CHAPTER: 2

LITERATURE REVIEW
2.1 DEVELOPMENT OF MEMBRANE:

With the development of synthetic asymmetric membrane in 1960 at the University of California by Sourirajan and Loeb, ultrafiltration has emerged as a viable separation process. Upto sixties, the membranes were classified as tortuous or sponge like until the advent of nucleopore membrane from General Electric Corporation [2]. These membranes were thinner, less porous and more flexible. In the late 1960s asymmetric non-cellulosic ultrafiltration membranes developed that overcame some of the limitations of cellulosic ultrafiltration membranes.

Early studies to reduce the porosity were highly empirical. It was found in 1957 [35], that cellulose acetate has the greatest permeability and rejection. The first generation membranes, asymmetric structure resembling the Loeb/Sourirajan [36] RO membranes, were relatively water impermeable by present day UF membrane standards but nevertheless several order of magnitude more permeable than homogeneous gel membranes with comparable solute retentivity.

The 10 years period between 1965 and 1975 was one of the intensive R & D efforts to fabricate UF membranes which were more water permeable, more mechanically rugged and chemically durable [37]. Although cellulose acetate (CA) membranes form the basis of these research efforts, many polymers were screened for potential application as selective barriers [38] for a variety of aqueous separations. In general, these studies relate polymer structures of membrane material with product flux and solute rejection. This leads to the development of asymmetric high flux membranes [36] and hollow fibers which provide exceedingly high membrane area per unit volume [39].

Details about the methods and conditions for casting high flux cellulose acetate membrane and also synthesis of polymeric membranes were discussed...
in various literature [35-40]. The complete history and development of membranes were given by Kesting [35] and Schweitzer [41].

2.2 DIFFERENCE AMONG RO, UF and MF:

In the common membrane processes i.e. microfiltration, ultrafiltration and reverse osmosis- hydraulic pressure is applied to speed up the transport processes. Among membrane separation processes itself, the distinction between the various processes is somewhat arbitrary and has evolved with usage and convention. Reverse osmosis or hyper filtration retains all components other than solvent water itself, while ultrafiltration retains only macromolecules and micro filtration is designed to retain suspended particles in the “micron” range. Porter [42,43] has defined the process by the rated pore size or the molecular weight cut-off of the membranes as follows:

Pore size - (0.0001- 0.001 \(\mu\) m) – RO
- (0.001-0.02 \(\mu\) m) - UF
- (0.10 - 10 \(\mu\)m) - MF

In conventional usage, particles larger than 10 \(\mu\) m are best handled by conventional filtration processes.

2.3 SOLUTE SEPARATION BY ULTRAFILTRATION:

In UF, the solute passes less readily through the membrane than the solvent. The reason attributed to this may be classified as follows [8, 44]:

(i) The solute may be adsorbed on the surface of the filter and its pore (primary adsorption).
(ii) The solute may be retained within the pores (blocking).
(iii) It may be mechanically retained (sieving).
One of the problems found in UF is the marked decline of permeate flux with time. This is mostly attributed to a series of resistances. During UF process, membrane surface concentration increases which leads to an increase in osmotic pressure. This phenomenon essentially reduces the driving force. It has been shown by several investigators [45,46] earlier, that osmotic pressure controlled flux decline occurs within a few seconds from the start up of the operation. In some study conducted by Liu et. al on the application of membrane technology on black liquor from pulp mills using UF membranes, the observed total filtration resistance was evaluated for the intrinsic resistance, adsorption, pore plugging and concentration polarization [47].

Modeling of concentration polarization phenomenon with a view to evaluate the parameters governing it and the methods for its control has attracted considerable attention. Though analysis for micro and macrosolute polarization has been developed by Goldsmith et. al. [48], Gill et. al. [49], Dressner [50] and Blatt et. al.[7] – many areas still remain to be explored. Kozinski and Lightfoot [24] developed a theoretical model for predicting permeate flux through rotating disc, taking into consideration of the concentration dependent diffusivity and viscosity. Experiments and theory agreed reasonably well. Average physical properties are found adequate in many situations.

Bellucci and Drioli [51] and Swaminathan [52] carried out UF of protein solution of Bovine Serum Albumin (BSA). They showed that experimental results agreed well with gel polarization model [38]. Trettin and Dhosi [53] developed their theory essentially based on gel layer formation and proposed their integral model which was an effort in the unification of macromolecular theories with classical filtration theory. This model differentiates substantially compared to Shen and Probstein model [18]. Experiments with unstirred batch cell using BSA solution were performed to verify this model [19]. A summary of governing transport and sorption phenomenon in porous membrane
ducts under isothermal conditions was given in the review article by Belfort and Nagata [54].

Theories based on hypothetical boundary layer (film) or polarized gel layer mainly govern the studies till date. However recently, some theories like those based on leaky membrane concept and solute-solute or solute-membrane interaction have gained importance. The effect of concentration polarization is very detrimental from industrial point of view. These are summarized by Aimer and Sanchez [55]. In order to describe performance of an UF unit throughout the range of operating conditions, several theories, individually or cumulatively proved to be quite adequate [56, 57].

Extensive researches were carried out to reduce the concentration polarization and improve the flux behaviour. Bouzerar et. al (2003) have investigated the performance of two rotating disk prototypes for dynamic filtration for the treatment of various industrial effluents by micro-(MF), ultra-(UF) and nanofiltration (NF) [58]. Permeate fluxes were compared with those obtained on the same effluents using a vibrating shear-enhanced filtration system equipped with the same membrane or with regular crossflow filtration in tubular membranes. The permeate flux from the disk unit was seen to increase linearly with transmembrane pressure to reach 200 Lh⁻¹ m⁻² at 40 bar vs. 130 L h⁻¹ m⁻² for the VSEP equipped with the same membrane at its maximum frequency.

Satyanarayana et. al [59] (2000) has studied ultrafiltration of black liquor in three different modules, namely radial cross flow, rectangular cross flow and stirred cell over a wide range of operating conditions. A comparative analysis of flux decline for different modules was also presented using a simple resistance-in series model. According to their study the gradual decline may be considered as a combined effect of build up of deposited layer on the membrane surface and deposition of solute particles in the membrane pores. Effects of different operating
conditions, Reynolds no., feed concentration on permeate flux and observed rejection were investigated.

2.4 SOLUTE PURIFICATION BY DIAFILTRATION :

Ultrafiltration is most widely used as a means of fractionating solutions. A considerable purification of a certain solutes can be done by direct ultrafiltration, the flux will drop to uneconomically low values and the pumping power required will rise due to increase in viscosity of the retentate. Thus in order to achieve a further purification, one will have to resort to “diafiltration”. Diafiltration refers to the process of adding water to the retentate and continuing the elimination of membrane-permeating species along with the water during ultrafiltration. It can be conducted under either one of two modes: discontinuous or continuous diafiltration.

2.4.1 Discontinuous Diafiltration (DD) :

In DD, permeable solutes are first eliminated by conventional ultrafiltration. Water is added to the concentrated retentate to dilute it back to a certain volume, and re-ultrafiltered.

2.4.2 Continuous Diafiltration (CD) :

In this mode of ultrafiltration, water or other solution is added continuously to the feed tank or retentate line at the same rate as permeate flux. The total volume of the system and the concentration of the retained solute remain constant during CD. The concentration of the permeable solutes decreases in proportion to the volumes diluted and their individual rejections.
2.5 TREATABILITY OF PULP AND PAPER MILL EFFlUENT:

In conventional Kraft Pulping process, the large amount of black liquor (BL) generated is either discarded or treated in a destructive way to recover the inorganic chemicals with the waste of valuable organics. Ultrafiltration of BL has been proposed in diverse literature [60-63] for recovery of valuable organics, to meet a part of the water requirements and finally to tackle wastewater disposal problems due to enforcement of stringent environmental regulations. Woerner and McCarthy [64] suggested that to produce purified high molecular weight lignin, UF should be operated at low pressure and under high alkalinity. Purity of 80-90% of lignin was reported using a combination of ultrafiltration and diafiltration [60,65].

Because of high BOD, COD loading, high lignin, organic and inorganic content of Kraft black liquor, researchers have explored the treatability of the same and predicted the limiting flux phenomenon of Kraft black liquor using various UF modules. Sridhar, in his study [66] concluded that the phenomenon of polarized layer deposition as the key cause that reduces flux of black liquor through the membrane. Asymmetric cellulose acetate complex membrane with 500-molecular weight cut-off was used to treat black liquor with concentration up to 5%. A permeate flux of about 37.8 l/m² h at a pressure of 550 kPa was reported.

Bhattacharjee [67] made an attempt at predicting the flux of an asymmetric cellulose acetate membrane in a stirred batch cell. The UF flux was 45 l/m² h under the condition of 830 kPa and 20g/l total solid for the black liquor. Although the predicted flux values remained within 7% of the experimental flux values, the predictions were based on the few experimental data available, and an extension of the results could only be limited.
Ola Wallberg et al.[68] investigated the retention of lignin and the flux for three polymeric membranes with cut-offs of 4, 8 and 20 kDa, with the retention of lignin found to be 80%, 67% and 45% respectively. Liu et al.[47] reported the presence of more than 75% organics larger than 60,000 Da in black liquor obtained from a pulp mill in China using the UF procedure with a 60,000 cut-off membrane at pH 10 and 11. Various organic and inorganic membranes were studied to produce high permeate flux and endure long operation period.

Studies have been carried out for effective separation of dissolved solids such as lignosulphonates (LS) on one hand and clear reusable water on the other using membrane processes i.e. UF, RO and nanofiltration (NF) and effectively combine one such process with other. Some researcher [69] demonstrated that the total solids (TS) of spent sulphite liquor (SSL) could be concentrated from 6 % to 12 % with a flux of about 40 l/m².h by RO, and membrane lifetime of more than a year was obtained with efficient membrane cleaning of two to six times a week.

SSL from sulphite pulping industry offers much greater possibilities in the field of water recovery and chemical recovery by membrane separation [70]. Madson and Nielsen [71] carried UF of bleach plant effluent for color removal and fractionation, purification of lignosulphonates from SSL using Danish Sugar Corporations membrane filtration equipment. They reported 95% removal from bleach plant effluent. System for full scale plant has been developed to remove colour of the order of 90% of bleach plant effluent from Kraft paper mill [72].

It was reported [73] that a full-scale UF plant with a membrane area of 1,120 m² was installed at the Borregaard® Industries (Sarpsbog, Norway) calcium bisulphate pulp mill in 1981. The UF plant processes 50 m³/h of feed liquor with 12% solids, and produces a retentate stream of 16 m³/h and 22% solids. The nominal cut-off of the polysulfone membranes used in the plant was 20kDa. The membranes are cleaned
once a day by recycling an alkaline detergent solution through the plant, The average membrane lifetime was 15 months. Though the UF process has been used worldwide to recover LS from SSL, a complete, neat and economical technology has yet to be evolved. Further, pressure-driven membrane operations have a significant limitation in terms of flux decline [74], which is largely dependent on the type of polymeric membrane, solute species and operating conditions. The nature of membranes has an extremely important role to play in pressure-driven membrane separation processes.

Researchers have used UF to separate spent liquor into purified fractions of lignosulphonates and sugars [74-76, 66]. Reverse osmosis has also been extensively used for concentration of sulfite liquor and bleach plant effluent [66, 77-79]. Lignin recovery and fractionation by UF were studied by several researchers [80, 81].

Treatability of pulp and paper mill effluent was studied by researchers using other routes also. It is reported that, precipitation and chemical coagulation with lime, alum, aluminium chloride, or ferric sulphate results in good colour removal (60-80%) from pulp and paper mill effluents, but there are associated problems of handling and disposal of sludge [82-84]. Shawwa et al.[85] reported 90% removal of colour, COD, and AOX from bleached wastewater by the adsorption process, using activated coke as an adsorbent.

Paper and pulp industry effluent is one of the important environmental problems, which has been correlated with mutagenic and carcinogenic activity [86,87]. Industrial biotechnology applications help the elimination of environmentally hazardous wastes. Some application methods of biotechnologies such as Aspergillus sp. remove colour of effluent from pulp waste [88] and from kraft mill by Phanerochaete chrysosporium [89]. Still biological treatment will not remove all organics and the effluents of the biological purification stages exhibit COD values that may exceed discharge standards.
2.6 TREATABILITY OF DAIRY EFFLUENT:

The dairy industry makes extensive use of ultrafiltration for concentrating total milk proteins in cheese production or for protein concentration standardization [90, 91, 92]. Recently UF has been proposed to separate \( \alpha \)-lactalbumin from \( \beta \)-lactoglobulin [93]. However, protein transmission was hindered by membrane fouling due to micelle casein layer deposited on the membrane. Whey, WPCs and IWPCs cause severe membrane fouling, mainly as a result of proteins adsorption onto the membrane and/or within the membrane pores [94, 95].

In three recent articles, Al-Akoum et al. [96-98] have investigated the performance of a Vsep shear-enhanced dynamic filtration device for concentrating proteins in UHT milk (sterilized at ultra high temperature) by UF and separating casein micelles from whey proteins by microfiltration (MF) and UF. When using a 0.1 \( \mu \) m membrane, the permeate flux reached a plateau of 95 l/h.m\(^2\) at a mean transmembrane pressure of 100 kPa at initial concentration, a temperature of 45\(^\circ\)C and maximum frequency, higher than those reported in the literature using tubular ceramic membranes of same pore size [99]. In UF with a 50kDa membrane, the permeate flux reached 80 l/h.m\(^2\) at a TMP of 600 kPa, at maximum frequency. Similarly, when equipped with a 50kDa membrane, the Vsep was able to reach a volume reduction ratio (VRR) of 8.66 [96], higher than that reported in conventional cross-flow filtration. The good performance of the Vsep can be attributed to the high shear rate at the membrane induced by the rapid oscillating azimuthal motion of the membrane reaching an amplitude of 30 mm at periphery, at a reasonable frequency of 60.75 Hz. With milk, the time maximum shear rate at membrane was calculated to be \( 10^5 \) s\(^{-1}\) at periphery and \( 7\times10^4 \) s\(^{-1}\) when averaged over the membrane area.

Lu-Hui Ding et al. (2003) [100] investigated the performance in milk ultrafiltration of another dynamic filtration system consisting in a disk rotating
at high speed near a circular membrane. Such systems, which are commercially available both as laboratory pilots and industrial units, have been shown to be very efficient, especially in macromolecule recovery from cell suspensions [101-104]. A survey of commercial rotating disk systems has been made by Bouzerar et al. [105]. Lu-Hui Ding et al. (2003)[100] reported that disks equipped with vanes greatly increased the performance both in terms of permeate flux and of the energy consumed by the disk per m$^3$ of the permeate.

One of the important applications of milk is the casein preparation, which is achieved either by rennet coagulation or by isoelectric precipitation with an acid. The disposal of casein whey, having a biological oxygen demand (BOD) value of about 35,000-60,000 mg/L and chemical oxygen demand (COD) value of 80,000-100,000 mg/L as sewage cause severe environmental pollution problem. Moreover, the whey protein fractions containing a wide array of proteins namely $\beta$ -lactoglobulin ($\beta$-LG), $\alpha$ -lactalbumin ($\alpha$-LA), bovine serum albumin (BSA), lactoferrin, lactoperoxidase, glycomacropeptide, etc.,[106] some of which could have important end uses, are getting disposed off as sewage. Even in WPCs and individual whey protein concentrates (IWPCs), the unique nutritional, therapeutic and functional characteristics of the individual whey proteins are largely unrealized due to interactions between components and degradation during processing. There, thus has been considerable commercial interest in the production of individual whey proteins by a process which will not denature, but retain its nutritional and other properties. Extensive researches have been carried out during last few years keeping this perspective in view [107,108]. $\beta$ -Lactoglobulin is a better foam stabilizer than the other whey proteins and can be used in the production of confectionery, whereas $\alpha$ -lactalbumin can be used in infant formula and as a neutraceutical because of its high tryptophan content. It also provides enhanced whippability in meringue like formulations. In addition, $\alpha$ -lactalbumin has strong affinity for glycosylated receptors on
the surface of oocytes and spermatozoids and may, thus have strong potential as a contraceptive agent [109].

Extensive studies have been carried out by the researchers to demonstrate the feasibility of membrane systems for the separations of proteins with very similar molecular sizes. Van Reis et al. [110] used high performance tangential flow filtration (HPTFF) to separate bovine serum albumin (BSA) from an antigen binding fragment of a monoclonal antibody (Fab), achieving more than 900-fold purification and 90% yield of the BSA. In a previous work carried out by Zhang [111] regarding the study on the affinity cross-flow filtration process for separation of BSA from IgG molecules, the target protein BSA was recovered in more than 95% purity. Van Eijndhoven et al. [112] developed a membrane system for the separation of bovine serum albumin from hemoglobin, two proteins with essentially identical molecular weight, with more than 100-fold purification and nearly 70% yield. More recently, Cheang and Zydney [113] were able to obtain 100-fold purification and greater than 90% recovery of $\beta$-LG from a binary mixture with $\alpha$-LA. All these experimental data were obtained with model system consisting of an artificial mixture of two previously purified proteins.

Experimental studies with complex multicomponent feed streams are much more limited, and the overall performance of these systems is much less impressive. With an objective to purify $\alpha$-LA from acid casein whey, Muller et. al. [114] used a combined ultrafiltration-diafiltration process and an $\alpha$-LA purity of only 50% was obtained in the final permeate. Bottomley [115] described a two-stage membrane process for the purification of $\alpha$-LA from cheddar whey, but the final product still contained nearly 25% $\beta$-LG. Lucas et al. [116] demonstrated the extraction of $\alpha$–LA selectively from acid casein whey protein concentrate (WPC) at pH 7 by limiting $\beta$-LG transmission by chemically modifying the inorganic membrane by a polyethyleneimine coating bearing positive charges. Some studies of proteins fractionation are based on the physico-chemical environment and the charge of the solutes.
Mehra and Donnelly [117] showed the possibility of fractionating clarified or dialysed whey with cellulose membranes. The retentate was enriched with the high molecular weight proteins and the permeate was enriched with the low molecular weight proteins.

Cheang and Zydney in a recent study [118] demonstrated a complete analysis for the separation of $\alpha$-LA and $\beta$-LG from a complex mixture obtained from commercial whey protein isolate. The recovery of two products required the use of a two-stage membrane system (100kDa and 30kDa) with the performance in each stage optimized to achieve the required selectivity by proper selection of pH, buffer conductivity and filtrate flux. Two different diafiltration strategies were examined for the purification of $\alpha$-LA and $\beta$-LG from the whey protein isolate. Strategy I used a 100 kDa membrane in the first stage to remove the large BSA followed by a 30 kDa membrane that separated between the $\alpha$–LA and $\beta$-LG. Strategy II examined the reverse combination with purified $\alpha$–LA and $\beta$-LG obtained in the permeate solutions from stages 1 and 2, respectively. In both cases, the overall purification factor for $\alpha$–LA was greater than 10, with 95% yield in Strategy I and 85% yield in Strategy II. However, Strategy II gave a significantly more concentrated $\alpha$–LA product since the $\alpha$–LA was recovered directly from the first stage using only a single diafiltration. The yields for $\beta$-LG, the “middle” component in this system, were around 70% in both strategies, with an overall purification factor of 8 using Strategy I and about 4 using Strategy II.