CHAPTER 2

2. LITERATURE SURVEY

2.1 INTRODUCTION

Textile industry is one among the few large industries which consume considerable amount of water at different stages of textile processing (Hafez 2011), which result in a wide variety of wastewater characteristics. A broad range of more common effluent parameters identified by a survey of articles published in the literature (Bisschops 2003) are given in Table 2.1. With increasing environmental awareness, water quality before the discharge of effluents is emerging to be more stringent than ever in both developed and developing economies (Tufekci 2007). Though a wide variety of primary, secondary and tertiary treatment procedures for dye removal and salt recovery are available, each of these individual operations contain certain limitations (Robinson 2001).

Table 2.1: Prevalence of parameters describing textile wastewaters (Bisschops 2008).

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Percentage of articles reporting the parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD</td>
<td>&gt;90%</td>
</tr>
<tr>
<td>pH, Colour, Suspended Solids</td>
<td>60-65%</td>
</tr>
<tr>
<td>BOD$_5$</td>
<td>50%</td>
</tr>
<tr>
<td>TKN, Conductivity, Metals, TOC, Cl$^-$</td>
<td>20-30%</td>
</tr>
<tr>
<td>TDS, Grease, Alkalinity, Surfactants</td>
<td>15-20%</td>
</tr>
<tr>
<td>Hardness, Sulphide, Total Solids</td>
<td>10-15%</td>
</tr>
<tr>
<td>Turbidity</td>
<td>&lt;10%</td>
</tr>
</tbody>
</table>
On the one hand, textile industry contributes significantly to the overall economic growth of developing countries such as India by providing employment opportunities, industrial production and exports (Tanange 2010). On the other hand, negative impact of the discharged pollutants from textile industries on the ecosystem at different locations in the country, where textile industry clusters have evolved over a period of time cannot be overlooked either (Rajaram 2008). For example, in Tiruppur south India, a dyeing industry cluster, which currently has more than 400 dyeing units in the same place, was found to pollute both surface water in Noyyal river and the groundwater in the region (Geetha 2008)

The Central Pollution Control Board (CPCB) of India in a recent survey has admitted that the common effluent treatment plants installed in Tiruppur and other industrial clusters fail to comply with the effluent standards (CPCB 2005). The conflict of interest between the dyeing industries on one side and the urban community which utilizes the groundwater for drinking purposes and the agricultural community which depends heavily on the river water for their survival on the other has aggravated social tensions (Appaswamy 2010). Cost effective dye effluent treatment technologies for handling millions of liters of different dye wastewaters everyday are yet to emerge. It is in this context that studies on advance methods of wastewater treatment assume a great significance (CPCB 2007).

Membranes play a significant role in any advanced dye wastewater treatment system. Microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) membranes are used in these processes. The prevention of membrane fouling in these advanced membrane separation processes is a critical challenge for ensuring their economic viability. Recent achievements in this direction with a special focus on textile wastewater treatment have been provided in this literature survey.
2.2 FOULING PROCESSES AND MODELS

2.2.1 Factors influencing membrane fouling

A conceptual understanding of fouling processes from general literature (Schafer 2005) would be very helpful for understanding the specific issues in dye wastewater treatment. Physicochemical factors that influence membrane fouling may be classified into three major categories namely a) feed water composition, b) membrane properties and c) hydrodynamic operating conditions (Tang 2011). Wherever biodegradation processes are involved, biofouling should also be considered (Drews 2010; Le-Clech 2006; Meng 2009).

The process of membrane fouling depends heavily on the nature and composition of feed. The four main types of feed dependent membrane fouling are as follows: a) inorganic fouling, b) organic fouling, c) fouling due to suspended solids and colloids and d) biofouling. In addition to the foulant types mentioned above the physicochemical parameters like pH, temperature and minor residual surfactants also influence fouling behavior.

The pore size of the membrane is an important parameter that influences membrane selection for a specified feed stock. The pore sizes of membranes depend on the monomer composition, method of preparation and modification. Membranes supplied by individual suppliers are available with widely different pore sizes and properties. The typical pore sizes and other properties of membranes are given in Table 2.2 as an indication (Wagner, 2001). While RO membranes are pore free membranes, the NF membranes have pores size up to 2 nm, the UF and MF membranes have significantly larger pore sizes. An increased the pore size of membrane would lower the pressure requirement would decrease and also increase the complexity of fouling. Apart from pore size, other physicochemical properties of membranes such as roughness, surface charge, hydrophilicity and surface functional groups also see to influence membrane fouling.
The hydrodynamic conditions can influence both the operating efficiency and membrane fouling. In addition to transmembrane pressure (TMP), cross flow velocity (CFV), temperature and flux rate also influence membrane fouling. Membrane modules and their design features have a significant effect on the overall efficiency of the process. Reactor design features become even more important for membrane bioreactors.

**Table 2.2:** Typical pore sizes and other properties of membranes (LMWC-Low molecular weight cutoff, HMWC-High molecular weight cutoff, CA-Cellulose acetate, PSO-Polysulfone, PES-Polyether sulfone, PVDF-Polyvinylidene fluoride, PP-Polypropylene) (Wagner 2001)

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Reverse Osmosis (RO)</th>
<th>Nanofiltration (NF)</th>
<th>Ultrafiltration (UF)</th>
<th>Microfiltration (MF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness (μm)</td>
<td>150</td>
<td>150</td>
<td>150 - 250</td>
<td>-150</td>
</tr>
<tr>
<td>Thin film (μm)</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>Pore size (μm)</td>
<td>&lt;0.002</td>
<td>&lt;0.002</td>
<td>0.2 - 0.02</td>
<td>4 - 0.02</td>
</tr>
<tr>
<td>Rejection of HMWC, LMWC sodium chloride glucose amino acids</td>
<td>HMWC monosaccharides, disaccharides, oligosaccharides polyvalent neg. ions,</td>
<td>Macro molecules, proteins, polysaccharides virus</td>
<td>Particles, clay bacteria</td>
<td></td>
</tr>
<tr>
<td>Membrane material(s)</td>
<td>CA, PSO, PES, Thin film</td>
<td>CA, PSF, PES Thin film</td>
<td>Ceramic PSO, PVDF, CA PP</td>
<td>Ceramic PSO, PVDF</td>
</tr>
<tr>
<td>Membrane Module</td>
<td>Tubular, spiral wound, plate-and-frame</td>
<td>Tubular, hollow fiber, spiral wound</td>
<td>Tubular, hollow fiber spiral wound</td>
<td>Tubular,</td>
</tr>
<tr>
<td>Operating pressure (bar)</td>
<td>15-150</td>
<td>5-35</td>
<td>1-10</td>
<td>&lt;2</td>
</tr>
</tbody>
</table>
(MBR). A recent review (Drews 2010) also illustrates the mutual interconnections and influence of feed stocks, membranes, reactor design and other operating parameters on the overall performance of MBR.

### 2.2.2 Characterization of fouling process

The flux reduction caused by any solute when compared to the pure water flux is given by the following equation.

\[
\text{Flux reduction (FR)} = 1 - \left( \frac{J_s}{J_w} \right)
\]

Where \( J_s \) refers to solution flux and \( J_w \) refers to pure water flux. These parameters measured under different experimental conditions provide primary information regarding membrane fouling. It is also possible to find correlations between flux decline due to a given solute and the pore size of the membranes (Lindau 1998). The fouling may also increase when the membrane separation processes is in progress. With time the solute adsorption would increase and enhance the pressure drop across the membrane (Zhu 2012). This is termed as normalized pressure drop (NPD).

The rate of change of flux with time is a quantitative indicator of the fouling process. Efforts have been made to estimate the fouling potential of different solute molecules, colloidal particles or biological components. The relative fouling potential of different molecules on a given membrane which is defined as modified fouling index (MFI) can be quantitatively estimated using the following expression.

\[
\text{Modified Fouling Index (MFI)} = \frac{\eta_{20^\circ C} \times \Delta P}{\eta_T \times P_A} \tan \alpha
\]

Where \( \eta_{20^\circ C} \) is the viscosity of feed water at 20°C, \( \eta_T \), the viscosity at the operating temperature, \( \Delta P \), the transmembrane pressure, \( P_A \) is the applied pressure (usually 210 Kpa) and \( \alpha \), the slope of \( t/V \) versus \( V \) (V-volume of permeate at time t).
The MFI values for different feeds have been calculated for RO (Vrouwenvelder 2003; Boerlage 2000) and NF (Vrouwenvelder 2003) membranes. The experimentally determined MFI values may further be used to find correlation between physicochemical properties of the molecules and their fouling potential (Koo 2012).

Membrane charge is an important parameter that determines the flux and fouling behavior of ionic solutions. The zeta potential of a membrane is the pH value of the solution at which the charge on the membrane surface is equal to zero. Various methods are available for calculating and measuring the zeta potential (Zhao 2010; Brant and Childress 2002). In the acidic region, the membrane tends to carry a positive charge due to the protonation of amide group. Such charges are responsible for the electrostatic interaction between the membrane and the foulant molecule. In an interesting work, electrochemical impedance spectroscopy has been used for characterizing the ion transport through the membrane (Bason 2007).

Fouling can also modify hydrophilicity of the membrane surface. Contact angle measurements have been employed as a tool for evaluating the modification of hydrophilicity (Zhao 2010; Brant 2002). The effluent organic matter adsorbed on the fouled membrane can be characterized either on the adsorbed mode or after the dissolution in appropriate solvent (Zhao 2010; Ivnitsky 2005; Pal I 2006; Jarusutthirak 2002) using Fourier transform infrared (FTIR) and other spectroscopic techniques.

The fouled membranes obtained under different exponential experimental conditions can be taken out and characterized using a broad range of surface analytical techniques such as scanning electron microscope (SEM) (Zhao 2010; Ivnitsky 2005; Chu 2004; Roudman 2000; Meng 2010). Typical SEM images showing inorganic, organic and biofouling are presented in Figs. 2.4a (Antony 2011), 2.4b (Zhao 2010) and 2.4c (Matin 2011). Inorganic salt layers, for example, can easily be distinguished from polymer such as organic films and microorganisms or biofilms.
Fig. 2.1: SEM images of the fouling SEM images of a) The CaCO$_3$ scaling on thin film composite-fouling resistance (TFC-FR) membranes under controlled conditions after 4 h (Inorganic fouling) b) Organic fouling by carbohydrates and protein. c) staphylococcal biofilm on the inner surface (Biofouling).

A closer evaluation of membrane fouling is possible using atomic force microscope (AFM) (Roudman 2000; Meng 2010). The fluorescent image obtained by confocal laser scanning microscopy (CLSM) indeed can provide much sharper images even at low level of membrane fouling (Ferrando 2005; Yun 2006). Monitoring of 3D images of membrane fouling is also possible and this can be owed to recent developments (Meng 2010; Hughes 2006). A less defined direct observation technique has also been used for membrane characterization (Pal 2006). A comprehensive review on the surface analytical technique for membrane characterization has been published recently (Meng 2010).
2. 2. 3. Fouling models

Any membrane has an inherent resistance to liquid flow. This is termed as membrane resistance \((R_m)\). During membrane separation, the retained solute concentration near the membrane develops a concentration polarization resistance termed as \(R_{cp}\). The fouling processes further enhance this inherent resistance. Basically, three modes of fouling resistances can be identified as shown in Fig. 2.3. The organic molecules can adsorb on the membrane pores leading to adsorption resistance \((R_a)\), if the particle size is smaller than the pore size (Fig. 2.1a). Larger molecules or colloidal particles can completely block the pores (Fig. 2.1b) resulting in higher resistance to flow (pore blocking resistance; \(R_p\)). Organic molecules, biological molecules and colloidal particles can form a porous gel structure or a more compact cake structure on the membrane surface (Fig. 2.1c). Inorganic salts may also lead to similar blocking influence with flux resistance gel layer resistance \((R_g)\). The overall experimental flux is given by eq. (2.3).

\[
J = \frac{\Delta p}{\eta R_{tot}}
\]  

(2.3)

where \(J\)-flux rate of the solution, \(\Delta p\)- applied pressure, \(\eta\)-viscosity \(R_{tot}\) - the sum of individual resistance values, given by eq. (4).

\[
R_{Tot} = R_m + R_{cp} + R_a + R_p + R_g
\]  

(2.4)

**Fig. 2.2:** Fouling mechanism a) Adsorption b) Pore blocking c) cake layer formation
The overall membrane fouling is the result of combination of any of the above fouling processes. Conditions do exist under which each of the above fouling mechanism can predominate. Efforts have been made to isolate individual resistance components such as particulate fouling (Boerlage 1997). Model solutions have been employed to evaluate the fouling behavior in UF and NF processes using the above resistance-in-series model (Aouni 2011). The same approach has also been employed to assess the fouling due to surfactants (Kaya 2011) and textile wastewater (Fersi 2009).

Even low concentration of organic molecules may adsorb on membrane surfaces and contribute to membrane fouling on RO membranes (Li 2011), NF membranes (Bruggen 2002; Bruggen 2002a) and UF membranes (Zhang 2008). All the membranes may be affected by adsorptive fouling in the initial stages (Subramani 2006). Modern membrane surfaces in industry generally contain charged functional groups. Beyond the isoelectric point (IEP) of each membrane, it is negatively charged. The organic molecules may also contain soluble ionic groups like carboxylic acids, sulphonic acids and amides. Change of pH can influence both membrane charge and the charge of the adsorbing organic molecules (Capar 2006a). The effect of surface charge (Bellona 2005) and molecular charge (Bruggen 1999) on membrane fouling has been studied. The electrostatic interaction between foulant molecular species may also be important (Tang 2007), which becomes membrane independent at higher flux rates (Guo 2012).

Pore blocking, gel formation and cake formation are generally interlinked. A qualitative description of membrane fouling by biomolecules covering all these mechanisms at different stages of development is available (Wang 2008). At very low foulant concentrations and low flux conditions, pore blocking mechanism would be predominant. Molecules like polysaccharides may tend to form gels on membrane surfaces (Wang 2011). As the feed concentration and complexity increases, pore blocking and cake formation occur simultaneously (Cogan 2009; Tang 2009; Huang 1998). Efforts have been made to model the fouling process involving pore blocking.
and cake formation pathways (Mondal 2010). A complete quantification of adsorptive resistance \( (R_a) \), pore resistance \( (R_p) \) and cake resistance \( (R_c) \) has also been attempted (Wu 2011).

2.3 MEMBRANE PROCESSES IN TEXTILE WASTEWATER TREATMENT

2.3.1 MF/UF membranes for pretreatment

MF and UF membranes can remove suspended particles, colloids and many biological molecules at significantly low pressure. Hence this process has almost become a standard unit operation before proceeding to further purification using NF and RO membranes (Bruggen 2004; Bruggen 2013). For the reclamation of rinsing waters of indigo dyeing process, MF filtration followed by UF filtration was found to be efficient (Uzal 2009). In another study sand filtration followed by MF was found to be useful pre-filtration for subsequent NF separation (Tahri 2012). UF pre-treatment stage can enhance the permeate flux of subsequent NF process by as much as 50% (Gozalvez-Zafirlla 2008).

Dye wastewater from the secondary treatment may contain hydrophobic impurities, which can reduce the flux rate and enhance membrane fouling in MF/UF membranes. Relatively more hydrophilic modified PVDF membranes can minimize membrane fouling (Srivastava 2011). Hydrophilic dynamic UF membranes using in situ addition of hydrophilic polymers like polyethylene glycol and polyvinyl alcohol can be efficiently used for preventing irreversible fouling by dye molecules (Amorim 2006).

Commercial MF/UF membranes used in dye wastewater treatment are generally polymeric membranes. Some attempts to use novel ceramic UF membrane for textile wastewater treatment are also reported (Barredo-Damas 2012; Jedidi 2011). Ceramic UF membranes are found to be suitable for long term operations (Barredo-Damas 2010; Barredo-Damas 2012).
2.3.2 Membrane bioreactors: The opportunities and challenges:

Membrane bioreactors (MBR) combine or integrate the process of biological treatment with membrane filtration. This option (Option-1 in Figure 1.1) can substantially simplify overall treatment process. Extensive original investigations and frequent reviews on membrane bioreactors appear in the literature from time to time (Chu 2005; Le-Clech 2006; Meng 2009; Drews 2010 and Huyskens 2011). These studies cover a wide range of fouling characteristics like factors influencing membrane fouling (Le-Clech 2006), influence of biological medium and feed stock (Meng 2009), the nature of cake formation (Chu 2005), MBR reactor design and influence of hydrodynamic parameters (Drews 2010) and other operating conditions (Huyskens 2011). It is beyond the scope of present review to discuss all these factors on MBR and membrane fouling.

The biological medium in which immersed MBR operates is indeed a multi component system which can significantly influence the fouling behavior of MF/UF membranes. Understanding and controlling membrane fouling in such a complex system are indeed quite challenging. The biological medium for example may contain high concentrations of mixed liquor suspended solids (MLSS). The extra cellular polymeric substance (EPS) can form hydrophobic gel and cake layer on membrane surface. Even the soluble microbial products (SMP) can contribute to membrane fouling through the pore blocking mechanism. High feed to microbial (F/M) ratio and high viscosity of the medium can also influence membrane fouling. These are some of the factors that are known to contribute to the overall membrane fouling in MBR’s (Fig. 4). Recent studies have also evolved strategies for controlling membrane fouling and hence enhance the overall performance of the MBR’s as indicated in this figure. Enhancement of hydraulic retention time (HRT), solid retention time (SRT) and generation of coarse gas bubbles near the membrane surface are some of the strategies that can reduce membrane fouling. Efficient back washing strategies are essential for
long term operation of membranes bioreactors (Fig. 4). Membrane modification and use of dynamic membranes are also being investigated.

**Fig: 2.3.** Favorable conditions mitigating membrane fouling (*HRT*-Hydraulic retention time, *SRT*- Solid retention time, *MLSS*-Mixed liquor suspended solids, *F/M*- Feed to microbial ratio, *EPS*-Extracellular polymeric substances, *SMP*- Soluble microbial products) (Meng 2009).

There are some recent reports on application studies of MBR’s in textile wastewater treatment (Lin 2012). The membrane fouling mechanism during synthetic textile wastewater treatment was found to depend on the type of membranes used. Cake layer formation was the principle mode of fouling on hollow fiber membrane while pore blocking was the main fouling path way on flat sheet membrane (Hai 2005).
The fouling due to EPS was found to be sensitive to pH (Sweity 2011; Yunpeng 2011). The influence of dye concentration and HRT on textile wastewater treatment has also been reported (Konsowa 2013). Dissolved oxygen in the medium and its role an anaerobic and aerobic process as well as mechanism of membrane fouling during textile wastewater treatment has received some attention (Spagni 2012, Wang 2011, Yun 2006). The use of powdered activated carbon (PAC) (Thanh 2012) and granulated activated carbon (GAC) (Hai 2012; Hai 2011) in fouling mitigation has also been established in recent studies. In addition to conventional bacterial bioreactors, continuous fungal bio reactors have also been evaluated for textile wastewater treatment (Hai 2008).

2.3.3 Reverse osmosis and recovery of pure water

RO membranes which are very compact when compared to UF and NF membranes do not undergo significant fouling by pore blocking mechanism (Wang 2008). However, these membranes also show fouling behavior due to humic acids (Nandy 2007), biological molecules (Matin 2011) and colloidal particles (Lee 2004). Higher concentration of colloidal particles can also lead to cake layer formation (Park 2008).

Synthetic textile effluents containing dye molecules exhibit fouling behavior on RO membranes (Li 2011). However, biologically treated textile effluents lead to relatively better separation on RO membranes when compared to NF membranes (Liu 2011). This is probably responsible for the better performance of RO membrane during pilot plant operations especially after biological treatment and pre-filtration with UF membranes (CPCB 2007).

Even low concentration of surfactants present in dye effluents can lead to flux reduction during RO process (Srisukphun 2009; Srisukphun 2010). Higher concentration of surfactants beyond critical micelle concentration (CMC) level however may form micelles and hence may not further enhance flux decline (Srisukphun 2009; Srisukphun 2010). Efforts to modify RO membrane using polyvinyl
alcohol (PVA) coatings (Kim 2004) and other related surface modifications (Kang 2012) may offer further scope in improving textile wastewater treatment.

2.3.4 Nanofiltration and salt recovery

Nanofiltration membranes with molecular weight cutoff (MWCO) of around 1000 Da or below generally show very good dye rejection above 95%. Molecular charge and polarity also have an effect on dye rejection (Bruggen 1999). The flux rate however decreases with increasing dye concentration as well as salt concentration. The flux rate however is closer to the pure water flux, when the dye solution was subjected to biological treatment (Bruggen 2001). UF filtration as a pretreatment further improves the flux rate during NF separation. The salt rejection decreases with salt concentration due to donnan effect. Monovalents salts like NaCl may easily pass through the membrane especially when the salt concentration is high (Capar 2006a; Koyuncu 2003; Koyuncu 2004; Koyuncu 2003). Under appropriate conditions NaCl salt rejection can reach as low as 15%. This is the basis for NF separation of RO concentrates to recover the NaCl solution in industrial units (shown as Option 2 in Fig. 1.1). Apart from reactive dyes other classes of dye molecules including metal complex dyes (Capar 2006b) and textile wastewaters from different sources (Lopes 2005; Aydiner 2010) have also been subjected to NF with high efficiency. Even anionic exchange resin regeneration effluent has been subjected to NF according to recent report (Salehi 2011). Low contaminated textile rinsing effluents can be directly treated by NF membrane for water recovery and reuse (Chen 1997; Florio 2005). The possibility of using NF as a pretreatment for RO has also explored (Nataraj 2009). However, more concentrated textile wastewater requires primary and secondary treatment before NF membrane separation.

Commercially available NF membranes with amide linkages can interact strongly with organic foulants. Many surface modifications of Polysulfone (PSf) and polyethersulfone (PES) base membranes by acrylate (Reddy 2005), PVDF (Akthakul 2004) and polyacrylonitrile (PAN) (Asatekin 2009) through interfacial polymerization
route have been found to exhibit better fouling resistance during dye wastewater treatment. Photografting (Akbari 2002; Akbari 2006) and plasma modification (Buonomenna 2009) approaches has also been employed for this purpose. Nanoparticles like zinc oxide (ZnO) and titanium dioxide (TiO$_2$) attached to NF membrane (Balta 2012) can also improve the NF membrane performance. A recent general review highlights the current approaches for the synthesis of thin film composite with improved resistance towards organic fouling (Lau 2012).

### 2.3.5 Hybrid processes and pilot plant studies

For the treatment of complex textile wastewater streams, integrated approaches involving multiple treatment stages would be certainly necessary. An interesting proposal for treating typical wastewater stream by all membrane integrated process was proposed in 2004 (Bruggen 2004b). This approach involves MF for removing organic impurities, a loose NF for recovery of salt solution and a tight NF stage (or RO) for recovery of pure water. In addition to these membrane processes already being used in textile industry, this scheme also suggests membrane distillation (MD) for further recovery of water from concentrated waste and membrane crystallization (MC) for the recovery of salt from the NF/RO reject stream (Fig. 2.4). In a recent review the progress made especially in MD and MC processes were highlighted (Bruggen 2013). Two or more membrane treatment stages have been studied as an integrated operation of real textile effluents. These include MF/UF (Khalid Iqbal 2007) and MF/NF (Tahri 2012; Barredo-Damas 2006; Fersi 2008). For the treatment of less contaminated rinsing effluents even a single NF treatment was found to be sufficient with appropriate choice of NF membranes (Florio 2005). A few other membrane separation based integrated processes are also indicated in the review work cited above (Bruggen 2004; Bruggen 2013). It appears that more and more membrane separation processes would indeed be integrated into the textile wastewater processes in future.
Extensive pilot plant studies of textile wastewater treatment have been carried out using one or more unit operations. Low concentrations of dyes in textile wastewater may be removed by direct ozonization followed by UF (Marcucci 2002). In presence of dye molecules ozonization removes the colour almost completely but the COD removal was only around 50% (Sundrarajan 2007).

For more concentrated textile wastewater, physiochemical as well as biological treatment are found to be generally necessary (Ciardelli 2001; Marcucci 2002). Eight different combinations of primary and secondary treatment steps such as chemical coagulation, activated sludge process, bio oxidation, electrocoagulation and sequential bioreactor on the overall techno economic feasibility have been evaluated (Manekar 2011). Ozonization can act as an efficient step after biological treatment to improve the water quality for membrane processes like reverse osmosis (Fu 2011; Qi 2011).
Many operating parameters can influence the bacterial decolourization and degradation of azo dyes (Saratale 2011). A wide range of bioreactors including bioflotation reactors, fixed bed biofilm reactors, flow jet aeration reactors in addition to the conventional activated sludge reactors have been evaluated for textile wastewater treatment (Papadia 2011). Biological aerated filter beds with and without ozone have also been used (Fu 2011).

2.4 CLEANING AND ACTIVATION OF MEMBRANE

Despite all the control methods adopted in membrane processes some level of fouling is bound to take place at shorter or longer time gaps. A broad spectrum of cleaning and reactivating procedures are available to recover the membrane performance (Hilal 2007). From the cleaning perspective membrane fouling can be broadly classified as reversible fouling, irreversible fouling and irrecoverable fouling. Reversible fouling can be reversed during the membrane separation process itself. Introduction of turbulent promoters, gas purging and air circulation can minimize membrane fouling. The flux can be stopped or flow direction can be reversed for a short period of time (for example, 3 sec/min) to enable the removal of foulant from membrane surface. These are called pulsing and backwashing respectively. After sufficiently long regular time intervals, the membrane can be rinsed and washed. The cleaning operation can be carried out either by cleaning in-place (CIP) or cleaning out of place (COP). A wide range of chemicals from anionic surfactants, disinfectants, acid and alkali or even commercial cleaning compositions recommended by membrane suppliers are commonly employed for membrane cleaning (Hilal 2007). MF/UF membranes containing relatively larger pores require relatively stronger cleaning operations at more frequent time intervals (Hilal 2007) especially when the concentration level in the feed is high. Quite similar cleaning procedures can be successfully employed for the treatment of NF and RO membranes as well.
Ultrasonic reflectometry (Li 2002) and lacer scanning microscopy (Spettmann 2008) has been introduced for in-situ monitoring of membrane fouling and identifying the effect of cleaning steps on membrane morphology. Amido black staining can also be used as an indicator of fouling spots on the membrane surface (Platt 2007). Streaming potential measurements have been suggested as a method of monitoring surface charges and isoelectric point values during the cleaning operation (Pontie 1998). A tool like atomic force microscopy (AFM) has also been used for close monitoring of different stages of cleaning (Li 2004).

In contrast to the extensive reports on general aspects of membrane cleaning, there are only few investigations which deal with cleaning requirements of different textile waste streams. Flux decline measurements due to fouling before and after different cleaning operation are the main mode of measuring the effectiveness of cleaning processes. In an interesting study the pore size distribution was found to change during a fouling-cleaning cycle (Kogutid 2002). Acid cleaning followed by base cleaning may sometimes be necessary for removing strongly held primary ink foulants from carpet dyeing process (Capar 2006). Strong chemical treatments like sodium hypochloride cleaning may be necessary for cleaning and disinfecting membranes in bioreactors while treating wastewater from denim producing textile industry (Yigit 2009). Hollow fiber membranes are covered by 50-200 µm mesh cages to prevent foulants from adsorbing on fine fibers (Hai 2006) during textile wastewater treatment. Appropriate membrane cleaning strategies may have to be evolved for different types of textile effluents and different membrane separation stages. Such specific investigations would certainly pave the way for commercially viable membrane processes.

2.5 INDUSTRIAL TEXTILE WASTEWATER TREATMENT: INDIAN EXPERIENCE

With financial as well as technical support, many individual textile units and clusters have taken initiatives for dye wastewater treatment in India (Dhodapkar 2007;
Nandyet 2007). Central pollution control board of India has also provided simple treatment strategies for these industries (CPCB 2007). Three distinct but interconnected strategies are currently under implementation with continuous evaluation and monitoring.

Complex textile units and common effluent treatment plants operated by industrial clusters do not segregate dye bath water and wash water. The effluent is subjected to UF after primary and secondary treatment. The permeate from UF is subjected to the RO which can recover up to 80% of water for reuse. The RO reject mainly contains inorganic salts and degraded organic products as shown in Fig. 1.1 (Main pathway). The monovalent salts like NaCl can be recovered from the RO reject using NF which leads to 9.1% water recovery along with NaCl as indicated in Option 2 of Fig. 1.1 (Vishnu 2008).

The common effluent treatment plants still face many challenges. The organic load is very high with wide variations in composition. Considerable organic residues after biological treatment need to be removed using ion-exchange resins. In such cases, the regeneration of the ion exchanger and handling the effluent becomes a problem. Hence, the CPCB is now in favour of treating the effluents locally with better control over effluent compositions as well as operation parameters of the effluent treatment plant (CPCB 2007).

The wastewater from the dye bath forms just 10% of total wastewater generated in dyeing units. Individual dyeing units (Fig. 2.5) can treat the small volume of dye bath wastewater separately (Ranganathan 2007). The treatment of this wastewater depends on whether NaCl or Na₂SO₄ is predominantly used in the dyeing process. The second strategy for dyeing units using NaCl involves simple filtration followed by NF membrane separation as shown in Fig. 2.5. This NF enables recovery of fairly concentrated NaCl solutions for reuse. The remaining 90% of the wastewater is treated by the routine treatment sequence as discussed in the first strategy. The NF membrane
fouling in such treatment can be properly evaluated for individual plants where the load composition is known or can be easily monitored.

If individual dyeing units employ Na$_2$SO$_4$ for dyeing, the RO reject after the conventional treatment stages indicated in the above strategy is subjected to multi effect evaporator (MEE) for further concentration and then sent to a crystallizer unit to recover the Na$_2$SO$_4$ salt. This third strategy involves high energy consuming MEE stage. The cake layer generated in the MEE contains both organic and inorganic constituents. The removal of this cake from time to time is also a serious challenge which requires specialized skills (Vergili 2012).

Many small dyeing and textile processing within Tiruppur region of south India have now installed effluent treatment plants as stipulated by CPCB (CPCB, 2007). Some detailed evaluations of the techno economic feasibility of these units have also been carried out. Manekar et al for example have evaluated the technical feasibility and cost effectiveness of the eight pretreatment strategies adopted by different effluent treatment units to achieve the requisite quality feed for UF/RO membrane separation process (Manekar 2011). The pretreatment stages evaluated include chemical coagulation, activated sludge process, sequential bioreactor, electrocoagulation, ozone treatment, catalytic oxidation, pressures and filter and active carbon adsorption. This study indicated that chemical coagulation and activated sludge processes still remain the cost effective pretreatment for complex textile effluents.

Dhodapker et al. (2007) studied the combined UF and RO operational efficiencies of seven small scale dyeing units in this region from their wastewater after tertiary treatment. These studies established the feasibility of using the RO permeate as boiler feed in the plant. In a further investigation, they have also shown that the unit operations in each effluent treatment plant can be further optimized to improve the overall operational efficiency (Nandy 2007).

Ranganathan et al. (2007) have studied the techno economical feasibility of effluent treatment plant (ETP’s) of four individual dyeing units in this region which
employ NaCl salt during dyeing process. These four units employ the NF separation for the treatment of dye bath effluent (Figure 6). The overall cost effectiveness was also evaluated. It should be noted that these dyeing units have to purchase the requisite quality water from other sources. When this aspect is taken into consideration, the overall effluent treatment indeed becomes cost effective as pointed out in this study.

Vishnu et al. (2008) have evaluated the recovery efficiencies of NaCl solution by NF separation (strategy 2) as discussed above and Na₂SO₄ salt by MEE and subsequent crystallization (strategy 3) as discussed above. They have shown that NaCl solution recovery is indeed more cost effective.

At present all the membrane separation processes namely MF, UF, RO and NF processes have found their place in pilot plants and industrial units. The recovery of 80% of water and significant quantity of NaCl as solution is also achievable on routine basis. The recovery of remaining water and achieving zero liquid discharge still remains a serious challenge. Solar pond evaporation is still the main process at this stage.
Fig. 2.5: Typical schematic diagram of advanced wastewater treatment technology for recycling of textile dyeing wastewaters (Ranganathan 2007).

2.6 CONCLUSIONS

Fouling control is one of the major challenges in the membrane processes of the textile wastewater treatment. Basic studies pilot plant investigations and industrial experiences highlighted in the present review lead to following conclusions and indicate the scope for further work.

1. In the case of very dilute solutions containing small quantities of organic molecules, UF or NF membranes can be directly used for water recovery. In all other cases, both the primary and secondary wastewater treatment processes become very important.
2. Chemical coagulation still continues to be the predominant primary treatment process. Polyelectrolytes are also used in addition to conventional inorganic coagulants. Electrocoagulation using iron electrodes could be a more controlled approach, which can produce less sludge and is also cost-effective. A few industrial units have already introduced electrocoagulation along with chemical coagulation. The experience from these units would indeed be very important.

3. Biological treatment is indeed the only cost-effective secondary treatment process in industrial use. Both anaerobic and aerobic processes can be sequentially used. Activated sludge process is the major approach used by many industries consuming very large volumes of wastewater on a daily basis. Optimization studies on biological processes, however, need greater attention.

4. A wide variety of conventional filters and specific filters are presently being used for removal of hardness and trace level iron removal. Ion exchange resins are also being used in dye wastewater treatment. Hence, there arises the need for selecting appropriate cost effective filters. Activated carbon filters, for example, can add considerable cost to the overall treatment process.

5. Ozonization is emerging as an effective technique for the removal of trace levels of organic impurities before membrane filtration stages. This is also called water polishing, and it considerably reduces membrane fouling.

6. Fouling of MF and UF membranes can be significant when the primary and secondary treatment processes are incomplete. The degradation products of biological material used in secondary treatment can also play a significant role in membrane fouling. Ceramic UF membranes are emerging as better options owing to their mechanical strength and wash ability.

7. Membrane bioreactors combine biodegradation and filtration in a single step. For long term operation, this process, however, demands a much better understanding of the role of fouling materials for each effluent. This promising approach requires further studies.
8. Feed composition is an important factor which would determine the overall process parameters. Individual wastewater treatment plants should focus on these aspects to minimize sludge generation and also to prevent membrane fouling. Common operating parameters may not be suitable for all the treatment plants and all types of effluents. It is also desirable to treat the concentrated dye bath wastewater separately. With proper optimization, the RO and NF separation processes have indeed become cost-effective in many small individual dyeing plants in India.

9. Fouling indexes and fouling control methods also need to be optimized for individual dye wastewater sources. It is better to adopt backwash and other time dependant methods to clean the membrane surface even at the reversible fouling stage.

10. Membrane modifications to achieve high flux rate and high dye rejection are in progress. A specific goal in this direction would be novel membranes which will allow recovery of Na₂SO₄, while maintaining high dye rejection.

11. ZLD is slowly emerging as the specification for dye waste treatment. Handling the final 10 percentage of concentrated sludge is indeed a critical challenge at present. Solar ponds are still predominantly used for drying the concentrated rejects. Development of cost effective alternatives to multi effect evaporators and membrane distillation units is indeed the need of the hour. Emerging approaches for RO concentrate handling like combined electrodialysis (Praneeth 2014; Oren 2010) and wind aided intensified evaporation (WAIV) approaches (Gilron 2003) may also find their place in future textile wastewater treatment processes for achieving ZLD.