CHAPTER 1

1. INTRODUCTION

1.1 TEXTILE WASTEWATER TREATMENT OVERVIEW

Textile industries employ a wide variety of dyes, inorganic salts and surfactants in various unit operations. Both simple salts such as NaCl and Na$_2$SO$_4$ and large cationic and anionic surfactants are used in dyeing industry. Though reactive dyes predominate the commercial dying process, many other water soluble and even insoluble organic dyes are still being employed. The inorganic salts interact with organic compounds resulting in complex water insoluble materials. The organic molecules themselves may undergo chemical modification during the dyeing operation. The effluent also normally contains bio-molecules generated by biofouling. Wherever biological treatment is used, additional bio-foulants are also induced. The composition of typical effluents from dyeing industry and the permissible limits of individual parameters (CPCB 2007; Ali 2008; Lin 1997) are presented in Table 1.1. This table indicates that the textile effluents contain substantially large excess of total suspended solids and (TSS) total dissolved solids (TDS) including chlorides and sulfates. The colour, biological oxygen demand (BOD) and chemical oxygen demand (COD) are also significantly exceed the permissible limits. There could be significant variation in all these parameters as summarized in a recent review (Varma 2012). The treatment of such complex effluent systems would naturally require several stages of effluent treatments (Crittenden 2005; Edzwald 2010; Fox 2004; Romero 2008; CPCB 2007; Metcalf 2003).

The wastewater treatment techniques are also undergoing significant changes in recent years, giving scope for further improvements in this field. Recent studies in primary treatment aim at the removal of insoluble organic and inorganic solids by sedimentation, adsorption (Rafatullah 2010; Safa 2011), coagulation (Verma 2012; Shi 2007; Lee 2006) and flocculation. Approximately 25 to 50% of the incoming biological oxygen demand (BOD), 50 to 70% of the total suspended solids (TSS), 65% of the oil and grease and 50 % of organic molecules are removed during primary treatments
involving municipal sewage (Metcalf 2003). Such generalization for textile wastewater from different sources with widely different compositions is not possible.

Secondary treatment involves the degradation and removal of biodegradable, dissolved and colloidal organic matter using chemical and/or biological oxidation. Among the chemical oxidizing agents, chlorine (Quader 2010) leads to the formation of chloride salt and chlorinated intermediates, which are well known carcinogens (Griffiths 1984). Advanced oxidation process (AOP) using oxidizing agents likes hydrogen peroxide ($\text{H}_2\text{O}_2$) and Fenton reagent (Lim 2011), ozone (Ciardelli 2001; Somensi 2010) and photo-assisted oxidation (Vilar 2011) were found to be effective for colour removal. Other advanced oxidation methods such as ultrasound (Mahamuni 2010) and photocatalysis (Maezawa 2007) have also been reported in literature. Also, electrochemical methods (Szpyrkowicz 2001; Zongo 2009) including electro-flotation (Merzouk 2011; Merzouk 2009; Balla 2010), electro-oxidation (Vlyssides 2000; Rajkumar 2006) and photo-assisted electro-oxidation (Raghu 2009) have also been reported. The cost effectiveness of these advanced oxidation processes in large scale operations however are yet to be established.

Biological oxidation is considered to be cost effective in the case of highly concentrated textile effluents. Decomposed organic materials from the degradation process are also biocompatible. Recent studies in this area have reported the use of biological material as adsorption columns (Charumathi 2012) and biological processes coupled with Fenton (Blanco 2012) and ozone (Fu 2011; Kanagaraj 2012; Qi 2011; Ledakowicz 2011). Both aerobic and anaerobic approaches can be used for textile wastewater treatment (Wallace 2001). Pilot plant studies on different types of bioreactors have also been reported (Papadia 2011). A comparative study of textile wastewater treatment by enzyme catalysis, coagulation and membrane filtration processes is also available (Khouni 2011).

Membrane separation processes occupy a central stage in tertiary wastewater treatment. Microfiltration (MF) and ultrafiltration (UF) membrane processes are
employed for the removal of larger particles and biologically degraded products (Fersi 2005; Bruggen 2005). Membrane bioreactors also use such MF and UF membranes (Badani 2005). Reverse osmosis (RO) is used to obtain water free from all organic and inorganic impurities (Al-Bastaki 2004). Nanofiltration (NF) membranes containing nonopores are used to isolate salt solutions containing monovalent cations and anions from the dye wastewater. This enables both the recovery and reuse of tonnage quantities of NaCl used in dyeing industries (Schoeberl 2004; Petrinic 2007; Lau 2007; Tang 2005; Gryta 2006). In recent times, high temperature membrane distillation is also being investigated for dye wastewater treatment (Gryta 2006; Criscuoli 2008) as part of zero liquid discharge (ZLD) strategy. It should however be noted that biological treatments introduce additional foulant materials into the system. Further efforts are needed to understand biofouling and optimize the operating conditions during membrane filtration stages for such effluents.

**Table 1.1: Typical actual and permissible level of parameters in effluents of textile industries** (CPCB 2007; IS 207 1998).

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Actual level</th>
<th>Permissible level</th>
</tr>
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<tbody>
<tr>
<td>pH</td>
<td>9.30</td>
<td>6.0-8.5</td>
</tr>
<tr>
<td>TSS (mg/L)</td>
<td>164</td>
<td>18</td>
</tr>
<tr>
<td>TDS (mg/L)</td>
<td>6000-9000</td>
<td>2100</td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>1300</td>
<td>250</td>
</tr>
<tr>
<td>BOD (mg/L)</td>
<td>800</td>
<td>30</td>
</tr>
<tr>
<td>TOC (mg/L)</td>
<td>386</td>
<td>&lt;20</td>
</tr>
<tr>
<td>Total Hardness (mg/L)</td>
<td>88</td>
<td>&lt;20</td>
</tr>
<tr>
<td>Chloride (mg/L)</td>
<td>3940</td>
<td>600</td>
</tr>
<tr>
<td>Sulfate (mg/L)</td>
<td>1395</td>
<td>100</td>
</tr>
<tr>
<td>Colour (HU)</td>
<td>250</td>
<td>50</td>
</tr>
</tbody>
</table>

Membrane separation processes occupy the centre stage in tertiary wastewater treatment. MF and UF membrane processes are employed for the removal of larger particles and biologically degraded products (Fersi 2005; Bruggen 2005). Membrane bioreactors also use such MF and UF membranes (Badani 2005). RO is used to remove
all organic and inorganic impurities from water (Al-Bastaki 2004). NF membranes containing nanopores are used to isolate salt solutions containing monovalent cations and anions from the dye wastewater. This enables recovery and reuse of tonnage quantities of NaCl used in dyeing industries (Schoeber 2004; Petrinic 2007; Lau 2009;

![Diagram of textile wastewater treatment plant](image-url)

**Fig. 1.1:** Typical stages generally used in textile wastewater treatment plant
Tang 2005; Gryta 2006). In recent times, high temperature membrane distillation is also being investigated for dye wastewater treatment (Gryta 2006; Criscuoli 2008) as part of zero liquid discharge (ZLD) strategy.

Typical unit operations employed by advanced textile wastewater treatment industry on pilot and commercial scale are indicated in Fig. 1.1. A few treatment plants also employ electrocoagulation (EC) as part of primary treatment. However, chemical coagulation (CC) is the predominant primary treatment method that is being widely employed. Aerobic biological treatment is the main process used for oxidative degradation of dyes. In some common effluent treatment plants (CETP) attempts are being made to replace the conventional secondary treatment by the membrane bioreactor (Option 1 in Fig. 1.1). Settling and sludge removal generally occurs after both these stages. The water is then subjected to multistage filters. Adsorption and ion-exchange columns are also used in some CETP which receive wastewater from different small scale treatment plants situated as a cluster. Further separation using UF and RO membranes lead to recovery of pure water (Fig. 1.1). The retentate from RO unit contains very high concentration of Na$_2$SO$_4$ or NaCl. The recovery of salt is achieved through energy intensive multi effect evaporator (MEE) and subsequent membrane crystallization (MC).

The recovery cost increase significantly in this stage. In the case of dyeing units employing NaCl, there is a cost effective second option of using NF separation which can recover NaCl along with water Option 2 in Fig. 1.1.

1.2 MEMBRANE TECHNOLOGY BACKGROUND

Membrane filtration is a promising water treatment technology which is used for obtaining pure water from natural and waste waters by pressure-driven flow. This technology has found practical applications in drinking water purification, desalination, wastewater recycling, and water softening and also in the food processing industry.

Membrane filtration is a separation process that purifies water by allowing water molecules to pass through the membrane, while other substances are caught on the
Several types of membranes are used in wastewater treatment application including MF, UF, NF and RO membranes. The separation performances of membranes are illustrated in Fig. 1.2. Synthetic membranes used for wastewater treatment can be prepared by both phase inversion and interfacially polymerization technique using organic and inorganic materials. Organic membranes account for the majority of membranes used and these are typically prepared from a polymer base, while inorganic membranes can be made of materials such as zirconia, zeolite, aluminum oxide, or titanium oxide. Membranes can also vary in cross-sectional structure, from symmetric to asymmetric to thin-film composite structures, depending on the method used to cast the membrane.

**Fig. 1.2:** *Comparison of the membrane separation for different substance*

Fig. 1.3 shows the gradient of these membranes from MF with largest pore-size that allows for the greatest passage of substances to RO membranes, which do not have
physical pores and filter only through diffusion. RO membranes can exclude all substances except water molecules, thus proving to be an useful technology for desalination. Fig. 1.3 specifically shows the size range of foulant that each membrane can filter and the example foulants within that size range.

**Fig. 1.3: Separation size ranges of different membrane technologies**  

1.3 FOULING IN MEMBRANE FILTRATION AND ITS EFFECTS

Membrane fouling refers to the blockage of membrane pores during filtration by the combination of sieving and adsorption of particulates and compounds onto the membrane surface or within the membrane pores. This increases the operating cost. Fouling can be broadly classified into reversible or irreversible, based on the attachment strength of particles to the membrane surface. Reversible fouling can be removed by backwashing process. But irreversible fouling cannot be removed with flushing,
backwashing, chemical cleaning, or any other means. Fouling also can be classified into four categories based on the type of foulants:

a) **Inorganic fouling/scaling:** It is caused by accumulation of inorganic particulates such as chloride salts, sulfate salts and metal hydroxides. Scaling is a major concern in reverse osmosis (RO) and nanofiltration (NF). RO and NF membranes reject inorganic species. Those species form a concentrated layer in the vicinity of membrane-liquid interface. This is referred to as concentration polarization (CP).

b) **Particulate fouling:** Algae, bacteria and certain natural organic matters fall into the size range of particles and colloids. However they are different from inert particles and colloids such as silts and clays. To distinguish the different fouling phenomena, particles and colloids are here referred to as biologically inert particles and colloids. These inorganic materials originate from weathering of rocks.

c) **Bio/microbial fouling:** It is due to formation of biofilms on the membrane surface. It is hard to prevent biofouling since even a few bacteria which get attached to the membrane can develop into a thick layer due to biological growth. Biofouling eventually influences membrane performance and life-span.

d) **Organic fouling:** Organic fouling is quiet predominant in membrane filtration when source water contains relatively high concentrations of natural organic matter (NOM), organic dye molecules and other chemicals released from the industrial processes. Surface water (lake, river) typically contains higher NOM than ground water. Organic fouling is believed to be the most significant factor for the flux decline.

The present research programme is specifically focused on flux decline and fouling of nanofiltration by textile dye wastewater with over all objectives of recovery of salt solutions. Specific literature survey focused on this topic carried out recently is presented in the next chapter (Chapter 2). The motivation (Chapter 3) and objectives and scope (Chapter 4) of the present work are outlined based on this literature survey.