

## **CHAPTER 1**

### **INTRODUCTION**

Membrane technology has become a dignified separation technology over the past decennia. The development of Membrane Science and Technology gains significant advantages in many industries. Efficient separation processes are needed to get high grade products (Bhattacharjee and Datta 1996, Rosberg 1997 and Huang and Koseoglu 1993). Membrane Technology is a kind of filtration process, which possesses extensive range of applications towards separation, purification and concentration of various chemicals. Membrane filtration processes involving microfiltration (MF), ultrafiltration (UF) and nanofiltration (NF) in potable water production have increased rapidly over the past decade. MF and UF are employed to remove microparticles and macromolecules, which generally include inorganic particles, organic colloids (i.e., microorganisms) and dissolved organic matter (DOM). (Zularisam et al 2006)

Membrane Separation Technology is most superior process compared to other conventional separation processes, as it is a highly selective process, efficient process, cost effective process etc., Further, there is no environmental hazard in this non-conventional technique.

#### **1.1 MEMBRANES**

Membrane in a broader sense is a region of discontinuity interposed between any two phases. This implies that membranes can be of gas, liquid, 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 can be classified according to their structures. Homogeneous or symmetric membranes each have a structure that is the same across the thickness of the membrane. These membranes can be porous or have a rather dense uniform structure. Heterogeneous or asymmetric membranes can be categorized into three basic structures integrally skinned asymmetric membrane with a porous skin layer, integrally skinned asymmetric membrane with a dense skin layer, and thin film composite membranes. (Pinnau et al 2000)

### **1.1.1 Historical Overview and Evolution of Polymeric Membranes**

Membrane phenomenon appears to start in 1748 by Abbe Nollet, who observed that a wet pig bladder inflated to the bursting point when placed in the carbon dioxide . In 1861 Thomas Graham did his first dialysis experiment using a synthetic membrane(Graham 1861). Later on he prepared the first polymeric membranes for separation of gases. He also discovered a permeability rate measuring device using flat membranes with a vacuum on one side, displacing a mercury column, and postulated a mechanism for the permeation process. Thomas Graham was considered as the father of membrane science due to his contribution towards the development of membrane separation process. Schoenbein in 1846 was the first to study cellulose nitrate membrane.

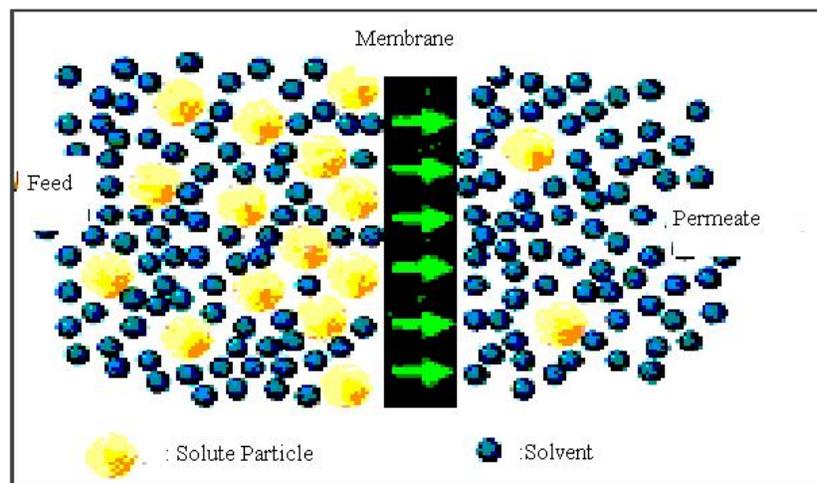
The osmotic phenomena was studied by Traube, Pfeffer and Vont-Hoff in membranes prepared by precipitating cupric ferrocyanide in a thin layer of unglazed porcelain. By the early 1930s microporous collodion membranes were commercially available. During the next 20 years, the early microfiltration membrane technology got extended to other polymers such as cellulose acetate, polysulfones etc, and the membranes found their significant

applications to obtain drinking water followed by industrial applications during 1960s by Sourirajan and Loeb.

## 1.2 MEMBRANE SEPARATION PROCESSES

Membrane processing is a technique that permits concentration and separation without the use of heat. Particles are separated on the basis of their molecular size and shape with the use of pressure (microfiltration, ultrafiltration, reverse osmosis and/or gas separation), a concentration gradient (dialysis) or an electrical gradient (electrodialysis) with a specially designed semi-permeable membranes.

Membrane separation is a kind of filtration technique. When effluent enters the system, two streams are formed namely concentrate, containing contaminate and permeate, containing dilute amounts of contaminate (Cartwright 1994) as shown in the Figure 1.1.



**Figure 1.1 Schematic representation of the membrane separation process**

A common illustration of all types of membrane separation processes is provided in Figure 1.2. However there are few differences exist between the various processes. The real separation mechanism can be based on differences in the size of the permeating components, or in the membrane affinity towards the feed solution constituents.

The solute chemical nature or electrical charges, as well as the vapour pressure of the different components in a mixture often play an important role in membrane separation processes. The two phases separated by the membrane, i.e., the feed and the permeate, may present either in the liquid or in the gaseous state. The driving force that is necessary for the transport may be transmembrane pressure gradient  $\Delta P$ , or a concentration or activity gradient  $\Delta C$  or  $\Delta a$ , respectively, or an electrical potential gradient  $\Delta E$ , or a temperature gradient  $\Delta T$ . Based on these driving forces, the membrane separation processes using membranes can be classified as shown in Table 1.1 (Mulder 1991).

# The Filtration Spectrum

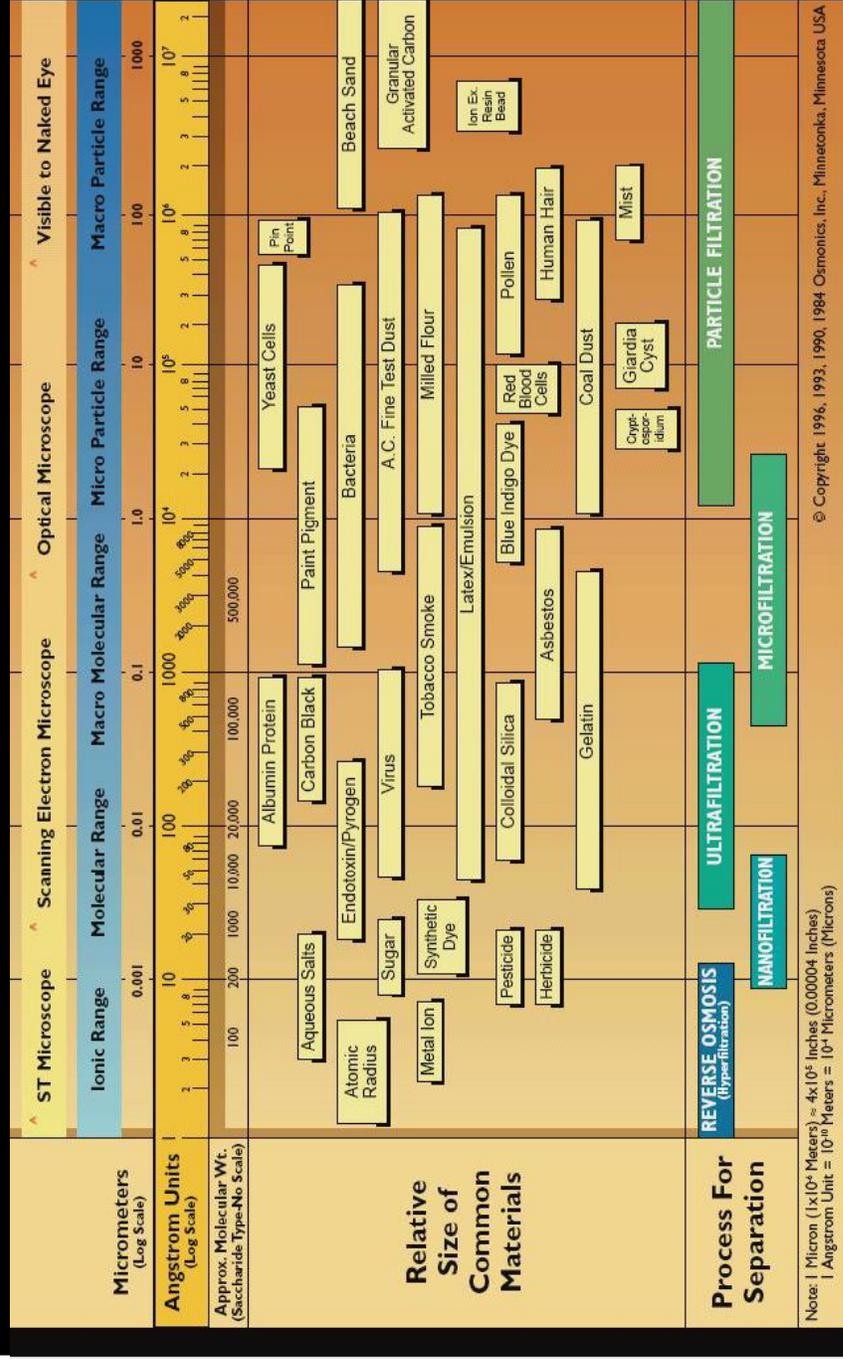


Figure 1.2 Filtration spectrum

**Table 1.1 Overview of membrane processes, driving force, separation mechanism and states of feed and permeate**

<b>Membrane process</b>	<b>Driving force</b>	<b>Feed state</b>	<b>Permeate state</b>	<b>Separation mechanism</b>
Microfiltration (MF)	$\Delta P$	Liquid	Liquid	Size
Ultrafiltration (UF)	$\Delta P$	Liquid	Liquid	Size
Nanofiltration (NF)	$\Delta P$	Liquid	Liquid	Size/ Affinity
Reverse osmosis (RO)	$\Delta P$	Liquid	Liquid	Size/ Affinity
Piezodialysis (PD)	$\Delta P$	Liquid	Liquid	Affinity
Gas separation (GS)	$\Delta P$	Gas	Gas	Affinity/ Size
Pervaporation (PV)	$\Delta P$	Liquid	Gas	Affinity
Dialysis (D)	$\Delta C$	Liquid	Liquid	Size
Osmosis (O)	$\Delta C$	Liquid	Liquid	Affinity
Liquid membranes (LM)	$\Delta C$	Liquid	Liquid	Chemical nature
Electrodialysis (ED)	$\Delta E$	Liquid	Liquid	Charge
Membrane distillation (MD)	$\Delta T, \Delta P$	Liquid	Liquid	Vapour pressure

Industrially important membrane separation processes and their operating principles are given in Table 1.1

**Table 1.2 Comparison of pressure-driven membrane processes**

Membrane process	Pore size (nm)	Material retained	Material passed	Pressure (bar)	Type of membrane
MF	> 50	Particles (bacteria, yeasts etc)	water, salts macromolecules	< 2	Porous
UF	1 – 100	Macromolecules, water, colloids, lattices solutes $M_w > 10,000$	water, salts and sugars	1-10	Microporous
NF	$\approx 1$	Solutes $M_w > 500$ , di- and multivalent ions	water, sugars, monovalent ions	5-20	Microporous
RO	Not relevant	All dissolved and suspended solutes (salts, sugars)	Water	15-80	Nonporous

The first four processes mentioned in Table 1.1 utilize a hydrostatic pressure difference as driving force and are closely related to each other. The ability to separate solutes, based on the pore size of microfiltration, ultrafiltration, nanofiltration, and reverse osmosis is given in Table 1.2 (Lonsdale 1982, Cadotte et al 1988, Eriksson 1988, Petersen 1993).

Ultrafiltration (UF) designates a membrane separation process, driven by a pressure gradient, in which the membrane fractionates components of a liquid as a function of their solvated size and structure. The membrane configuration is usually cross-flow. Due to the low energy requirement ultrafiltration is superior than the other conventional separation processes (Ilias et al 1995).

### 1.3 MEMBRANE PREPARATION

Membranes are prepared by adopting Several techniques depending on the type of membranes required. Few important membrane preparation techniques are discussed as follows.

Symmetric membranes are uniformly isotropic in nature through the cross section of the membrane. 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 membranes 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 Polymerization
- Thin film composite membranes
- UV- grafting
- Phase separation

In Interfacial polymerization, membranes are prepared by coating a reactive monomer on to a micro porous support or base membrane. The reactive monomer will get adsorbed on to the surface of the micro porous support membrane. This results in a densely cross linked thin membrane layer on the surface.

Thin film composite membranes are prepared by preparing a thin water insoluble layer and then packing it on to a porous 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.

Though several methods are available, phase inversion is a versatile technique for the preparation of asymmetric membrane and it has also been employed in our investigation. In this method, Polymer solution is prepared by dissolving a polymer in a suitable solvent. A thin film of polymer solution is made by casting the solution on to a glass plate by a 'doctor's blade' and the solvent is allowed to evaporate. After a predetermined evaporation time, the cast film along with the glass plate is immersed in a bath containing non-solvent, with considerable amount of solvent and surfactant, called as gelation bath. The water rapidly precipitates the top surface of the cast film forming an extremely dense permselective 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.

Prepared membranes suffer from fouling over a period of run. Fouling cannot be completely eradicate from the membrane but it can be controlled by means of several modification. UV grafting or photo functionalization is a versatile method to control fouling over other methods. The membranes are dipped in a monomer solution and the setup is exposed to uv radiation for a predetermined time. During irradiation the photochemical reactions occur and the monomer will gradually gets grafted on to the membrane surface.

Among various alternatives, photochemical surface modification has distinct advantages, i.e., it can be performed at mild reaction conditions and

low temperature, high selectivity is possible by choosing suited photoreactive groups or chromophores and respective excitation wavelengths (Ulbricht et al 1996). This method had been based on the intrinsic photoreactivity of the membrane polymers. As expected, the desired functionalization was always accompanied by more or less severe pore degradation of the membrane. Kaeselev et al reported that the best conditions of modification of PES UF membranes were at the highest monomer concentration and the lowest radiation energy. (Kaeselev et al 2002)

#### **1.4 MEMBRANE MODULES**

A variety of membrane types and configurations has been developed. The types of ultrafiltration modules commercially (Strathmann 1990) produced are

- Flat sheet membrane
- Tubular membrane modules
- Spiral wound membrane modules
- Hollow fibre membrane elements

The immersion type flat membrane module operates suction or gravity filtration while the membrane is being rinsed by aeration. Tubular membranes are based on either PVDF (polyvinylidene fluoride) or PSf (polysulfone). They are capable of continuous, reproducible processing cycles, which means they are cleanable, durable, easy to operate and a proven advance in technology. Spiral wound membrane technology was first introduced more than 30 years ago. Some of the many applications that employ the spiral wound membranes are Seawater desalination, Brackish Water treatment and Recovery of high purity water production, Dairy processing, Whey protein concentration. (Belforte et al 1988)

Hollow fiber membranes have been successfully employed in a wide variety of industries including food, juice, pharmaceutical, metalworking, dairy, wine and most recently municipal drinking water. Depending on the application, hollow fiber membranes can be highly practical and cost effective alternatives to conventional chemical and physical separation processes.

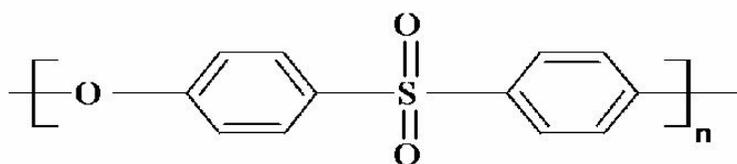
## **1.5 HOMO POLYMERIC MEMBRANES AND MODIFIED POLYMERIC MEMBRANES – A REVIEW**

### **1.5.1 Polyethersulfone**

The development of polyethersulfone membranes of asymmetric structure has found wide range of applications in many separation industries due to their high tolerance towards chemicals, extreme pH environments respectively and it is thermally stable. However, it is more susceptible to fouling due to its hydrophobic character. This fragility of the membrane material results in loss of flux over a period of time. Even the membrane life is reduced due to fouling and the choice of cleaning agents is extremely limited (Brousse et al 1976).

The performance of the polyethersulfone membranes are highly hindered by the fouling effects. This type of fouling can be reduced by modifying the membrane with hydrophilic monomer or a polymer. Many researchers modified the poly ether sulfone membranes adopting various techniques such as Functionalization, Blending, surface modification etc. In order to check the performance of the membranes a 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 (Bhattacharjee and Datta 1996).

Recently there is an increasing need for separation of proteins, humic substances, toxic metals and sediments from water source due to the increasing pollution. In the pharmaceutical and food industry, ultrafiltration membrane is required to have a high temperature and solvent resistances respectively. Polyethersulfone membranes has high water permeability and has high resistance towards wide range of pH, chemical tolerance and are thermally stable. However, fouling during filtration restricts its application (Van der Bruggen et al 2009).



**Figure 1.3 Polyethersulfone(PES)**

The effects of modification on morphology and performance of polyethersulfone membranes were investigated by (Van der Bruggen et al 2009).

The following advantages of polyethersulfone and its derivatives made it suitable for selecting it as membrane material.

- wide temperature limit: typically temperatures up to 90-320° C can be used, which would be an advantage for microbial and biotechnological applications.
- pH tolerances: pH range of 1-13, which is an advantage for cleaning purpose
- fairly good chlorine resistance: up to 200 ppm chlorine for short term sanitation purposes and up to 50 ppm chlorine for long-term storage of the membranes.

- easy to fabricate membranes in a wide variety of configurations and
- wide range of pore size, ranging from 10 to 200 Å and molecular cut-off from 1000 up to 500,000 Da.
- longer shelf-life for dope solution in processing industries
- longer life
- less shut-downs for cleaning
- longer continuous run
- lower surface defects

However, the limitations of polyethersulfone membranes are:

- More hydrophobic

### **1.5.2 Polyetherimide (PEI) Membranes**

Polyetherimides are well known for their photo resistant property and they are highly stable to photo chemical radiations. Polyimides are important, both scientifically and commercially, because of their combination of outstanding key properties, including thermal, thermo-oxidative stability, high mechanical strength, high modulus and excellent electrical properties.

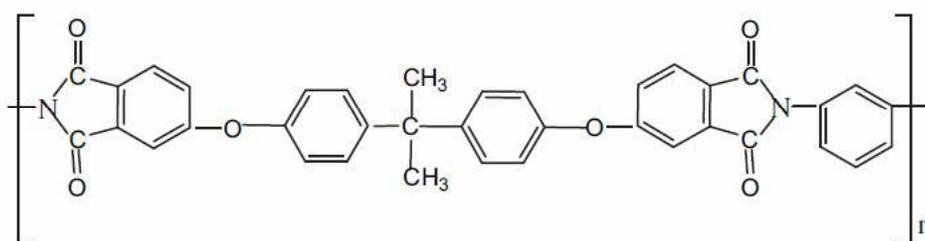
Polyimides are widely used as membrane material, matrix resins, adhesives, coatings, printed circuit board and insulators for high performance applications in the aerospace, automotive, electrical, electronics and packing industries.

The first report concerning polyimides was made by Bogert and Renshaw (1908). Commercially available poly imides are introduced by

Dupont (Sroog et al 1965). Later variety of polyimides were prepared and reported by General electric. (Amancio- filco et al 2008)

The second generation polyimides are highly thermofusible. The aromatic imide units provide high performance properties such as resistant towards heat, chemicals etc. Kim et al (2001) prepared integrally skinned uncharged PEI asymmetric nanofiltration membranes by the dry/ wet phase inversion method. Sulfonated polyetherimide has been reported for developing proton exchange membranes (PEM) Polyetherimide asymmetric membranes was prepared for gas separation. (Serfaty 1984)

Wang et al (1995) have determined the relationship between the mass ratio of non solvent additive to solvent in a membrane casting solution and its coagulation value in preparing asymmetric membranes by wet or dry/wet phase inversion process. The equation developed may be used to indicate a variation of phase separation behavior of the membrane casting solution with a coagulant by the introduction of a nonsolvent additive in the solution.



**Figure 1.4 Polyetherimide (PEI)**

Nagendran et al (2008) have prepared membranes from a casting solution polyetherimide, CA and PEI in 1-methyl-2-pyrrolidone (NMP) as solvent by immersing them in mixtures of water and NMP. Using a model for

mass transfer in the quaternary system, it was possible to explain the effect of the nonsolvent.

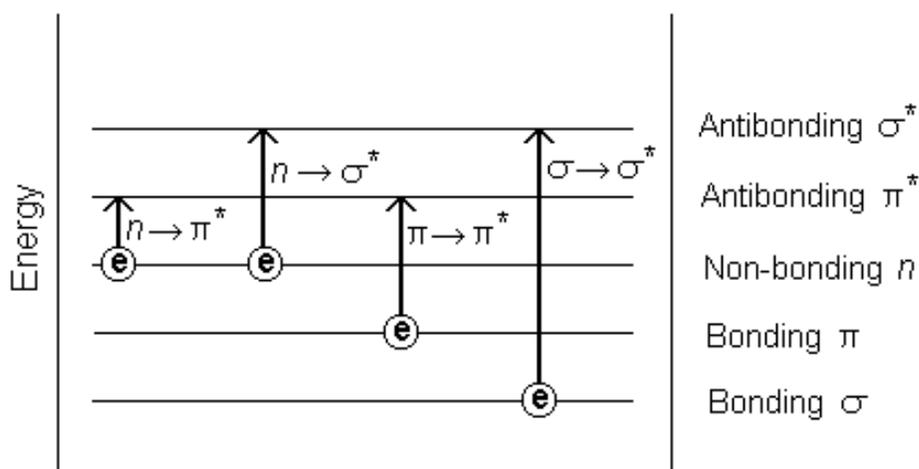
### 1.5.3 UV – assisted photochemical graft Polymerization

Photo-chemical reactions in the most general sense are reactions induced by radiations like ultraviolet rays having wavelength of 100–400 nm, visible rays with wavelength of 400–760 nm and infrared rays having wavelength 780–20,000nm (Susanto et al 2007). Molecules will undergo electronic transitions if it absorbs the radiation

There are three types of electronic transition which can be considered;

- Transitions involving  $\pi$ ,  $\sigma$ , and  $n$  electrons
- Transitions involving charge-transfer electrons
- Transitions involving  $d$  and  $f$  electrons

Possible electronic transitions of  $\pi$ ,  $\sigma$  and  $n$  electrons are;



**Figure 1.5 Schematic representation of electronic transition**

### **$\sigma \rightarrow \sigma^*$ Transitions**

An electron in a bonding  $\sigma$  orbital is excited to the corresponding antibonding orbital. The energy required is large. For example, methane (which has only C-H bonds, and can only undergo  $\sigma \rightarrow \sigma^*$  transitions) shows an absorbance maximum at 125 nm. Absorption maxima due to  $\sigma \rightarrow \sigma^*$  transitions are not seen in typical UV-Vis. spectra (200 - 700 nm)

### **$n \rightarrow \sigma^*$ Transitions**

Saturated compounds containing atoms with lone pairs (non-bonding electrons) are capable of  $n \rightarrow \sigma^*$  transitions. These transitions usually need less energy than  $\sigma \rightarrow \sigma^*$  transitions. They can be initiated by light whose wavelength is in the range 150 - 250 nm. The number of organic functional groups with  $n \rightarrow \sigma^*$  peaks in the UV region is small.

### **$n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ Transitions**

Most absorption spectroscopy of organic compounds is based on transitions of  $n$  or  $\pi$  electrons to the  $\pi^*$  excited state. This is because the absorption peaks for these transitions fall in an experimentally convenient region of the spectrum (200 - 700 nm). These transitions need an unsaturated group in the molecule to provide the  $\pi$  electrons.

The light absorption by substances or materials is often described by the Lambert–Beer law. However, efficiency of light absorption can also depend very much on concentration, matrix effects and other factors.

The current and emerging technical applications of UV–vis irradiation are all based on at least one of the following advantages

- high selectivity of chemical reactions or processes under mild condition (ambient temperature or also much below),
- typically no need for added catalysts or special solvents,
- applicable to very small and (relatively) large scales.

The main technical applications of photo-irradiation with artificial light sources are the following

- chemical synthesis
- UV-curing of coatings
- photo-polymerizations
- photo-lithography
- disinfection, for instance water or wastewater treatment

The primary analysis using photo-irradiation for preparation of a composite membrane involves the coating of the surface by a thin film can be traced back to Steuck's work (Steuck 1986). Hayes (Hayes 1988) group showed that a photo-cross-linked membrane from a Polyimine containing benzophenone tetracarboxylic dianhydride exhibited very high permeation rates while still being able to effectively separate several combinations of gases. Immobilization of glucose oxidase into poly(vinyl alcohol) membrane in the presence of UV light sensitive diazoresin and sodium benzoate sensitizers was done by Liu (Liu et al 1990).

Rühe and co-workers have reported the synthesis of photo-cross-linkable polymer hydrogels using benzophenone as photo-reactive side group of the polymer chain (Murata et al 2004 and Toomey et al 2004). Photo-excitation of benzophenone and subsequent hydrogen Abstraction. Recently, photo-irradiation was integrated into phase separation technique for

membrane formation (Kang et al 2000). Photo-cross-linking was performed by irradiation of a film of a solution of polyimide containing benzophenone. It was reported that such cross-linking preserved the structure of cast solution film until immersing into a non-solvent bath.

Composite membranes for catalysis processes prepared by immobilizing of semiconductor titanium dioxide and organometallic coordination compounds containing cobalt(III) and vanadium(V) via photo-cross-linking polymerization of acrylic monomers have been intensively investigated (Bellobono et al 1994,1997 and Kita et al 1994) reported that the gas permeability of the PI membrane decreased after irradiating with UV light. However, the permselectivity was higher than that of the uncross-linked PI with similar permeability.

Recently, photo-initiated cross-linking of hydrophilic monomers on to a porous membranes were also used to prepare low fouling membranes. Modified polymeric membranes were found to possess less fouling behavior, than their unmodified analogues and the protection is extended to wide range of retentate pH values (Gancarz et al 2000, Potnis 1992). The impetus for development of new polymers or modification for existing polymers has been proved by the need for higher flux with high permselectivity.

Transformation of neutral polymers into charged ones is a reason for introducing chemically active groups on membrane polymers. In case of polymers with excellent permeabilities like polyethersulfone, these properties should not be lost by chemical reaction. UV-assisted photochemical graft polymerization technique is used by many researchers to modify poly(ether sulfone) (PES) UF membranes. since, this exhibit *reduced interaction* with natural organic matter(proteins), as a route to reduce the fouling caused by proteins. UV-assisted photochemical graft polymerization is also employed for surface modification to reduce NOM fouling on reverse osmosis and

nanofiltration membranes by Belfer et al 1999,2001 and Kilduff et al 2000. Poly(ether sulfone) membranes are selected for their photosensitivity and because they offer attractive features for water treatment applications, including wide pH tolerance and good resistance to oxidants, including chlorine under water treatment conditions (Zeeman and Zydney 1996)

The charged ultrafiltration membranes are more interesting than uncharged 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 non-charged 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.

Out of all these advantages, photopolymerization is always accompanied by a reaction called photo scission of the polymeric back bones which results in the loss of thermal stability. But even this can be overcome by blending the reactive polymer with an photoinactive polymers.

#### **1.5.4 Polymer Blends as Membrane Material**

Membranes which are grafted via photochemical reactions have low thermal stability. By blending the base polymer(photosensitive) with a suitable additional polymer(photo-inactive) the thermal stability will gets increased to a greater extent.

Membranes prepared from homopolymers lack certain qualities such as low flux, poor mechanical strength, hydrophobic nature etc., These drawbacks could be eliminated by blending two or more polymers having

desired properties. Blending of a miscible hydrophilic polymer with a chemically or thermally stable hydrophobic polymer has been investigated for achieving stable polymeric materials with improved hydrophilicity (Chiou and Paul 1994).

Membranes from homogeneous blends of these polymers can be prepared by phase inversion. Chen et al (1996) have prepared mechanically stable, partially charged hydrophilic membranes from blends of aminated polysulfone or sulfonated polysulfone with polysulfone.

Blending is used to modify the polymeric material, developing new types of materials and it shows great potential for applications in membranes too (Bikson et al 1994, Baoguo and Hongliang 1996 and Xiuli and Hua 1997). Polyvinylpyrrolidone (PVP), a hydrophilic polymer is known to form blends with polysulfone (Tam et al 1993), polyethersulfone, polyimide, and polyetherimide (Roesink 1989).

Polymer blends have provided an efficient way to fill new requirements for material properties. Blending is done for a variety of reasons including creating materials with enhanced thermal and mechanical behavior. Blends of CA and polysulfone have been prepared by (Sivakumar et al 1995). They characterized the blends by pure water permeability and separation of metal ions in aqueous medium. The great majority of useful blends are immiscible, and in these blends, mechanical properties can be optimized by controlling the blend morphology (Sourirajan and Matsura 1985).

Cellulose acetate as a matrix polymer was blended with polyethyleneimine in a mixture of solvents to prepare a modified microfiltration membrane (Chen et al 2004). The prepared membranes have homogeneously microporous structure, large internal surface area, high pore interconnectivity and mechanical stability.

## 1.6 CHARACTERIZATION OF MEMBRANES

The characterization of the membranes is essential in order to enhance their performance in the separation and technology processes. Membranes were characterized in terms of compaction, pure water flux, contact angle, membrane hydraulic resistance, molecular weight cut-off, fouling-reversible, fouling irreversible and morphological studies. The pore size and inner structure of pores of the membranes play an important role in deciding the type and performance of membranes. Since membrane performance is governed by its characterization, many attempts were made on characterization of membranes. The necessity and effect of compaction on the water flux of ultrafiltration membranes have been studied by Persson et al (1995). The effect of grafting on the performance of polyethersulfone ultrafiltration membranes in terms of water permeability and solute rejection has been studied by Masahide et al 2003.

Kim et al (1990) examined the effect of the density of the hydrophilic group on the pure water flux and water content of membranes. The change in flux was elucidated by considering pore volume change and the site of graft chains. The membrane performance was evaluated by the water flux and the rejection of dextran using a polyacrylonitrile ultrafiltration membranes by Nouzaki et al (2002). Johnson and Johnson (1995) determined the water flux for hydrophobic/hydrophilic ultrafiltration membranes with increasing time. Mulder (1991) concluded that membrane compaction would lead to a denser structure with smaller 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 1980).

The performance of ultrafiltration and microfiltration were determined by protein separation Opong and Zydney (1990). The hydraulic permeability of the protein deposit decreased with increasing the filtration pressure. Water content is directly dependent on the porosity of membranes and it is an index of membrane hydrophilicity and flux and studied by Prabhakar and Misra (1986), Tamura et al (1981), and also Mohan group, Mahendran et al (2004).

The molecular weight cut-off (MWCO) was constructed by measuring the separation values of polyethylene glycol solutes of varying molecular weights. The method for determining the concentration of polyethylene glycol was given by Sabde et al (1997). It is used as an indirect method for determining the pore size of the membrane.

## **1.7 APPLICATIONS OF ULTRAFILTRATION PROCESSES**

Conventional separation techniques such as precipitation, ozonation, biological treatment possesses has lots of disadvantages such as usage of chemicals, huge man power, energy expensive etc,. Whereas, the advanced membrane technology finds widespread applications in the areas of ultrapure water, food technology, animal blood processing, clarification of juice, down stream processing, membrane bio reactors, electrodeposition of paints, oil and latex emulsion treatment, pulp and paper industry etc., (Jonsson and Tragardh 1990). The physical process of separation by ultrafiltration membranes was studied to improve the colour and turbidity removal of the textile effluent (Rosa Maria Ribeiro, 2002).

Cellulose acetate and polysulfone based membranes have been largely used for the treatment of sea water for the production of drinking water. (Jones and Wilson 1998 and Pryor et al 1998). In microbiology, ultrafiltration finds wider usage in the separation and concentration of foot-

and-mouth virus. Stirred cell, flat sheet and spiral configurations of 50 -300 KDa MWCO ultrafiltration membranes made of acrylate polymers were used for the concentration of virus and a maximum of 94% recovery has been achieved (Adikane et al 1997).

Ultrafiltration provides macro-molecular separation for particles in the range of 20 - 1000 Å. 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. Further, impetus for the application of membranes comes from biotechnology, there is an increasing need for the separation of proteins and peptide drugs from biological broths and blood. The treatment of distillery effluent and removal of color is a major problem with sugar industries. Satyajai Mayor (1999) has studied the use of membranes at various stages of effluent treatments in detail. It has been proved that the economics works out to be reasonably satisfactory to the distillery.

Membranes were used to treat waste waters in various mining and mineral sectors like metal leaching solutions, ore washing, flotation process water, acid mine drainage, refinery operations etc., (Awardalla and Kumar 1994). Precious and rare earth metals such as Au, Se and U etc., have been extracted from their dilute solutions. 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.

### **1.7.1 Rejection of proteins by ultrafiltration membrane process**

The rapid growth in the field of biotechnology has led to an increase in the demand for efficient, large-scale protein rejection processes. The major advantage of ultrafiltration processes over conventional processes is high throughput of product. Fane et al (1983) explained ultrafiltration of proteins through partially-permeable membranes. The flux and rejection are time-dependent, flux shows an initially rapid and then a more gradual decline that is attributable to loss of porosity by internal adsorption followed by surface adsorption.

Iritani et al (2002) examined the dynamic behavior of dead-end ultrafiltration of dilute aqueous BSA protein solution. The concentration distributions in the filter cake, accumulated on the membrane surface in dead-end ultrafiltration of protein solutions, were measured using the principle of inclined ultrafiltration where a large amount of filter cake is formed. Balakrishnan and Agarwal (1996) concluded that a high degree of protein separation is generally obtained at low fluxes, corresponding to low transmembrane pressures.

Dynamic ceramic ultrafiltration membrane was characterized in terms of ovalbumin protein solution, the linear velocity along the membrane, bulk protein concentration, pressure and pH in the feed solution were studied in detail (Matsuyama et al 1994). In various industrial fields, such as food and medical industries and bio industry, it becomes increasingly important to separate solution constituents such as proteins, enzymes, antibodies, hormones, and blood proteins (Nakao et al 1988).

Magueijo et al (2002) have reported protein ultrafiltration (UF) and its dependence on UF operating conditions. Cellulose acetate (CA) asymmetric membranes are made in laboratory by the phase-inversion method

and characterized in terms of pure water permeability and molecular weight cut-off (MWCO) (10000 Da for 98% of rejection). Permeation experiments were carried out for solutions of reference solutes in order to characterize the membranes and for lysozyme solutions under different operating conditions. The influence of the ionic strength in the permeation flux and protein rejection is studied by performing permeation tests with a solution of lysozyme ( $0.3 \text{ kg/m}^3$ ) containing different NaCl concentrations.

The transmission of the major chicken egg with proteins ie, ovalbumin and conalbumin, were found to depend on the transmembrane pressure; transmission decreased with increase in transmembrane pressure (Gosh et al 2000). Mukai et al (1998) have conducted ultrafiltration of mixtures of bovine serum albumin and egg white lysozyme using membranes which were almost completely retentive for BSA but permeable for lysozyme. Chiang et al (1993) have reported a two-step process involving diafiltration and affinity separation for purification of lysozyme.

The contributions of individual protein species to the apparent critical flux were evaluated as well as the separation performance by Ghan et al (2002). For mixtures of globulin/lysozyme and BSA/lysozyme the larger retained protein tend to control the critical flux behaviour. Causseranda et al (2002) determined the apparent MWCO of ultrafiltration membranes using a mixture of dextran protein solutions. Tests were conducted with a flat-sheet membrane with an effective filtration area.

### 1.7.2 Fouling behavior of membranes

The undesirable formation of a layer on the surface of the membrane during filtration is known as fouling. Surface property of a membrane holds a key factor in fouling as it determines the interaction between proteins and materials (Ho et al 1999). The contact of synthetic materials, particularly polymers, with biological environment usually induces nonspecific protein adsorption, which is generally unfavorable in bioinstrumentations such as medical devices, biosensors, chromatographic supports and membrane modules due to the negative affect on their performance(Lee et al 1997 and siegers et al 2004). Flemming and Schaule(1988) confirmed that the first irreversible attachment of cells occur within a few minutes of contact between a membrane and feed, they also detected a biological affinity of different membrane materials towards bacteria.

Fouling is of different types, according to the sites, fouling are classified into external and internal fouling. Fouling can be of inorganic, organic, bio according to the nature of foulant. Fouling which can be removed by washings is considered as reversible fouling, whereas irreversible fouling cannot be recovered by washings or by chemical treatment. If so, the surface layer will get damaged or the life of the membrane will get reduced.

Biofouling of reverse-osmosis membranes with wastewater was reported by Ghayeni et.al., (1998) and Ridgway et al.(1983,1985) . Protein and carbohydrate represented as much as 30% and 17% respectively of the dry weight of the biofilm. Electronmicroscopy revealed that the biofilm on the feed water side surface of the membrane was 10 to 20 mm thick and was composed of several layers of compacted bacterial cells.Ridgway (1991) confirmed that bacterial adhesion is regulated by the physico-chemical properties of both feed and the polymeric membrane surface. Generally

proteins form a layer on the surface of the membrane by intermolecular disulfide linkages.

The morphology of the membrane surface can influence the formation of the fouling layer. Riedl et al(1998) used an atomic force microscopy technique to measure membrane surface roughness, and scanning electron microscopy to assess the fouling layer. Finally they concluded as, smooth membranes produced a dense surface fouling layer whereas biofilm on rough membranes was much more less. Scott et al. (2000) found that the use of corrugated membranes enhanced the flux in a more efficient way by promoting turbulence near the wall region resulting in mixing of the boundary layer and hence reducing fouling.

A fouling-resistant reverse osmosis membrane that reduces microbial adhesion was reported by Jenkins and Tanner (1998) modified membranes were superior in filtration process than unmodified membranes. Scientists should therefore be able to minimize microbial adhesion by controlling the surface chemistry of polymer membranes, through, for example, the inclusion of hydrophilic groups.

Belfer (1988) described a simple method for surface modification of commercial composite polyamide reverse osmosis membranes. ATR-FTIR provided valuable information about the degree of grafting and the micro structure of the grafted chain on the membrane surface. It was shown that some of the modified membranes conserved their previous operating characteristics, flux, or rejection, but exhibited a higher resistance to humic acid.

A desirable surface for biological needs should promote favorable properties to non-specifically repel all proteins, which can be obtained by immobilizing hydrophilic polymers since many studies demonstrate the

increase of surface hydrophilicity can availablely reduce protein adsorption (Lee et al 2000). Among all the technologies for concentration or purification of protein solution, ultrafiltration takes an increasing important role. However, membrane fouling caused by nonspecific protein adsorption and deposition induces severe decline in permeate flux with operation time and a serious impact on the efficiency and economics of the protein recovery process.

Jarusutthirak et al (2002) isolated different fractions of organic matter in the waste water (Ghayeni et al 1998). Each fractions exhibited different characteristics in fouling of nanofiltration (NF) and UF membranes. For example, the colloidal fractions gave a high flux decline due to pore blockage and hydrophobic interactions were very important for hydrophobic membranes causing a reduction in permeate flux.

Various techniques such as chemically or radiation induced grafting and plasma polymerization have been explored for the modification of ultrafiltration membrane (Taniguchi et al 2004). In comparison, surface modification seems to be a promising technique because of its facile operation, high efficiency, and low cost. The surface modification technique can be described as follows: hydrophilic polymer is blended in membrane casting solution, and during the subsequent phase inversion process, the hydrophilic segments of the additive are segregated to the membrane surface spontaneously whereas the hydrophobic parts are firmly entrapped in the membrane matrix.

By choosing appropriate recipe and processing parameters, the obtained membrane will be homogeneously modified at both external and internal surfaces, and the hydrophilic property of the additive will endow the membrane with favorable long-term stability (Hancock et al 2000).

## 1.8 SCOPE AND OBJECTIVES OF PRESENT INVESTIGATION

Though several reports on the properties and performance of various membranes are available, membranes suitable for specific environment and applications with improved properties such as antifouling properties, fouling due to concentration polarization and due to gel layer formation, have not been reported deeply. Hence, in the present investigation, an attempt has been made to develop UF membranes with improved low fouling properties by photo functionalization. In this study, Polyethersulfone (PES) have been chosen as the base polymer for photofunctionalization. Since, photo chemical reactions are always accompanied with photo chain scission reaction, Polyetherimide, a photo inactive polymer is chosen for blending with the base polymer. Polyethersulfone (PES) and Polyethersulfone / Polyetherimide blend membranes are subjected to UV irradiation in the presence of two different hydrophilic monomers such as Acrylic acid and N-vinyl Pyrrolidone.

The objectives of the present investigation are,

- Studies on solution blending of PES with PEI at various blend compositionss
- UV- assisted photo grafting of PES/PEI blends with acrylic acid and N-vinyl pyrrolidone as monomers individually
- Studies on the effect of irradiation time on photo grafting
- Confirmation of grafting by Infra-Red(IR) spectroscopy and Thermo gravimetric analysis(TGA)
- Characterization of the above blended and grafted membranes in terms of compaction, pure water flux, contact angle, hydraulic resistance, molecular weight cut-off and morphology

- Studies on the applicability of the above membranes for the separation of
  - Proteins such as trypsin, pepsin, egg albumin and bovine serum albumin from aqueous streams.
- Anti fouling studies of the membranes with BSA
  - Reversible and irreversible fouling
  - Flux recovery after hydraulic washing and chemical cleaning