Chapter 1

INTRODUCTION

1.1 INTRODUCTION TO MEMBRANES

Cleaner and greener processes are preferred in any industrial production/processing unit in view of increasing environmental pollution. Every complete industrial unit includes one or more separation processes. Compared to equilibrium governed separation processes, e.g., adsorption, distillation, evaporation etc., rate governed membrane based separation processes have gradually become attractive alternatives in many industrial applications. In membrane based separation processes two bulk phases are physically separated by a membrane phase. Using an applied transmembrane pressure, the feed is separated into two phases: permeate (the materials that go through the membrane) and retentate (the portion of the feed retained by the membrane). The transport of materials between permeate and retentate phases is controlled by the nature of the membrane (principally molecular weight cut-off) and the operating conditions (transmembrane pressure, velocity etc.).

A membrane is a semi-permeable barrier separating two phases (feed and product stream) where selective transport of species through the membrane takes place. The application of membrane techniques involves a number of advantages in terms of low energy and chemical consumption (less environmental pollution), increase capacity, separation in continuous mode with the possibility to integrate membrane processes with other unit processes. The separation is carried out in mild conditions. Membranes for industrial separation processes can be classified according to the driving force that causes permeate flow through the membrane. The relevant driving forces are pressure difference, temperature difference, concentration difference, electric potential difference. The driving forces corresponding to the respective membrane process are listed in Table 1.1.

Table 1.1: Driving forces and their respective membrane process

Driving force	Membrane separation process
Pressure difference	Microfiltration Ultrafiltration Nanofiltration Reverse osmosis
Temperature difference	Membrane distillation
Concentration difference	Dialysis Membrane extraction
Electric potential difference	Electro dialysis

1.2 CLASSIFICATION OF MEMBRANES

The focus of the present work is based on pressure driven membrane separation process in which flux through the membrane is induced by an applied pressure difference between the bulk solution and the permeate side. Membrane processes in this category include reverse osmosis, nanofiltration (NF), ultrafiltration (UF) and microfiltration (MF) which are becoming increasingly widespread in water treatment and wastewater reclamation/reuse applications (Drewes et al., 2003; Fusaoka et al., 2001; Mohammad & Ali, 2002). Classification of membrane based separation processes can also be made based on the operating pressure, membrane pore size and molecular weight of solutes to be separated and is tabulated in Table 1.2.

Table 1.2: Classification of membranes based on the operating pressure, membrane pore size and molecular weight of solutes

Membrane process	Operating pressure (atmospheres)	Pore size (Å)	Molecular weight of solute to be separated
Microfiltration	2-4	>1000	>100000
Ultrafiltration	6-8	20-1000	1000-100000
Nanofiltration	15-25	5-20	200-900
Reverse osmosis	>25	2-10	<100

1.3 SOME IMPORTANT CONCEPTS RELEVANT TO MEMBRANE SEPARATION

1.3.1 Feed

The influent or the feed, also referred to as the feed stream, to a membrane process is the stream that is to be treated.

1.3.2 Permeate

The effluent or permeate, also referred to as the filtrate or the product stream, is the liquid that has passed through the membrane.

1.3.3 Concentrate

The concentrate or the retentate, also referred to as the reject, is the waste stream that is retained by the membranes.

1.3.4 Flux

Flux is the volume of water that passes through a membrane per unit of time and per unit surface area of the membrane.

1.3.5 Molecular Weight Cut Off (MWCO)

The molecular weight cutoff (MWCO) or nominal molecular weight cutoff is an alternative means of measuring which particles will or will not pass through a membrane. MWCO indicates that 90% of the species with a molecular weight larger than the MWCO will be rejected. Molecular weight is measured in Daltons.

1.3.6 Membrane Fouling

Membrane fouling is the reduction of the flux through a membrane caused by the buildup of solutes. The fouling of a membrane can take place either at the surface (macrofouling) or inside the pore (pore fouling or micro fouling). Fouling can be reversible (restored by air scouring or chemical cleaning) or nonreversible.

1.3.7 Transmembrane Pressure

The transmembrane pressure (TMP) is defined as the difference between the average feed/concentrate pressure and the permeate pressure. It is effectively the driving force associated with the process and is an overall indication of the feed-pressure requirement for a given operation.

1.3.8 Membrane Permeability

Permeability of a membrane is the combination of flux and transmembrane pressure defined as the flux per unit pressure of driving force. The pure water flux through the membrane is directly proportional to the applied pressure difference. Membrane permeability indicates how porous the membrane is, and the permeability is measured by conducting experiments with distilled water. Permeate flux values at various operating pressures are measured and the slope of flux versus pressure plot gives the permeability. The membrane permeability is denoted by L_p and it is expressed in m/(Pa·s).

1.3.9 Dead-End and Cross-Flow Filtration

In dead-end filtration, the bulk solution is pressurized through the membrane. Thus, permeate will be forced through the membrane and the bulk solution will decrease in volume since the feed is contained in a batch cell. The feed flows at right angles to the membrane. In dead-end filtration the pressure is constant over the whole membrane area. In dead-end filtration, no retentate is continually removed. The schematic of dead end filtration is given Fig. 1.1. In dead-end filtration, the cake grows with time and consequently the flux decreases with time (Scott, 1995).

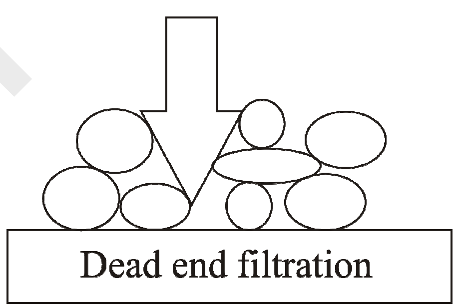

Figure 1.1: Schematic illustration of dead end filtration

In cross-flow filtration the bulk solution is pumped tangentially at a high pressure along the membrane surface. The feed flows across the membrane surface. The pressure will not be constant over the whole membrane area as there will be a pressure drop along the membrane surface. In cross-flow mode, the feed is introduced at one end of the membrane feed channel and the retentate is returned at the other end of the membrane feed channel. The schematic illustration of cross-flow filtration is given in Fig. 1.2. Flux decline is relatively small in case of cross-flow filtration.

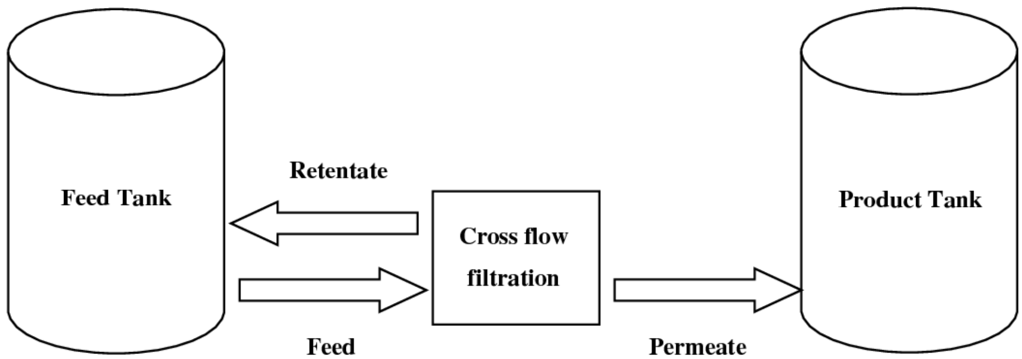

Figure 1.2: Schematic illustration of cross-flow filtration

Cross-flow filtration has several advantages in comparison to dead-end filtration namely, high shear force near the membrane surface, feed stream recycling, low fouling tendencies, minimizing the cake layer formation over membrane surface and stable flux.

1.3.10 Concentration Polarization

The basic operation of membrane separation leads to an accumulation of the retained solutes and a depletion of the permeating components adjacent to the membrane forming a boundary layer. This phenomenon is more commonly known as concentration polarization (Blatt, et al., 1970). The polarization of the solutes leads to a decrease in the available driving force of the preferentially permeating solutes across the membrane and leads to an increase of the retained solutes. The accumulation of solutes at the membrane surface adversely affects the membrane performance in terms of reduction in permeate flux and separation efficiency. Concentration polarization is of considerable interest since high permeate rate is most desirable in filtration processes (Song & Elimelech, 1995). The reduction in performance is manifested by a fall in flux with time, the extent of the effect varies with the type of separation.

1.3.11 Solution – Diffusion Mechanism

At the feed side, the components are being dissolved in the membrane and transported by diffusion through the membrane with driving force acting inside the membrane. At the permeate side the components leave the membrane. Separation results from differences in the solubility of the components into the membrane material and differences in velocities of diffusion through the membrane (Wijmans & Baker, 1995). The driving force is solely activated by properties of the membrane material, like chemical affinity, and not of porosity (the geometry) of the membrane. Because the transport is a result of the solubility and the diffusivity, the separation process is called 'solution-diffusion' mechanism.

1.3.12 Darcy's Law

Solvent flow through the membrane is quantified by Darcy's law. It describes the governing equation, for solvent flow through a porous medium (Hoffman, 2003; Belfort et al., 1994).

1.3.13 Stagnant Film Theory

The film theory describes the relationship between the bulk, permeate and membrane surface concentration and the flux. It assumes a film of constant thickness is formed over the membrane surface (Auddy et al., 2005; Zydney, 1997).

1.3.14 Kedem-Katchalsky Equation

Kedem-Katchalsky model includes convection in the solute transport mechanism within the membrane (Kargol, 2001; Kargol, 1996). According to Kedem-Katchalsky model solute flux is a sum of diffusive and convective transport.

1.3.15 Types of Motion Through Membranes

This includes Permeation, Knudsen diffusion and convection.

1.3.15.1 Permeation

This is the chief mode of transport for reverse osmosis membranes because RO membranes are dense membranes with very low pore size. Permeation involves three steps.

(a) Dissolution-of the species in the membrane matrix,

(b) Diffusion-through the membrane matrix,

(c) Desorption-of the species from the membrane matrix to the permeability side.

1.3.15.2 Knudsen diffusion

This is the chief transport mechanism for gases. Gas molecules are transported under rarefied medium. Knudsen diffusion is valid for $(d/\lambda) < 0.2$. where, d=pore diameter, λ= mean free path.

1.3.15.3 Convection

This is the chief transport mechanism for ultrafiltration and microfiltration membranes because of higher pore size. Convection is the viscous flow occurring through the pores. Convection is valid for $(d/\lambda) > 20$. where, d=pore diameter, λ= mean free path.

1.4 ADVANTAGE OF MEMBRANE SEPARATION PROCESSES

Membrane based separation processes have several advantages over conventional separation processes such as, i) high efficiency; operational simplicity and flexibility; ii) physical separation process with unique separation capabilities; iii) high selectivity and compatibility; iv) low energy and chemicals consumptions; v) treatment of heat sensitive materials e.g., fruit juice; vi) mild operating condition (non-thermal process); vii) no phase change; viii) less capital and operating cost; ix) good stability and modularity; x) easy control and scale-up.

1.5 APPLICATION OF MEMBRANE SEPARATION PROCESSES

Advances in development of new membranes with better thermal, chemical and improved transport have led to new applications. Pressure driven membrane based separation processes are used for separation in extensively varying industrial processes which includes bio-separation, chemical industries, dairy, drinking water, food processing, pharmaceutical, petrochemicals, pulp and paper, sugar, tannery, textiles, water treatment etc.(Ghosh & Cui, 2000; Rai et al., 2008; Benitez et al., 2008; Nenov et al., 2008; Van Der Horst et al., 1995; Guo et al., 2010; Meier-Haack et al., 2003;Jacangelo et al., 1997; Rai et al., 2006; Cakmakce et al., 2008; Mänttäri et al., 2008; Hamachi et al., 2003; Cassano et al., 2001; Tang & Chen, 2002).

1.6 MAJOR LIMITATIONS OF MEMBRANE SEPARATION PROCESSES

In spite of various benefits, membrane based separation processes have certain drawbacks during operation that leads to decline in flux. This is primarily due to concentration polarization and membrane fouling (Schulz & Ripperger, 1989).

1.6.1 Concentration Polarization

A concentration boundary layer develops during membrane separation, leading to accumulation of solutes near the membrane surface and the phenomenon is called concentration polarization.

Consequences of concentration polarization are as follows,

- Increase in solute concentration on the membrane surface leads to an increase in the osmotic pressure of the solution, thereby reducing the effective driving force for the solvent flow (Bader & Veenstra, 1996; Gekas & Olund, 1988; Kim & Hoek, 2005; Lyster & Cohen, 2007; De & Bhattacharya, 1997).
- For certain macromolecules like proteins, a gel with constant gel concentration may also form on the membrane surface. Since the bulk concentration of

higher molecular weight solute is much less than that of the gel layer concentration, a concentration boundary layer forms from the bulk of the solution up to the gel layer. Formation of cake or gel type layer on the membrane surface that offers an additional resistance to the permeate flow, in series to that of hydraulic membrane resistance (De & Bhattacharya, 1997; Karode, 2000).

- Changes in physico-chemical properties of solution with solute concentration such as viscosity, diffusivity and density within the boundary layer which adversely affects the permeation rate (Gill et al., 1988; Field & Aimar, 1993; Aimar & Sanches, 1986).
- Membrane permeability may be reduced to a larger extent, due to the partial or complete pore blocking (Kimura et al., 2004; Wiesner & Chellam, 1999). Concentration polarization may lead to fouling due to deposition of retained material on the membrane material as well as adsorption inside the pores leading to pore blocking (Seminario et al., 2002). All these factors lead to a decrease in system performance i.e., throughput of the system.

All of these phenomena hinder permeate flow. These flux reducing phenomena cannot be avoided completely in any membrane separation process but the effects can be minimized to a certain level.

1.6.2 Irreversible Membrane Fouling

Concentration polarization can facilitate irreversible membrane fouling by altering interaction among solvent, solute and membrane. Membrane pores may be completely or partially blocked by the solute particles. There may also be solute adsorption at the pore mouth or inside the pores leading to pore clogging. All these factors result in the reduction of membrane permeability. This loss of permeability cannot be recovered even after thorough washing causes irreversible fouling.

1.7 WAYS TO REDUCE CONCENTRATION POLARIZATION

Extensive research has been carried out to reduce fouling and thereby improve permeate flux. There are several approaches to reduce the concentration polarization in membrane processes and thereby increases the membrane performance in terms of permeate quality and flux. A very simple way to address the problem is to increase the cross flow velocity of the retentate stream over the membrane surface in the membrane channel. This sweeping action of the tangentially flowing feed over the membrane surface results in the removal (atleast partially) of the solute particles accumulated over the membrane surface leading to a decrease in the concentration polarization and a reduction of the osmotic pressure of solutes over the membrane surface.

The major approaches to reduction of concentration polarization and flux enhancement are:

i) Hydrodynamic modification and use of turbulent promoters to improve mass transfer (Krstic et al., 2007; Auddy et al., 2004), unsteady flows (Mercier et al., 1997), spacers, back flushing and cleaning also lead to flux improvement (Lim, 2003).

ii) Addition of air/gas to the liquid stream to increase turbulence near the surface of the membrane thereby suppressing boundary layer formation (Cui & Wright, 1996).

iii) Vibration of flat sheet reverse osmosis membrane to reduce fouling (Shi & Benjamin, 2009).

iv) Application of external body force such as dc electric field (Sarkar et al., 2009; Henry et al., 1977), magnetic field, etc.

v) Modification of membrane surface, e.g., by plasma treatment to reduce fouling (Tyszler et al., 2006).

1.7.1 Change of Hydrodynamic Conditions

By modifying the membrane surface, interaction between the solute and membrane can be changed to minimize fouling. But, once the cake or gel-type layer is formed, the only alternative left is to change the system hydrodynamics so that mass transfer can be improved. Hydrodynamics in the flow channel can be altered either by steady state technique or by imposing instability to the flow. In the steady state technique, high cross flow velocity or stirring can be used.

1.7.2 Turbulent Flow

An increase in cross flow velocity in the flow channel is the simplest way to reduce concentration polarization and fouling on the membrane surface. With increase in cross flow velocity, membrane surface concentration decreases by forced convection due to increased turbulence. The associated decrease in the osmotic pressure or the reduction in the gel layer thickness (in case of gel-controlled separation) results in an enhancement of permeate flux. However, high turbulence may create increased axial pressure drop which may, in turn, decreases the transmembrane pressure drop and increases the pumping overhead (Belfort et al., 1994).

1.7.3 Unsteady Flows and Induction of Instabilities

The observation that introduction of instabilities in the flow channel results in an enhancement of mass transfer was first reported by Thomas in 1973 (Thomas, 1973). Hydrodynamic instabilities can be caused by (i) turbulent promoter, (ii) gas sparging, (iii) pulsatile flow.

1.7.3.1 Turbulence promoter

The function of turbulent promoters is to generate local turbulence in the flow channel leading to lesser accumulation of solute particles over the membrane surface, thereby augmenting the permeate flux. A variety of turbulence promoters have been investigated. The insertion of rods, wire ring, glass beads, baffles, doughnut disk baffles, and moving balls in the flow channel has been identified to minimize fouling (Hiddink et al., 1980; Najarian & Bellhouse, 1996; Costa et al., 1993; Mackley & Sherman, 1993; Krstic et al., 2007; Howell et al., 1993). Turbulent promoters create instabilities close to membrane-solution interface where the solute build up is much higher. Introduction of intermittent jets (Arroyo & Fonade, 1993), screw threaded flow parameters (Millward et al., 1995); static mixers (Hiddink et al., 1980), etc. are also some examples of successful use of turbulence promoters.

1.7.3.2 Gas sparging

Gas sparging, the injecting gas bubbles into the feed, has recently been identified as an effective technique to enhance the performance of ultrafiltration and microfiltration membrane(Cui & Wright, 1996; Cui & Wright, 1994; Cabassud et al., 1997; Mercier-Bonin et al., 2001; Ghosh et al., 1998). The addition of air to the liquid stream increases both the turbulence at the surface of the membrane and the superficial cross flow velocity within the system, suppressing boundary layer formation, leading to an enhancement of the filtration process. Different gas-liquid two-phase flow patterns are described and air bubbling and other factors that influence the phenomena of flux enhancement have been probed in detail (Mayer et al., 2006). Gas bubble enhanced membrane processing has been applied to MBR, hybrid membrane processes for surface water polishing, bioprocesses separations and cell harvesting (Cui et al., 2003). Experimental studies conducted so far aim to improve knowledge of the gas-sparged hollow fiber ultrafiltration (HFUF) process with the ultimate goal of process optimization, through experiments with precisely controlled flow distribution and well-characterized hydrodynamic conditions. It was observed that gas sparging in HFUF membrane systems can increase the permeate flux up to 102% (Smith & Cui, 2004). Lee et al. have also reported the use of air slugs to improve the cross-flow filtration of bacterial suspensions (Lee et al., 1993).

1.7.3.3 Pulsatile flow

Application of pulsed flow is found to be effective to reduce concentration polarization and fouling (Wang et al., 1994; Finnigan & Howell, 1990). Pulsed flow may be generated by vibration of porous plate above the membrane surface, pump vibration or ultrasound. Bauser and his coworkers have used periodic sequence of pumping pulses keeping mean flow constant during microfiltration of whey and observed improvement of flux by about 38% (Bauser et al., 1986).

1.7.4 Plasma Treatment

Hydrophobicity in membrane materials can cause severe fouling problems (Koh et al., 2005). Therefore, membrane modification is usually done to increase the resistance of the membrane towards fouling. Among the various surface-modification techniques, low temperature plasma treatment is regarded as the most advantageous one. For the design and development of surface-modified polymer membranes, the capability of plasma to change the physical and chemical properties of polymeric surfaces without affecting the bulk properties of the base material is advantageous. Plasma treatment is generally carried out using gases like argon, hydrogen, carbon dioxide, helium, oxygen, ammonia, etc. (Der Bruggen, 2009; Pal et al., 2008; Gancraz et al., 1999; Kim et al., 2002; Lue et al., 2007; Tran et al., 2007; Tyszler et al., 2006; Ulbricht & Belfort, 1996; Wavhal & Fisher, 2002; Yu et al., 2005).

1.8 TANNERY-MAJOR SOURCE OF POLLUTION

The major focus of the present study is to develop distinct methods to treat different effluent from a tannery which will be introduced in subsequent chapters. The tannery is considered one of the major polluting industries owing to the intrinsic nature of the technologies that are employed for manufacturing of leather. Leather industries generate large volume of liquid effluent from each processing steps. Wastewater treatment is by far the most important environmental challenge being faced by tanneries. Each tannery operation e.g., soaking, liming, deliming, bating, pickling, degreasing, tanning, neutralization, dyeing, fatliquoring, finishing, etc., produces huge quantities of polluting effluent and is extensively chemical consuming. The sequence of steps involved in leather manufacturing is presented in Fig. 1.3. The generated wastewater contains appreciable amount of organic and inorganic materials leading to water and soil pollution. The lack of effective rules and regulations as well as poor treatment practices has further aggravated the pollution problem caused by the tanning industry over the years.

The effluent generated from a tannery has a very high pollution load which contains higher concentrations of total dissolved salts, suspended solids, chlorides, etc. The effluent from tanneries are highly colored, foul smelling, contain a heavy sediment load including toxic metallic compounds, chemicals, biologically degradable materials and large quantities of putrefying suspended mater. Many authors have done a thorough characterization of different streams generated by tanneries (Tünay et al., 1995; Orhon et al., 1999; Rivela et al., 2004).

In addition, dyes and leather-lubricating oils used in different processes of a tannery are also found in the effluent. It is reported that approximately 50% of the chemicals used in these processes turn up into wastewater or sludge (Thanikaivelan et al., 2002).

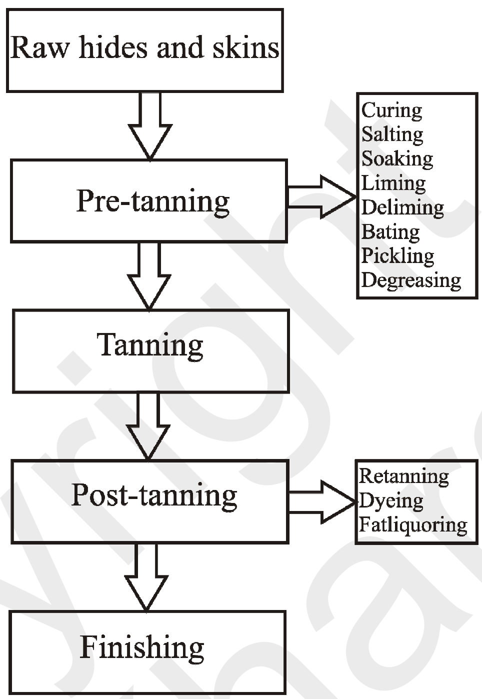

Figure 1.3: Steps involved in leather manufacturing

The tannery discharges include different types of waste, primarily in the form of liquid effluent containing organic matters, chromium, sulfide, ammonium, and other salts, which affect the quality of the environment and are toxic to the flora, fauna and human health (Scholz & Lucas, 2003). Serious deterioration in the quality of groundwater takes place as a result of the effluents discharged from the tanneries. Also, the chemicals used mainly for the preservation of leather, have been a matter of great concern because they are highly toxic. Standard methods are not available for handling and safe disposal of tannery effluents in view of the fact that they depend on the many distinct steps involving a variety of different chemicals employed for leather making and depending on the type of leather produced. Due to increased awareness of environmental conservation, government policy is becoming stricter and appropriate treatment protocol for treatment of tannery wastewater has become an important social issue (Purkait et al., 2005). When unprocessed effluents are discharged to environment without prior treatment they create severe ecological imbalance. To partially balance the effluent treatment costs, reuse of water and recovery of chemicals to the maximum extent possible would be advisable (Cheremisinoff, 2002). The effluents generated are therefore treated conventionally or using modern techniques.

1.9 CONVENTIONAL TREATMENT METHODS FOR THE TREATMENT OF TANNERY EFFLUENTS

In several states in India, especially in Tamil Nadu, the state government has issued order to tannery industries for having a zero discharge plant. Varieties of conventional treatment techniques are available to remove pollutants from wastewater with an objective to separate wastes from water (Garrote et al., 1995; Munz et al., 2009; Haydar & Aziz, 2009; Song et al., 2000; Song et al., 2001; Song et al., 2004). Wastewater treatment processes can be considered separation processes which includes physical, chemical and biological processes. Sedimentation, flotation and screening are examples of physical processes where physical forces are applied in order to remove floating and settleable solids found in wastewater. Coagulation, flocculation, adsorption, disinfection, pH adjustment and dechlorination are typical chemical processes that are designed to bring about some form of change by means of chemical reactions, while biological processes include biological digestion. Biological treatment may not always be suitable for wastewaters with intermittent flows, wastes containing substances toxic to biological growth and wastewaters containing non-biodegradable impurities. In these processes, microorganisms, particularly bacteria, convert the colloidal and dissolved carbonaceous organic matter into various gases and into cell tissue, which is then removed in sedimentation tanks (Grady et al., 1999). The limitations associated with conventional methods are significant due to the fact that they are land and labor intensive and have often been found to be quite expensive.

Thus, conventional methods like biological treatment, adsorption, coagulation, etc., have various limitations (Bellona & Drewes, 2007; Frenzel et al, 2006; Mo et al., 2007; Scott & Ollis, 1995). Therefore, the needs for effective and economical removal of unwanted materials have resulted in search for newer methods and materials that might be useful in this field (Veriansyah & Kim, 2007). To fulfill the requirements of recycling of valuable components from waste streams and concentration of waste volume for further waste elimination process, membrane processes offer a probable solution.

1.10 ADVANCED TREATMENT OF TANNERY EFFLUENT USING MEMBRANE PROCESSES

Membrane technologies have become very attractive today as a viable alternative to the wastewater treatment for the recovery of valuable components as well as reuse of water (Fusaoka et al., 2001; Drewes et al., 2003). Membrane processes include reverse osmosis, ultra-low pressure reverse osmosis, nanofiltration (NF) and ultrafiltration (UF) (Drewes et al., 2003; Fusaoka et al., 2001) and are often chosen, since these applications achieve high removals of constituents such as dissolved solids, organic carbon, inorganic ions, and regulated and unregulated organic compounds (Braghetta et al., 1997).

Mechanism of separation is of fundamental importance. On this basis membranes may be categorized as dense or porous. Dense membrane processes comprise reverse osmosis (RO), electro dialysis (ED) and nanofiltration (NF). Separation by dense membranes relies to some extent on physico-chemical interactions between the permeating components and the membrane material, achieving separations of the highest selectivity. Porous membranes in contrast achieve separation mechanically, i.e. by sieving, and are therefore, mechanistically closer to conventional filtration processes. Ultrafiltration (UF) can remove colloidal and dissolved macromolecular species, and as such their ability to reject material is defined by the molecular weight cut-off in Daltons (i.e., the relative molecular weight) of the rejected solute, rather than its physical size (Christopher et al., 2004).

Thus, the major advantage in membrane based separation over conventional separation processes is that it is a physical separation process and no chemicals are required. They are less energy intensive requiring no phase change and working conditions are mild with the possibility of easy scale-up.

1.11 SPECIFIC MEMBRANE PROCESSES FOR THE TREATMENT OF TANNERY EFFLUENT

During tannery processing, 30 to 40 liters of effluent per kg of skin or hide is discharged. In the case of finishing operation, this quantity can reach up to 50 liters per kg (Dutta, 1999). This implies that tanneries must have their own facilities for treatment of wastewater in their site itself and the treated water should be reused in the plant.

In this regard, membrane based separation process offer a promising alternative to the conventional chemical intensive processes (Cassano et al., 2001). Usually the top skin layer of the membrane governs the separation performance of a membrane. Literature search indicates two routes of research attempts in this field. The first one is to collect the effluent discharged from different process streams except the chrome tanning stream, because of high toxicity of tanning effluent and the combined effluent is treated (Jain et al., 2006). Here, this common effluent is subjected to a series of hybrid treatment processes including pretreatment by coagulation, coarse filtration, nanofiltration and reverse osmosis. The second trend suggests treatment of effluent emerging from individual unit operations (Espantaleón et al., 2003). This scheme recovers both water and useful chemicals that can be recycled to the upstream unit directly which reduces the operating costs of the plant. Individual treatment scheme helps in better recovery of chemicals. Treatment of effluent from each process streams separately is desirable than mixing all the effluents together in a common header for treatment. This idea was first conceptualized by Cassano et al. generated substantial research work aiming at the treatment of specific effluent.

The role of membranes for treating individual tannery process effluents is now well accepted. The treated water has two streams. Chemical rich stream can be recycled thus lowering the operating cost. The other stream which has quite low COD (chemical oxygen demand) content can be recycled as process water. The sludge that is generated in this case can be used as fertilizer. Various applications of the membrane based processes, e.g., microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) on different effluent streams of the beam house are reported in literature. It is reported that reverse osmosis could also be employed for the treatment of exhausted liquor coming from pickling unit, after an appropriate pretreatment, to recover the salt component in the retentate. The permeate solution could be employed for the preparation of soaking baths or as washing water.

Similarly, Alves and Pinho suggested ultrafiltration as suitable process to decolorize the wastewater emerging from dyeing unit of the tannery (Alves & Pinho, 2000). Das et al. attempted a hybrid separation process involving gravity settling, coagulation by alum followed by nanofiltration and reverse osmosis for treatment of soaking effluent discharged from a tannery (Das et al., 2007). Bes-Piá et al. reported reclamation of pickling wastewater from a tannery by means of nanofiltration (Bes-Piá et al., 2008). The viability of using nanofiltration membranes for elimination of chromium content present in tannery effluents is also investigated (Ortega et al., 2005). Pilot scale studies have also been carried out for removal of toxic chemicals from spent tanning effluent (Hafez et al., 2002). Ahmed et al., studied the behavior of membrane with respect to the composition of the solution at various stages and reported on tanning and liming bath by employing nanofiltration solution (Ahmed et al., 2006). Galiana-Aleixandre et al. have used nanofiltration for the pickling effluent and the feasibility of the process is evaluated (Galiana-Aleixandre et al., 2005). In these works, energy intensive reverse osmosis and nanofiltration process are used. For the recovery and recycling of primary resources, membrane processes offer good opportunities (Cassano et al., 2007).

1.12 FACTORS AFFECTING MEMBRANE PERFORMANCE

The main operational disadvantage of membrane based separation is reduction of permeate flux with time due to membrane fouling, caused by the accumulation of feed components on the membrane surface (termed as concentration polarization) due to transmembrane pressure drop and adsorption inside the pores causing pore blocking. The pore blocking can further be classified as complete, intermediate and partial (Bai & Leow, 2002; Field et al., 1995). Mathematical descriptions of blocking rules are first proposed by Hérmia (Hérmia, 1982). He derived the equations for each of these blocking rules from the first principles for unstirred batch cell.

Concentration polarization offers resistance against the solvent flux. The fouling also depends on the concentration of the organics in the feed. Thus, a higher concentration of organics would increase membrane fouling. At constant applied pressure, fouling causes a decline in permeate flux over time. Although periodic membrane cleaning generally restores the permeate flux, membrane replacement become eventually inevitable resulting in higher operational and maintenance costs. Foulants can be categorized into several groups such as sparingly soluble (inorganic) salts, organic substances, colloidal and particulate matter and biological growth. Natural organic matter such as humic acid is considered to be one of the major causes of membrane fouling. Fouling of membranes is generally a function of initial flux and feed water composition, and that the flux decline was likely more dependent on the foulant deposited and foulant interaction rather than on the virgin membrane properties. Some potential mechanisms have been identified as contributing to the flux decline in the fouling studies (Schäfer et al., 2000).

Back diffusion of one foulant type may be hindered by the presence of the concentration polarization of fouling layer of other types of foulants. During filtration, permeate flow brings the solute towards the membrane surface, convective flow transports the solute along the membrane surface tangentially, and Brownian diffusion and shear-induced diffusion simultaneously transport the solute back to the bulk fluid. However, for small particles shear-induced diffusion is negligible (Belfort et al., 1994). Adsorption of dissolved macromolecules on colloidal surfaces can disturb electric double layer interactions and alter van der Waals forces among colloids and between colloids and membranes, as well as cause steric hindrance effects. A number of studies on colloidal transport in porous media have shown that natural organic matter can play an important role in facilitating the transport of natural and model colloids (Akbour et al., 2002; Amirbahman & Olson, 1993). Moreover, interactions between the organic foulants and the membrane surface can modify membrane surface properties, like membrane surface roughness, hydro-phobicity and charge, and are shown to affect flux behavior (Bellona & Drewes, 2007; Childress & Elimelech, 1996; Vrijenhoek et al., 2001). These changes can significantly modify the fouling behavior of colloidal particles by either increasing or decreasing (depending on the molecular characteristics of the organic foulant) colloidal aggregation in the concentration polarization layer and their deposition on the membrane surface.

Fouling of a membrane can occur by deposition of particles inside or on top of the membrane. The flux decline using the blocking rules valid for batch mode was developed by Hérmia. Here, intermediate pore blocking followed by cake filtration was the dominant fouling mechanism. Analysis showed that both standard and intermediate pore blocking models fitted the data well indicating deposition of particles inside as well as on the pore mouth causing decline in permeate flux. Clarification of very dilute suspensions of fine particles using microfiltration membranes is being increasingly applied in water-purification processes (Madaeni & Fane, 1996). One of the critical issues in the development of effective processes is a rapid flux decline attributed to pore-blocking phenomena arising from particles reaching the membrane as well as the formation of the filter cake (McCarthy et al., 2002). The steps of membrane blocking during dead end microfiltration of protein (BSA) solution are reported in literature (Bowen et al., 1995). They observed at high pressure, fouling of membrane consists of complete pore blocking followed by cake formation. At lower pressure, cake formation took place earlier. A simple and convenient filtration model has been developed to describe the blocking phenomenon of the membrane pores (Iritani et al., 2005). Jonsson et al. studied fouling in microfiltration membrane during filtration of BSA in cross flow mode (Jonsson et al., 1996). Various membranes with different average pore sizes (0.9 and 0.2 µm) were studied. Ruohomaki and Nystorm analyzed the flux decline during MF of humic acid using 0.7 µm ceramic filters (Ruohomaki & Nystrom, 2000). Studies of protein fouling during microfiltration have shown considerable differences between filtrate flux data and predictions of the classical pore blockage, pore constriction, and cake filtration models. Therefore, a new mathematical model was developed for permeate flux which accounts for initial fouling due to pore blockage and subsequent fouling due to the growth of a protein cake or deposit over these initially blocked regions (Ho & Zydney, 2000). Their results indicated complete pore blocking for initial filtration followed by cake filtration were the mechanisms for flux decline and the model parameters were evaluated by optimization of the experimental permeate flux profiles. The model was shown to be in excellent agreement with experimental data obtained during the stirred cell filtration of bovine serum albumin solutions through polycarbonate track-etched microfiltration membranes. Rai et al. analyzed the cross flow ultrafiltration data of depectinized mosambi juice using various membranes (Rai et al., 2006). They observed that complete or partial pore blocking might occur during first few minutes of the filtration, the growth of the cake type of layer over the membrane surface by the higher molecular weight solutes dictated the long term flux decline.

Concentration polarization is mostly reversible in nature since majority of flux decline due to concentration polarization can be recovered after membrane cleaning. However, sometimes it is impossible to remove the adsorbed solute from membrane. This type of fouling is known as irreversible fouling. The membrane fouling increases with an increase in the organic concentration in the effluent. Increase in solute concentration over membrane surface also leads to an increase in the osmotic pressure in the solution. This leads to a decline in permeate flux. Thus, accumulation of solute over the membrane surface can lead to adsorption or cake or gel type layer formation on the membrane surface. These factors reduce the membrane performance in terms of its productivity. Generally, the identification of mechanism and quantification of flux decline during continuous cross flow mode are based on considering one fouling mechanism at a time. However, it is entirely possible that more than one mechanism for flux decline coexist.

1.13 BACKGROUND OF PROPOSED RESEARCH

Membrane separation processes are being increasingly integrated with conventional technologies as hybrid membrane systems to make products energy efficient and with minimum environmental impact. Many treatment processes using membranes are proposed for discharged tannery effluents. The role of membranes for treating these effluents is now well accepted. A hybrid treatment scheme includes treatment of tannery effluent using coagulation and membrane operation is anticipated. For implementing any process scheme in any industrial application a detailed parametric study is required along with the development of mathematical models. However, scant data are available on such detailed experimental study along with theoretical interpretations. Keeping this in mind, in the present work, a combination model is adopted for treatment for tannery effluent generated from individual units from a tannery.

In literature, treatment of individual tannery effluents namely, soaking, liming, deliming-bating, tanning and dyeing effluent had already been carried out using hybrid membrane separation process (Das et al., 2007; Das et al., 2007; Das et al., 2008; Das et al., 2006; Cassano et al., 2001). Three effluents from individual units of a tannery namely pickling, fatliquoring and degreasing are now selected for treatment.

First the effluent undergoes appropriate pretreatment followed by membrane separation process. Suitable membranes are selected based on stirred batch cell experiments. Once the process scheme is selected, experiments are carried out in cross flow mode in three flow regimes (laminar, turbulent and laminar regime with turbulent promoters). Experiments are performed to observe the effects of various process parameters in detail. Theoretical models are developed and used for prediction of process outputs. The phenomenological equations for transport through membranes using the solution-diffusion model are based on the fundamental statement that flux is proportional to a gradient in chemical potential. The numerical solutions of the model equations coupled with the experimental data add insights to this complex process and will be important for scale up for the ultimate use in the industrial design of the process.

A variety of flux enhancement techniques have been attempted and their efficacy in terms of increases in permeate flux has been probed in detail, e.g., the use of air-sparging and plasma treatment. The effect of body forces on flux enhancement during air-sparging in a flat sheet module has been investigated. Important insights into the process are obtained by accurately measuring the deposition pattern of solutes as functions of various operating parameters. Ar-O_2 plasma treatment is used to treat poly-ether-sulfone (PES), essentially a hydrophobic membrane that is widely used for a number of separation applications. The surface changes are quantified and experiments confirm the enhancement of flux through the treated membranes.

1.14 OBJECTIVE OF THE WORK

The primary objective of the proposed research is to carry out systematic investigations for purification of tannery waste-waters for recycling utilizing membrane separation processes and an in-depth theoretical analysis that can subsequently be used for scale up. By tuning the processing conditions and through hydrodynamic modification of flow over the membrane surface using turbulent promoters, significant reduction in concentration polarization and hence flux enhancement are achieved. Induction of two phase flow by addition of air to the liquid stream to increase turbulence at the surface of the membrane suppresses the formation of boundary layer and has shown to be quite effective. Further, plasma modification of membrane surface has resulted in enhanced hydrophilicity of commercially available membranes making them less susceptible to fouling.

The specific objectives are itemized below:

- ✓ Evaluation of the feasibility of specific membrane based separation processes for the treatment effluent from pickling, degreasing and fatliquoring units of a tannery.
- ✓ Depending upon the permeate quality of ultrafiltration/nanofiltration, the use of subsequent filtration (reverse osmosis) is considered leading to the design of hybrid or sequential membrane processes for each of these effluent.
- ✓ The effects of incorporating turbulent promoters in the flow path are investigated with the aim to improve permeate flux (throughput of the system).
- ✓ To develop theoretical models for membrane fouling that would be used to predict permeate flux and permeate quality.
- ✓ Use of air-sparging and plasma treatment for further flux enhancement in specialized cases.

1.15 ORGANIZATION OF THE THESIS

The thesis is divided into six chapters. The brief content of each chapter is given below.

Chapter 1 provides an introduction and a detailed literature review of membrane separation in general and tannery effluent treatment in particular. In this chapter, the need for membrane based separation technology and its basic theory, application, major limitations and ways to overcome those drawbacks are described. The review includes a detailed discussion about separate treatment strategy for tannery effluent which is identified as a major source of environmental pollution. The discussion includes tannery effluent treatment using conventional methods and alternate treatment techniques using membrane separation processes. Selection of suitable membranes for treatment of individual tannery effluent is discussed.

Chapter 2 deals with the treatment of pickling effluent from a tannery. The pickling effluent being highly acidic in nature cannot be discharged as such to the surrounding atmosphere. First, a suitable membrane is selected based on the results of dead-end filtration. A scheme is proposed to treat pickling effluent using a hybrid separation technique that includes suitable coagulation followed by ultrafiltration in cross flow mode. The membrane filtration experiments are carried out in laminar, laminar with turbulent promoter and turbulent flow regimes in cross flow mode. Effect's of transmembrane pressure drop, cross flow velocity on the permeate flux and quality are studied. A combined model based on osmotic pressure and Kedem-Katchalsky mechanism is used to predict transport coefficients relevant to the ultrafiltration process.

Chapter 3 discusses the treatment of degreasing effluent generated from a tannery. A scheme is proposed to treat the degreasing effluent using a hybrid separation technique that includes suitable coagulation and single step nanofiltration. A theoretical model is proposed using a combination of osmotic pressure and solution diffusion model for nanofiltration. Three relevant transport coefficients, namely, the effective osmotic coefficient, solute diffusivity and solute permeability through the membrane are obtained by comparing the model predicted results with experimental data of permeate flux and permeate concentration. The flow regimes encompass the laminar and turbulent zones, including laminar flows with turbulent promoters and the flux enhancement due to the hydrodynamic modifications are also quantified.

Chapter 4 presents a scheme for the treatment of fatliquoring effluent generated from a tannery, using gravity settling, two step coagulation process and nanofiltration followed by reverse osmosis. A detailed parametric study highlighting the effects of transmembrane pressure drop and cross-flow velocity has been performed in the three different flow regimes as explained before. A combination of osmotic pressure and solution diffusion model is used to analyze the data further.

Chapter 5 describes two different ways of flux enhancement, namely, air-sparging and plasma treatment to reduce contaminant deposition thereby enhancing the flux and separation. Image analyzing video microscopy is used to accurately quantify the change in deposition thicknesses on the membrane surface as functions of the operating parameters. The use of air-sparging to reduce deposition on the membrane and consequent fouling during ultrafiltration and nanofiltration has been studied with a model solute (pectin) and an industrial effluent (degreasing effluent from tannery). Once the effectiveness of the method is established with the model solute (pectin), the same technique is successfully used to treat degreasing effluent from a tannery. In the second part of Chapter 5, a detailed description of argon-oxygen (Ar-O_2) plasma treatment of polyethersulfone (PES) membranes is presented. The aim is to enhance hydrophilicity of the membranes leading to less deposition of solute particles and subsequent flux enhancement. An appreciable decrease in contact angle and increase in permeability of the treated membranes are accurately quantified. Relevant experimental data involving polyethylene glycol (PEG) as the model solute are presented as well.

Finally, **Chapter 6** highlights the important conclusions and scope for related further research.