Pre-Treatment of Textile Industry Wastewater Using Ceramic Membranes

A Dissertation

submitted in partial fulfilment of the requirement
for the award of degree of

Master of Technology
In
Environment Science and Technology

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CERTIFICATE

This is to certify that the thesis entitled, "**Pre-Treatment of Textile Industry Wastewater Using Ceramic membranes**" submitted by **Ms. Priyanka Saini** (Roll No. 601201017) in partial fulfilment of the requirements for the award of the degree of **Master of Technology** in **Environment Science & Technology** at **Thapar University, Patiala** is an authentic work carried out by her under our supervision and guidance.

To the best of our knowledge, the matter embodied in this thesis has not been submitted to any other university/ institute for award of any degree or diploma.

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DECLARATION

I, the undersigned, hereby declare that the research work presented in the M.Tech project entitled "**Pre-Treatment of Textile Industry Wastewater Using Ceramic Membranes**" has been carried out by me under the supervision and guidance of ***Dr. A.S. Reddy, Associate Professor and Head (School of Energy and Environment) and Dr. Vijaya Kumar Bulasara, Assistant Professor, Chemical Engineering Department**, **Thapar University, Patiala***.

Further, I declare that no part of this Dissertation has been submitted for a degree or any other qualification of any other university or examining body in India/elsewhere.

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ACKNOWLEDGEMENT

I would like to express my deepest gratitude to **Dr. A.S. Reddy**, Associate Professor and Head, School of Energy and Environment, Thapar University, Patiala, under whose guidance I had the privilege to complete this thesis. I wish to express my deep gratitude towards him for providing individual guidance and support throughout the thesis work.

I convey my sincere thanks to my co-guide **Dr. Vijaya Kumar Bulasara,** Assistant Professor, Chemical Engineering Department, Thapar University Patiala for the encouragement and cooperation.

I am also thankful to, **Mr. Amarpreet Singh Arora** and **Mr. Harpreet Singh Bhangu** for their kind help and suggestions at various stages of my work.

My greatest thanks are to all who wished me success especially my parents. Above all I render my gratitude to the Almighty who bestowed self-confidence, ability and strength in me to complete this work for not letting me down. I do not find enough words with which I can express my feelings of thanks to my dear friends for their help, inspiration and moral support which went a long way in successful competition of the present study.

Finally, I would like to extend my gratitude to all those persons who directly or indirectly helped me in the process and contributed towards this work.

At last but not the least, I am thankful to the authors, whose work I have consulted and quoted in my thesis report.

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ABSTRACT

Textile dyeing processes are among the most environment unfriendly industrial processes, because they produce coloured wastewaters that are heavily polluted with dyes, textile auxiliaries and chemicals. The wastewaters originating from dyeing processes are generally characterized by the high content of color caused by the dyestuffs; salts; chemical oxygen demand (COD) deriving from additives such as acetic acid, detergents and complexing agents; suspended solids including fibers; high temperature and broadly fluctuating pH. Since textile is one of the major industries and it utilizes a huge volume of water, membrane technology can be an efficient and cost-effective method for treating textile effluents. Membrane separation process is a novel separation technology with high separation efficiency, low energy consumption, easy operation, and no pollution.

In the present work, ceramic membranes have been evaluated for their suitability in removing COD, colour, conductivity, TDS, turbidity etc. to treat the wastewaters of textile processing. A low-cost ceramic membrane has been prepared in laboratory using paste method. The prepared membrane had a porosity of 40% with an average pore diameter of 274 nm. The water permeability of the membrane was 1376 L/m^2.h.bar. The prepared membrane showed excellent corrosion resistance against basic medium. Two types of wastewater, namely, sulphate containing and chloride containing textile dye bath effluents have been collected from a cotton mill located in Ludhiana. The wastewater has been analysed for contaminants before and after the dead-end microfiltration experiments. Complete (100%) removal of TSS was obtained for both types of wastewater. Considerable removal of COD, TDS, BOD and color has been achieved in the microfiltration process. The results showed that the prepared membrane has a very good potential to be used for pretreatment of textile dye bath effluent prior to NF/RO.

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LIST OF ABBREVIATIONS

ADBW	Acid Dyebath Wastewater
AOP	Advanced Oxidation Process
APHA	American Public Health Association
BOD	Biological Oxygen Demand
CA	Cellulose Acetate
CF	Coagulation–Flocculation
CFMF	Crossflow Microfiltration
CFV	Crossflow Velocity
COD	Chemical Oxygen Demand
Da	Dalton
ED	Electrodialysis
EDTA	Ethylenediaminetetraacetic Acid
IS	International Standards
kPa	Kilopascals
MF	Microfiltration
MW	Molecular Weight
MWCO	Molecular Weight Cutoff
NF	Nanofiltration
NPOC	Non-Purgeable Organic Carbon
PES	Polyethersulfone
PSD	Particle Size Distribution
PTFE	Polytetrafluoroethylene
PVDF	Polyvinylidene Difluoride
PVP	Polyvinylpyrrolidone
SDS	Sodium Dodecyl Sulphate
TH	Total Hardness
TMP	Transmembrane Pressure
UF	Ultrafiltration

CHAPTER 1
INTRODUCTION

1.1 MOTIVATION

The textile chemical processing industry has importance of its own, being one of the basic needs of society and currently it is in the midst of a major restructuring and consolidation phase with the emphasis on product innovation, rebuilding and environmental friendliness. The textile industry has a major impact not only on the nation's economy but also on the economic and environmental quality of life in modern community. Textile industry is one of the oldest and heaviest polluters in the world. Textile effluents have been subjected to a considerable extent of research for many years due to the fact that they are generated in huge volumes in addition to being quite complex in nature due to the presence of several dyes and auxiliary chemicals. The textile industry consists of a number of processes employed for converting fibers of natural origin such as cotton, silk and wool, and of synthetic origin such as nylon; first into fabrics by weaving and knitting and then into the final products by applying wet processes such as dyeing, sizing, printing, and finishing. These stages involve treating the fabric with chemical baths including dispersing agents, salts, emulsifiers, leveling agents, and in some cases heavy metals, and often require additional washing, rinsing, and drying steps, and hence they imply a large consumption of fresh water, energy, chemicals and a large production of waste streams. In terms of waste generation and environmental impacts, wet processing is the most significant textile operation. The wastewaters originating from dyeing processes are generally characterized by the high content of colour caused by the dyestuffs; salts; chemical oxygen demand (COD) deriving from additives such as acetic acid, detergents and complexing agents; suspended solids including fibers; high temperature and broadly fluctuating pH **(Allegre et al., 2006).**

Various methods can be applied to treat cotton textile effluents and to minimize pollution load **(Rameshbabu et al., 2007)**. Traditional technologies to treat textile wastewater include various combinations of biological, physical, and chemical methods and even advanced treatment but these methods require high capital and operating costs and suffer from the limitation of not being able to treat highly coloured wastewaters resulting from textile processing **(Ranganathan et al., 2007)**. Colour removal by conventional treatment methods was found to be inadequate because most textile dyes have complex aromatic structures that resist degradation. They all are stable to light, oxidising agents and aerobic digestion. Membrane based separation process has gradually become an attractive alternative **(Fersi et al., 2005).** The application of membrane filtration processes not only enables high removal efficiencies but also allows reuse of water and some of the valuable waste constituents **(Marcucci et al., 2002).**

As the environmental regulations became stringent and the cost of freshwater is increasing day by day, reclamation of wastewater becomes more and more necessary. Membrane filtration technology assisted with the physico-chemical pre-treatment methods is reported to be one of the most promising technologies for the reclamation of textile effluents **(Bes-Pia et al., 2002).** The significant drawback of membrane technology is the flux decline caused by membrane fouling. Implementation of the right pre-treatment process is very important to minimize flux decline and hence maintain an efficient membrane separation process **(Bruggen et al., 2005).** In the present study, ceramic membranes evaluated for their suitability in removing COD, colour, conductivity, TDS, turbidity etc. and to treat the wastewaters of textile processing. Permeate quality will be analysed from the membrane process.

1.2 IMPORTANCE

The potential scarcity of water supplies on the earth has become one of the most challenging problems of human beings. The world population is ever increasing, creating the need for more production of goods, leading to more industrialization, and hence more water consumption through the industrial processes. Today, approximately half of the available water is being used for domestic purposes, and the other half is consumed by the industrial and agricultural activities. In addition to fresh water shortage, industrial activities lead to the most severe environmental pollution problems via discharge of wastewaters into the receiving water bodies. Although treatment of these wastewaters before discharging is obligatory by the relevant environmental protection legislations, all the industrial facilities in the world do not have treatment plants nor do the existing ones have adequate treatment efficiencies **(Arnal et al., 2008)**. As a result, the water quality in the receiving environments is rapidly deteriorating. The shortage of water supplies also forces the industrialists to pay even more for their fresh water consumption and wastewater generation. All these facts force the industrialists to consider the recovery and reuse of their wastewaters, at least to a certain extent.

1.3 TEXTILE INDUSTRY AND WASTEWATER GENERATION

1.3.1 Textile Industry

Textile industries are one of most complicated manufacturing industries because of its fragmented and heterogeneous character. The textile industry uses a large quantity of chemicals, water and produces large volumes of wastewater from different processes occurs in textile industries. The chemical reagents used are very diverse in chemical composition, ranging from inorganic compounds to polymers and organic products.

Textile industry can be classified into three categories viz., cotton, woollen, and synthetic fibers (polyester, acrylics) depending upon the used raw materials. As shown in **Figure 1.1**, the textile industry consists of a number of processes employed for converting fibers of natural origin such as cotton, silk and wool, and of synthetic origin such as nylon; first into fabrics by weaving and knitting and then into the final products by applying wet processes such as dyeing, sizing, printing, and finishing. Cotton, which is the world’s most widely used fiber, is also the substrate that requires the most water in its processing. The dyeing of one kilogram of cotton with reactive dyes demands 70 to 150 L water, 0.6 to 0.8 kg NaCl and around 30–60 g dyestuff **(Allegre et al., 2006).** The main environmental impact comes from wet processes of the industry.

Wastewater from printing and dyeing units is often rich in colour, containing residues of reactive dyes and chemicals, such as complex components, many aerosols, various waste chemical pollutants such as sizing agents, wetting agents, complexing agents, dyes, pigments, softening agents, stiffening agents, fluorocarbon, surfactants, oils, wax and many other additives which are used throughout the processes. These pollutants contribute to high suspended solids (SS), chemical oxygen demand (COD), biochemical oxygen demand (BOD), heat, colour, acidity, alkalinity and other soluble substances.

Textile industries typically generate 200–500 L of wastewater per kg of finished product **(Marcucci et al., 2001)**. In order to reduce water consumption, wastewater treatment is necessary for water reuse in the textile industries **(Jahangiri et al., 2012)**. Different techniques currently used for the treatment of textile effluents are based on carbon adsorption, filtration, chemical precipitation, photo degradation, biodegradation and electrolytic chemical treatment. Activated sludge process offers high efficiency in COD removal, but does not provide complete colour elimination and suffer frequently from operational problems like appearance of bulking.

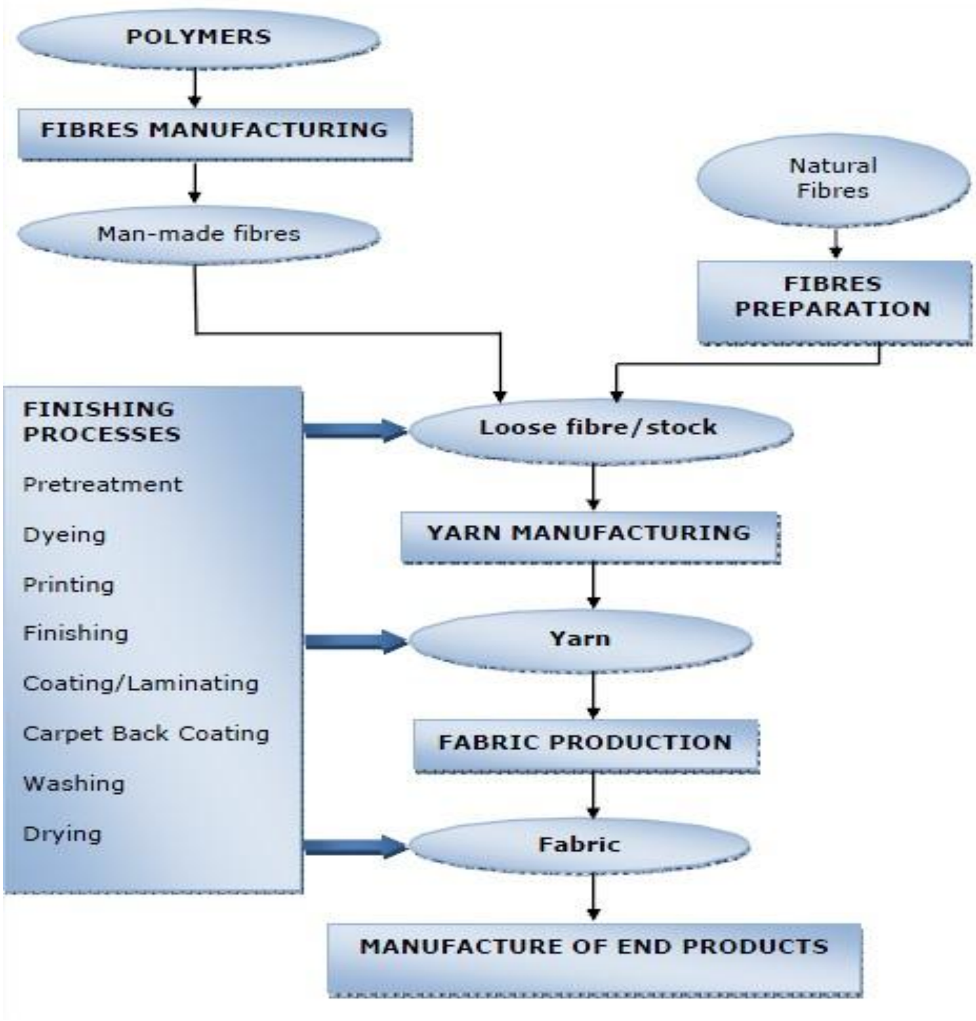

Figure 1.1: Layout of processes in the textile industry **(Sources of pollution, prevention and abatement: textiles industry)**

Advanced oxidation methods (ozonation, photo-fenton, UV etc.): Ozone combinations are the most commonly applied advanced oxidation methods used prior to biological treatment to enhance biodegradability and remove colour in textile wastewaters. Membrane filtration and advanced oxidation processes appear to be the indispensable alternatives for the tertiary treatment of the effluent from biological treatment.

1.3.2 Overview of the Textile Processes

Textile industries receive and prepare fibers, transform fibers into yarn, thread, or webbing; convert the yarn into fabric or related products; and dye and finish these materials at various stages of production. Textile processing industries include pre-treatment (desizing, scouring, bleaching, mercerising, washing) drying, dyeing, printing and finishing processes. Various processes involved in a typical cotton mill are shown in **Figure 1.2**.

1.3.3 Different Types of Processes in Textile Processing Industries

Desizing: Sizing applied to warp yarns prior to weaving or warp knitting by the slashing process must be removed prior to dyeing or finishing assuring even and uniform application of the dye or finish. Sizes can consist of starches, modified starches, and adhesives based on synthetic organic polymers. Starches and modified starches may generally be removed by dilute acid or enzyme treatment, whereas synthetic adhesive sizes can be removed by specialized short washing treatments.

Bleaching: It involves elimination of unwanted colour from textiles. These are three processes: sodium hypochlorite bleaching; hydrogen peroxide bleaching and sodium chlorite bleaching. Hypochlorite is one of the oldest industrial bleaching agents. For bleaching, textiles are soaked with bleaching agents and then temperature is raised to the recommended levels. Then the textiles are thoroughly washed and dried.

Mercerization: It is carried out by treating cotton material with a strong solution of sodium hydroxide (about 18–24%) and washing-off the caustic after 1 to 3 min, while holding the material under tension. Cotton is known to undergo a longitudinal shrinkage upon impregnation with this solution. This process provides lustre and strength to textiles.

Dyeing: It is the treatment of fiber or fabric with chemical pigments/dyes to impart colour. In this process, water is used to transfer dyes and in the form of steam to heat the treatment baths. Cotton, which is the world’s most widely used fiber, is a substrate that requires a large amount of water for processing.

Drying: The purpose of drying process is to reduce or eliminate the water content of the yarns or fabrics after wet processes applied in dyeing. In the textile mill, drying process is applied via contact driers at a temperature of 140^{o}C in order to reduce the water content of the rope from 68% to 7–8%.

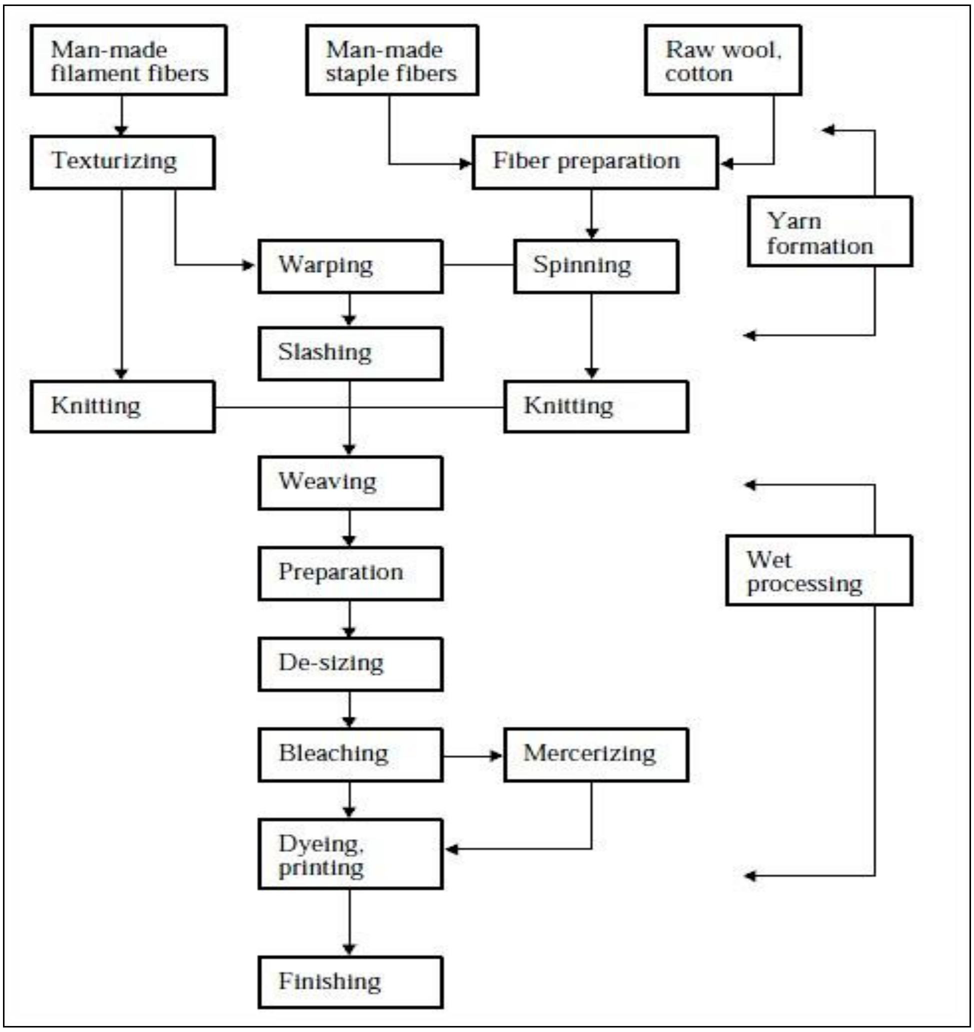

Figure 1.2: Various steps involved in processing textile in a cotton mill **(Rameshbabu et al., 2007)**

According to the dyeing properties, the dye classes are acid, basic, direct, disperse, mordant, reactive, sulfur and vat dyes (shown in **Table 1.1**). Each dye class is suitable to a specific type of fiber and hence the fixation rate of each class of dye is different.

Printing: It is generally defined as ‘localized dyeing,’ i.e., dyeing that is confined to a certain portion of the fabric that constitutes the design. It is a form of dyeing in which the essential reactions involved are the same as those in dyeing. In dyeing, colour is applied in the form of a solution, whereas in printing, colour is applied in the form of a thick paste of the dyes.

Finishing: Both natural and synthetic textiles are subjected to a variety of finishing processes. This is done to improve specific properties in the finished fabric and involves the use of a large number of finishing agents for softening, cross-linking, and waterproofing. All of the finishing processes contribute to water pollution. Among the products that are used in textile finishing, the most ecologically friendly ones are formaldehyde-based cross-linking agents that bestow desired properties, such as softness and stiffness that impart bulk and drape properties, smoothness, and handle, to cellulosic textiles.

Table 1.1: Different dye classes with respective fibres **(Pollution prevention and abatement handbook: Sources of pollution, prevention and abatement: textiles industry)**

Dye class	**Fibres**
Acid	Wool and nylon
Azoic	Cotton and other cellulosic
Basic	Acrylic
Direct	Cotton and other cellulosic
Disperse	Polyester, other synthetics
Reactive	Cotton and other cellulosic
Mordant	Natural fibres after pretreating with metals
Sulphur	Cotton and other cellulosic
Vat	Cotton and other cellulosic

1.3.4 Wastewater Generated in Textile Operations

The common constituents of wastewater generated from various textile processes are shown in **Table 1.2**.

Table 1.2: Wastewaters generated from textile processing **(Rameshbabu et al., 2007)**

Various Textile Processes	**Constituents of Wastewaters Generated**
Fiber preparation	Little or no wastewater generated
Desizing	BOD from water-soluble sizes; synthetic size; lubricants; biocides; anti-static compounds
Scouring	Disinfectants and insecticide residues; NaOH; detergents; fats; oils; pectin; wax; knitting lubricants; spin finishes; spent solvents
Bleaching	Hydrogen peroxide, sodium silicate or organic stabilizer; high pH
Mercerising	High pH; NaOH
Dyeing	Metals; salt; surfactants; toxics; organic processing assistance; cationic materials; colour; BOD; sulfide; acidity/ alkalinity; spent solvents
Printing	Suspended solids; urea; solvents; colour; metals; heat; BOD; foam
Finishing	BOD; COD; suspended solids; toxics; spent solvents
Product fabrication	Little or no wastewater generated

CHAPTER 2
MEMBRANE SEPARATION PROCESS

2.1 INTRODUCTION

The first membranes produced in Germany in 1920 were used for the filtration of bacteria on laboratory scale. Later in 1960s, the development of the synthetic asymmetric membrane at the University of California, Los Angeles, by Loeb and Sourirajan in 1962 for the separation of salt from seawater has lead to a significant development of the membrane technology. Since then, the application areas have been widely spread in many industries, among which beverage, food, pharmaceutical, electronics, paper and textile are only a few. In addition to being used in several industrial production stages, membranes have been widely used in the treatment of wastes and the recovery of valuable materials like dyes, metals, and water. Drinking water treatment is another area where membrane separation processes have recently been introduced. The popularity of the membrane technology in environmental applications has emerged due to the potential scarcity of fresh water supplies and the stringent environmental regulations. Meanwhile, the rapid development of the membrane material science over the recent years has also helped the widespread use of membrane technology due to the availability of membranes from a wide range of materials of different structures, including synthetic polymers, cellulose-based natural products and others like inorganic, ceramic and metals. In the past several decades, many techniques have been developed to find an economic and efficient way to treat the textile dyeing wastewater, including physicochemical, biochemical, combined treatment processes and other technologies. In dyestuffs manufacturing industry, the membrane separation technology is applied in the improvement of conventional processes and treatment of wastewater for the purpose of waste minimization, energy and water saving. Currently, the membrane separation process is often used for treatment of dyeing wastewater mainly based on membrane processes such as reverse osmosis (RO), ultrafiltration (UF), nanofiltration (NF) and microfiltration (MF). The membrane discussion in this chapter is limited to the pressure-driven membranes since this study is based on their performances for textile wastewater treatment and recovery.

2.2 DEFINITION AND BASIC PRINCIPLES

Membrane separation process is a new separation technology, with high separation efficiency, low energy consumption, ease of operation, and no pollution. However, this technology is still not large-scale promoted because it has the limitation of requiring special equipment, and having high investment and the membrane fouling (**Ranganathan et al., 2007**). This has a wide range of applications in the textile industry. Various types of dyes and chemicals can be recovered from the textile effluent using this technology and a large proportion of wastewater can be reused. Since textile is one of the major industries and it utilizes a huge volume of water, membrane technology can be an efficient and cost-effective method for treating textile effluents.

The membrane is a physical barrier that allows certain compounds to pass through, depending on their physical and chemical properties. It is a permeable and semi-permeable phase, thin polymeric/ ceramic/metallic solid, which restricts the motion of species. Membranes can remove particles, ions and other substances in certain size ranges. It commonly consists of a porous support layer with a thin dense layer on top that forms the actual membrane.

Common types of membrane processes based on membrane pore size (**Figure 2.1**) are described below:

- Microfiltration
- Ultrafiltration
- Nanofiltration
- Reverse Osmosis
- Electro-dialysis

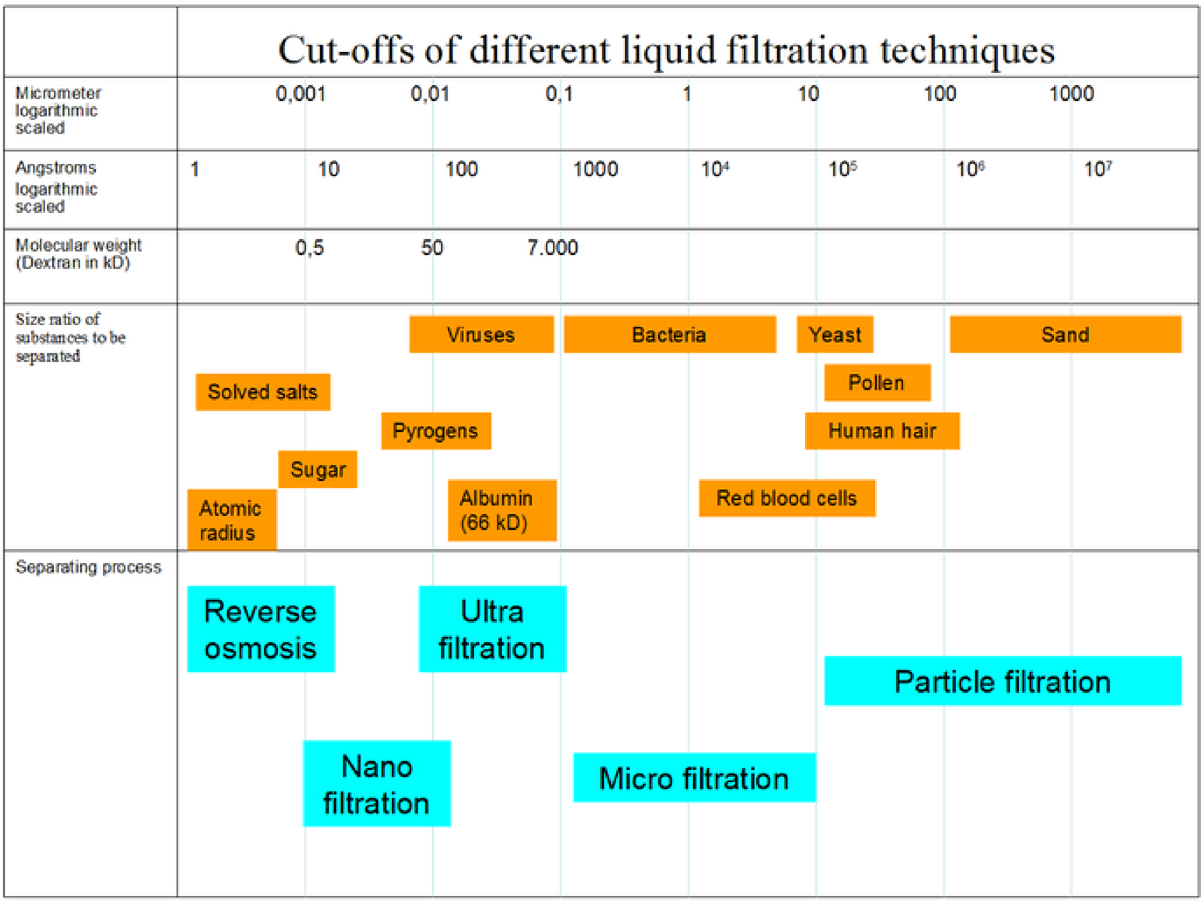

Figure 2.1: Size ranges of different membrane processes **(Baker, 2004)**

Membrane materials can be categorised as either *dense* or *porous*, and by the mechanism by which separation is actually achieved. Separation by dense membranes relies to some extent on physicochemical interactions between the permeating components and the membrane material, and relate to separation processes having the highest selectivity. NF, ED and RO are dense membranes.

Porous membranes, on the other hand, achieve separation mechanically by size exclusion (i.e. sieving), where the rejected material may be either dissolved or suspended depending on its size relative to that of the pore. MF & UF are porous membranes.

2.3 PERFORMANCE OF MEMBRANES

The performance of a membrane is defined in terms of two factors: flux and selectivity.

Flux: It is the volumetric flow-rate of the fluid passing through per unit area of the membrane per unit time.

$$J = \frac{1}{A} \times \frac{dv}{dt} \qquad (2.1)$$

Where, J: flux (L/m^2.h)
A: effective membrane area (m^2)
dv/dt : permeate flow rate (L/h)

Selectivity: It is named as retention for solutes and particles in liquids and gases; the fraction of solute retained in the feed by the membrane is given by:

$$R = \frac{C_f - C_p}{C_f} \qquad (2.2)$$

Where, R: retention
C_p: solute concentration in the permeate (mg/L)
C_f : solute concentration in the feed (mg/L)

2.4 MEMBRANE OPERATION

Membrane processes (**Figure 2.2**) can be operated as:

- Dead-end filtration (in-line filtration)
- Cross-flow filtration

Dead-end filtration refers to filtration at one end. The entire fluid flow is forced through the membrane under pressure. As particles accumulate on the membrane surface or in its interior, the pressure required to maintain the required flow increases, until at some point the membrane must be replaced. A problem with these systems is frequent membrane clogging. Dead-end filtration is generally suitable for concentrated suspensions, and not appropriate for the filtration of very fine and dilute suspensions or production of very pure filtrates **(Baker, 2004)**.

In *cross-flow filtration* the feed solution is circulated across the surface of the filter, producing two streams: a clean particle-free permeates and a concentrated retentate containing the particles. The equipment required for cross-flow filtration is more complex, but overcoming the problem of membrane clogging lets membrane lifetime is longer than with in-line filtration and it is widely used in water and wastewater treatment.

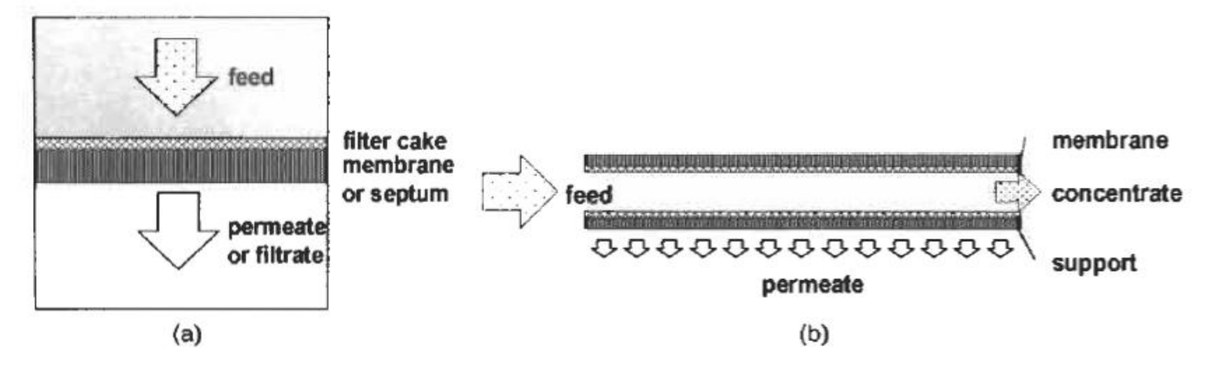

Figure 2.2: Schematic representation of (a) dead-end; and (b) cross-flow filtration mode **(Baker, 2004)**

Two streams are produced in a membrane separation process; one stream, called the permeate, is depleted in certain components and a second stream, called the retentate, is concentrated in them. The term permeate is used in membrane technology instead of filtrate, representing the portion of the feed solution passing through the membrane. The term retentate, which is used interchangeably with the term concentrate, represents the portion of the feed solution that is retained on the high-pressure side of the membrane.

Transmembrane pressure (TMP) is the driving force for the pressure-driven membrane processes, and it is defined as the pressure difference across the membrane.

$$\text{TMP} = \frac{P_{in} + P_{out}}{2} - P_p \qquad (2.3)$$

Where, P_{in}: inlet pressure (feed pressure)

P_{out}: outlet pressure (retentate pressure)

P_p: permeate pressure (atmospheric pressure)

2.5 MEMBRANE CONFIGURATION

Module is a complete unit comprised of the membranes. The module is the base for membrane installation and process design. The most common types of membrane modules are shown in **Figure 2.3**.

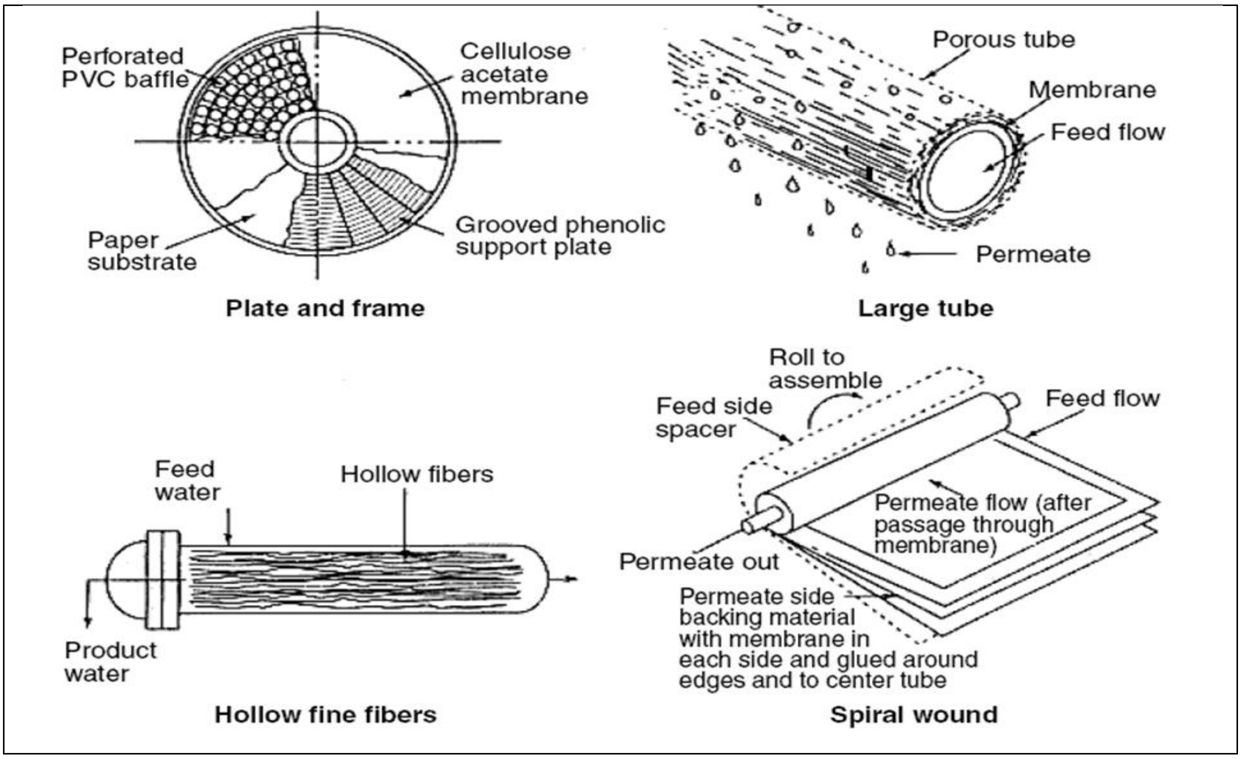

Figure 2.3: Different types of membrane modules. (**Sincero & Sincero, 2003)**

Plate-and-frame module: The structure is simple and the membrane replacement is easy. In this, Sets of two membranes are placed in a sandwich. A suitable spacer is placed to promote turbulence of the feed fluid and the module diameter is 20–30 cm.

Tubular module: A number of membranes of tubular shape are encased in a container. The feed solution always flows through the centre of the tubes, while, the permeate flows through the porous supporting tube. Membranes have a diameter of about 5 to 15 mm. They have the following features.

- Low packing density of the module
- Simple pre-treatment of feed liquid
- Easy cleaning

Spiral-wound module: Membrane and permeate-side spacer material are then glued along three edges to build a membrane envelope. The feed flows axial through the cylindrical module parallel along the central pipe. The permeate flows radially towards the central pipe.

Here, the features include:

- A compact structure

- High-pressure durability
- Less contamination
- Minimum concentration polarization

Hollow-fibre (capillary) module: It consists of a large number of fibres assembled together in a module. Membranes are self-supporting. The packing density is very high. Its diameter is generally below 0.1 µm and chances of plugging are very high.

Arrangements can be:

- **Inside-out** where the feed solution passes through the bore of the fibre and the permeate is collected on the outside of the fibre
- **Outside-in** where the feed solution enters the module on the shell side of the fibres and the permeate passes into the fibre bore

2.6 PRESSURE-DRIVEN MEMBRANE SEPARATION PROCESSES

Membranes are generally classified in broad categories by their ability to remove particles, ions and other substances in certain size ranges. The type of the driving force applied across the membrane leads to a basic classification of membrane separation processes, as shown in **Table 2.1**. As seen, there are four commonly accepted pressure-driven membrane separation processes, defined based on the size of the material they will remove from the solvent. Ranking from the largest to the smallest pore size, these are microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). As the pore size gets smaller, the hydrodynamic resistance of the membranes increases, which necessitates the application of higher pressures across the membranes. MF is well understood as the fine end of the particle filtration, with pore sizes ranging from 0.05 to 10 µm, which are visible under a microscope. UF, NF and RO membranes do not have holes as such, but rely on higher pressures to defuse a liquid or gas through the molecular structure of the medium.

The molecular spacing can be controlled during manufacturing to permit the creation of membranes having any desired molecular weight cut-off (MWCO) level, which is a means of determining the size of the largest molecule able to permeate a UF, NF or RO membrane. **Table 2.2** shows the ranges of material sizes retained, the pressures required, the typical fluxes obtained and the separation mechanisms used by each membrane separation process.

Table 2.1: Membrane Processes According to their Driving Forces **(Reynolds et al., 2002)**

Membrane Processes	**Driving Force**
MF/ UF/ NF/ RO	Pressure difference
Pervaporation	Concentration difference
Dialysis	
Liquid membranes	
Gas separation	
Membrane distillation	Temperature difference
Thermo-osmosis	
Electro-osmosis	Electrical potential difference
Electrodialysis	

Table 2.2: Specifications of pressure driven membrane processes (Mulder, 1996)

Process	**Retained Particle Size**	**Pressure Required, Bar**	**Typical Fluxes Obtained, L/M^2/H/Bar**	**Separation Mechanism**
MF	0.05–10 µm (micro particles)	0.1–2	>50	Sieving
UF	1–100 nm (macro particles)	1–10	50–100	Sieving
NF	0.5–5 nm (molecules)	5–20	1.4–12	Solution diffusion
RO	<1 nm (molecules)	10–100	0.05–1.4	Solution diffusion

2.6.1 MICROFILTRATION (MF)

When pressure-driven flow through a membrane or other filter medium is used to separate micron-sized particles from fluids, the process is called MF. The MF process is used in a wide variety of industrial applications where particles of a size greater than 0.1 µm can be retained. However, the irregular nature of the membrane pores and the irregular shape of the particles to be filtered point out the difficulty in defining sharp cut-off of size during filtration

(Scott, 1996). The separation in MF process is achieved by sieving mechanism when the particle sizes are greater than the pore size, that they are collected on the surface of the membrane rather than inside the pores, thus forming a cake layer. This sieving mechanism is sometimes called surface filtration. In case the particle sizes are smaller than the pore sizes then they can enter the interior of the filter medium, which is called the in-depth filtration (**Davis, 1992**). In both types of filtration, the particle build up results in an increased resistance to flow, and the permeate flux decreases if the TMP is kept constant. As the sizes of the particles retained by MF are larger than the sizes of solutes retained by NF or RO, the osmotic pressure for MF process is negligible, and the required TMP is relatively small, generally less than 2 bar. The permeate flux is typically larger for MF than for other membrane processes as the pore sizes are larger. MF is often applied in dead-end filtration mode in the analytical laboratories, which is one of the most important application areas of MF process today. On the other hand, cross-flow application is preferred for larger scale applications to ensure longer media life. Sterilisation and clarification are the main applications of MF processes in food and pharmaceutical industries. Removal of particles for ultra pure water production in semiconductor industry and cell harvesting in biotechnology are among the other applications (**Mulder, 1996**).

2.6.2 ULTRAFILTRATION (UF)

UF is primarily a size-exclusion based pressure-driven separation process. UF membranes have typically pore sizes ranging from 1 to 100 nm, and are capable of retaining medium to large size dissolved molecules in the molecular weight range of 300 to 300000 Da. These MWCO values are only approximate because the same molecules can have different sizes depending on the solution properties like pH and ionic strength. In addition, physico-chemical interactions between the solute, solvent and the membrane surface would also affect the retention performance (**Scott, 1996**). Typical species rejected by UF are sugar, biomolecules, polymers, and colloidal particles, where the separation mechanism is sieving (**Kulkarni et al., 1992**). UF is similar to MF based on the separation principle, however UF membranes have a much higher hydrodynamic resistance due to their structure. Since UF membranes do not typically reject salts, osmotic pressure differentials are small as compared to RO membranes. UF operates at TMP of 1–10 bars, and typical permeate fluxes are lower than those of MF. UF processes are widely used for feed clarification, concentration of rejected solutes and fractionation of solutes. Some applications may require the separation of high molecular weight components from low molecular weight ones. Typical examples of applications are the food and dairy, pharmaceutical, textile, chemical, metallurgy, paper and leather industries. The applications of UF process in food and dairy industry are highly diverse, such as the concentration of milk, cheese making, recovery of whey proteins, concentration of egg products and the clarification of fruit juices and alcoholic beverages (**Mulder, 1996**).

2.6.3 NANOFILTRATION (NF)

The term NF was first used nearly a decade ago to define the membranes which had already been referred to as “loose RO” due to their more open network structure. Therefore, NF is said to be in the area between the separation capabilities of RO and UF membranes. The typical pore size of NF membranes is 0.5–5 nm, and the applied pressures are typically 5–20 bar, which are lower than the RO process, but yield higher fluxes (**Mulder, 1996**; **Scott, 1996**). NF membranes can retain low molecular weight solutes such as inorganic salts or small organic molecules such as glucose and pollutants such as pesticides, and dyes. NF typically has partial salt retention and rejects molecules from 500 to a few thousands Da. The retention of divalent ions (Ca^{2+}, Mg^{2+}) by NF process is generally higher than the retention of monovalent ions (Na^+, K^+, Cl^-). This is because most NF polymers have formal charges, which exclude higher valence ions more than monovalent ions from passing through the membrane (**Paulson, 1995**). The application of NF and RO are obviously different, NF is the preferred process when a high retention is not required for NaCl (**Mulder, 1996**). The typical rejections of NF are 60% for NaCl, 80% for calcium bicarbonate and 98% for magnesium sulphate, glucose and sucrose (**Scott, 1996**). Among the widely spreading application areas of NF process are the water softening, removal of trihalomethanes and natural organic matter, retention of dyes and metals, and wastewater treatment and recovery. NF process has recently emerged as a feasible alternative to the conventional treatment methods in the environmental engineering field due to its unique separation ability and possibility of valuable material recovery.

2.7 MEMBRANE FOULING AND CLEANING

Fouling can be defined as irreversible deposition of materials onto or into the membrane causing loss of flux and altered rejection**.** The major drawback hindering the use of membranes is the reversible and irreversible fouling that impedes the flux of clean water through the membranes. The consequence of membrane fouling is a reduction of permeate production rate and/or an increase in solute passage across the membrane with time. Fouling also causes increase in energy consumption as trans-membrane pressure can increase substantially due to fouling. In addition, fouling increases downtime and may shorten membrane lifespan. The membranes are too expensive to be replaced for reasons of fouling.

Membrane fouling can be caused by:

- Particulate deposition (colloidal fouling)
- Adsorption of organic molecules (organic fouling)
- Inorganic deposits (scaling)
- Microbial adhesion and growth (bio-film formation)

The extent of fouling is strongly dependent on the type of the membrane processes involved and the feed employed. The flux decline is most severe in MF and UF membranes. The fouling causing components of the feed solutions are the soluble inorganic compounds, colloidal or particulate matter, dissolved organics, chemical reactants and micro-organisms. When fouling occurs, the membrane requires cleaning to restore the membrane properties.

Membranes and most fouling materials are likely to carry negative charges. Therefore, electrostatic repulsion is a major force to keep membrane and fouling materials apart. Hence, increasing the electrostatic repulsion is expected to enhance the membrane cleaning by increasing the charge density of fouling materials. As molecular weight and mass/charge ratio of solutes, ionic strength, and the concentration of divalent cations increases, hydrophobic attraction tends to increase, so does the potential of membrane fouling. On the other hand, increases in charge density and polarity of solutes, and pH will increase electrostatic repulsion between the membrane and solutes, which reduces the adhesion between membrane and fouling materials and enhances the cleaning efficiency.

Membrane cleaning is an essential step in maintaining the permeability and selectivity of a membrane process. Cleaning techniques for membrane restoration could be broadly categorized into three types: physical, chemical and physico-chemical methods. Important cleaning parameters that vary with foulant and membrane material are type of cleaning agent, pH, concentration, temperature and time. Chemical cleaning methods depend on chemical reactions to weaken the cohesion forces between the foulants and the adhesion forces between the foulants and the membrane surface. However, as a rule, mineral deposits are removed by acidic solutions and organic compounds by alkaline solutions. The choice of chemical cleaning agents not only depends on type of foulants present in the membrane system, but also depends on the chemical resistance of the membrane material.

Physical cleaning methods depend on mechanical forces to dislodge and remove foulants from the membrane surface. Physical methods used include forward flushing, reverse flushing, backwashing, vibrations, air sparge and CO_2 back permeation. MF and UF used in pre-treatment to RO are more frequently cleaned by physical cleaning and less frequently by chemical cleaning. Cleaning frequencies reported in literature varied widely. Physical cleaning frequency is approximately every 40 min with a chemical clean scheduled every 6 months. An air backwash frequency of 15–20 min is sufficient for hollow-fibre MF membranes. In a UF evaluation study; backwashing was able to achieve an average flux recovery of 86.5%**.** It was observed in the same study that flux restoration could be achieved even when backwash was reduced from 10 to 1 min.

2.8 CERAMIC MEMBRANES

Ceramic membranes are a type of artificial membranes made from inorganic materials (such as alumina, titania, zirconia oxides, silicon carbide or some glassy materials). They are used in membrane operations. By contrast with polymeric membranes, they can be used in separations where aggressive media (acids, strong solvents) are present. They also have excellent thermal stability which makes them usable in high-temperature membrane operations. Like polymeric membranes, they are either dense or porous. Ceramic membrane presents several advantages over organic membranes. It can be applied at high temperatures, upto 600^o C and in a wide range of pH, as well as, in the presence of organic solvents, thus increase its potential of applications. Also the ceramic membranes are biological resistant and minimize the possibility of fouling by microorganisms during the separation process (**Silva, 2009**). Despite the brittleness characteristics of the ceramic materials, if it is handled properly to prevent the direct impact, ceramic membrane have longer lifetime when compared with polymeric membranes. Ceramic membrane can easily cleaned by chemical process or using vapor at high temperature (**Fontes et al., 2005**). Thanks to these properties ceramic membrane can be used in the treatment of several industrial effluents, including textile industry.

In contrast to many polymer membranes the ceramic membranes are a perfect match for this demand due to their extremely high chemical and physical stability, their outstanding separation characteristics and their long working life. Ceramic materials are generally very stable chemically, thermally and mechanically, and in addition are frequently bio inert. They are therefore ideal materials for many applications in the chemical and pharmaceutical industry or in water and wastewater processing. The medium to be filtered flows through the channels of the membrane carrier. Particles are retained if their size exceeds the radius of the membranes pores, building up the concentrate. The filtrate permeates through the pores and it is subjected to subsequent process stages.

Many are the advantages deriving from the ceramic membrane use: they separate mixtures physically. They are ecologically friendly and more favourable than other separation technologies. No additives are necessary and the process temperature is not limited. Filtration with ceramics is a mild, highly selective process without phase transformation. Running costs are limited by closed production cycles and continuous processes. Ceramic membranes offer:

- Chemical, mechanical and thermal stability
- Ability of steam sterilisation and back flushing
- High abrasion resistance
- High fluxes
- High durability
- Bacteria resistance
- Possibility of regeneration
- Dry storage after cleaning

CHAPTER 3

LITERATURE REVIEW

Review of literature has been carried out on following aspects.

3.1 Membranes Used in Textile Wastewater Treatment

Reclamation of textile wastewaters have become a widespread application of membrane technology since the environmental regulations for wastewater discharge are getting more stringent and the scarcity of fresh water supplies on earth are increasing, which in turn, have been forcing textile manufacturers to focus on water recycling. Although membrane technology requires an initial high setup cost, it is outweighed by the significant cost savings achieved through the reuse of chemicals, dyes and water. The costs can be reduced by the implementation of pre-treatment processes and regular cleaning to eliminate fouling problems and by choosing the most appropriate membrane system (**Tang and Chen, 2002**). Several approaches consisting of individual or combined membrane processes have been offered for advanced treatment of textile wastewaters, including microfiltration (MF), ultrafiltration (UF) and nanofiltration (NF). However, a systematic approach to investigate the most suitable solution for the textile industry seems to be lacking in terms of the kind of effluent to treat, the type of the membrane to use, and the process combinations to use (**Bottino et al., 2000**). In an attempt to contribute to the existing efforts for filling this gap, this study involves the development of the most suitable combinations of membrane processes for the reclamation of the effluents.

3.2 Treatment of Textile Processing Industry Wastewaters by Microfiltration

Microfiltration processes use porous membranes to separate suspended particles with diameters between 0.1 and 10 μm, thus yielding a relatively higher flux than the other membrane separation technology. Thus, microfiltration (MF) membranes fall between UF membranes and conventional filters (**Baker, 2004**). MF membranes comprise the largest fraction of total membrane production due to their increasing usage in recent years. MF provides a simple clarification of the effluent by removing suspended solids (**Bottino et al., 2000**) and colloidal dyes (**Buckley, 1992**). Therefore, its application alone has been reported to be inadequate for water recycling, making it more generally adopted in pre-treatment for further membrane processes (**Bottino et al., 2000**). MF has been gaining a wider acceptance for the pre-treatment stage since it is economically more competitive than conventional methods such as coagulation, flocculation, sedimentation and filtration (**Vedavyasan, 2000**). Microfiltration can also be used as a pre-treatment for nanofiltration (NF) or reverse osmosis (RO). The use of MF to remove colloidal species from the exhausted dye bath effluents before NF has been proposed in the past studies (**Treffry-Goatley et al., 1983**). The separation in MF process is achieved by sieving mechanism when the particle sizes are greater than the pore size, that they are collected on the surface of the membrane rather than inside the pores, thus forming a cake layer. This sieving mechanism is sometimes called *surface filtration.* In case the particle sizes are smaller than the pore sizes then they can enter the interior of the filter medium, which is called the *in-depth filtration* (**Davis, 1992**). In both types of filtration, the particle build up results in an increased resistance to flow, and the permeate flux decreases if the trans-membrane pressure (TMP) is kept constant. The influence of operating conditions on membrane fouling in cross flow microfiltration of particulate suspensions was studied by **Harit et al. (2000).** A process was developed based on the observed effects of the operating parameters on the cross-flow microfiltration (CFMF) performance that enables operation at very low internal fouling and high flux for as long as 160 min after estimating all important parameters (internal and surface fouling, cake mass, height, porosity, and particle size distribution (PSD) at constant trans-membrane pressure (TMP) mode using tubular ceramic MF membrane modules. **Latif et al. (2002)** explored the use of microfiltration membrane separation processes to remove the suspended solid (mainly due to dyes in the painting and colouring processes) from wastewater of batik industry. The results showed that the dye concentration, pH of dye, and the operating pressure were found to affect the filtration process. **Vander et al. (2004)** used microfiltration as pretreatment of used finishing baths, followed by dual nanofiltration (NF). The influence of operative conditions on membrane fouling and flux during dead-end microfiltration was studied by **Wang et al. (2006).** In their experiments, two membranes were used, of which, one was the PVDF membrane with pore size of 0.1 μm, and the other was the PTFE membrane with pore size of 0.1 μm. Results showed that temperature, pressure and concentration had a significant influence on microfiltration membrane flux. **Fersi et al. (2009)** investigated the parameters that determine the flux decline of textile wastewater by membrane technologies, where MF and UF processes were studied in order to be investigated as pre-treatment for the NF process in the case of textile effluent treatment. **Nigmet et al. (2009)** focused on the applicability of microfiltration (MF)/ultrafiltration (UF) as a pretreatment to nanofiltration (NF) for the reclamation of rinsing waters of indigo dyeing process. Two different MF alternatives, single 5 mm MF and sequential 5 mm and 0.45 mm MF, were evaluated as pre filtration to improve the performance of the proceeding UF stage. Single stage 5 mm MF followed by 100 kDa UF was selected as the best prefiltration train to NF that permits the textile producer to reclaim indigo dyeing wastewater.

3.3 Treatment of Textile Processing Industry Wastewaters by Ultrafiltration

Ultrafiltration (UF) is generally applied in the separation of macromolecules with a molecular weight of 1000 Dalton or above **(Erswell et al., 1988)**. Although UF has been successfully applied in many industries, its use in textile industry has been limited due to the variability of rejection performances, which makes direct reuse impossible **(Watters et al., 1991)**. UF performance is highly dependent on the type of membrane material and the feed composition as well as the shape and size of the macromolecules. In UF process, the removal of polluting substances is never complete, i.e., 21–77% COD, 31–76% colour, and 32–94% surfactants. However, even in the best case, the permeate quality cannot meet the reuse requirements for the dyeing of light colours. Hence, the UF permeates have been accepted only for minor processes in textile industry when salinity is not a problem **(Bottino et al., 2000)**. On the other hand, several applications of the UF process have been reported for the separation of certain dyes, such as indigo, direct, disperse and reactive dyes. Dye rejection performances as high as 90–100% had been obtained in these studies, whereas, UF performance was shown to be significantly variable, i.e., 34–93%, for total waste streams from dye house **(Watters et al., 1991)**. Therefore, further filtration by either NF or RO would be required for water recovery (**Tang and Chen, 2002).** In a UF study, textile wastewater was studied for reuse purpose and the proposed treatment scheme was the sequential application of cross flow UF and NF by **Barredo et al. (2006).** They concluded that UF is an appropriate technique as a pretreatment of a NF/RO process for textile wastewater reuse. In their study, membrane selection and operating conditions were considered as important issues to optimize the process technically and economically. Nevertheless, these parameters were accepted as they had minor effects on COD and colour removal efficiencies. **Małgorzata and Krystyna (2007)** used ultrafiltration membranes made of cellulose acetate (CA), polysulfone (PES) and polyvinylidene fluoride (PVDF) for separation of dyes from micellar solutions. The best separation of the dyes was obtained when the ionic surfactant, charged opposite to dye, was used alone or in the mixture with the non-ionic surfactant. **Barredo et al. (2010)** evaluated the performance of tubular ceramic ultrafiltration membranes treating integrated raw effluents from a textile mill, at different operating conditions (transmembrane pressure, pH, and molecular weight cut-off). They concluded that higher membrane fouling rates were observed for the highest cut-off as well as for the highest applied pressures. **Simonic (2009)** studied the removal efficiencies for colour and COD using two hydrophobic and one hydrophilic commercial UF membranes with or without a flocculation pre-treatment. The colour and COD removal efficiencies were up to 98% and 61%, respectively.

3.4 Treatment of Textile Processing Industry Wastewaters by Nanofiltration

Nanofiltration membranes retain low molecular weight organic compounds, divalent ions, large monovalent ions, hydrolyzed reactive dyes, and dyeing auxiliaries. Harmful effects of high concentrations of dye and salts in dye house effluents have frequently been reported **(Tang and Chen, 2002; Koyuncu, 2002; Bruggen et al., 2001; Jiraratananon et al., 2000; Erswell et al., 1988)**. A two-step nanofiltration process has been developed, which is able to recover 90% of the industrial waste stream and to reduce the colour content with 99.8**% (Frank et al., 2002)**. Cross flow nanofiltration using thin film composite polysulfone membrane was used to recover the electrolyte solution and reject the colour by using a synthetic textile effluent of reactive dye and NaCl solution (**Tang and Chen, 2002).** They worked on the mechanism controlling flux and rejection by varying the four main parameter viz. cross flow velocity, initial dye concentration, feed pressure, and electrolyte concentration. Results showed that the osmotic pressure did not significantly affect the flux or rejection. At low pressures up to 500 kPa, relatively high fluxes were obtained, thus, a high quality of reuse water could be recovered. Nanofiltration has been applied for the treatment of coloured effluents from the textile industry. A combination of adsorption and nanofiltration can be adopted for the treatment of textile dye effluents. The adsorption step precedes nanofiltration, because this sequence decreases concentration polarization during the filtration process, which increases the process output **(Chakraborty et al., 2003)**. The effects of operating conditions (operating pressure, feed flow rate, concentrating ratio of the wastewater, recovery ratio of the process, membrane fouling and cleaning) on the nanofiltration membrane have been reported by **Liu et al. (2004)**. Another investigation was performed with the biologically treated textile effluents by **Bes-Pia et al. (2004)**, where ozonation was further tested in the pre-treatment stage for NF. A COD removal efficiency of 43% was accomplished with low ozone doses in 60 min ozonation period, which, in turn, resulted in an increase of NF membrane life. NF processes were also used for textile waste recovery and reuse, pulp and paper water recovery and reuse, dye and ink concentration and recovery, water softening, removal of natural organic matter, heavy metals and plating salts concentration etc. (**Uzal et al., 2006**). **Goksen et al. (2006)** described the effect of pH on nanofiltration performance for the reclamation of acid dye bath wastewaters (ADBW) of carpet manufacturing industry. In their work, wastewater originally having acidic pH (5.0–5.9) was subjected to pre-filtration through 1.0 μm microfiltration (MF) media prior to nanofiltration (NF). Colour was removed completely and turbidity was rejected by 79–92% in all alternatives. However, COD, total solids, total hardness and conductivity were partially removed in single NF without pH neutralization. In order to have energy and cost effective separation of dyes, a combination of advanced oxidation process (AOP) using Fenton's reagent and nanofiltration (NF) was proposed by **Banerjee and DasGupta, (2007)** for removal of dye from aqueous solution. Acrylic grafted nano membrane was reported to be potentially capable to separate dyes from coloured textile effluent **(Amini et al., 2011)**. NF process has recently emerged as a feasible alternative to the conventional treatment methods in the environmental engineering field due to its unique separation ability and possibility of valuable material recovery. The performance of Nanofiltration (NF) as a post treatment after coagulation–flocculation (CF), for treating a mixture of effluents coming from different textile industry operations was studied by **Ellouze et al. (2012)**.

3.5 Treatment of Textile Processing Wastewater with Combinations of Various Membrane Processes

The use of effective pre-treatment processes such as coagulation, sand filtration, disinfection, flotation, or other membrane processes (MF and/or UF) is fundamental to guarantee a good and constant performance of the NF and RO systems **(Marcucci et al., 2003)**. **Ciardelli et al. (2000)** applied a process train consisting of sand filtration, UF and RO for treating the dyeing and finishing effluents of a textile plant, which were pre-treated in an activated sludge system. The sand filtration achieved a satisfactory reduction of suspended solids and slight reduction of colour. The quality of UF permeate was realized to be adequate for feeding the RO membranes. Finally, the RO step produced permeate with much better quality with respect to the process water quality currently in use. Therefore, they concluded that the permeate could be reused in all production steps, including the most demanding ones concerning water quality such as dyeing of light colours. In order to determine the most suitable kind of membrane for the production of permeate with the desired quality for reuse, **Marcucci et al. (2003)** chose two approaches for the textile effluents downstream of a biological activated sludge process, i.e., UF+RO and MF+NF, which were tested alternatively after the pretreatment stage of sand filtration. In the first case, sand filtration and UF stages made it possible to achieve a turbidity-free effluent, as required to minimize RO membrane fouling. Sand filtration and UF removed COD partially (less than 30%), and colour poorly (5%). The RO permeate was of excellent quality where 95% COD removal was achieved. The dyeing tests revealed very high quality of the dyeings with RO permeate, which achieved better results than the well water currently used as the process water. In the second case, sand filtration and MF removed 99% of suspended solids and 80% of turbidity, whereas only 36% of COD and 13% of colour were removed. The NF membrane achieved complete removal of the COD left, and a very high fraction of the remaining colour. The dyeing tests performed with NF permeate gave satisfactory results even if the water quality was worse than RO permeate in terms of salt content and chlorides. They finally concluded that both permeates from the two-stage membrane systems could be used as process water for the textile industry, and about 60–65% of the plant effluents could be recycled using this kind of advanced treatment systems. Similarly**, Bruggen et al. (2001)** tested two options for textile wastewater recovery, i.e., direct NF, which was performed with simulated dye baths, and sand filtration followed by NF, which was performed with biologically treated effluent. In the first case, they observed problems with high osmotic pressures and hence the need for a membrane configuration with double pass was reported. In the second case where a biological treatment and sand filtration preceded NF, acceptable water flux was obtained and the salt concentrations were low enough to avoid the problems with build-up of the osmotic pressure. Moreover, the tested process train allowed the retentions to be sufficiently high to make the recirculation of the permeate possible. Another investigation was performed by **Bes-Pia et al. (2004)** with the biologically treated textile effluents, where ozonation was further tested in the pretreatment stage for NF. A COD removal efficiency of 43% was accomplished with low ozone doses at 60 min ozonation period, which, in turn, resulted in an increase of NF membrane life. Implementation of UF alone as an alternative to NF or RO has been proven to be insufficient to achieve the desired permeate quality for reuse. **Bes-Pia et al. (2002)** tested UF against NF after chemical precipitation for the reclamation of wastewaters of a printing, dyeing and finishing textile industry. A COD reduction of 50% in the chemical precipitation stage was reported, where 200 mg/L of coagulant and 1 mg/L of anionic flocculant were used. None of the UF membranes with MWCO ranging from 5000 to 100000 Da could effectively reduce COD. On the other hand, the NF membranes produced permeates almost free of organic matter, which were suitable for reuse in the industry. Improvement of UF performance by a suitable pre-treatment process was investigated by **Marcucci et al. (2002)**. In their study, the performance of the physicochemical processes (clariflocculation and ozonation) followed by UF treatment, which was applied directly to the textile wastewater was compared with another process train composed of sand filtration and MF followed by NF, which was applied to the biologically treated effluent. The configuration with UF as the final membrane process revealed good performance of the clariflocculation and ozonation steps where a turbidity removal of 49% and a colour removal of 71% were achieved. In the UF step, 27% of turbidity and 30% of total solids were removed. In addition, a satisfactory COD removal of 66% was accomplished and the total colour removal reached 93%. The dyeing tests performed with 50% UF permeate and 50% well water provided successful results, suggesting a limit of 50% for the contribution of recycled water into the process water. In the second configuration with NF as the final membrane process, the sand filtration and MF steps removed the suspended solids completely; turbidity to 78%, and COD was removed partially to 30%. The NF membrane removed the remaining COD and colour almost completely. The results of the dyeing tests conducted with 100% NF permeate suggested that NF permeate was reusable in all dyeing cycles, even for light colours. In another study with similar approach, **Rozzi et al. (1999)** tested two different process combinations for the reclamation of a textile effluent subjected to biological treatment. The first combination was MF coupled with NF and the second one was clariflocculation plus multimedia filtration coupled with low pressure RO. They observed that the qualities of the final permeates produced by both treatment schemes were acceptable for water reuse. However, the requirement of an additional pre-treatment step consisting of coagulant addition to the first treatment scheme was reported in order to assure acceptable duration of filtration cycles.

As seen from all the studies summarized here, a pre-treatment step is very important for the development of the best process train for a given textile effluent, and therefore the pre-treatment process must be optimized to ensure minimized flux decline. In a study performed by **Dhale and Mahajani (2000)** NF was tested after pre-filtration through a 50 µm membrane for the recovery of a highly coloured disperse dye bath waste and a drastic flux decline of 80% was observed accompanied with 98% colour and 70% COD rejection efficiencies. Although the selected process train produced a permeate which had suitable quality for recycling into the process, the severe flux decline makes this process train unfeasible, thereby necessitating the implementation of alternative pre-treatment processes to ensure better permeate flux. Most of the studies mentioned above have shown that the recovery of textile wastewaters with membrane technology currently proposes a combination of two or more processes and hence the costs involved have caused a limitation on the broad application of the technique **(Bottino et al., 2000)**. Furthermore, the presence of several applications downstream of an already existing biological treatment would raise the question of whether there is a limitation of the applicability of membrane technology for the textile plants, which possess a biological treatment plant. To this end, achievement of the reclamation of the textile effluents with good permeate qualities and minimized flux declines in the most simple and energy efficient integrated process combinations would be of great value for spreading the membrane applications. In an attempt to achieve this target, **Bottino et al. (2000)** performed a comparison of a number of approaches consisting of MF, UF, NF and RO for the treatment of several streams generated in different textile processes and at different purification stages. According to their results, NF and RO produced high quality permeates, with a very high removal of COD, i.e., 79–81% by NF and 89–91% by RO. Similarly, colour was removed at greater than 96% by both processes. They considered that the degree of removal was good enough for the NF permeate to be reused in all wet textile processes, including the most demanding ones. Moreover, they observed that the removal performances were only slightly dependent on the quality of the feed concerning flows (prior to or after biological treatment), and suggested the viability of a single-step membrane process as nanofiltration for the specific application, which allows for significant reduction of treatment costs. On the other hand**, Rautenbach et al. (2000)** reported the requirement of cascaded, all membrane processes for the achievement of high water recovery rates, which should be around 100% for most industries. To this end, it is obvious that each particular textile effluent should be handled individually for the development of the most suitable process or process combinations for its recovery to the degree of quality required for the dyeing process.

Sostar et al. (2005) studied about the feasibility of the combination of physicochemical treatment with nanofiltration (NF) and/or reverse osmosis (RO) for water reuse. In fact, dead-end filtration by microfiltration (MF), ultrafiltration (UF), NF, and RO tests showed that a primary physicochemical treatment (coagulation/flocculation) was necessary to limit membrane fouling. Then, NF and/or RO experiments were performed and investigated at different operating pressures. Results showed that NF allowed the higher flow rate, 90 $L.h^{-1}.m^{-2}$ at 18.5 bar transmembrane pressure. **Joonghwan et al. (2007)** used chemical coagulants such as HOC-100A, alum, and ferric chloride for pretreatment of the feed water to membrane processes. Under optimum conditions, for all the coagulants used, about 90% of materials were removed from the solution when checked with the UV absorbance of the solution before and after treatment. **Zeng et al. (2008)** applied ultrafiltration and reverse osmosis combined membrane processes for in the textile wastewater treatment and reuse. As a pretreatment, ultrafiltration had good performance on removal of turbidity and organic matters with high molecular weight, which could guarantee good quality of feed water for reverse osmosis. **Anissa et al. (2009)** discussed about the hybrid flotation membrane. Various ways of hybrid flotation–membrane filtration such as flotation–microfiltration (MF), flotation–ultrafiltration (UF), flotation–nanofiltration (NF), and flotation–reverse osmosis (RO) were also addressed. The authors concluded that hybrid flotation–NF/RO is a new technology for wastewater treatment which produces high quality water with greater recovery and lower energy and reagents. Use of flotation in combination with MF/UF has reduced membrane fouling, and lead to a reduction in operation cost and improved the efficiency of membrane performance. **Nouha et al. (2012)** treated different combination of selected dyeing cycle baths using the combination of microfiltration (MF) with nanofiltration (NF) in order to reuse the treated water in the dyeing process. The pretreatment by MF lead to a 50% of pollutant retention except for salts which did not exceed 13%. The addition of NF lead to a high quality of treated effluent with retention of salt, colour, suspended matter and COD respectively by 47–52%, 100%, 99.9% and 73–85% depending on the effluent load. They concluded that the use of MF as a pretreatment prior to NF improves the treatment effectiveness by increasing the operating time and the permeate flux.

The membrane literature involves many studies investigating the effects of the factors such as MWCO, porosity, morphology, surface charge and membrane hydrophobicity; the solute characteristics such as the molecular weight (MW), molecular size, charge and hydrophobicity; the solution chemistry such as pH, ionic strength, hardness, and organic matter; and the system operating conditions such as the applied pressure, temperature, cross flow velocity and recovery ratio on the membrane separation performance **(Yen et al., 2002; Akbari et al., 2002; Koyuncu, 2002; Qin et al., 2004; Bellona and Drewes, 2005)**.

Due to the complexity of membrane systems, researchers have been trying to formulate and apply modelling approaches that can describe the retention of solutes at membrane pores through steric exclusion, electrostatic exclusion, solution-diffusion and adsorption **(Kargol, 2001; Vander and Vadecasteele, 2001; Mohammed and Ali, 2002)**. It has been proposed that rejection of non-charged compounds can be predicted based on their MW **(Ozaki and Li, 2002).** In addition, it has been confirmed that the MW is a poor predictor of rejection for compounds other than non-charged and hydrophilic type **(Kiso et al., 2001)**.

The adsorption of hydrophobic compounds onto the membranes is reported to be an important factor in the rejection of micropollutants during membrane applications **(Bellona et al., 2005)**. The hydrophobicity of membranes is determined by their contact angle measurements. The rejection of compounds by MF having MWCO, which is much larger than the MW of the compound, has been explained by adsorption **(Chang et al., 2002)**. According to the results of these studies, hydrophobic-hydrophobic interactions between the solute and the membrane play an important role in the rejection of hydrophobic compounds.

3.6 Treatment of Textile Processing Industry Wastewaters with Ceramic Membranes

Ultrafiltration using ceramic membranes can be a suitable process for removal of natural substances. Previously reported experiments were dedicated to evaluating the suitability of ultrafiltration through ceramic membrane for water treatment with a focus on the separation of natural organic matter. The effects of the membrane operating time and linear flow velocity on transport and separation properties were also examined. **Urbanowska et al. (2014)** carried out the experiments, using a 7-channel 300 kDa MWCO ceramic membrane, with model solutions and surface water at trans-membrane pressure of 0.2–0.5 MPa. The results revealed that a loose UF ceramic membrane can successfully eliminate natural organic matter from water. Comparison of ceramic and polymeric membrane permeability and fouling using surface water was studied by **Hofs et al. (2011)**. The trans-membrane pressure (TMP) was increased at a constant flux of 150 L m^{-2} h^{-1} due to membrane fouling by direct filtration with lake water was investigated for four ceramic (Al_2O_3, ZrO_2, TiO_2, SiC) and a PES/PVP polymeric microfiltration membrane. Removal of non-purgeable organic carbon (NPOC) is around 30% for the ceramic membranes, and 13–25% for the polymeric membrane. The higher degree of fouling on the polymeric membrane is partly due to its lower volume/area ratio, compared to ceramic membranes. **Alventosa-Delara et al. (2012)**

used ultrafiltration (UF) ceramic membrane to decolorize Reactive Black 5 (RB5) solutions at different dye concentrations (50 and 500 mg/L). Transmembrane pressure (TMP) and cross-flow velocity (CFV) were modified to study their influence on initial and steady-state permeate flux (J_p) and dye rejection (R). The effectiveness of ultrafiltration treatment was evaluated through dye rejection coefficient. The results showed significant dye removals, regardless of the tested conditions, with steady-state R higher than 79.8% for the 50 mg/L runs and around 73.2% for the 500 mg/L runs. **Jedidi et al. (2009)** developed a new mineral porous tubular membrane based on mineral coal fly ash. This membrane was applied to the treatment of the dying effluents generated by the washing baths in the textile industry. The performances in term of permeate flux and efficiency were determined and compared to those obtained using a commercial alumina microfiltration membrane. Almost the same stabilised permeate flux was obtained (about 100 L h^{-1} m^{-2}). The quality of permeate was almost the same with the two membranes: the COD and color removal was 75% and 90% respectively. Much work has been done on the dyeing water treatment by a new method of the combination of crossflow microfiltration, flocculation and ceramic membrane technique with some successful results caused by the advantages of the combination. The kind of flocculation and its dosage was studied by **Xu et al. (2002)** to treat some wastewater. Compared with organic membrane, ceramic membrane has exceptional performance of cleaning and regeneration. The results showed that the dynamic filtration equipped with ceramic plate membrane as the filtration membrane has great advantages and wide applications in membrane separation. A study reported the results of ultrafiltration experiments on model dye solutions containing anionic dyes and anionic surfactant. **Nowak (2010)** used the ceramic membrane modules CeramINSIDE (TAMI Industries) of various cut-off values (1, 5, 8, 15, and 30 kDa) in the experiments. The suitability of ceramic membranes for the decolourization of dye solutions was evaluated. Seven anionic organic dyes of molecular weights ranging from 327 to 1084 Da were used in the tests. The anionic surfactant (sodium dodecyl sulphate, SDS) was added to the dye solutions. The experiments were conducted at 0.03–0.1 MPa with the use of a laboratory and semi-pilot UF installation. The effect of the molecular weight of the dyes as well as the SDS presence in the separated solutions (in the range below the CMC) on the process efficiency was studied. It was found that membrane properties (permeability and dye separation factor) were almost identical for membrane modules of cut-off equal to 1, 5, and 8 kDa. For high-molecular-weight dyes above 600 Da, retention amounted to 95–98% and was slightly influenced by the presence of SDS in the dye solution. Ceramic membranes with a cut-off of 15 and 30 kDa exhibited insignificantly poorer properties. **Bhattacharya et al. (2010)** developed crossflow microfiltration (CMF) using ceramic membrane, from a low cost composition of α-alumina and clay in the tubular multichannel configuration with filtration area of 0.045 m^2. It was used alone, and in combination with different physicochemical techniques, viz. adsorption and chemical coagulation for treatment of wastewater collected from the sulphur dyeing process of a garment processing industry. The concentrated effluent was enriched with sulphur black dye, with turbidity 5912 NTU and COD of 3910 mg/L. Adsorptive treatment was carried out using a biosorbent prepared from the roots of an aquatic weed, E. Crassipes. Chemical pretreatment was carried out using different inorganic coagulants. Effect of different transmembrane pressures (TMP) in the range of 0.4–1.2 kg/cm^2 was observed and constant pressure filtration was conducted at 1 kg/cm^2 TMP. Performance of the single stage CMF process was compared with that of two stage processes in terms of the permeate quality, viz. COD, color, turbidity and TSS etc., and permeate flux. Encouraging result was found after microfiltration of the biosorbent treated feed as well as, effluent pretreated with aluminium sulphate. Dye removal was about 99%, with 80% reduction of COD. The chemical pretreatment process considerably increased the permeate flux compared to the single stage process.

3.7 Gaps Identified In the Existing Literature

- More research is required to reduce membrane fouling as it is the major drawback in membrane technologies. Fouling should be studied in detail to understand the causes of flux decline and to develop new approaches for minimizing the flux declines.
- The effect of wastewater pH and the operational conditions on the membrane performance need to be studied more to improve the efficiency of membrane processes.
- The selection of membrane for different types of wastewaters was not studied in detail.
- In addition to water, other valuable auxiliary chemicals can be recovered, thereby reducing effluent treatment costs, which has not been clearly studied.
- The literature lacks information about the reclamation of dyeing wastewaters by membrane processes, which is an important subcategory of textile industry.

3.8 Objectives of the Present Study

The main aim of this work is to study the use of microfiltration ceramic membranes for pre-treatment of effluents from textile industry. The specific objectives of this work include the following.

- Preparation of low-cost ceramic microfiltration membranes.
- Ceramic membrane characterization for porosity and pore size.
- Collection and characterization of wastewater from textile industry.
- Treatment of wastewater by dead-end microfiltration process.
- Analysis of permeate after treatment.

CHAPTER 4

METHODOLOGY

In order to achieve the research objectives, experimental work has been carried out on the following work elements.

- Preparation of ceramic membranes
- Characterization of textile industrial wastewater containing sulphates and chlorides
- Treatment of sulphates and chlorides containing textile dye bath wastewater using lab scale permeation apparatus
- Characterization of treated water

4.1 Raw Materials Used for Ceramic Membrane Fabrication

Seven inorganic raw materials viz. kaolin, feldspar, quartz, sodium carbonate, pyrophyllite, boric acid and sodium metasilicate were used in the fabrication of ceramic membrane supports. Kaolin was obtained from CDH Ltd., India, feldspar and pyrophyllite from National Chemicals, India, quartz from Research-lab Fine Chem Industries, India, sodium metasilicate from SD Fine-chem Ltd., India and the other inorganic precursors (sodium carbonate and boric acid) were obtained from Merck Ltd., India. Composition of raw materials used for the fabrication of ceramic microfiltration membranes is presented in **Table 4.1**. This composition has been chosen as it was reported to have the lowest average pore size and good corrosion resistance (**Bulasara et al., 2011**).

4.2 Preparation of Ceramic Membranes

The ceramic microfiltration membranes were fabricated manually by paste method. As shown in **Figure 4.1**, the fabrication methodology consisted of the following hierarchical steps: mixing of raw materials to make a paste; casting of the paste into circular moulds; drying of the raw discs; sintering; polishing and cleaning of the membranes. All the raw materials except water were taken based on the above composition (**Table 4.1**) with a total dry weight of 20 g per each membrane. These raw materials were manually mixed and ground to make a uniform powder and then mixed thoroughly using a laboratory blender. This dry mixture was taken into a petri dish and water was added to it (approx. 5 ml for each membrane) and was mixed to form a uniform paste. The paste was then transferred to a circular mould (stainless steel) to make disk type flat membranes. Weights (2 kg each) were placed on the wet membranes to recover structural deformations for about 12 hours and then the membranes were dried in open for 24 hours at ambient conditions (25°C). Then, the membranes were dried in a muffle furnace at 100°C for 12 hours to remove the moisture content of the membranes. Finally, the membranes were sintered at 900°C for four hours. During the sintering process, the temperature of the furnace was raised in two steps. Initially, heating was carried out at a slower rate (1°C/min) up to 250°C to avoid bending/cracking of membranes followed by a slightly higher heating rate (2°C/min) up to the sintering temperature (900°C). Sintering was carried out for four hours and the membranes were allowed to cool down slowly to the room temperature. The sintered membranes were polished on silicon carbide abrasive paper (No. C-220) to obtain a smooth surface finishing with required dimensions (52.5 mm diameter and 4.5 mm thickness) and were subjected to ultrasonic cleaning for 15 minutes to remove any loose particles created during surface polishing. After cleaning the membranes with de-ionized water, they were dried in a hot air oven to make them moisture free.

Table 4.1: Composition of raw materials used in the preparation of ceramic membranes

Material	**Composition on dry basis (wt %)**	**Composition on wet basis (wt %)**
Kaolin	40	32
Feldspar	15	12
Quartz	15	12
Pyrophillite	10	8
Sodium carbonate	10	8
Boric acid	5	4
Sodium metasilicate	5	4
Water	–	20

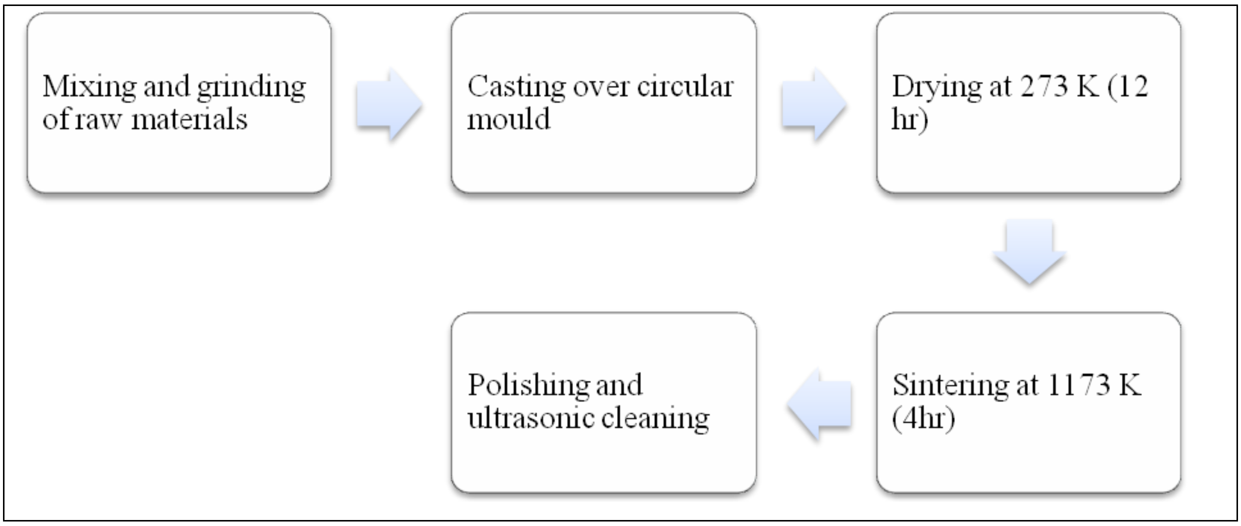

Figure 4.1: An outline of ceramic membrane preparation procedure.

4.3 Characterization of Textile Dye Bath Effluents (Feed)

Characterization of textile wastewater containing sulphates and chlorides was carried out by referring to the APHA manual and IS standards. Parameters for characterization are shown in **Table 4.2**.

Table 4.2: Analytical techniques for testing of textile wastewater parameters

S. No	Parameter	Method (with reference from APHA manual, 22nd edition)	Part No.
1.	BOD	5- day BOD test	5210 B
2.	COD	Open reflux method	5220 B
3.	Colour	Spectrophotometric Method	2120 C
4.	Chlorides	Argentometric method	4500-Cl^- B
5.	Sulphates	Gravimetric with ignition of residue	4500-SO_4^{2-} C
6.	pH	Electrometric	4500-H^+
7.	Conductivity	Electrometric	2510- B
8.	Turbidity	Nephilometric	2310 B
9.	Total dissolved solids	Gravimetric method	2540 C
10.	Total suspended solids	Gravimetric method	2540 D

S. No	Parameter	Method (with reference from APHA manual, 22^{nd} edition)	Part No.
11.	Sulphide	Idometric method	4500-S^{2-}
12.	Alkalinity	Titration method	2320 B
13.	Total hardness	EDTA Titrimetric Method	2340 C
14.	Calcium hardness	EDTA Titrimetric Method	3500 C

4.4 Treatment of Textile Wastewater Using Lab-Scale Permeation Apparatus

Firstly, liquid (water) permeation experiments were carried out to evaluate the membrane performance and identify the presence of defects in the interior of the membranes using a laboratory made permeation setup (shown in **Figure 4.2**) of capacity 85 ml. The setup consisted of a Teflon tubular cell with flat rectangular Perspex base plate. The membrane was placed in the membrane housing provided on the base plate and was sealed with epoxy resin. The cell was pressurized with compressed air and water flow rate was measured at various transmembrane pressures. The hydraulic permeability and corresponding pore diameter and porosity of the membranes were also determined. All permeation experiments were conducted at room temperature (25°C). After that same permeation experiments were carried out for treatment of textile cotton Dyebath containing sulphates and chlorides at two different pressure (i.e. at 15 psi and 30 psi) and flux data was recorded for each experiment and represented in graphical form to obtain the membrane performance on Dyebath wastewater.

4.5 Characterization of Treated Water (Permeate)

Characterization of textile wastewater after treatment using ceramic membranes was carried out by referring APHA manual and IS standards. Parameters for characterization were the same as those shown in **Table 4.2**.

Figure 4.2: Lab Scale Permeation Apparatus

CHAPTER 5

RESULTS AND DISCUSSIONS

5.1 Membrane Characterization

Membrane characterization was studied using various preliminary methods. The surface characterization was performed by scanning electron microscopy (SEM). The mean pore size of the bulk membrane was estimated from water permeation experiments. Membrane porosity was obtained by pycnometric method. Finally, the prepared membranes were tested for their corrosion resistance by measuring their weight loss after keeping them in standard (0.1 N) solutions of HCl and NaOH respectively for a period of 7 days.

5.1.1 Surface Characterization

Figure 5.1 presents the SEM surface micrograph of the membrane. This figure shows that the pores are unevenly distributed on the surface of the membrane.

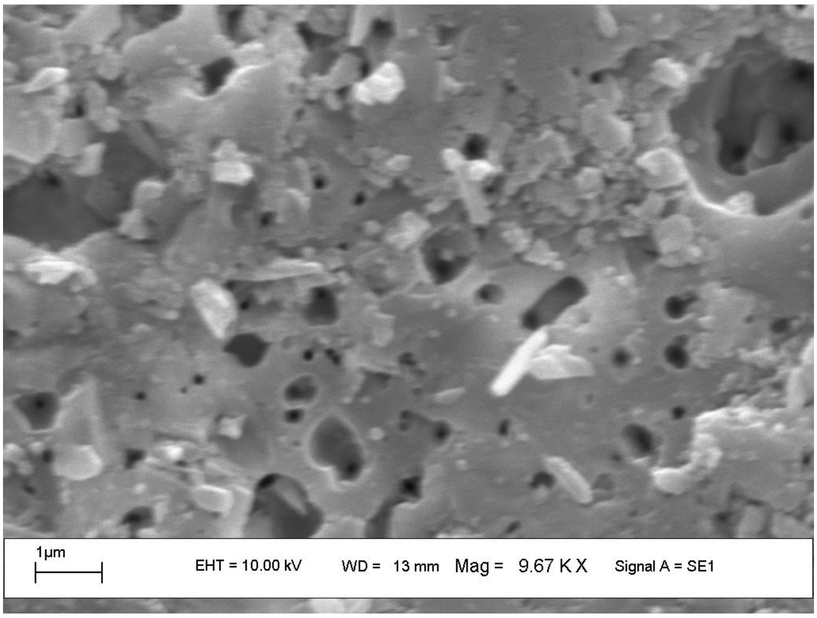

Figure 5.1: Surface SEM Image of the Ceramic Membrane

5.1.2 Porosity Estimation

Bulk porosity of the ceramic membrane was estimated by pycnometric method using water as the wetting medium. In this method, the dry membrane was wetted by water for about 15 minutes in a sonication bath and the weight gain was measured. Thereby, the volume of water absorbed into the pores was evaluated to get the pore volume. The ratio of pore volume to the total volume of the membrane gives the bulk porosity of the prepared membrane.

$$\text{Porosity, } \varphi = \frac{\text{Volume of pores}}{\text{Total volume of the membrane}} \tag{5.1}$$

Using the above equation, porosity was found to be 0.4021.

5.1.3 Water Permeation

Based on the liquid permeation data, hydraulic permeability (L_h) and the average pore radius (r) can be estimated according to the following expression.

$$J = \frac{n\pi r^4 \Delta P}{8\mu l} = L_h \Delta P \tag{5.2}$$

Where J is the flow density (flux) of permeated water, n is the pore density (number of pores per m^2), μ is the water viscosity, l is the pore length (m), ΔP (Pa) is the transmembrane pressure difference. Here L_h is the slope of the straight line fitted for 'J'versus 'ΔP' (**Figure 5.2**). By using the porosity, $\varepsilon = n\pi r^2$ in Equation (5.3), the corresponding pore radius can be obtained as follows.

$$r = \left[\frac{8\,\mu l}{\varepsilon}\, L_h\right]^{0.5} \tag{5.3}$$

As shown in the figure (**Figure 5.2**), the slope of the straight line was 1376.7 which is the value of hydraulic permeability (L_h). By substituting this value and the values of other variables in Equation (5.3) gives the average pore radius from which the pore diameter can be evaluated. The average pore diameter as obtained from the above calculation was 274.18 nm.

The water permeability of the membrane was found to be 1376.7 L/m^2.h.bar. The membranes had an average pore size of 274.18 nm with a porosity of 40.21%.

5.1.4 Corrosion Test

The prepared membranes were tested for their corrosion resistance by keeping them in standard (0.1 N) solutions of hydrochloric acid (HCl) and sodium hydroxide (NaOH) for a period of one week. These membranes were then washed with water and were dried at a temperature of 393 K for four hours to take their dry weight. The weight loss of the membranes was measured in order to evaluate their corrosion resistance. No weight loss was observed for the membrane placed inNaOH solution but a considerable amount (5%) of weight loss was observed for the membrane placed in HCl solution. Results showed that the prepared membranes have better resistance to alkaline (base) atmosphere and are very much suitable for alkaline cotton Dyebath wastewater.

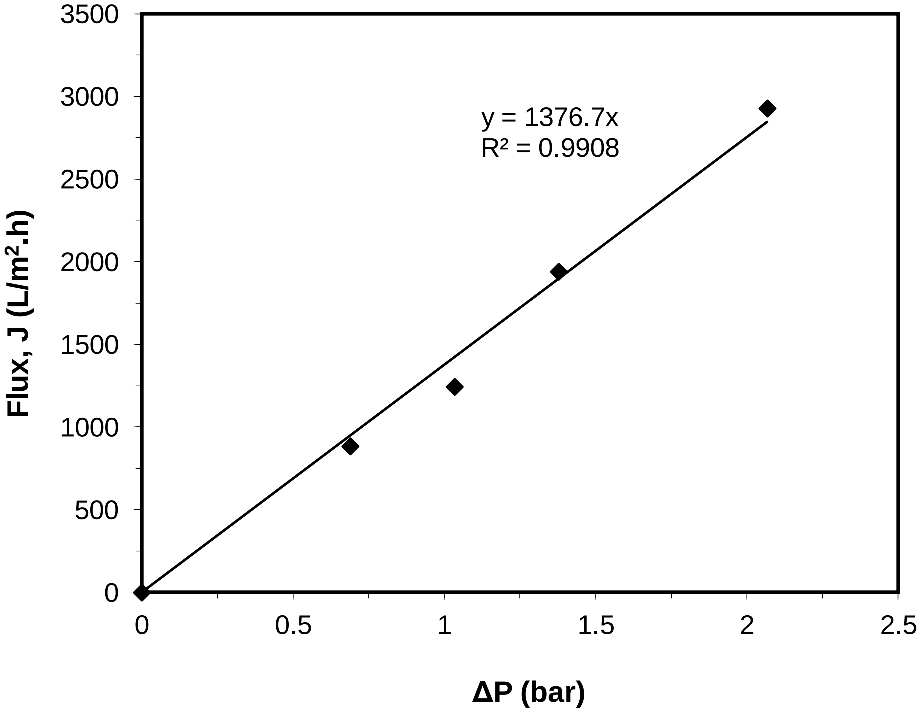

Figure 5.2: Water Flux Data for the Ceramic Membrane**.**

5.2 Wastewater (Feed) Characteristics

Various parameters are studied for sulphate containing waste water from cotton dye bath processing of textile industry. Values obtained for each parameter is given below in **Table 5.1**.

Table 5.1: Values for Each Parameter before Treatment of Sulphate Containing Dyebath

S. NO.	PARAMETER	RESULT
1.	pH	11.34
2.	Conductivity	24.54 mS/cm
3.	Turbidity	0.85 NTU

S. NO.	PARAMETER	RESULT
4.	Colour	2400 Pt.Co unit
5.	Chlorides	749.56 mg/L
6.	Total Dissolved Solids (TDS)	20,800 mg/L
7.	Total Suspended Solids (TSS)	45 mg/L
8.	Sulphates	12,950 mg/L
9.	COD	4,650 mg/L
10.	BOD	990 mg/L
11.	Alkalinity	4500 mg/L
12.	Sulphide	33 mg/L
13.	Total Hardness	3500 mg/L as $CaCO_3$ Eq.
14.	Calcium Hardness	1500 mg/L as $CaCO_3$ Eq.

Various parameters are studied for Chlorides containing waste water from cotton dye bath processing of textile industry. Values obtained for each parameter is given below in **Table 5.2**.

Table 5.2: Values for Each Parameter before Treatment of Chlorides Containing Dyebath

S. NO.	PARAMETER	RESULT
1.	pH	11.85
2.	Conductivity	69.4 mS/cm
3.	Turbidity	0.61 NTU
4.	Colour	3480 Pt.Co unit
5.	Chlorides	43836.4 mg/L
6.	Total Dissolved Solids (TDS)	50548 mg/L
7.	Total Suspended Solids (TSS)	120 mg/L
8.	Sulphates	690.7 mg/L
9.	COD	3800 mg/L
10.	BOD	780 mg/L
11.	Alkalinity	3700 mg/L
12.	Sulphide	34.3 mg/L
13.	Total Hardness	3200 mg/L as $CaCO_3$ Eq.
14.	Calcium Hardness	1200 mg/L as $CaCO_3$ Eq.

5.3 Dead-End Microfiltration Experiments and Results

The applicability of dead-end microfiltration (MF) was tested for cotton dye bath wastewater. A lab scale filtration apparatus (**Figure 4.2**) providing dead-end filtration was used to pre-treat the wastewater. All MF experiments were conducted at room temperature (298 K). The flux data of the textile wastewater through the ceramic membrane is presented in graphical form. The filtrate were collected and analysed for various parameters. The filtration rates were determined by dividing the total volume of the filtrates by the time periods of filtration. The calculated values represent cumulative filtration rates since the filtration rates decreased with time of filtration due to the accumulation of material on the membrane. The membrane during microfiltration experiments was subjected to washing and back-flushing by water.

5.3.1 Sulphate Dyebath Wastewater

Figure 5.3 shows the flux profiles of the permeate at a trans-membrane pressure of 15 psi. The dotted line above the permeate flux data represents the pure water flux. The permeate flux declined exponentially with time due to the effect of membrane fouling.

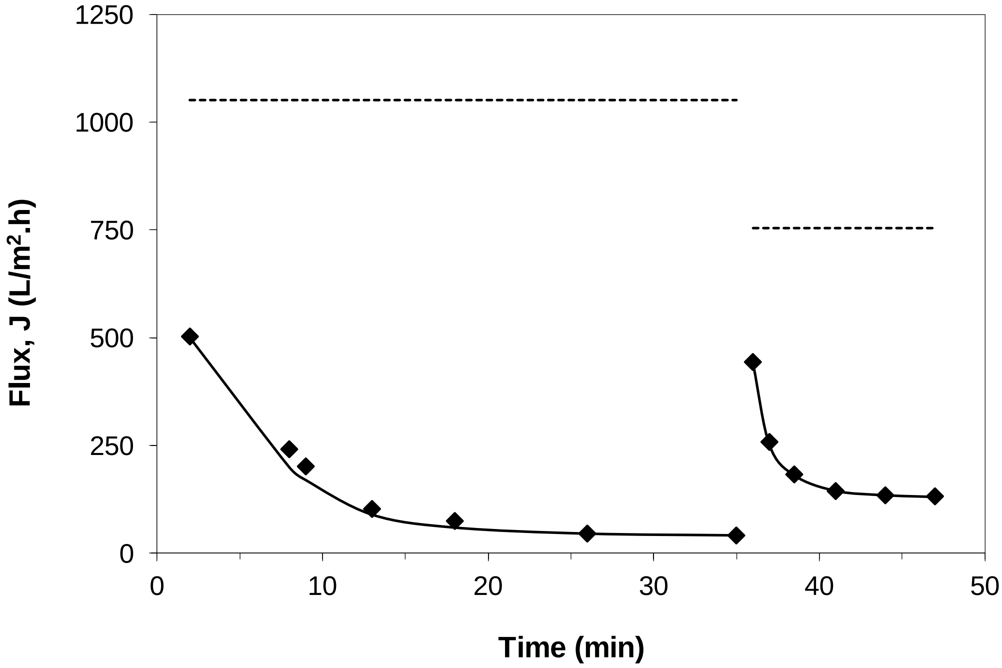

Figure 5.3: Sulphate Containing Dyebath Wastewater Flux Data at 15 Psi Pressure

A similar observation was noticed for a trans-membrane pressure of 30 psi (**Figure 5.4**).

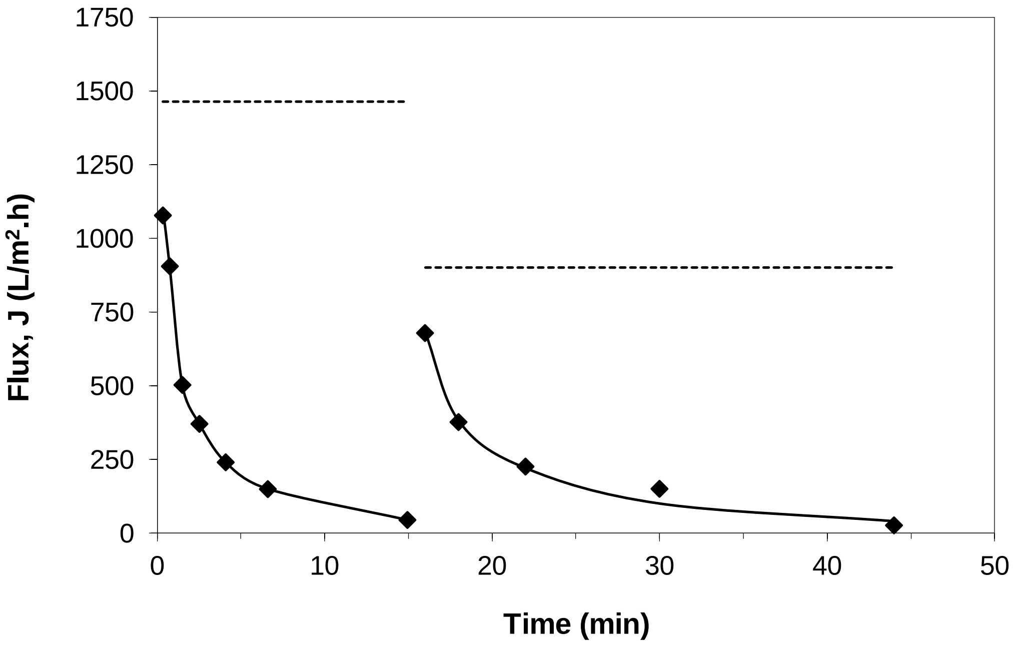

Figure 5.4: Sulphate Containing Dyebath Wastewater Flux Data at 30 Psi Pressure

5.3.2 Chloride Dyebath Wastewater

Figure 5.5 shows the flux profiles of the permeate at a trans-membrane pressure of 15 psi. The dotted line above the permeate flux data represents the pure water flux. The permeate flux declined exponentially with time due to the effect of membrane fouling.

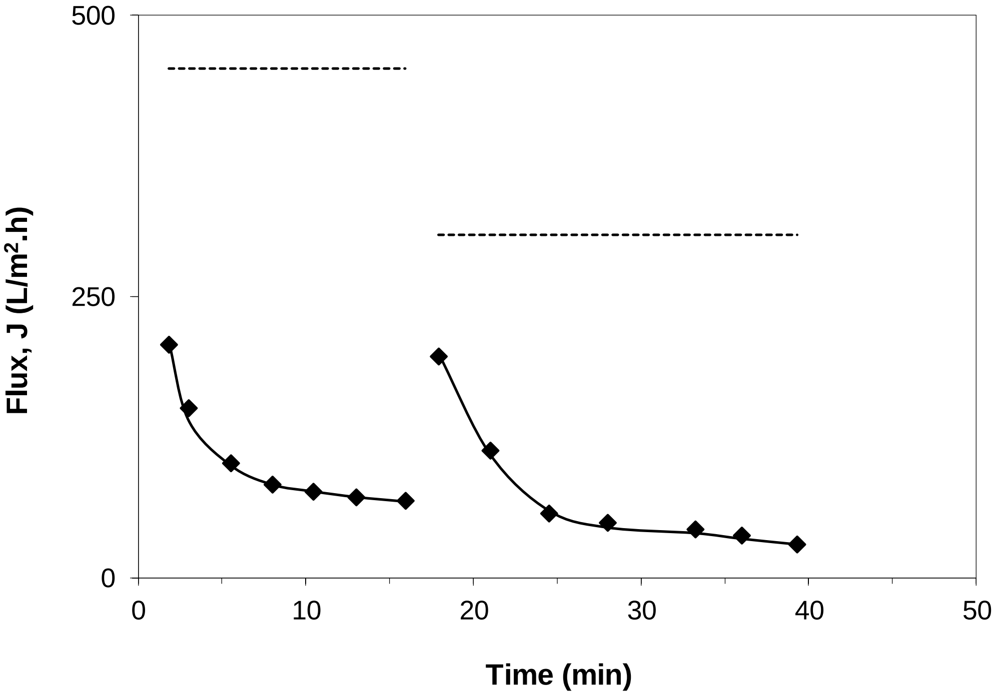

Figure 5.5: Chloride Containing Dyebath Wastewater Flux Data at 15 Psi Pressure

A similar observation was noticed for a trans-membrane pressure of 30 psi (**Figure 5.6**).

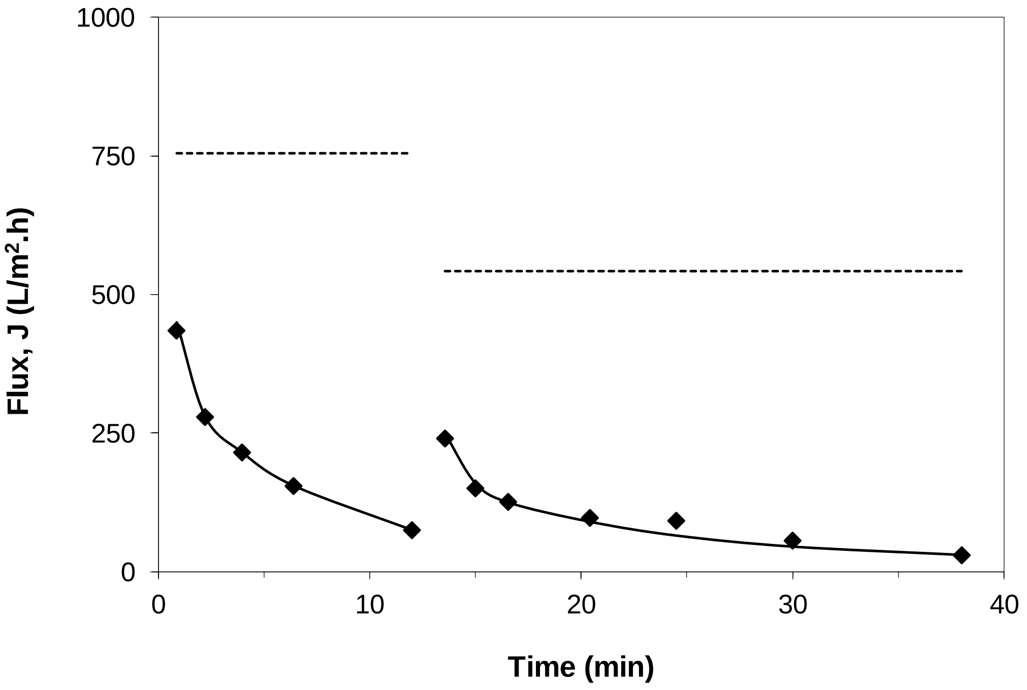

Figure 5.6: Chloride Containing Dyebath Wastewater Flux Data at 30 Psi Pressure

5.4 Treated Water (Permeate) Characteristics

Characterization of textile wastewater after treatment using ceramic membranes was carried out by referring APHA manual and IS standards. Permeate characteristics for sulphate rich and chloride rich wastewater are shown in Tables 5.3 and 5.4 respectively.

Sulphate rich wastewater originally had COD of 4650 mg/L, TSS of 45 mg/L, TDS of 20,800 mg/L, BOD of 990 mg/L, Colour of 2400 Pt.Co unit, Sulphate of 12950 mg/L, Chloride of 749.56 mg/L, Hardness of 3500 mg/L. After pre-treatment, the permeate had no TSS, however, it had COD of 3580 mg/L, TDS of 14356 mg/L, BOD of 601 mg/L, Colour of 1790 Pt.Co unit, Sulphate of 8606 mg/L, Chloride of 501.4 mg/L, Hardness of 3300 mg/L.

The Chloride rich wastewater originally had COD of 3800 mg/L, TSS of 120 mg/L, TDS of 50,548 mg/L, BOD of 780 mg/L, Colour of 3480 Pt.Co unit, Sulphate of 690.7 mg/L, Chloride of 43836.4 mg/L, Hardness of 3200 mg/L. After pre-treatment, the permeate had no TSS, however, it had COD of 2870 mg/L, TDS of 41,585.6 mg/L, BOD of 521.5 mg/L, colour of 2670 Pt.Co unit, Sulphate of 498.6 mg/L, Chloride of 34503.8 mg/L, Hardness of 3000 mg/L.

The percentage removal of some important contaminants during the pre-treatment process is shown in Figure 5.7. From this figure, it can be seen that the TSS was completely removed, while, TDS removal was 31% and 18% respectively, for sulphate and chloride wastewater. The percentage removal of most of the contaminants was slightly higher for sulphate containing dye bath wastewater than the chloride containing wastewater.

Table 5.3: Values for Each Parameter before and after Treatment of Sulphate Containing Dyebath

S.NO.	PARAMETER	BEFORE	AFTER
1.	pH	11.34	10.39
2.	Conductivity	24.54 mS/cm	23.5 mS/cm
3.	Turbidity	0.85 NTU	0.67 NTU
4.	Colour	2400 Pt.Co unit	1790 Pt.Co unit
5.	Chlorides	749.56 mg/L	501.4 mg/L
6.	TDS	20,800 mg/L	14356 mg/L
7.	TSS	45 mg/L	0 mg/L
8.	Sulphates	12,950 mg/L	8606 mg/L
9.	COD	4,650 mg/L	3580 mg/L
10.	BOD	990 mg/L	601.6 mg/L
11.	Alkalinity	4500 mg/L	4180 mg/L
12.	Sulphide	33 mg/L	29.1 mg/L
13.	Total Hardness	3500 mg/L as $CaCO_3$ Eq.	3300 mg/L as $CaCO_3$ Eq.
14.	Calcium Hardness	1500 mg/L as $CaCO_3$ Eq.	1350 mg/L as $CaCO_3$ Eq.

Table 5.4: Values for Each Parameter before and after Treatment of Chlorides Containing Dyebath

S.NO.	PARAMETER	BEFORE	AFTER
1.	pH	11.85	10.39
2.	Conductivity	69.4 mS/cm	65.8 mS/cm
3.	Turbidity	0.61 NTU	0.48 NTU
4.	Colour	3480 Pt.Co unit	2670 Pt.Co unit
5.	Chlorides	43836.4 mg/L	34503.8 mg/L
6.	TDS	50548 mg/L	41585.6 mg/L
7.	TSS	120 mg/L	0 mg/L
8.	Sulphates	690.7 mg/L	498.6 mg/L
9.	COD	3800 mg/L	2870 mg/L
10.	BOD	780 mg/L	521.5 mg/L
11.	Alkalinity	3700 mg/L	3400 mg/L
12.	Sulphide	34.3 mg/L	31.5 mg/L
13.	Total Hardness	3200 mg/L as $CaCO_3$ Eq.	3000 mg/L as $CaCO_3$ Eq.
14.	Calcium Hardness	1200 mg/L as $CaCO_3$ Eq.	1050 mg/L as $CaCO_3$ Eq.

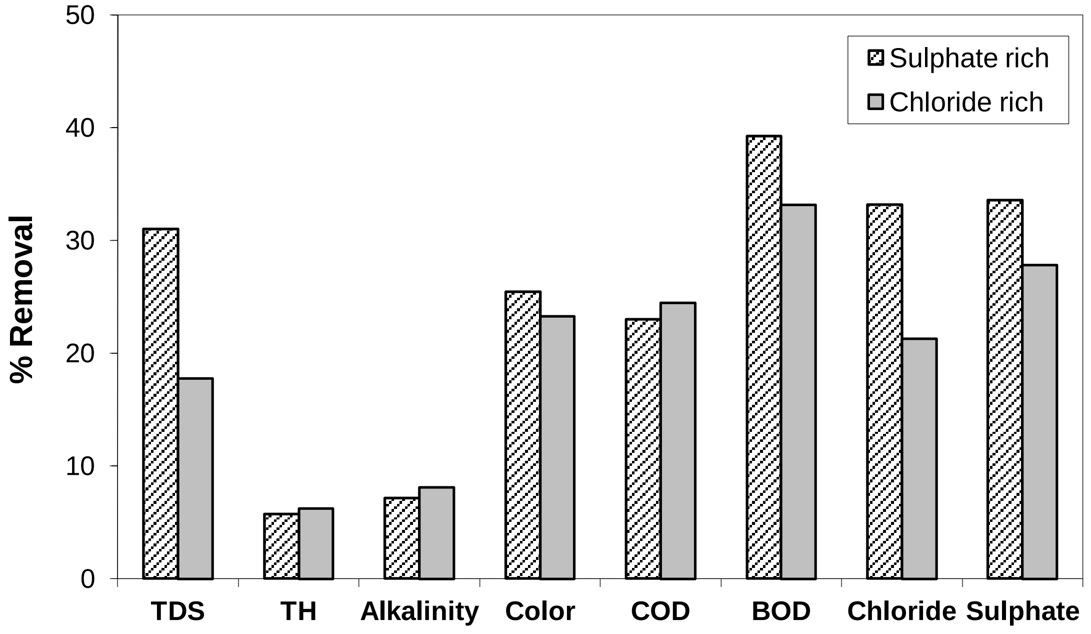

Figure 5.7: Efficiency of pre-treatment process

CHAPTER 6
CONCLUSION AND FUTURE WORK

The prepared ceramic microfiltration membrane was successfully applied for pretreatment of two types of textile dye bath effluents, one containing chlorides and the other containing sulphates. During the pre-treatment process, TSS was completely removed, while, TDS, COD and BOD were reduced drastically. For the sulphate rich wastewater, about 23 % removal of COD, 21% removal of Turbidity, 25% removal of Colour, 33% removal of Chloride, 31% removal of TDS, 100% removal of TSS, 34% removal of Sulphate, 39% removal of BOD, 11% removal of Sulphide, 10% removal of Calcium Hardness were noticed. In a similar way, for the chloride rich wastewater, about 24 % removal of COD, 21% removal of Turbidity, 23% removal of Colour, 21% removal of Chloride, 18% removal of TDS, 100% removal of TSS, 28 % removal of Sulphate, 33% removal of BOD, 8% removal of Sulphide, 12.5% removal of Calcium hardness were noticed. However, the MF membrane was unable to remove metal ions and colour up to the required standards. Therefore, further treatment of the permeate by means of NF or RO is necessary to meet the disposal/reuse standards.

Regarding all the discussions and conclusions of this study, the following future work is recommended:

1. The performance of the ceramic membranes (applied for water recovery from the dyeing effluents of cotton textile industry in the present work) should be tested for other textile wastewaters of different processes with similar characteristics in an attempt to generalize the conclusions obtained in this study.

2. A detailed study regarding the effect of pH on the separation performance of the membranes for the recovery of dyeing effluents should be performed. In this way, it should be determined whether the pH is effective on the wastewater or on the membrane characteristics, or both.

3. Membrane characteristics is very important in evaluation of its performance, therefore a detailed study is recommended for membrane characterization, for which measurement of zeta potential for the determination of membrane surface charge, measurement of contact angle for determining whether the membrane is hydrophilic or hydrophobic, or even the preparation of the membrane itself may be required. A more detailed characterization of the wastewater is also required for understanding the mechanisms of rejections better.

4. Fouling should be studied in detail to understand the causes of flux decline and to develop new approaches for minimizing the flux declines.

5. Economical feasibility of the ceramic membranes should be studied.

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