which can be defined as the pure water permeability of the fresh membrane.

The permeate flux J, passing through the membrane can be described by the equation

$$J = L_P . \Delta P \qquad (2.6)$$

$_P$ is the hydraulic membrane permeability and ΔP is the TMP. Combining equations 2.5) and (2.6) gives equation (2.7) for hydraulic resistance R_m

$$R_m = 1/(\mu . L_P) \qquad (2.7)$$

2.15.3 Mass transfer (film theory) model (pressure independent region)

When the process deviates from any of the condition mentioned in the earlier sections 2.15.1 and 2.15.2, flux becomes independent of pressure. The asymptotic pressure–flux relationship is due to the effects of concentration polarization. Under these conditions, the Hagen-Poiseuille model and Darcy's law no longer adequately describe the membrane process. One of the widely used theory for modeling flux in pressure-independent, mass transfer-controlled systems is shown schematically in Figure 2.10. As solution is ultrafiltered, solute is brought to the membrane surface by convective transport at a rate J_s, defined as:

$$J_s = J\,C_b \qquad (2.8)$$

Where: J = permeate flux (volume/time)

C_b = bulk concentration of the rejected solute

The resulting concentration gradient causes the solute to be transported back into the bulk of the solution due to diffusion effects. Neglecting axial concentration gradients, the rate of back-transport of solute will be given by:

$$J_s = D\frac{dC}{dX} \qquad (2.9)$$

Where: D = diffusion coefficient

$\frac{dC}{dX}$ = Concentration gradient over a differential element in the boundary layer.

A steady state, the two mechanisms will balance each other. Both equations (2.8) and (2.9) can be equated and integrated over the boundary layer to give:

$$J = \frac{D}{\delta} ln \frac{C_g}{C_b} \tag{2.10}$$

Where: C_g = gel layer thickness

C_b = bulk concentration of the rejected solute

δ = thickness of the boundary layer (D/k)

k = mass transfer coefficient, having the same units as the flux J and calculated as:

$$k = \frac{D}{\delta} \text{ where } \quad J = k \ln \frac{C_g}{C_b} \tag{2.11}$$

In this model, there is no pressure term. This model is valid only in the pressure-independent region. The flux will be controlled by the rate at which solute is transferred back from the membrane surface into bulk fluid. C_g and C_b are fixed physicochemical properties of the feed. flux can only be improved by enhancing k as much as possible, such as by reducing the thickness of the boundary layer. Flux will become independent of pressure and only increase if the back-transport mechanism reduces the gel layer thickness δ.

A number of qualitative relationships correlating the mass transfer coefficient to physical properties, flow channel dimensions, and operating parameters exists in literature [22-24]:

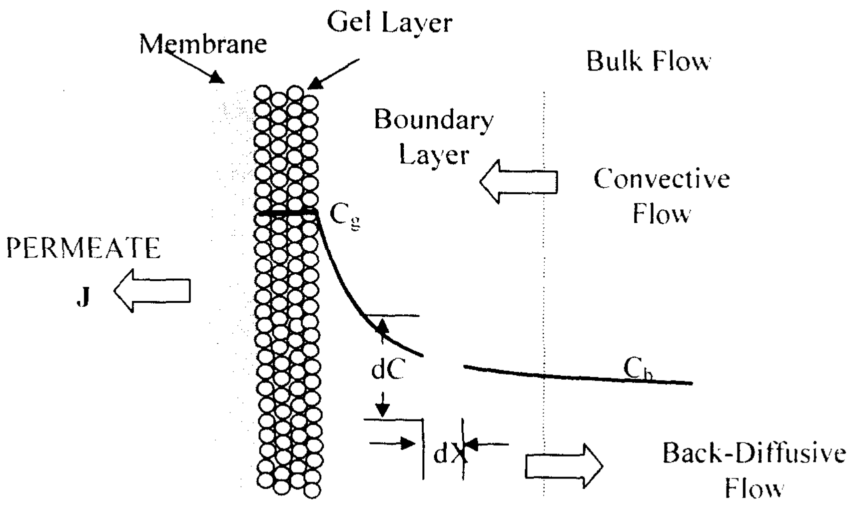


Figure 2.10.Schematic of concentration polarization during UF of colloidal and macromolecular solutes, showing the built-up of the polarized (gel) layer and associated boundary layer.
Source: Cheryan. (1998) [22]

2.16 Design factors to improve flux

The major emphasis in the design of equipment and its operation is to reduce the effects of concentration polarization. Figure 2.11 shows several such methods. Among the approaches shown in the first tier, reducing solids in the feed may be counterproductive in the long run, since then a greater volume of feed has to be processed. The lowest possible pressure should be used, especially in UF and MF. To reduce solute concentration at the membrane surface, mixing can be enhanced near the membrane surface by using paddle mixers (commonly done in laboratory-scale apparatus, but impractical for industrial equipment) or by using static mixers (e.g., the kinecs mixer) in large tubular designs, or mesh-spacer turbulence promoters, which are used in spiral-wound and some plate designs. "Scouring balls" in large tubular units are also recommended. Substantial improvement in flux can be obtained with this device. In both turbulent and laminar flow, flux increases with velocity. For flow rate Q, although the effect is more pronounced in turbulent flow. Increase in temperature causes an increase in diffusion coefficient (D) and decrease in viscosity (μ) from equation 2.19 would enhance flux. Another cost effective way is to decrease the channel height (diameter) so as to maximize the shear rate. However, there are several other methods of enhancing flux, e.g., by moving the membrane instead of the liquid or subjecting the liquid to different types of perturbation to minimize fouling and polarization [19, 27].

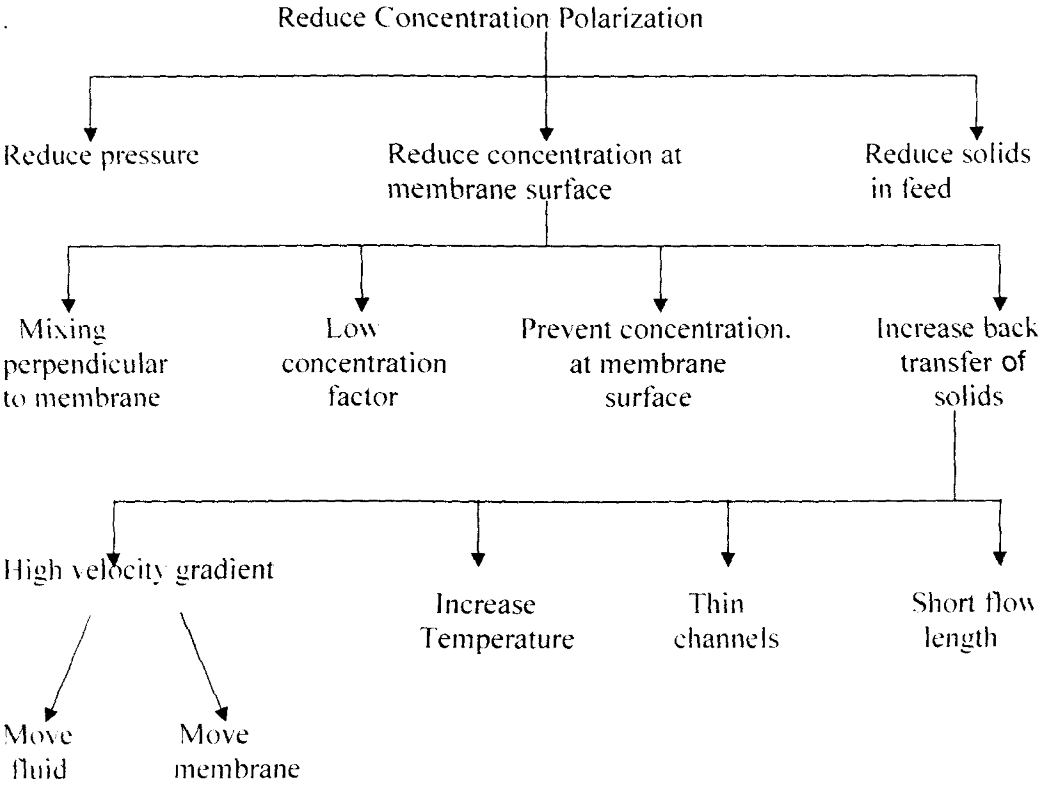


Figure 2.11 Methods to maximize flux [adapted from Cheryan, 1998] [22]

2.17 Membrane fouling

Membrane fouling is the irreversible alteration in the membrane caused by specific physical and/or chemical interactions between the membrane and various components present in the process stream and is attributed to the decay in filtrate flux and an alteration in membrane selectivity. Extensive membrane cleaning or replacement of the membrane needs to be done to restore the original flux. The effect of membrane fouling is very similar to concentration polarization except that the concentration polarization is a (reversible) boundary layer phenomenon arising from the bulk mass transfer limitations in the membrane device. Therefore, adjusting the device design and operating conditions can control concentration polarization. Its effects can be reduced or even eliminated by sufficiently increasing the rate of solute mass transfer back away from the membrane.

In contrast, membrane fouling occurs because of specific physical or chemical (attractive) interactions between the various particles and the membrane. The rate and extent of membrane fouling is typically a function of the device fluid mechanics, but simply increasing the rate of solute mass transfer cannot in general, eliminate fouling. Fouling cannot be termed as totally "irreversible". The changes in membrane properties caused by fouling can often be reversed by back-flushing, application of very high cross-flow velocities, or chemical cleaning. However, the mechanical and/or chemical forces required of all components present in the process stream could foul the membrane. The nature and extent of the fouling are determined by the specific physical and chemical (molecular) characteristics of the individual components and the membrane. Fouling in many processes may be caused by species present only in trace amounts, and their concentration may be virtually independent of the main components involved in the actual separation, while the fouling seen in many biological separations is often caused by trace amounts of aggregated and/or denatured protein.

One of the major problems involved in developing a fundamental understanding of membrane fouling is the difficulty in identifying the actual foulant and in distinguishing between the symptoms of fouling and the effects of concentration polarization and membrane compaction. Many investigators have (somewhat arbitrarily) attributed the rapid flux decline seen at the start of a given filtration process to concentration polarization. Any long-term flux decline is then attributed to membrane fouling. However, fouling can also develop very quickly. For example, the characteristic time for protein adsorption to solid surfaces can often be as short as several seconds. In addition, the presence of a long-term decline in the filtrate flux is not itself, conclusive evidence for membrane fouling. Such long-term flux decline could also reflect an alteration in the feed stream (e.g. a slow increase in fluid viscosity or an accumulation of retained solute) or a slow physical or chemical alteration of the membrane structure or composition.

Physical changes in the membrane can be caused by compaction or deformation. Chemical changes may be induced by displacement of wetting agent, surface modifications, blended polymers, or other components present in the membrane. Chemical degradation can also be a problem in some systems if the pH, temperature, or chemical composition of the feed or cleaning agents is incompatible with the membrane chemistry. The rate and extent of membrane fouling in any given system will be determined by the strength of the intermolecular interactions between the macro solutes and the membrane in combination with the effects of the various hydrodynamic (and body) forces acting on the macro solutes. The hydrodynamic forces not only determine the rate of macro solute transport toward the membrane (and thus the local macro solute concentration in the immediate vicinity of the membrane surface), they can also directly contribute to membrane fouling through the physical deposition of macro solutes [19, 20, 27].

2.17.1 Characteristics of fouling

Flux of a real world feed stream is usually much lower than flux of the pure solvent (e.g., water) for several reasons as follows:

(a) *Changes in membrane properties* - These can occur as a result of physical or chemical deterioration of the membrane. Since membrane processing is a pressure-dependent process, it is possible that, under high pressures, the membrane may undergo a "creep" or "compaction" phenomenon. Chemical deterioration, on the other hand, could occur if the pH, temperature, and other environmental factors are incompatible with the particular membrane. Harsh and frequent cleaning regimes, sometimes necessary in food and biological applications, will decrease membrane lifetime significantly.

(b) *Changes in feed properties* - Solvent transport through porous MF and UF membranes are usually considered a viscous flow phenomenon governed by the Hagen-Poiseuille equation or mass transfer relationships. Thus, since the feed stream's viscosity and density increase and diffusivity changes as solids levels increase, flux should be lower than that of water, purely from hydrodynamic considerations. This can be easily predicted and taken into account.

(c) *Concentration polarization* - Flux-depressing effects due to membrane fouling are frequently confused with flux-lowering phenomena associated with concentration polarization. In theory, concentration polarization effects should be reversible by decreasing the transmembrane pressure, lowering the feed concentration, or increasing cross-flow velocity or turbulence. If this can be done, the cause of lower flux is polarization and not true fouling [24, 35, 38].

2.17.2 Factors affecting fouling

Since fouling in its true sense is a result of specific interactions between the membrane and various solutes in the feed stream, and perhaps between the adsorbed solute and the other solutes in the feed stream, it is difficult to establish general rules or theories about the nature and extent of fouling that will be universally applicable. Each component of a feed stream will react differently with the membrane: conformation, charge, zeta potential, hydrophobic interactions, and other factors will have a significant bearing on these membrane-solute interactions. Certain process engineering factors, such as cross-flow velocity, pressure, and temperature can also have a bearing on fouling. It should be recognized that all these general categories – membrane material properties, solute properties, and operating parameters – can interact with each other and give rise to quite different effects in combination than if these factors were studied individually or with model systems. Nevertheless, some general observations can be made that should help understand the mechanisms of fouling [22, 23, 36].

2.18 Membrane cleaning

Cleaning is the removal of foreign material from the surface and body of the membrane and associated equipment. All membranes will foul during operation, causing the membrane performance (flux and/or selectivity) to drop below some minimally acceptable level. At this point the foulants must be removed from the membrane structure using an appropriate cleaning procedure. To make the process economically attractive (without replacing the membrane regularly), several methods have been proposed to clean and regenerate the membrane performance back to its original level. Usually detail information on the operational limits for different membranes should be obtained directly from the manufacturer [34, 44].

2.18.1 Chemical cleaning

A large number of different cleaning solutions have been developed for specific applications. In general, the different chemicals in these solutions can be classified as acids, alkalis, surfactants, sequestrates (chelator), or enzymes. Table 2.9 lists typical cleaning reagents and their modes of action.

2.18.2 Physical method

Physical cleaning saves operational costs, as it does not incur additional cost for the purchase of chemicals. Chemical cleaning as far as possible is avoided in the food processing industries so as to avoid any contamination in the final food product. Physical cleaning is widely practiced in such industries and cleaning protocols are followed at regular intervals. Some foulants can be effectively removed from the membrane surface by mechanical means. One way is by removing transmembrane pressure and circulating feed solution through membrane module. Rinse solution could also be circulated at relatively higher shear rate. Periodic back flushing with pulsing can clean hollow-fiber membranes and some flat-sheet membranes with appropriate feed-channel. Forcing rubber sponge balls through the lumens of the large-bore tubes can clean tubular membrane modules. Pulsed electric fields technique was very effectively used to remove particulate foulant when the membrane and particles had like charges. Low operating pressure and high cross-flow velocity, which can create a high degree of turbulence concentrate layer on the membrane surface, could be destroyed and flushed away.

Table 2.9 Typical cleaning reagents and their modes of action.

Foulant	Reagent	Time and Temperature	Mode of action
Fats and oils, proteins, polysaccharides, bacteria	0.5 N NaOH with 200 ppm Cl_2	30-60 min 25-55 °C	Hydrolysis and oxidation
DNA, mineral salts	0.1 M-0.5 M Acid (acetic, Citric, nitric)	30-60 min 25-35 °C	Solubilization
Fats, oils, biopolymers, proteins	0.1 % SDS emulsifying, 0.1 % Triton X-100	30 min-overnight 25-55 °C	Wetting, suspending, dispersing
Cell fragments, Enzyme breakdown Fats, oils, proteins	detergents	30 min-overnight 30-40 °C	Catalytic (proteolysis)
DNA	0.5 % DNAase	30 min-overnight 30-40 °C	Enyme hydrolysis
Fats, oils, and grease	20-50% ethanol	30-60 min 25-50 °C	Solubilization

Source: Cheryan, 1998 [22]

One of the physical methods for cleaning-in-place of fouled membrane is to pulse the process fluid itself inside the membrane module. Periodic gas sparging using pressurized inert gaseous like nitrogen into a tubular membrane could reduce fouling and this is also a method of cleaning-in-place [22, 23, 25].

2.19 Previous application of ultrafiltration on concentration of lattices

2.19.1 Studies on the ENR latex concentration by ultrafiltration

Epoxidised natural rubber (ENR) latex is structurally modified latex of an original cis-polyisoprene latex structure (Figure 2.1), which has an oxygen atom, incorporated into its structure.

The presence of oxygen [O] in the ENR makes it resistant to oil, chemical and environmental degradation (ozone, heat and water) resulting in improved properties when it is made into products such as rubber hose or car components. ENR 20, 50 and 60 denotes the percentage of epoxidization from the original NR structure (Figure 2.1) to epoxidized structure (Figure 4.1). Epoxidation of natural rubber (NR) alters its physico-chemical properties.

In epoxidised natural rubber (ENR) latex for eample, the difference in the specific gravity between the rubber and the serum phase is too small to affect concentration either by centrifuging or creaming methods. Further, prolonged heating of ENR latex gives rise to stability problems and could also lead to the formation of open-ring products. For these reasons, the use of evaporation to concentrate ENR latex is precluded.

The process of ultrafiltration was tested and found to be a workable alternative to ENR latex concentration by Nambiar. J., [17]. Ultrafiltration is a low pressure (1–10 bar) membrane processes which relies on particle-size as the primary factor affecting separation.

A composite preservation system consisting of 3 parts per hundred of non-ionic surfactant, Teric and 0.4% ammonia were added to stabilize the ENR latex before the concentration by ultrafiltration was carried out.

During ultrafiltration, process fluid is pumped across the surface of a semi-permeable membrane. Low molecular weight particles like water, salts, sugar and most surfactants pass through the membrane and thereby concentrated. Particles larger than about 0.001 – 0.002μm (10 Å – 200 Å) are retained during ultrafiltration. Concentration levels between 60 and 65% could be routinely achieved from an initial DRC of 30%. The types of ultrafiltration equipment tested were a plate and frame unit and a tubular membrane system. The relationship between flux, which is indicative of the efficiency of ultrafiltration, and key operating parameters like feed concentration: temperature and pressure were studied at some length.

Comparisons of flux between membranes with different pore-size were carried out, and the effectiveness of clean-in-place feature to reduce membrane fouling was gauged. The cost of ultrafiltration of ENR latex was estimated for both pilot-scale and commercial level production. The operating cost for commercial production were two-thirds lower than pilot plant scale.

2.19.2 PVC latex concentration

Shen and Mir [18] employed the use of tubular ultrafiltration system to dewater polyvinyl chloride latex (PVC). PVC is a form of synthetic latex manufactured from emulsion polymerization. There were two major industrial applications for this process. The first is the concentration of dilute latex from 0.5% to 25% solids or more for pollution control measures. The second major application is the concentration of in-process latex streams from 30% to above 50%, replacing the evaporator by the ultra filtration process.

Several technical parameters of interest such as flux characteristics, concentration polarization, latex stability, and membrane cleaning was investigated. Performance data with PVC and styrene butadiene rubber (SBR) lattices were collected in laboratory and pilot plant studies. Techniques to enhance latex stability with respect to ultra filtration processing conditions have been established. Effective cleaning and reuse of tubular membranes by solvent soaking and mechanical cleaning have been demonstrated. Due to the high flux performance obtainable with stable latex feeds, especially PVC latex emulsions, the tubular ultrafiltration process is also very energy efficient process. Comparison of operating energy costs among ultrafiltration and evaporative methods for PVC latex dewatering were obtained. It is shown that the energy cost for the ultrafiltration process is only a fraction of that for the more energy-intensive thermal evaporation process.

Membrane cleaning protocols were also established. Two membrane solvent cleanings were performed. The first cleaning was after 20 batch runs (after 350hrs of membrane processing time), and the second cleaning was performed after 32 batch runs (after 755hrs of membrane processing time). At each cleaning, membranes were exposed to solvent twice. The solvent exposure may either be in soaking mode, where the solvent was simply pumped into the system and left for one hour or so, or in the recirculation mode, where the solvent was continuously pumped through the tubular membranes for 1 hr. These cleaning cycles were able to bring about over 80% process flux recovery compared to new membranes.

2.19.3 Removing protein from HDPNR latex by Rotary Disk Membrane Module

Protein constitutes up to about 1.5% by weight of latex. Some of these proteins cause allergenic reaction to the user when they are made into products like examination gloves. It is quite customary to remove these proteins by biological means by incubating the natural rubber latex with proteolytic enzyme in the presence of surfactant(s). These proteins get hydrolyzed from the latex and removed by centrifugation. The latex which had its protein removed by this process is called highly deproteinized natural rubber (HDPNR). However this process which uses the conventional surfactants, showed low mechanical stability and poor processability, that is nonuniformity and crack formations of the film from HDPNR. A part of the properties was presumed to be derived from the particle-size distribution, because the successive centrifugation of HDPNR latex resulted in the loss of smaller rubber particles.

Tanaka and Kawasaki [19] exploited the use of membrane separation technique as an alternate method to remove the hydrolyzed protein to subsequently concentrating the latex as well.

The HA-latex was incubated with 2.0% w/v surfactant(s) (KP-4093, Kao Co.) and 0.24% w/v proteolytic enzyme (KP-3939, Kao Co.). The reacted latex was diluted to 15% DRC with deionized water followed by concentration to 30% DRC with a rotary disk membrane module.

The rotary disk membrane module, which was developed by Nitto Denko Co. and Hitachi Plant Engineering & Construction Co., Ltd., was applied to the washing of latex. It consisted of five disks equipped with ultrafiltration membrane made of polysulphone at both sides with 0.28 m^2 area, which is installed in a 10L tank and was operated under the pressure of 0.5kgf/cm^2 rotating at 300rpm. The washings were repeated three times, subsequently the latex was concentrated to 60% DRC in a similar way. The nitrogen content of the rubber was 0.035%.

Treated HDPNR latex by membrane separation technique showed the same particle-size distribution as the untreated latex and its mechanical stability and process ability were better than that obtained by conventional centrifugation.

2.19.4 Cross flow filtration of latex emulsion on a pilot scale using organic and inorganic membranes with different cut-off values

Novalic et.al [20] worked on increasing the concentration of a *ca.*1 wt% styrene butadiene latex emulsion resulting from an industrial production using cross-flow filtration. In order to avoid the occurrence of solid waste resulting from precipitation by adding $Al_2(SO_4)_3$ on one hand, and to recover value added products on the other, the emulsion can be concentrated and recycled using cross-flow filtration.

This study investigated the process performance using different types of membrane. The permeate flux were in the range of 2.36×10^{-5} - 0.14×10^{-5} $m^3/s.m^2$ when emulsion was concentrated up to ~40 wt%. Although three different membrane types, one organic and two inorganic with varying cut-off values (20,000, 50 000 and 0.2μm) were used, no significant differences in average permeate flow were observed. The concentration of the latex emulsion was seen to have the greatest effect on the permeate flux, and with increasing concentration, the flux was observed to drop to ~0. In contrast to this, during continuous testing over a period of nearly two months, using two emulsions of 15 wt% and 1 wt%, respectively, the permeate flow rate remained practically stable.