CHAPTER 1

INTRODUCTION

Traditional and conventional methods being used, in various industries like sugar, textile, chemical, paper and pulp and tanneries to treat liquid wastes, are screening, filtration, gravity sedimentation, centrifugation, disinfection etc., They are found to be tedious, troublesome, inefficient in product recovery and consume lot of energy and emphasized the advent of innovative, energy-saving technology. Membrane separation technology was found to satisfy the needs of the industries by circumventing the above drawbacks.

Membrane separation technology in its modern incarnation was born from the development of the synthetic asymmetric polymeric membrane in 1960 at the University of California, Los Angels, by Sourirajan and Loeb. Separation technology based on membrane, a relative new comer on the separation has demonstrated the potential of saving enormous amount of energy in the processing industries compared to conventional separation systems.

The significant advantage of membrane filtration over conventional methods such as precipitation, distillation etc., are that the solutes are not heated or chemically altered and frequently membrane filtration is less costlier than competitive processes (Riley et al 1972, Rosberg R. (1997).
1.1 MEMBRANES

In a broader sense, “a membrane is a region of discontinuity interposed between two phases”. This implies that, membranes can be gas, liquid or solid or combination of these phases. Thus, the interfaces of two immiscible liquids, of a gas and a liquid, or of a gas and a solid would not ordinarily be considered as membrane structures. Membranes vary in their make up from relatively crude structure of a screen to extremely fine configurations only one molecular layer thick, as in the fatty acid spreading in water (Hwang and Kammermeyer 1975, Mathias Ulbrich 2006). The term ‘Synthetic Membrane’, refers to those polymeric barriers, irrespective of the void volume or physical state, which have been restructured prior to utilization in a membrane separation process (Kesting 1971).

1.1.1 Historical Overview and Evolution of Membranes

The studies on biological membranes, their properties and performance led to the origin and growth of synthetic membranes. The versatility of the biological membrane is a result of the evolutionary process of the living system, whereas the science and technology of the synthetic membrane is linked to the short history of polymer science (Cabasso 1989). Biological membranes including the membranes of the skin, lungs, heart collagen, liver collagen, kidney glomerular membrane etc., are composed primarily of lipids and proteins (Jain and Wagner 1980). A schematic representation of the biological membrane showing proteins embedded in the lipid bilayer is illustrated in Figure 1.1.
Followed by the material transport across bio-membranes, membrane phenomena appears to be started in 1748 by Abbe Nollet, who placed “spirits of wine“ in a vessel, mouth of which was closed with an animal bladder and immersed in pure water. Nollet observed, the swelling of bladder, demonstrating the permeability of waste through bladder to wine. However, the history of synthetic polymeric membranes began after the inversion of cellulose nitrate in 1846 by Schonbein. Bechhold prepared the first series of membranes by varying cellulose nitrate concentration in 1906. The osmotic phenomena was studied principally by Traube, Pfeffer and Vont-Hoff in unglazed porcelain. By the early 1930s microporous collodion membranes were commercially available. During the next 20 years, the early microfiltration membrane technology got extended to other polymers such as cellulose acetate and membranes found their significant applications to obtain drinking water followed by industrial applications during 1960s.
1.2 MEMBRANE PROCESSES

Membrane processes can appear deceptively simple. All that required is a circuit containing a pump to pressurize and re-circulate the process stream and a membrane module in which to perform the filtration. Fundamentally, each membrane system is based on the same concept. Once effluent enters the system, two streams are formed: concentrate, containing the contaminant in the concentrated form and permeate, containing dilute amounts of contaminant (Cartwright 1994), as shown in the Figure 1.2.

![Figure 1.2 Schematic representation of a membrane process](image)

Membrane processes may differ in their basic operating mode and areas of application. However, they share several features that make them attractive in the separation of molecular mixtures. Separation is performed by physical means at ambient temperature without damaging or chemically altering the constituents. This is important in the food and drug industries, as well as in down-stream processing of bio-products where temperature-sensitive substances must often be handled. They are equally well suited for large-scale continuous operations, including, desalination of sea water and batch-wise treatment of very small quantities like isolation and purification of valuable drugs (Strathmann 1990). Although membranes and membrane processes were first introduced as an analytical tool in chemical and
biomedical laboratories, they developed into industrial products and methods with significant technical and commercial impact (Lansdale 1982).

Membrane separation processes differ greatly with regard to membranes, driving forces, areas of application, and industrial or economic relevance. The driving force in these processes may be a hydrostatic pressure gradient (microfiltration, ultrafiltration, reverse osmosis, or gas separation), a concentration gradient (dialysis) or an electrical potential gradient electrodialysis. Industrially important membrane separation processes and their operating principles are tabulated in Table 1.1.

There are many different ways of classifying and cross-correlating membranes and membrane separation processes. Useful range of separation processes, showing the range of particle or molecular size covered by each process, visualization techniques and the relative sizes of common materials are illustrated in Figure 1.3.

Ultrafiltration has been an industrial process for over three decades. With the advances in asymmetric membranes and improved engineering designs of ultrafiltration modules, in many industrial applications, ultrafiltration systems are favoured over other conventional separation processes due to their low energy requirement (Illias et al 1995). Membrane separations are now effectively used in the separation of particles from solution, salts from water, toxins from blood, separation of a gas from a mixture of gases etc., Further, membranes are used in various industries such as chemical, food, pharmaceutical and metal–finishing industries focus has been made on the preparation of polymer based ultrafiltration membranes for specific applications.
Table 1.1 Size of materials retained, driving force and type of membrane

<table>
<thead>
<tr>
<th>Process</th>
<th>Size of materials retained</th>
<th>Driving force</th>
<th>Type of membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microfiltration</td>
<td>0.1-10µm microparticles</td>
<td>Pressure differences</td>
<td>Porous</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0.5-2 bar)</td>
<td></td>
</tr>
<tr>
<td>Ultrafiltration</td>
<td>1-100 nm macromolecules</td>
<td>Pressure differences</td>
<td>Microporous</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(1-10 bar)</td>
<td></td>
</tr>
<tr>
<td>Nanofiltration</td>
<td>0.5-5 nm molecules</td>
<td>Pressure differences</td>
<td>Microporous</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6 bar</td>
<td></td>
</tr>
<tr>
<td>Reverse osmosis</td>
<td>&lt; 1 nm molecules</td>
<td>Pressure differences</td>
<td>Nonporous</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(10-100 bar)</td>
<td></td>
</tr>
<tr>
<td>Dialysis</td>
<td>&lt; 1 nm molecules</td>
<td>Concentration difference</td>
<td>Nonporous or microporous</td>
</tr>
<tr>
<td>Electrodialysis</td>
<td>&lt; 1 nm molecules</td>
<td>Electrical potential difference</td>
<td>Nonporous or microporous</td>
</tr>
<tr>
<td>Pervapouration</td>
<td>&lt; 1 nm molecules</td>
<td>Concentration differences</td>
<td>Nonporous</td>
</tr>
<tr>
<td>Gas permeation</td>
<td>&lt; 1 nm molecules</td>
<td>Partial pressure</td>
<td>Nonporous</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Difference</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(1-100 bar)</td>
<td></td>
</tr>
<tr>
<td>Membrane distillation</td>
<td>&lt; 1 nm molecules</td>
<td>Partial pressure</td>
<td>Microporous</td>
</tr>
<tr>
<td></td>
<td></td>
<td>difference</td>
<td></td>
</tr>
</tbody>
</table>
Figure 1.3 Filtration spectrum - Various membrane processes, range of particles, membrane pore size and scanning region
1.3 POLYMER MEMBRANES

Based on the separation of water from wine using animal bladder by Abbe Nollet, Fick prepared artificial semi permeable membranes made from an ether-alcohol solution of cellulose nitrate called colloidion. Efforts to control membrane pore size led to the development of artificial membranes. Manegold, Michaels and McBain in 1920s prepared membranes, using regenerated cellulose or cellophane. Those cellophane membranes were used for kidney dialysis, which became the first practical application of synthetic membranes. This paved a way for many other researchers to look into polymers for the preparation of membranes. The simple conditions for polymers to be eligible for the preparation are governed by their availability, capable of forming dense or porous film, correct hydrophilic/hydrophobic balance and a moderate ionic character/dielectric constant. During 1950s due to the breakthrough in membrane technology, scientists, engineers and entrepreneurs intensified the research on the preparation of homopolymeric membranes due to their separation efficiency. Based on the pore size of the membranes, classifications were carried out as microfiltration, ultrafiltration, nanofiltration and reverse osmosis.

1.4 MEMBRANE PREPARATION

Several membrane preparation techniques are available which could be applied depending on the type of membranes required. Some important membrane preparation techniques are discussed as follows.

Symmetric membranes are uniformly isotropic in nature through the cross section of the membranes. These membranes can be porous or dense, but the permeability of the membrane material does not change from point to point within the membrane. The dense membranes are prepared by
solution casting and thermal melt pressing while the porous membrane by irradiation, stretching and leaching. The surface layer performs the separation and is the principal barrier to flow through the membrane. Asymmetric membranes are prepared by the following techniques.

- Interfacial composite membranes
- Solution cast composite membranes
- Plasma polymerization
- Phase inversion

Interfacial composite membranes are prepared on a microporous support membrane. In this method an aqueous solution of reactive prepolymer is deposited in the pores of the micro porous support membrane followed by immersion in a water immiscible solvent solution containing a reactant. This results in a densely cross linked thin membrane layer. The Classification of synthetic membranes is shown in Figure 1.4

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**Figure 1.4 Classification of synthetic membranes**
Solution cast composite membranes are prepared by preparing the thin water insoluble layer and then packing it on microporous support. In plasma polymerization, a support membrane is kept in an inert gas atmosphere at low pressure. When monomer vapour is introduced in the atmosphere at 200-300 milli torr for 1-10 min, an ultrathin polymer film is deposited on the porous membrane sample held in the plasma field.

Although several methods are available, phase inversion is a versatile technique for asymmetric membrane preparation and it has also been employed in our investigation. In this method, polymer solution is first cast using a ‘doctor blade’ to produce a thin film on a glass plate and the solvent is allowed to evaporate. After a predetermined evaporation time, the cast film is immersed in a bath of non-solvent, containing considerable amount of solvent and surfactant. The water rapidly precipitates the top surface of the cast film forming an extremely dense perm selective skin. As the cast film, which was in homogeneous sol phase, is converted to gel by non-solvent, the process of formation of membrane is called phase inversion. Since, the casting solution and the conditions of formation can be varied widely to get controlled structures, the phase inversion process is an extremely versatile technique for asymmetric membrane formations.

1.5 MEMBRANE MODULES

The first requirement in any membrane process is a membrane capable of the function needed, but successful implementation requires packaging of the membrane in a module whose configuration is engineered for specific application. Membranes may be formed as flat sheets, tubes of relatively large diameter, or hollow fibers based on the nature of feed. Important economic considerations in their design and operation include the cost of the supporting and containing vessels, power consumption in fluid
pumping and how much of the module hardware can be reused when the membrane replaced. The types of modules commercially produced are plate and frame, spiral-wound, tubular and hollow fiber (Strathamann 1990).

1.6 ASYMMETRIC MICROPOROUS FLAT SHEET MEMBRANES FOR ULTRAFILTRATION APPLICATION - A REVIEW

Since, colloidal separations are dominated by ultrafiltration process, it follows that membrane cost is highest for this process. This is obviously related to the difficulty of producing these highly structured species (Kesting 1971). Ultrafiltration offers the following advantages over competing processes: there is no heat added and hence heat-labile substances are not harmed; energy requirements are lower than that for lyophilization or evaporation and no chemical denaturation as in the case of salt precipitation or solvent extraction; concentration and purification may be achieved in one step, e.g., enzyme recovery, using diafiltration to wash away unwanted or excess media; the permeate is especially suitable for specialized fermentation broths or final product recovery systems, e.g., by ion exchange, chromatography, adsorption etc., the ultrafilter may be used either directly as a continuous reactor by attaching cells or enzymes to the membrane or by retaining cells and enzymes with the membrane.

1.6.1 Cellulose Acetate Membranes

The development of cellulose acetate membranes of asymmetric structure has wide application in desalination. However, it is more susceptible to chemical and bacteriological agents. This fragility of the membrane material results in heavy and costly installations for the pretreatment of water, difficulties in the storage of the membrane and in the case of accidental
clogging or blocking, the choice of cleaning agents is extremely limited (Brousse et al 1976). A mathematical model based on steady-state mass balance over a boundary layer, coupled with the results from irreversible thermodynamics, is proposed for ultrafiltration of PEG 600 using a cellulose acetate membrane. The model has been developed by taking into account the solvent permeability, solute permeability, and reflection coefficient and can be utilized to predict the value of rejection at any operating condition were taken into account while developing this model (Bhattacharjee and Datta 1996).

On the basis of separation curves, the pore size and pore size distribution of cellulose ultrafiltration membranes are determined (Schwarz and Hicke 1989). Recently there is an increasing need for separation of proteins and peptide drugs from biological broths due to the development of Biotechnology. In the pharmaceutical and food industry, ultrafiltration membrane is required to have a high temperature resistance and solvent resistance. Cellulose acetate membrane has high water permeability and easy manufacturing as an advantage. However, a fairly narrow pH range, compaction and biodegradation limit to expand its applied field (Kurihara and Himeshima 1991).

The effects of pretreatments on morphology and performance of cellulose acetate membranes were investigated by Wang et al (1994). Cellulosic membranes were also prepared and used to effect separation of proteins such as BSA and Immuno-γ-globulin (Net et al 1994). The buoyancy studies of macrovoid pore formation in dry-cast cellulose acetate membranes were investigated by Mathew et al (2002). Flat sheet cellulose acetate membranes were prepared and the compaction at modest pressure and loss of permeability was reported recently. The results show the range of hydraulic pressure suitable for maximum efficiency.
The following advantages of cellulose acetate and its derivatives made it suitable for selecting it as membrane material.

- Moderate flux and high salt rejection properties
- Relatively easy to manufacture and cost effective
- Renewable source of raw material
- Non-toxicity

1.6.2 Polycarbonate Membranes

Polycarbonate (PC) is a family of thermoplastics that possess high performance properties as engineering materials. PC is a transparent, mechanically rigid, tough and exhibits excellent thermal oxidative resistance. In view of their chemical, mechanical thermal and hydrostatic stability, polycarbonate polymers are of practical interest as membrane materials for a wide variety of ultrafiltration applications. The effects of thermodynamic conditions during formation of asymmetric polycarbonate was studied by Hacerlioglu et al (2003). The following characteristics are exhibited by polycarbonate.

- Wide temperature limit: typically temperature up to 75-125°C can be used, which would be an advantage for Microbial and Biotechnological applications.
- Wide pH tolerances: can be exposed to a range of 1-13.
- Fairly good chlorine résistance: Most manufactures permit the use of up to 200 ppm chlorine for short sanitation purposes and up to 50 ppm for long-term storage of the membranes.
Wide range of pore sizes ranging from 10 to 200 Å and molecular cut-off from 1kDa up to 500 kDa are available for ultrafiltration applications.

1.6.3 Sulfonated Polycarbonate Membranes

The adaptability of the membrane processes to wide range of applications stems from the development of new polymers or modifications of the existing polymers (Potnis 1992). The impetus for development of new polymers or modification of existing polymers has been proved by the need for higher flux coupled with high perm selectivity. Polycarbonate membrane possesses excellent mechanical, biological and chemical stability, as well as are tolerant to a wide range of temperature and pH. Wan-Jin Lee et al (2000) have studied the electrical properties of sulfonated polycarbonate membranes.

Transformation of neutral polymers into charged ones is a reason for introducing chemically active groups on membrane polymers. In case of polymers with excellent film-forming properties like polycarbonate, these properties should not be lost by a chemical reaction. Membranes prepared from these ion exchange polymers provide higher water content. Thus chemical modification improves the hydrophilic of the hydrophobic polymer. Rejections are high when the solute concentration is low and become lower with higher concentration, which is the typical trend of the charged membrane. Thus, these membranes can remove low content of inorganic solute at low pressure of ultrafiltration range, resulting in energy saving.

The membranes modified by direct sulfonation had the lowest surface energy and the shortest graft chain length and exhibited the highest volumetric flux with BSA solution. It was also easier to clean and exhibited
the highest initial flux (Nabe et al 1997). The chemical reactions for the modification are membrane preserving, i.e., they do not alter the membrane characteristics considerably. The surface charges of the membranes are changed and it depends on the substitute and on the completion of the reaction. The charged ultrafiltration membranes are more interesting than non-charged membranes for practical applications, as they have three variables: sign, density of charges, and pore size (Kobayashi and Fujii 1992). The charged membrane is able to expel charged solutes and colloids having the same sign as the membrane surface, so that it is less fouled than the noncharged membrane, by the gel layer formation on the membrane surface (Nakao et al 1988). It is therefore useful to apply a charged ultrafiltration membranes to the separation and permeation of constituents such as proteins, enzyme and water-soluble polymer.

When the positively charged UF membrane (sulfonated) is used for separation of proteins (BSA) at pH=4 the fouling is reduced due to repulsion of positively charged proteins at pH=4. When the negatively charged UF membrane (aminated) is used for separation of proteins at pH=7 the fouling is reduced due to repulsion of negatively charged proteins at the same pH.

When negatively charged NF membrane is used for separation of metals, the fouling of the membrane increases due to the positively charged metal ions. Thus this is the difference between charged UF and NF membrane.

1.6.4 Polymer Blends as Membrane Material

More than 99% of membranes used in separation applications nowadays are made from polymers that were originally developed for different applications (Mockel et al 1999). Membranes used in ultrafiltration applications often need to possess both good thermal and chemical resistance.
Unfortunately, polymers fulfilling these requirements best, PC, PES and Polysulfone exhibit high hydrophobicity and in practice leads to a significant loss of performance due to the effects of adsorption. Often polymers do not fit the demand for special applications when they are used in their original chemical form. This problem can be solved either by blending the polymer or by chemical modification (Hinke and Staude 1990). The term polymer blend is used for any mixture of two polymers without any chemical bonding between them, though a degree of compatibility between the polymers is necessary for IPNS (Thomas and Sperling 1978). Thus, polymer blending is a proven tool to obtain new type of material with a wide diversity of properties intermediate between those of pure components along with economic advantages. It is simpler and more feasible technique than combining different polymer segments via copolymerization and formation of interpenetrating networks (IPN).

Polymer blends have provided an efficient way to fulfill new requirements for material properties. Blending is done for a variety of reasons including creating materials with enhanced thermal and mechanical behaviour. The great majority of useful blends are immiscible, and in these blends, mechanical properties can be optimized by controlling the blend morphology (Sundararaj and Macosko 1995). The synthesis of a polymer blend membrane is motivated by the desire to superimpose requisite properties upon the transport properties of a base polymer (Sivakumar et al 1996).

Munari et al (1998) have worked on the preparation and characterization of Polysulfone-Polyvinyl Pyrrolidone (PSF-PVP) based membranes. Several hollow fibre ultrafiltration membranes from PC have been produced by Hacerlioglu et al (2003). Sivakumar et al (1996) have prepared ultrafiltration membranes by blending Polysulfone with cellulose acetate.
In view of the better performance of cellulose acetate, polycarbonate and sulfonated polycarbonate as membrane material these polymers have been chosen in the present investigation to prepare asymmetric, microporous, flat-sheet membranes by phase inversion technique for ultrafiltration applications. The flow diagram for the preparation of membrane by phase inversion method is shown in Figure 1.5.

**Figure 1.5 Preparation of membrane- phase inversion method**
1.7 MEMBRANE CHARACTERIZATION

The technology of separation processes using porous membranes continually finds more applications. The choice of membrane depends on the feed solution to be separated, for which knowledge of the pore size distribution and the internal structure of the membrane is essential when making a choice of the appropriate membrane (Jackson 1995). Thus, membrane characterization is a very important part of membrane research and development because the design of membrane processes and systems depends on reliable data relating to membrane properties.

Characterization of ultrafiltration membranes is of great interest today, both as tool in choosing the proper membrane for the filtration system and in the development of new and better membranes (Zhang et al 1989). In addition to chemical compatibility, the supporting layer must combine high surface porosity with minimal pore diameters (Walch 1983). Membrane permeability depends on the chemical nature of the base polymer and also on its morphological structure i.e., the thickness and porosity (size, number and distribution of the pores) of the skin layer and on the structure of the porous sub-layer (Bottino et al 1984). Yunlan et al (1987) have developed a mathematical method for the study of the effect of water permeability, solute rejection, and other parameters of synthetic membranes on membrane performance. Kuixiang et al (1995) have investigated on the effects of storage time and prefiltration of the fiber casting polymer solutions on the performance characteristics of polycarbonate hollow fiber ultrafiltration membranes.

Porous microfiltration or ultrafiltration membranes are generally characterized in terms of their transmembrane flux, pore size, pore size distribution and molecular weight cut off. Measurements of the water permeability of several commercial ultrafiltration membranes as a function of
pressure and temperature have shown that the convective flux of water was proportional to the pressure and inversely proportional to the viscosity (Nguyen et al 1979). Mulder (1991) concluded that membrane compaction will lead to a denser structure with small pores. Transmembrane flux and membrane solute retention are determined in filtration tests. Transmembrane flux is generally measured as a function of applied hydrostatic pressure with ultra-pure water. Molecular weight of the polymer and the casting solution composition could affect the pore size and pore size distribution on the surface of the resulting membrane (Nguyen et al 1981). The whole investigation is summarized in Figure 1.6.

Investigation on preparation of novel polymeric membranes with superior properties

New membrane material PC is used which is a thermoplastics and possess high performance as engineering materials

Preparation & Characterization:  
- Solution blending of CA/PC and CA/SPC  
- Preparation of UF blend membranes based on CA, PC & SPC  
- Characterization in terms of compaction, PWF, water content, Rm, MWCO, Morphology.

Membranes can be used in the separation of proteins & toxic heavy metal ions.

Membranes thus prepared found to have efficient separation of proteins & heavy metal ions and can be attempted by large scale after necessary modification of the system.

Figure 1.6 Flow diagram of whole investigation
Matz (1972) has studied the mechanism of the development of porous structure in anisotropic cellulose acetate membranes using microscopic studies. For the design of appropriate membrane separation processes, information is needed on the behaviour of the components as a function of the charge, hydrophobic properties and size, the physico-chemical environment these components are present and their interaction with the membrane and its properties such as charge, hydrophobicity and pore size (Timer et al 1998).

Besides membrane thickness and pore radii, pore size distribution and pore density are the other key factors determining the permeability of a ultrafiltration membrane (Mockel et al 1999). The primary characteristic of a membrane is its pore distribution, which defines selectivity and solvent flow determined in terms of their molecular weight cut off, wherein, the rejection of a given membrane for various molecular mass components is determined in filtration tests to investigate the molecular weight transport profiles of ultrafiltration membranes using a synthetic polymer or globular proteins with a distribution of molecular weights (Cooper and van Derveer 1979; Sueoka et al 1983; Issid et al 1992).

The ultrafiltration behaviour of PEGS has been investigated with respect to their partial retention by CA membranes (Papamichael and Kula 1987). Globular proteins were better probes as compared to synthetic linear polymer in the determination of the molecular weight cut-off of membranes (Tam and Tremblay1991). The structures of porous membranes are determined by electron microscopy. Scanning electron microscopy gives a clear picture of membrane structure (Gittens et al 1973; Walch 1983).

Based on the survey of literature, it was decided to systematically characterize the membranes in terms of compaction, pure water flux,
membrane hydraulic resistance by measuring the pure water flux of the membranes at different transmembrane pressures, water content, molecular weight cut-off by using globular proteins of varied molar masses as solute probes and membrane morphology by scanning electron microscopy.

### 1.8 APPLICATIONS OF ULTRAFILTRATION MEMBRANES

Membrane separation processes exploit the physical properties of solute solubility and the solute diffusion coefficient through the membrane to achieve highly selective separations of materials that are only slightly different in physical properties. The membrane separation technologies possess characteristics, which make them attractive for industrial pollution control applications (Cartwright 1985; Sweeney 1985).

Ultrafiltration provides macro-molecular separation for particles in the 20 to 1000 Angstrom range (up to 0.1 micron). All the dissolved salts and smaller molecules pass through the membrane. Items rejected by the membrane include colloids, proteins, microbiological contaminants and large organic molecules (Vigneswaran and Fane 1998). Most ultrafiltration membranes have molecular weight cut-off values between 1kDa and 100 kDa. Transmembrane pressures are typically 1 to 7 bar (15 to 100 psi). Today membranes are used on a large scale to provide potable water from the sea; to clean industrial effluents and recover valuable constituents; to concentrate, purify, or fractionate macromolecular solutions in the food and drug industries; to release drugs at a controlled rate of medium (Strathamann 1990; Barker et al 1984) etc. Typical applications of Ultrafiltration membranes are concentrating proteins from milk whey, or recovery of colloidal paint particles from electrocoat paint rinse waters.
Further impetus for the application of membranes comes from biotechnology where the substrates and/or products are concentrated and purified by means of synthetic membranes. Due to the development of biotechnology, there is an increasing need for the separation of proteins and peptide drugs from biological broths and blood (Higuchi et al 1991). The advantages are large-scale separation and easy operation of the membranes.

The water reuse applications involving ultrafiltration include electro deposition primers, oil-water separation in metal cutting operations, color removal from kraft mill effluents and laundry wastes (Bhattacharyya et al 1975). The use of ultra filtration for the separation of low molecular weight ionic solutes with charged membranes (Bhattacharya et al 1974; Bhattacharyya et al 1975), modest molecular weight organic solutes complex suspensions of a nonionic surfactant, inorganic and particulates (Bhattacharyya et al 1975) and organic macromolecular and colloids (Porter and Nelson 1972), has been reported in the literature. Ultrafiltration is one of the best techniques for the concentration of macromolecular solutions (Nakao et al 1986). Bioprocess operation as cell removal, whole-broth clarification, and downstream recovery and purification of byproducts from invariably dilute and often complex aqueous mixtures.

Ultrafiltration is a process increasingly applied in liquid industrial waste treatment, food processing (fruit juices, cheese whey, milk, starch factory effluent) and pharmaceutical and medical industries. The superiority of the drinking water treatment by membrane ultrafiltration resides in the excellent quality of the water produced, especially as concerns the various parameters relative to the suspended-soled and bacteriological content (Letournuer and Mehra 1993). In various industrial fields such as food and medical industries and bio industry, it becomes increasingly important to
separate solutions constituents such as proteins, enzymes, antibodies, hormones and blood proteins (Nakao et al 1988).

Ehsani et al (1997) have studied the fractionation of ternary mixtures of ovalbumin, conalbumin and lysozyme and natural egg white protein solutions at different pH and two ionic strengths with unmodified and UV modified polysulfone ultrafiltration membranes was also studied. Jaffrin et al (1997) investigated the ultrafiltration of albumin-ethanol solutions on PSU hollow fibre membranes (30 kDa) to identify the mechanism responsible for the observed permeate flux reduction in presence of ethanol. Mukai et al (1998) have conducted ultrafiltration of mixtures of bovine serum and egg white lysozyme using membranes which were almost completely retentive for BSA but permeable for lysozyme. The effects of gas sparging on permeate flux, single protein transmission and protein fractionation have been investigated by Li et al (1997) and Li et al (1998). Experimental results show that gas sparging can increase permeate flux and improve the efficiency of protein fractionation.

Conventional treatment methods for removal of heavy metals from metal finishing operations are usually energy-intensive and costly (Ahmadi et al 1994). Further reverse osmosis is not preferred, since all the other constituents would also be retained by the membrane. However, in ultrafiltration processes high fluxes can be obtained at relatively low pressures. Unfortunately, ordinary ultrafiltration methods are not effective in removing solutes having molecular weights less than about 0.3 kDa (Sriratana et al 1996). Micellar enhanced ultrafiltration with synthetic surfactants is a recently developed technique which can remove heavy metals and other low molecular weight ions from waste streams at relatively lower cost without a phase change (Smith et al 1995; Hanra and Prabhakar 1996; Kim et al 1998; Fillipi et al 1998).
Concentration and recovery of heavy metals such as Hg(II), Cd(II), Cu(II), Pb(II), Co(II), Ni(II) and Ca(II) etc., have been carried out using various complexing agents including polymethacrylic acid, carboxymethyl cellulose (Mundkur and Watters 1993), polyacrylic acid (Bodzek et al 1999), polyethyleneimine (Nguyen et al 1981; Juang and Chen 1996; Uludag et al 1997) etc. Natural ligands such as cholesterol (Huang et al 1994), alginic acid (Solpan and Sahan 1998), lecithins (Huang et al 1994), etc., have also been used as complexing agents in the separation of heavy metals using ultrafiltration technique.

Since, several workers had extensively used polyethyleneimine with better efficiency of separation, it has been chosen as the complexing agent in the present investigation.

Kim and Vigneswaran (1991) have conducted studies on the treatment of starch waste water by anaerobic digestion coupled with membrane separation process. Juang et al (1993) have conducted low-pressure batch ultrafiltration for the removal of dyes from aqueous solutions at 22°C and reported that ultrafiltration is an ideal way to achieve these goals by selection of a membrane with appropriate molecular weight retention characteristics. Cheryan and Rajagopalan (1998) have investigated the membrane processing of oily streams by ultrafiltration. Vigneswaran and Fane (1998) have used ultrafiltration membranes to remove bacteriological and dissolved organics from water and reported a 100% removal of bacteria and virus (Phages of *Shigella* and *E. coli*) and a significant removal of organics (60-70%).

There are various methods of separation of toxic metals from aqueous solution such as coagulation and filtration with or without sedimentation, coagulation assisted micro-filtration, Lime softening, sorption on granules
activated alumina. Each of these traditional methods of treatment involve substantial cost and are often difficult to proper control, especially for small treatment systems and hazardous check-up operations (Papdiamas et al 1997).

Thus, ultrafiltration membranes find a wide range of applications from food and pharmaceuticals to waste water reclamation and hence, in the present investigation attempts have been made to study the performance of the membranes based on cellulose acetate, polycarbonate and sulfonated polycarbonate for specific applications of proteins and metal-ion rejections.

1.9 SUCCESS, NEED AND FOCUS ON MEMBRANE RESEARCH

In the initial stage, membrane technology, suffered from less operational reliability, less selectivity, high expenditure and less productivity etc., To circumvent the above problems, a series of attempts were made to prepare defect free high flux, ultra thin reverse osmosis membrane by Loeb and Sourirajan (1963). The flux of the membranes were ten times higher than that of any available membranes then and made reverse osmosis a practical technology.

However, membrane selectivity, which is the ability of the membrane to make the required separation, remained as a key problem in many membrane techniques. In this direction, Loeb-Sourirajan membranes produced in 1960-63 had high fluxes and were able to remove 97-98% of the dissolved salt. Further, interfacial composite membranes prepared by Cadotte were able to remove 99.8-99.9% of the dissolved salt (Cadotte and Petersen, 1981). Similarly microfiltration, ultrafiltration and electrodialysis membranes are generally able to perform the selective separation. However, in general,
membrane selectivity still remains as unsolved problem in cases of gas separation and pervaporation to some extent.

Productivity on separation performance per unit cost is an important issue in most of the membrane separation processes. Membrane materials, membrane configuration and membrane packaging efficiency constitute the problem of productivity and cost of membrane system. Likewise, reliability is the most generally significant problem in membrane processes. The causes of reliability problems vary from process to process. The various methods of separation of toxic substances are summarized and is shown in Table 1.6.

### Table 1.2 Various methods of separation of toxic substances

<table>
<thead>
<tr>
<th>Process</th>
<th>Features</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorption</td>
<td>Gas or liquid solutes accumulates on solid surface</td>
<td>It is widely used in various industries</td>
<td>Thermal regeneration</td>
</tr>
<tr>
<td>Precipitation</td>
<td>Removal of dissolved inorganic compounds</td>
<td>Extraction of metal is made simple in this method</td>
<td>Process may generate toxic sludge requires proper disposal.</td>
</tr>
<tr>
<td>Ozonation</td>
<td>Organic compounds can be recovered eg., phenol, cyanides etc.,</td>
<td>Requires short time for removal</td>
<td>Ozone has short half-life.</td>
</tr>
<tr>
<td>Solvent extraction</td>
<td>compounds insoluble in water can be removed</td>
<td>oils can be removed</td>
<td>selection of proper solvent.</td>
</tr>
<tr>
<td>Ion exchange</td>
<td>Removes ionic species</td>
<td>Trace quantities can be removed</td>
<td>Expensive</td>
</tr>
<tr>
<td>Adsorption on activated carbon</td>
<td>Highly porous amorphous solids used based on the principle of adsorption</td>
<td>Non-polar and cheap</td>
<td>Combustible.</td>
</tr>
</tbody>
</table>
1.10 SCOPE OF THE PRESENT INVESTIGATION

Membrane technology has its leaps and bounds over several industrial processes and applications. In particular, ultrafiltration and reverse osmosis membranes have ruled over most of the conventional separation processes, because of their several advantages. However, due to the drawbacks discussed earlier, membrane technology has still to be refined for specific environment and applications, so as to maintain the efficiency and effectiveness of the operation.

Hence, to develop high performance UF membranes, for desired application, attention has been given on several aspects of the system. Thus, the properties of cellulose acetate, polycarbonate and sulfonated polycarbonate are found to be suitable hydrophobic/hydrophilic balance, appropriate crystalline/amorphous character. The presence of additive PEG 600 in the blend membranes is expected to play key role in the selectivity, permeability and structure of the resulting membranes.

Hence, it was proposed to modify cellulose acetate and polycarbonate with sulfonated polycarbonate individually and in presence of various concentration of PEG 600 as additive.

In order to prepare membranes with superior properties, such as chemical, mechanical and thermal stability, an investigation on preparation of novel polymeric membranes with the following objectives were made

- Solution blending of cellulose acetate-polycarbonate and cellulose acetate-sulfonated polycarbonate
• Preparation of blend ultrafiltration membranes based on cellulose acetate, polycarbonate and sulfonated polycarbonate

• Study on the effect of additive concentration on polymer blend compositions on the performance of membranes.

• Characterization of the novel membranes in terms of
  o compaction
  o pure water flux
  o water content
  o membrane hydraulic resistance
  o molecular weight cut-off
  o membrane morphology

• Application of the membranes
  o separation of proteins such as trypsin, pepsin, egg albumin and bovine serum albumin
  o separation of toxic heavy metal ions such as Copper (II), Nickel (II), Zinc (II) and Cadmium (II) ions from aqueous streams.