RECOVERY AND REUSE OF INDIGO DYEING WASTEWATER USING MEMBRANE TECHNOLOGY

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ABSTRACT

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The objective of this study is to develop a membrane-based generic treatment scheme for wastewaters of indigo dyeing process of denim industry, based on water reuse. For this purpose, firstly the performances of microfiltration (MF), coagulation, and ultrafiltration (UF) processes were evaluated as pretreatment alternatives and the best pretreatment alternatives appeared to be single stage 5 μm MF and sequential 5 μm MF followed by 100 kDa UF providing high permeation rate and high color retention. These two pretreatment alternatives were compared based on the performance of nanofiltration (NF) using NF 270 membrane, and the best pretreatment process was evaluated as 5 μm MF that provided 87-92% color and 10% chemical oxygen demand (COD) retention.

After the pretreatment tests, three different NF (NF 270, NF 90, Dow Filmtec, USA and NF 99, Alfa Laval, Denmark) and two different reverse osmosis (RO) membranes (HR 98 PP and CA 995 PE, Alfa Laval, Denmark) were tested to produce reusable water. Permeate COD and color performances of the tested NF and RO membranes were similar and satisfactory in meeting the relevant reuse criteria, while permeate conductivity was satisfactory only for HR 98 PP RO membrane and for NF 90 membrane. On the other hand, NF 270 membrane was superior to the other membranes in terms of permeation rate. For NF 270 membrane; cumulative color, COD and conductivity retentions were found to be 93 %, 92 %, and 60 %, respectively.

When the developed process chain (5µm MF+ NF 270) was also tested for a dilute indigo dyeing wastewater, it was found out that the developed scheme works similarly and is generic for indigo dyeing wastewaters.

Keywords: Textile wastewater, Indigo dyeing, Pretreatment, Membrane filtration, Color retention, Flux, Fouling

ÖZ

İNDİGO BOYAMA ATIKSULARININ MEMBRAN TEKNOLOJİLERİ KULLANILARAK GERİ KAZANIMI VE YENİDEN KULLANIMI

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Bu çalışmanın amacı, denim endüstrisi kaynaklı indigo boyama atıksuyunun yeniden kullanımı hedefi ile membran esaslı jenerik bir arıtma süreci geliştirilmesidir. Bu amaçla öncelikle önarıtım alternatifi olarak mikrofiltrasyon (MF), koagülasyon ve ultrafiltrasyon (UF) proseslerinin performansları değerlendirilmiş ve en iyi önarıtım alternatifi olarak yüksek atıksu akıları ve renk giderim değerleri nedeniyle tek aşamalı 5 µm kesikli MF ve ardışık olarak 5 µm kesikli MF ardından 100 kDa UF görülmüştür. Bu iki önarıtım alternatifi, NF 270 membranı ile nanofiltrasyon (NF) performansı açısından karşılaştırılmış ve en iyi ön arıtım prosesi, % 87-92 renk ve % 10 kimyasal oksijen ihtiyacı (KOİ) sağlayan 5 µm MF olarak değerlendirilmiştir.

Ön arıtım deneylerinin ardından, üç farklı NF (NF 270, NF 90, Dow Filmtec, ABD ve NF 99, Alfa Laval, Danimarka) ve iki farklı ters ozmoz (RO) (HR 98 PP ve CA 995 PE, Alfa Laval, Danimarka) membranları yeniden kullanılabilecek su elde etme hedefi ile değerlendirilmiştir. Test edilen NF ve RO membranlarının permeat KOİ ve renk performansları birbirlerine benzer olarak ilgili yeniden kullanılabilirlik kriterlerini sağlarken, permeat iletkenlik kriterinin ise sadece HR 98 PP RO membranı ve NF 90 membranı için sağlandığı görülmüştür. Öte yandan, NF 270 membranı permeat akı değerleri açısından diğer membranlara göre çok üstündür. NF 270 membranı için kümülatif renk, kimyasal oksijen ihtiyacı (KOİ) ve iletkenlik giderimleri sırasıyla % 97, % 93, ve % 60 olarak tespit edilmiştir.

Geliştirilen proses zinciri (5µm MF + NF 270) seyreltik indigo boyama atıksuyu için de test edildiğinde bu sürecin benzer performans gösterdiği ve indigo boyama atıksuları için jenerik olduğu bulunmuştur.

Anahtar Kelimeler: Tekstil atıksuyu, Indigo boyama, Önarıtım, Membran, Renk giderimi, Akı, Tıkanma

To My Parents

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ABBREVIATIONS

AOPs	: Advanced Oxidation Processes
CFV	: Cross-flow Velocity
COD	: Chemical Oxygen Demand
Da	: Dalton
J_{cwc}	: Clean Water Flux of Washed Membrane
J_{ww}	: Wastewater Flux
J_{cwi}	: Clean Water Flux of Virgin Membrane
MBR	: Membrane Bioreactor
MF	: Microfiltration
MWCO	: Molecular Weight Cut Off
NF	: Nanofiltration
PS	: Polysulphone
RO	: Reverse Osmosis
rpm	: Revolution Per Minute
TMP	: Trans Membrane Pressure
TRMF	: Total Recycle Mode of Filtration
TSS	: Total Suspended Solids
UF	: Ultrafiltration

CHAPTER 1

INTRODUCTION

1.1. General

In recent years, water has become scarce in many populated areas of the world with increasing urbanization and industrialization. Today, because of regulations that are more stringent and increasing freshwater costs, industries often face a shortage of available water sources [1, 2]. Therefore, industries should not only consider the treatment of generated wastewaters, but also develop methods to minimize waste generation with an integrated approach [3]. This increases the effort for reclamation and reuse of wastewater coming from industrial activities.

Textile industry, which generally uses large volumes of water and hence long sequence of wet processing stages consumes many resource inputs and produces quantities of wastewater. The main sources of wastewater are rinsing waters from fiber preparation and continuous dyeing, alkaline waste from preparation, and batch dyeing waste containing large amounts of salts, acid or alkali chemicals [4, 5, 6].

Denim is one of the most important sub sectors of the textile industry and indigo is the major dye used along with huge amount of water consumption [7]. Turkey being one of the most important textile and clothing producers and exporters in the World, has the World’s second largest denim fabric factory, after India. The statistics of the last 6 years show how the denim fabric sector has grown in Turkey in terms of foreign trade. With the quality, speed and talent for meeting demands, Turkey exports denim products all over the world. It is inevitable that Turkey will expand its market share in the world in future, since it has brought its traditional buildup from the woven fabric sector into the denim sector [8, 9]. As a result of increase in denim production, water consumption of the industry is increasing day by day, and in turn wastewater generation.

In the treatment of textile wastewaters, conventional methods (e.g., coagulation/flocculation, biological treatment, and sand filtration) may be used, but "new" techniques may also be required. Although conventional treatment systems provide effluents within the required discharge limits, the final effluents are not usually suitable for the reuse in the textile processes. Among non-conventional treatment methods, advanced oxidation techniques are gaining interest as a further treatment in order to obtain reusable water within the process. The interest in these systems grows rapidly due to the fact that they provide reuse opportunity. Literature contains many reports on advanced oxidation processes (AOPs), such as ozonation, Fenton's reagent oxidation, electrodialysis, and etc., to investigate the possibility of textile wastewater reuse [12, 13]. Another non-conventional technique, which is defined as the most promising method, is of course membrane filtration. Recent literature on the subject clearly indicates that pressure-driven membrane processes are very satisfactory in providing reusable effluent [14].

A number of pressure-driven membrane processes have been investigated for advanced textile wastewater treatment, including microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). These processes can be used to remove a wide range of components, ranging from suspended solids to small organic compounds and ions. In most cases, more than one compound is removed at the same time by using membrane processes. In several studies, NF and RO membranes were used for the treatment and reuse of textile effluents. These membranes were found to be suitable for the effective removal of ions and larger species from dye bath effluents providing permeate quality which is satisfactory and acceptable for water reuse [15, 16, 17]. This advantage leads to a large number of applications in various fields [14]. Even if the application of membrane processes to textile wastewater treatment and reuse has been proved effective from a technical point of view, to date this kind of application has been restricted to studies on a pilot scale [18].

The implementation of pressure-driven membrane processes has some limitations which are the high investment and operation costs and the occurrence of fouling. Depending on the type of the foulant, a strategy or a combination of strategies can be chosen to maintain the performance of the membrane. Chemical cleaning, hydraulic rinsing and electrical cleaning methods can be utilized as a solution for membrane fouling. Besides these cleaning methods, application of a pretreatment alternative could also be used to prevent membrane fouling and extend membrane life and consequently, to decrease the costs of membrane modules. The most important pretreatment alternatives are biological treatment, MF and UF processes [19].

Wastewater coming from indigo dyeing process is characterized by a moderate amount of chemical oxygen demand (COD), pH, suspended solids, dissolved solids and a dark blue color [6]. The water insoluble indigo dye that causes dark blue color is a vat dye and considered as a recalcitrant substance that causes environmental concern [14, 20]. In general, for treatment of vat dyes, chemical coagulation is the most widely used method. However, this method produces large amount of sludge which pose handling and disposal problems. The other option; AOPs although effective are costly in terms of installation, operation and maintenance costs [21]. Conventional biological processes are not very effective in the complete removal of vat dyes (including indigo) therefore not satisfactory in providing the desired effluent quality especially when water reuse is of concern. In recent years, the investigators have tested various non-conventional biological treatment methods (eg., sequential anaerobic/aerobic and fungi assisted processes) for the complete treatment of indigo dyeing wastewaters [22]. However, all these treatment processes have found to be far from providing reusable water containing vat dyes and especially indigo dye.

This study is concerned with the treatment of indigo dyeing wastewater by membrane processes. Although there are number of studies published in the literature about the treatment of some other types of colored textile effluents by membrane processes, the removal of color and of course other constituents, from indigo dyeing effluents for reuse purposes is relatively unclear [1, 2]. Indigo dye which is soluble in water at elevated pHs posses different characteristics than other textile dyes, therefore its removal by membrane processes requires special attention.

1.2. Objective of the Study

The overall objective of this research is to develop a membrane-based generic treatment scheme for wastewaters of indigo dyeing, targeting on water reuse. The indigo dyeing process is composed of pre-rinsing, dyeing, post-rinsing and softening operations. In the pre-rinsing, fabric is washed for several times for the removal of impurities and then subjected to dyeing which is followed by post-rinsing. In the post rinsing, dyes and chemicals that are not fixed on to the fibers are removed in a number of sequential rinsing tanks. Pre and post-rinsing stages consume high amount of water and therefore generate large volumes of wastewater. The major part of the pollution in these wastewaters comes from the post-rinsing tanks and especially from the first post-rinsing tank as it removes residual dye and other chemicals from the cotton fibers coming from the dye bath solution.

In the present study, treatability of the first post-rinsing stage wastewater by membrane filtration was investigated as it would be representative of the whole post-rinsing wastewaters. Throughout the study, real wastewater samples were obtained from a textile mill located in the Central Anatolia Region, which produces denim fabric, and utilized in the experiments. By the way, the studies were not limited to the first post-rinsing tank effluent. An additional set of investigations were also carried out with composite wastewater from all post-rinsing tanks in order to be able to extend the results from the first part of the study to the composite wastewater from indigo dyeing.

1.3. Indigo Dyeing Process in the Plant

The textile mill from which wastewater samples were obtained produces denim textile starting from raw cotton. This plant is an integrated one with spinning, dyeing, sizing, weaving and finishing of cotton. The plant produces 20000 tons of cotton fiber; 45 million meter of woven fabric and 12 million meter of denim annually with a daily water consumption of about 3500-5000 ton/day. In the plant, more than one third of the wastewater volume originates from the dyeing operations which are composed of pre-treatment, dyeing, pre- and post-rinsing, softening and drying. Dyes used either individually or sequentially in more than 400 recipes are indigo, indanthrene, sulphur and disperse dyes [23, 24].

Among the dyeing recipes applied, indigo dyeing is one of the most common ones. According to the annual production report for the year 2006, the share of indigo dyeing in the total dyeing operations was 20 percent. A typical indigo dyeing recipe applied in the plant is given in Table 1.1. In the indigo dyeing process, high amounts of caustic and reducing agent ($Na_2S_2O_4$) are utilized for the reduction of indigo dye at high pH condition.

Table 1.1. Typical indigo dyeing recipe applied for the production of wastewaters used in experiments

Indigo Dyeing Recipe	**Amount (%)**
Indigo dye	34
Complexing agent	3
Sodiumsulphite ($Na_2S_2O_4$)	31
Caustic (NaOH)	29
Stabilizing Agent	1

1.4. Scope of the Study

This study covers the investigation of the most suitable membrane based treatment scheme for the indigo dyeing post-rinsing wastewaters. The first part of the research focused on the comparison of the performances of coagulation, MF and UF pretreatment alternatives while the second part was about the determination of best NF or RO alternative in order to produce reusable water.

Before pretreatment tests, a detailed characterization of the wastewater in terms of COD, color, total suspended solids, pH, alkalinity, conductivity and particle size distribution was carried out. After wastewater characterization, pretreatment tests that aimed at the determination of best pretreatment process were initiated. The selection of the best pretreatment process was mainly based on the removal efficiency (MF, UF, coagulation) and permeates flux (MF, UF) achieved by the alternatives tested. MF experiments were performed under two modes of operation; dead-end and cross-flow. In dead-end MF tests, the best MF membrane sequence and the effect of pH was determined. In these experiments, different pore sized filters were evaluated as single and sequential stages to achieve the highest performance in terms of color retentions and fluxes. According to the results of dead-end MF, cross-flow MF tests were conducted. In the cross-flow MF, the effect of cross-flow velocity (CFV) and transmembrane pressure (TMP) were evaluated for the second stages of sequential MF alternatives. Coagulation tests were performed as an alternative pretreatment option to MF. The performance of two coagulants; alum and ferric chloride were investigated. Optimum pH and coagulant doses were determined. The alternatives specified in the MF tests were evaluated in the further UF tests as a sequential pretreatment stage. At this stage, the performances of five different UF membranes were examined in terms of their color retentions and permeate retentions.

In the second part of the study, NF performance was investigated for reuse purposes in terms of permeate flux, color, COD and conductivity retentions. In NF experiments, firstly the effect of membrane type was evaluated with three different NF membranes. Then, the effect of pretreatment alternatives on the performance of NF membranes that were selected in the first part of the study was investigated.

In addition, the effect of two different wastewater pH (pH 7.2±0.4 and 9.7±0.2) and wastewater composition on the performance of NF was investigated. In order to extend the applicability of the findings for the first post-rinsing tank effluents to all type of indigo dyeing process rinsing waters, additional NF tests were conducted for composite effluent from all post-rinsing tanks. For this purpose, the performance of the pre-selected membrane sequence in the previous stage was tested for the composite indigo dyeing wastewater. The overall results from this part of the study considered to be a generic treatment for the indigo dyeing wastewaters.

Due to high conductivity values of post-rinsing tank wastewaters of indigo dyeing process, sequential stage NF (double-pass NF) and RO experiments were also employed to increase the reuse potential and / or to improve the quality of permeate water. In RO experiments, the performance of two different RO membranes were compared with NF membranes, in terms of permeate flux, color, COD and conductivity retentions.

CHAPTER 2

MEMBRANE TECHNOLOGY

2.1.General

Membrane processes have been the technology of choice for water and wastewater treatment over the past decades and is playing an increasing role in sustaining water supplies. When the technology is evaluated in terms of the criteria for sustainable development it gets a favorable ranking. The major force of the technology is the fact that no additional chemicals are required and reliable product quality can be achieved [25, 26].

Although the membrane processes generally provide a better product quality and gaining more attention today, one of the major disadvantages of these processes is the cost. Very often a combination of conventional water treatment processes with membrane processes results in reliable and cost effective treatment combined with high product water quality. Another disadvantage of membrane processes is that in many applications their long term reliability is not yet proven. Furthermore, membrane processes sometimes require excessive pretreatment due to their sensitivity to concentration polarization and membrane fouling due to chemical interaction with water constituents. And, also membranes are mechanically not very robust and can be destroyed by a malfunction in the operating procedure [27].

Membrane separation processes are used in a wide range of applications, to produce potable water from the surface waters, to clean industrial effluents and recover valuable constituents and to fractionate macromolecular solutions. Membrane processes may be very different in their mode of operation, structures and driving forces used for the transport of the different chemical components but they have several features in common which make them attractive as a separation tool [28]. In most of the membrane processes used in water and wastewater treatment the driving force is a pressure difference across the membrane [25]. In the following sections, pressure-driven membrane processes are described in detail since the present study bases on this type of membrane process.

2.2. Pressure-driven Membrane Processes

Pressure-driven membrane processes use the pressure difference as a driving force to transport the solvent (usually water) through the membrane. Particles and dissolved components are partially retained on the membrane related to their properties such as size, shape, and charge. Pressure-driven membrane processes can be classified by these properties and pressure exerted on the membrane [14].

As indicated before, generally, four types of pressure-driven membrane processes are distinguished MF, UF, NF and RO. Although these processes are related to each other, each of them has its specific characteristics. As we go from MF through UF and NF to RO, the size of the particles or molecules separated diminishes and consequently the pore sizes in the membrane must become smaller. This implies that the resistance of the membranes to mass transfer increases and the applied pressure has to be increased to obtain the same flux. However, no sharp distinction can be drawn between these processes. The schematic representation of the separation range in these processes is given in Figure 2.1 [25].

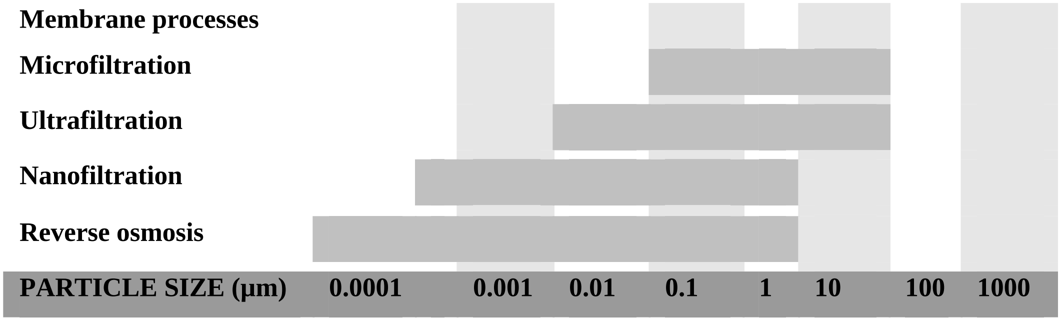


Figure 2.1. Filtration spectrum and separation range of membrane processes [29]

Membrane operations may be conducted under two modes of operations, i.e. dead-end (in line) or cross-flow filtration. The schematic representation of these two operation systems are given in Figure 2. 2.

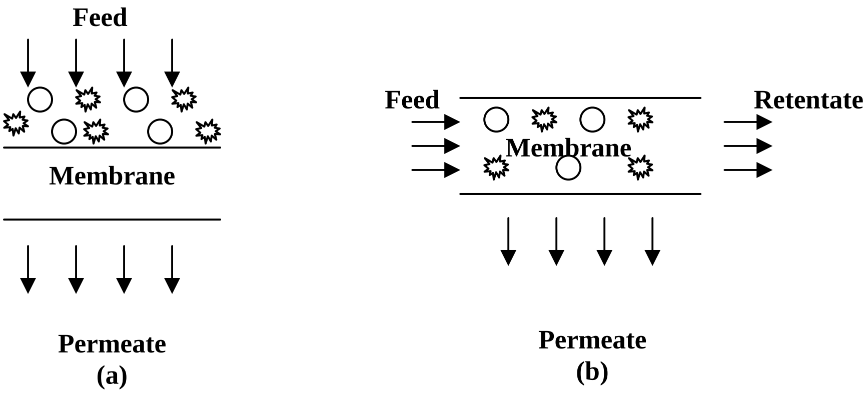


Figure 2. 2. Schematic representation of (a) dead-end and (b) cross-flow filtration

In the dead-end filtration, the feed suspension flows perpendicularly through the membrane surface and all the suspended particles larger than the pore size of the medium are retained by the membrane. Most dead-end filtration processes are carried out in batch mode and therefore the mass of the filter cake grows until all the cells are deposited, or until the capacity of the filter has been reached, in which case further filtration is not possible. The filtration rate decreases with filtration time due to the hydraulic resistance of the filter cake [30]. In contrast; cross-flow membrane filtration is the operation with two effluent streams. Only a part of the feed suspension passes through the medium as recovered product, and the other part flows tangentially along the medium surface, forming the so-called cross-flow.

Dead-end membrane filtration is a promising technology in the field of water purification. This is due to its high selectivity, economic scalability and low chemical composition. Furthermore, compared to cross-flow filtration it has low capital and energy costs. However, membrane performance is often limited by cake formation. Deposition of particulate matter from the filtered liquid causes an increase in the hydraulic resistance of the membrane system. Hence, the effort needed increases as the filtration progresses. This raises the operating costs, due to extra energy consumption and the necessity of periodic cleaning. However in cross-flow filtration some of the particles in the permeating liquid may be carried away by the tangential flow (cross-flow) and thus will not deposit on the membrane surface. Therefore, cross-flow filtration may be expected to have higher permeation fluxes over a longer period of time than dead-end filtration. The need to provide the cross-flow however incurs additional energy consumption [31]. For industrial applications, a cross-flow mode is preferred because of the lower fouling tendency relative to dead-end systems. In the cross-flow operation, the feed flows parallel to the membrane surface with the inlet feed stream entering the membrane module at a certain composition [32]. The cross-flow filtration is influenced by complex effects of a great number of parameters, e g. CFV, TMP, membrane resistance, layer resistance, size distribution of the suspended particles, particle form, agglomeration behavior and surface effects of the particles etc [33].

2.2.1. Microfiltration

MF is a membrane process which most closely resembles conventional coarse filtration. The pore sizes of MF membranes range from 0.05 to 10 μm and may be prepared from a large number of different materials based on either organic (polymer) materials or inorganic (ceramics, metals, glasses) materials. Typical operating pressures of MF systems are in the range of 0.1 and 2 bar [25].

MF is used in a wide variety of industrial applications and the most important applications today are still based on dead-end filtration cartridges and single membranes applied in all kind of laboratories. For the larger scale applications, dead-end MF will slowly be replaced by a cross-flow MF. One of the main industrial applications is the sterilization and clarification of all kinds of chemicals in the food and pharmaceutical industries. MF is also used to remove particles during the processing of ultrapure water in the semiconductor industry. New fields of application are biotechnology and biomedical technology, especially in cell harvesting [19, 25].

2.2.2. Ultrafiltration

UF employs membranes with pore sizes ranging from 0.05 μm to 1 nm. As MF membranes, UF membranes can be considered as porous membranes where rejection is determined mainly by the size and shape of the solutes relative to the pore size in the membrane and the transport of solvent is directly proportional to the applied pressure. The operating pressure of UF systems typically ranges from 1 to 10 bar [25].

UF membranes are currently used in a very wide range of applications in the food, pharmaceutical, biomedical, biotechnological, pulp and paper, and chemical industries and also used extensively in the treatment of a variety of wastewaters from both industrial and municipal [34]. UF systems are less complicated in design; allow higher water flux rates at low pressures and protect and lengthen lifetime of further NF and RO processes. Therefore the acceptability of UF process (with or without MF) as a pretreatment to NF/RO processes is very high due to economic reasons [35, 36].

2.2.3. Nanofiltration

NF removes substances that are too small to be removed by UF. NF membranes' molecular cut-off typically ranges from 200 to 1000 Daltons. When compared to RO membranes, NF membranes provide several advantages such as low operation pressure, high flux, and high retention of multivalent ions [33, 34]. The typical operating pressure of NF systems typically ranges between 5 and 20 bar [25].

NF membranes are quite similar to RO membranes only difference being a more open network structure. This implies that the retention for monovalent salts as Na^+ and Cl^- become much lower but the retention for bivalent ions such as Ca^{2+} and CO_3^{2-} remains very high. It is clear that the application of both processes is different; when a high retention is required for NaCl with high feed concentrations RO is the preferred process. Since the water permeability is much higher in NF the capital cost for a certain application will be lower. In Table 2.1, comparison of retention characteristics of NF and RO membranes is given [25].

Table 2.1. Comparison of retention characteristics of NF and RO membranes [25]

Solute	**RO**	**NF**
Monovalent ions (Na, K, Cl, NO_3)	> 98%	< 50%
Bivalent ions (Ca, Mg, SO_4, CO_3)	> 99%	> 90%
Bacteria and viruses	> 99%	< 99%
Microsolutes (Mw > 100)	> 90%	> 50%
Microsolutes (Mw < 100)	0-99%	0-50%

NF membrane processes have found wide applications for the treatment of industrial wastewaters such as, pulp and paper industry, textile industry, and electroplating industry etc., involving material recovery, reuse, and for pollution prevention [25, 37].

2.2.4. Reverse Osmosis

RO membranes can be considered as being intermediate between open porous type of membrane and dense nonporous membranes. RO membranes are dense membranes without predefined pores. As a result, permeation is slower and rejection is not by sieving, but a solution diffusion mechanism. The low permeability of RO membranes requires high pressures and consequently, relatively high energy consumption [14, 25]. Typical RO pressures are in the range of 10 to 100 bar [14].

RO can be used in principle for a wide range of applications, which may be roughly classified as solvent purification (permeate is the product) and solute concentration (feed is the product). Most of applications are the purification of water, mainly the desalination of brackish and especially seawater to produce potable water. RO is also used as a concentration step particularly in the food industry, the galvanic industry and the dairy industry [25]

As is the case with UF membranes, RO and NF membranes are not always categorized by molecular weight cut off (MWCO), these membranes are normally evaluated against solutions of sodium chloride and magnesium sulphate. In the selection of the membrane, treatment objective will be the major limitation.

Turbidity, hardness and color are targeted contaminants that can be removed by NF and RO processes. RO will provide the same treatment as NF, in addition to greater total dissolved solid removal. Thus, RO/NF processes can remove a broad spectrum of contaminants and can be used beneficially to treat potable water and industrial wastewaters [35].

2.3. Types of Pressure-Driven Membranes

Membranes are made of various materials, including metals, ceramics, polymers, and even liquids. Cellulose polymers are inexpensive and widely used. More recent polyamide thin-film composite membranes are more chemically robust, have longer life, possess greater rejection of dissolved salts and organics, and operate at lower pressures. They are, however, more expensive than cellulose membranes. Ceramic and metal oxide membranes are traditionally used for UF and are commonly available in tubular form. Although ceramic and metal oxide membranes are more costly than other types, they are used for many industrial processes because they can withstand very high temperatures [38, 39].

A number of module designs are possible and all are based on two types of membrane configuration: i) flat; and ii) tubular. Plate and frame and spiral wound modules involve flat membranes whereas tubular, capillary and hollow fiber modules are based on tubular membrane configurations. The choice of module configuration, as well as the arrangement of the modules in a system is based solely on economic considerations with the correct engineering parameters being employed to achieve this [25]. The characteristics of all the modules can be compared qualitatively and this comparison is shown in Table 2.2.

Table 2.2. Comparison of characteristics of membrane modules [25]

	Tubular	**Plate-and-Frame**	**Spiral wound**	**Capillary**	**Hollow Fiber**
Packing Density	low	------------	---------	---------->	very high
Investment	high	------------	---------	---------->	low
Fouling tendency	low	------------	---------	---------->	very high
Cleaning	good	------------	---------	---------->	poor

Two types of membrane configuration used extensively for water and wastewater treatment are hollow-fiber and spiral-wound. In a hollow-fiber element, fibers made of porous polymer material are bundled together and sealed in a pressure vessel. Spiral-wound elements usually range from 2 to 10 inches (5 to 25 cm) in diameter and 10 to 60 inches (25 to 152 cm) in length. The membranes are rolled up around the tube in the form of a spiral. Feed water is pumped through the layers, and product water passes through the membranes and follows the spiral configuration to the central perforated tube. Water that does not penetrate the membrane exits the element as concentrate [39].

2.4. Membrane Fouling

During an actual membrane separation, the performance of the membrane can change with time, and often a typical flux time behavior may be observed: the flux through the membrane decreases over time [25]. Flux decline can be caused by several factors, such as concentration polarization, adsorption, gel layer formation and plugging of the pores. All these factors induce additional resistances on the feed side to the transport across the membrane.

In pressure-driven membrane processes various types of resistances contribute with different extent to the total resistance. The total resistance to permeate flow is comprised of two components: (i) membrane resistance and (ii) resistance of the retained particles. Membrane resistance is usually a constant value, depending on membrane physical and chemical properties. Therefore, the flux of a pure solvent through the membrane, in the absence of retained particles, is proportional to the applied pressure. Resistance of the retained particles is attributed to the frictional drag force resulting from the passage of permeate through the dense layer of particles which are stationary in the transverse direction. This resistance is a function of the extent of particle accumulation and structure of the retained particle layer, and therefore depends on filtration performance [25, 40, 41].

As liquid passes through the membrane, particles accumulate in the vicinity of the membrane surface and form a thin layer in which the particles are stationary in the transverse direction with respect to the membrane surface and named as concentration polarization resistance [25, 41]. The effect of concentration polarization (reversible fouling) is very severe in MF and UF both because the fluxes are high and the mass transfer coefficients are low [25].

With porous membranes it is possible for some solutes to penetrate into the membrane and block the pores, leading to the pore blocking resistance. After the membrane pores have been blocked, further deposition of particles on the membrane surface will form a cake layer. The cake layer is an immobile layer of retained particles packed at maximum density on the membrane surface. Cake formation creates an additional resistance layer to the permeate flow. The flux decreases as the thickness of the cake layer increases with time [25, 42]. Finally, a resistance can arise due to adsorption phenomena (irreversible fouling). Adsorption can take place upon the membrane surface as well as within the pores themselves. The extent of these fouling phenomena is strongly dependent on the types of membrane process and feed solution employed [25].

The characteristics and location of the deposited materials can play an important role in determining the extent and reversibility of permeate flux decline. Reductions in permeate flux and procedures for maintaining permeate flux must be considered in both the design and operation of membrane facilities Roughly three types of foulant can be distinguished; organic precipitates (macromolecules, biological substances, etc), inorganic precipitates (metal hyroxides, calcium salts, etc) and particulates [25, 35].

2.5. Methods to Reduce Fouling

Flux decline has a negative influence on the economics of a given membrane operation, and for this reason measures must be taken to reduce its incidence [25].

The cause and prevention of fouling depend greatly on the feed water being treated, and appropriate control procedures must be devised for each plant [43]. Strategies to minimize the effect of fouling can be divided into two groups: avoidance and remediation. Remediation is usually done by chemical, mechanical and hydraulic cleaning at regular times. Membranes are often cleaned when a given pressure increase (10-15 percent) is exceeded. Membranes can be cleaned at high or low pH, using polar or non-polar solvents, at varying temperatures, and with varying materials, depending on the particular foulants. Typical membrane cleaning agents commonly used are acids, alkalis, chelatants, detergents, formulated products and sterilizers. Also the use of various kinds of turbulence promoters will reduce fouling. It is also possible to avoid fouling by using an adequate pretreatment. In the simplest form pretreatment involves micro-straining with no chemical addition and include pH adjustment, coagulation / precipitation, slow sand filtration, adsorption on activated carbon and pre-microfiltration and pre-ultrafiltration [20, 25, 35, 42, 43].

CHAPTER 3

TEXTILE INDUSTRY

3.1.General

The textile industry is one of the oldest and the most widespread industries in the world. Textile establishments receive and prepare fibers; transform fibers into yarn, thread, and convert the yarn into fabric or related products; and dye and finish these materials at various stages of production. The process of converting raw fibers into finished apparel and non-apparel textile products is complex; thus, most textile mills specialize for the production of one of these processes [5].

In a textile processing plant, water is a vital raw material not only for the boilers supplying steam for heating and drying purposes, but also for all the wet processes such as scouring, bleaching, dyeing, printing and finishing. Among these processes, dyeing is of primary concern from the environmental pollution point of view. It consumes and generates a large portion of the textile industry’s total water and wastewater. The primary source of wastewater in dyeing operations is spent dye bath and rinsing waters. Such wastewater typically contains by-products, residual dye, and salts. Of the 700,000 tons of dyes produced annually worldwide, about 10 to 15 percent is disposed of in effluent from dyeing operations [5]. Dyeing processes use different types of salts for different purposes and salts are not removed by conventional wastewater treatment processes and are therefore ultimately discharged in the final effluent.

The main environmental concern of the textile industry is the amount of wastewater discharged with a high pollution loading. According to the European Integrated Pollution Prevention and Control Bureau estimates, the textile industry releases more than 0.2 million of tons of salts in the environment every year. More than 7000 different compounds and additives are used for the preparation of textile materials, and up to 1 kg of these substances are used for each kilogram of fabric [11]. In Turkey, textile dyeing and finishing sector has an estimated annual production capacity of 2 million tones and the water usage estimated at 250 million tones per year [44].

Cotton is the most commonly used fiber worldwide and has the highest water demand. In 2000, the estimated amount of annual cotton yarn production in Turkey was around 788,000 tons and cotton fabric production was $1403*10^6$ m [45]. Reactive dyeing of 1 kg of cotton requires about 150 L of water, 0.6 kg of NaCl, and 40 g of reactive dyes. Reactive dyes are similar to indigo dyes considered in the present study as regards the application procedure which is consuming high salt and water. One can easily imagine the huge amount of pollution generated from the denim producing industry in Turkey [11].

3.2. Types of Dyes

Dyes may be classified in several ways (e.g., according to chemical constitution, application class, end-use). The primary classifications of dyes are based on the fibers to which they can be applied and on the chemical nature of each dye. Factors that companies consider when selecting a dye include the type of fibers being dyed, desired shade, dyeing uniformity, and fastness (desired stability or resistance of stock or colorants to influences such as light, alkali, etc) [5].

With respect to the chemical nature, practically, textile dyes are classified into acid, basic, direct, disperse, reactive, sulphur or vat dyes (Table 3.1). The acid dyes are so named because of the presence in their molecules of one or more sulphonic acid or other acidic groups. Acid dyes are water-soluble anionic dyes that are applied to nitrogenous fibres such as wool, silk, polyamide (nylon) and modified acrylic fibres from acid or neutral baths. Attachment to the fiber is attributed at least partly to salt formation between anionic groups in the dyes and cationic groups in the fiber. Basic dyes, which are water soluble in aqueous solution, yield colored cations. A number of these dyes were later to become more important for application to acrylic fibres [46].

Most common dyes in use today are the reactive and direct types for cotton dyeing, and disperse types for polyester dyeing. Reactive dyes react with fiber molecules to form chemical bonds. Direct dyes can color fabric directly with one operation and without the aid of an affixing agent. Direct dyes are the simplest dyes to apply and the cheapest in their initial and application costs although there are tradeoffs in the dyes' shade range and wet-fastness. Direct and reactive dyes have a fixation rate of 90 to 95 percent and 60 to 90 percent, respectively. A variety of auxiliary chemicals may be used during dyeing to assist in dye absorption and fixation into the fibers. Vat dyes, such as indigo, are also commonly used for cotton and other cellulosic fibers [5]. In the proceeding section detailed information is given about vat dyes as they are of concern in the present study.

3.2.1. Vat Dyes and Their Application

Vat dyes are water insoluble compounds that contain anthraquinone and indigoid ring structures (Figure 3.1). Important subclasses of vat dyes include: indanthrones, flavanthrones, pyranthrones, dibenzathrones, benzathrone acridones, anthraquinone carbazoles and anthraquinone oxazoles [47].

Table 3.1. Dye classification [5, 46]

Dye Class	Characteristics	Application	Dye Fiber Attachment Mechanism/ Typical Fixation (%)	Dyeing Method
Acid	Anionic, water soluble	Nylon, wool	Ionic bond, Van der Waals/80-93	Fibre placed in acidified aqueous media pH 2.5–7 dye added and temperature 100–110 °C
Basic	Cationic, water soluble	Acrylic, nylon, silk cotton, wool	Ionic Bond/ 97-98	Fibre placed in acidified aqueous dye bath at pH 5–6.5 and temperature 105 °C
Direct	Anionic, water soluble	Cotton	H-Bond/ 70-95	Fibre placed in dye bath slightly alkaline and electrolyte at temperature 100 °C
Disperse	Colloidal dispersion, very low water solubility	Polyester, nylon, acetate, cellulose, Acrylic	Solid solution formation / 80-92	Fibre placed in acidified dye bath pH 5.5 temperature 130–210 °C
Sulphur	Colloidal, insoluble	Cotton	Dye precipitated fibre / 60-70	Fibre placed in dye bath dissolved in alkaline sodiumsulphur, dye displaced to fibre with electrolyte, dye precipitate in situ with air or peroxide
Reactive	Anionic, water soluble	Cotton, silk, nylon, wool	Covalent Bond / 60-90	Fibre placed in dye bath add salt to displace dye to fibre add alkali to cause reaction between dye and fibre
Vat	As sulphur	Cotton	As sulphur dye / 80-95	As sulphur dye

In the application of vat and sulphur dyes a complicated application procedure (reduction and oxidation mechanisms) required because they are insoluble in water and have no affinity for cellulose fibres in such a state. Thus, these dyes have to be reduced into “leuco form”. Before dyeing it has to be converted into the water-soluble form and after absorption into the fibres to be dyed, should be re-oxidized to the original water insoluble dye pigment form in the fibres [48].

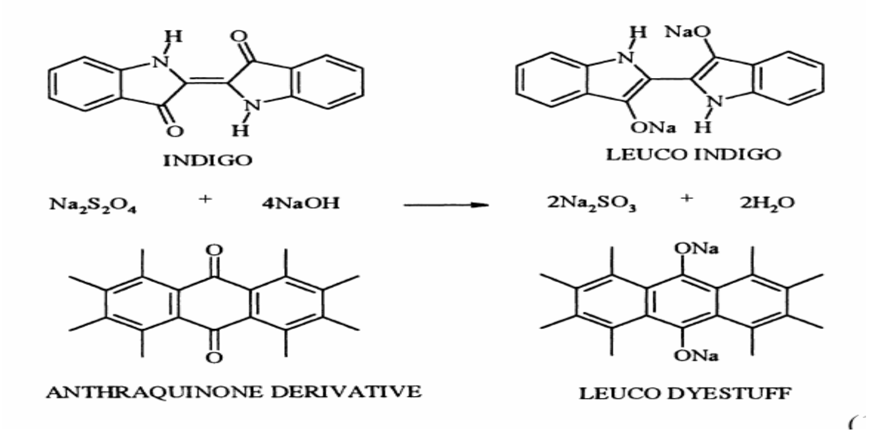


Figure 3.1. Chemical structures of vat dyes; indigo and anthraquinone [49]

The conversion of the vat dye into the leuco form is a heterogeneous reaction that comprises the following stages: diffusion of molecules of the reducing agent to the surface of dye particles, sorption of the reducing agent, chemical reaction between the dye and reducing agent on the surface with the formation of a leuco compound [48]. In conventional vat-dyeing processes, the dye is reduced in a high alkaline medium (pH 11-14) using powerful reducing agents among which sodium dithionite ($Na_2S_2O_4$) is of major importance. Because of the individual molecular structures of different dyes, concentrations of reducing agents and alkali, temperature and timing, each dye requires an individual procedure. Carbonyl groups in these structures are reduced to their soluble leuco form in the dye bath with sodium hydroxide or with sodium hydrosulfite, and then insolubilized in the fiber by oxidation with air or with various oxidizing agents. Solubilized leuco esters of vat dyes that do not require reduction before application to fibers have also been developed [47].

Depending on dye bath pH, the reduced form of the dye molecule exists in unionized, mono-/di-ionized, multi-ionized form, or as mixtures of the forms. High dye bath pH values (such as 12-13 or more), result in a high level of ionization of both, the vat dyes and the cotton. The soluble form of the dye is fully ionized to give a negatively charged dye anion with associated positively charged sodium cations. High pH also ionizes the hydroxyl groups on cotton, thus giving it a negative charge. The control of the reduction process is carried out by measuring the redox potential, while the kinetics and thermodynamics of the reduction oxidation of vat dyes on cellulose material can be controlled by cyclic voltammetry [48].

Vat dyes are particularly substantive to cellulosic fibres, but may also be applied to other fibers such as polyamides. Before application of vat dyes, cotton fabrics are usually desized, scoured, bleached and mercerized. The latter process affords deeper shades with the vats. Although these dyes are noted for their excellent fastness to washing and to chlorine, certain shades on fabric accelerate degradation on exposure to light. Substantivity of vat dyes to fibers has been attributed to hydrogen bonding and Van der Waals forces, but enough anomalies exist to preclude a simple relationship between vat dye substantivity and molecular structure [47].

3.2.1.1. Indigo Dye

The indigo dye which had been used both for painting and dyeing textiles such as wool and linen was discovered years ago during treatment of the plant *Indigofera tinctoria*. Its major industrial application is the dyeing of cloths (blue jeans) and other blue denim. It has also been employed as redox indicator in analytical chemistry and as a microscopic stain in biology [50]. Indigo is a dark blue crystalline powder that melts at 390–392°C. It is insoluble in water, alcohol, or ether but soluble in chloroform, nitrobenzene, or concentrated sulfuric acid. The chemical structure of indigo corresponds to the formula $C_{16}H_{10}N_2O_2$. Intra- and inter-molecular hydrogen bonding are responsible for indigo's extremely low solubility in water, dilute acids and dilute alkalis, as well as its high melting point. Indigo is readily reduced by various reagents, such as sodium dithionite, hydroxyacetone and hydrogen, or by electrochemical methods. In an alkaline medium the yellow-brown sodium salt of leuco indigo is produced, which can be converted by acids to the so called white indigo. The reduction potential (~ 600 mV) of indigo dye lies between that of vat dyes and sulphur dyes. The mechanism of reduction oxidation in this dyeing is presented in Figure 3.2.

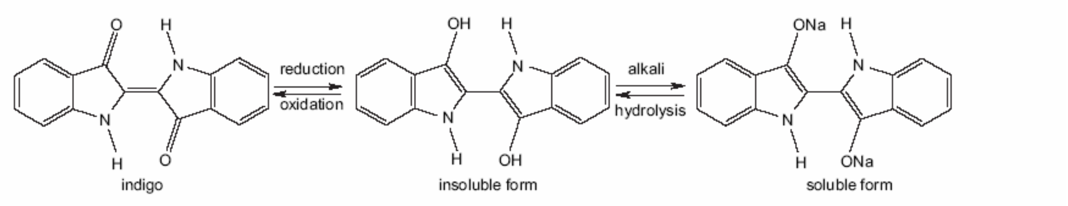


Figure 3.2. The mechanism of indigo dyeing [48]

In the coloration of cellulosic fibres, indigo hold a large part of the dyestuff market. About 33000 tons of vat dyes (including indigo) are being used annually since 1992. The situation will remain constant in the near future mainly because vat dyes yield colored fibers of excellent all round fastness, particularly to light washing and chlorine bleaching. Reactive dyes have not yet achieved the popularity of anthraquinone vat dyes that were invented a century ago. Thus, at present, there is no true alternative to this class of dye [51].

CHAPTER 4

LITERATURE

4.1. Textile Effluent Treatment

The methodology required for integrated water management in a textile finishing company depends largely on the nature of the operations and on the composition of the processing baths and waste water. The dyeing step has the largest risk for environmental pollution, because this step often requires high concentrations of water, dyes, and salts [3].

Effluents from textile industry are of complex composition and usually require more than a single treatment technology to achieve and maintain compliance with currently enforced environmental legislations. Current treatment interventions comprise physical treatment, physicochemical technologies and biological ones [52]. Each treatment alternative has its advantages and disadvantages. In the selection of the treatment alternative; the effluent characteristics and the treatment target should be considered together.

The physicochemical technologies for the treatment of textile effluents include different methods of precipitation (chemical precipitation, sedimentation), adsorption (on activated carbon, biological sludge), AOPs, electrochemical processes, filtration, or membrane processes separately or combinations of these processes [10]. Physicochemical treatment techniques are effective for color removal but use more energy and chemicals than biological processes [53]. However, as a result of the low biodegradability of most of the dyes and chemicals used in the textile industry, their biological treatment by conventional biological systems does not always meet with great success: in fact most of the dyes resist biological treatment [10]. The most important textile effluent treatment techniques are briefly discussed in the following sections.

4.1.1. Biological Treatment

Color is the first contaminant to be recognized in textile wastewaters and the main color causing substance is obviously the dyes used in textile processes [54]. In the literature, there are tremendous numbers of articles/ reports published about the treatment of colored textile effluents by biological means. In a recent one, Manu and Chaudhari (2003) reported decolorization of a simulated cotton dyeing wastewater containing indigo and azo dyes under anaerobic conditions using mixed bacterial cultures, and indicated that COD removal of 90% and color removal of up to 95% can be achieved [21].

In the treatment of textile wastewaters the main problem of using conventional biological systems is the adsorption of the dyes onto (the weak negatively charged) activated sludge or be flocculated, due to their water-insoluble nature (disperse and vat dyes), their high molecular weight (direct dyes) or their cationic nature (basic dyes). At this point, simple biological treatment processes are insufficient for obtaining the required water quality for discharging or reuse in the process [51]. In addition to the adsorption problem of dyes, most of the dyes are very difficult to treat, since these dyes (azo, basic, disperse, reactive) are recalcitrant organic molecules, resistant to aerobic digestion, and are stable to light, heat and oxidizing agents [54].

Recent research efforts have been concentrated on a sequential anaerobic–aerobic treatment of textile effluents. It has been suggested to combine the anaerobic cleavage of the dyes with an aerobic treatment system for the amines formed. Most of the color was removed in the anaerobic part. Aerobic bacteria were used to degrade these amines and the majority COD were removed in the subsequent aerobic processes [55, 56]. Kapdan and Alparslan (2005) investigated the treatability of a textile wastewater in Turkey by an anaerobic packed column – activated sludge sequential treatment system. They obtained over 85% color and about 90% COD removal efficiency at 48 h retention time [56]. In another study, applicability of anaerobic–aerobic sequential system for the treatment of three structurally dissimilar reactive azo dyes was investigated. It was reported that the majority of color removal occurs in the anaerobic stage. On the contrary in some other studies, the anaerobic phase was reported to give low COD removal. Most of the COD was removed in the subsequent aerobic phase, including the decolorized metabolites formed from anaerobic phases [57].

The overwhelming majority of the current publications in the field of the removal of synthetic dyes from waters by biological means have been dealing with the various aspects of the application of innovative microbiological methods and techniques, with the search for new microorganisms providing higher decomposition rates and with the elucidation of the principal biochemical and biophysical processes underlying the decolorization of dyes. This trend unambiguously proves the decisive role of microbiological processes in the future technologies used for the removal of dyes from waters. The widespread application of combined techniques using microbiological decomposition and chemical or physical treatments to enhance the efficacy of the microbiological decomposition can be expected in future. Some new results indicate that gene manipulation; the creation of recombinant strains with higher biodegradation capacity will be applied in the future [58].

4.1.2. Advanced Oxidation Processes

AOPs have been broadly defined as near ambient temperature treatment processes based on highly reactive radicals, especially the hydroxyl radical (OH), as the primary oxidant. Clearly, the OH radical is among the strongest oxidizing species used in water and wastewater treatment and offers the potential to greatly accelerate the rates of contaminant oxidation. The generation of OH radicals is commonly accelerated by combining ozone (O_3), hydrogen peroxide (H_2O_2), titanium dioxide (TiO_2), heterogeneous photocatalysis, UV radiation, ultrasound, and (or) high electron beam irradiation. Of these, O_3–H_2O_2, O_3–UV, H_2O_2–UV, and heterogeneous photocatalytic processes hold the greatest promise to detoxify water and wastewater and specifically textile wastewaters [59, 60]. The major drawbacks of AOPs are the formation of oxidation by products and limited information about the full scale applications [61].

4.1.3. Coagulation (Chemical Precipitation)

Dyeing wastewaters which contain large amounts of dyestuff together with significant amounts of suspended solids, dispersing agents, salts and trace metals can be treated by coagulation and certain color and COD removal can be achieved [62, 63]. Destabilization of colloidal or suspended particles is usually brought about by adjusting the solution pH value and by adding chemicals named as coagulants and also high molecular weight polymers of cationic, anionic or nonionic character [64]. For treatment of vat dyes, the dye type used in this study, chemical coagulation is the most widely used method. Water insoluble vat dyes are removed in a pretreatment step using coagulants-flocculants like lime, alum, ferrous sulfates and polyelectrolyte and in the following activated sludge process, the other contaminants are eliminated. However, the basic disadvantage of physicochemical methods (coagulation) is the producing large amount of sludge which pose handling and disposal problems [65].

4.1.4. Adsorption on Powdered Activated Carbon

Adsorption process is usually combined with the chemical or biological treatment as a polishing step for the removal of color and COD. Powdered activated carbon has been the most widely used adsorbent for removal of recalcitrant organic compounds including the textile dyestuffs from wastewaters despite its high price and regeneration requirements because of its large specific surface area and high adsorption capacity. There is a growing interest in using low cost, commercially available materials for the treatment of wastewater. A wide variety of low cost materials, such as clay minerals, orange peel, wood and wasted biomass are being evaluated as viable substitutes for activated carbon to remove dyes from colored effluents. The main drawbacks of adsorption process are high cost and difficult adsorbent regeneration [66, 67, 68].

4.1.5. Electrochemical Processes

In general, because of the relatively large capital investment and the expensive electricity supply, electrochemical water or wastewater treatment technologies did not find a wide application [69]. However, in the literature, electrochemical oxidation is also reported as an effective method in the oxidation of dyes in textile wastewaters or as a feasible detoxification and color removal pretreatment stage for biological post treatment. Electrochemical oxidation is found as capable of destroying the chromophore groups of dyes found in textile effluents at short treatment times and low energy consumption. However, this is accompanied by a moderate degree of mineralization [70, 71, 72].

4.1.6. Membrane Bioreactors

A membrane bioreactor (MBR) is a combination process of biological reactor coupled with membrane separation device and commonly regarded as innovative technology for wastewater treatment and reclamation. The two-fold effect of biological treatment and subsequent membrane filtration makes this process a powerful and efficient tool for the purification of industrial wastewater. In recent years, the interest in the application of MBRs to textile wastewater treatment for water reuse has increased and MBR technology is shown as a reliable and feasible in alternative to other conventional systems [73, 74].

The effectiveness of an MBR-based treatment concept for textile wastewater has been demonstrated in the literature by several researchers [75, 76]. However, these studies have also indicated that treatment with an MBR might not be sufficient to attain reuse standards. Therefore, additional post-treatment steps including oxidative processes and NF for upgrading the MBR-treated wastewater should be investigated. With an MBR and subsequent NF, it is possible to meet all requirements for reuse [73].

4.2. Membrane Filtration

Textile effluents treated with conventional methods still contain significant amount of color causing substances, inorganic salts and microorganisms and additional treatment should be needed before reuse. For this, generally, membrane processes are preferred as a further treatment stage. Fersi et al. (2005) studied the reuse potential of a textile plant effluent after a biological treatment process and the results of this study showed that more than 90% of color, turbidity and TDS were removed from the treated water accompanied with a reduction of high COD. The authors reported that the NF process provide a permeate water that have a sufficient good quality for reuse in the process [77].

Kim and Lee (2006) investigated the treatment and reuse of dyeing process wastewaters by a hybrid system consisting of pre-treatment (coagulation, activated sludge process, MF) followed by NF or RO. Membrane processes have been screened for the treatment and reuse of effluents mainly from textile dye baths due to large amounts of water consumption for reuse purposes. They reported that in the treatment of dyeing process wastewaters NF or RO membranes effluent after MF, were useful for the reuse of wastewater in terms of water quality and membrane fouling [78]. Van der Bruggen et al. (2001) investigated the possibility of using NF to improve the wastewater quality to the standards that are used for the dyeing of wool. Four different samples from the wastewater treatment sequence (biological treatment plant effluent, dyeing machines) of a textile factory were filtrated with three different NF membranes. The samples were a used and untreated metal complex dye bath, a used and untreated acid dye bath, a sample from the storage tank (containing a diluted mixture of the previous baths), and the effluent of the biological treatment. Authors reported NF as to be a realistic method in the textile industry for direct treatment of dye baths, but the biologically treated dye baths showed a more efficient color removal. For direct NF of used dye baths, two membrane passages would be needed to provide the required permeate quality [79].

In addition to the use of biological treatment plants as a pretreatment to membrane processes, physicochemical processes are also utilized as a pretreatment alternative. Suksaroj et al. (2005) investigated the feasibility of a physico-chemical treatment and NF/RO combination was studied for the cotton and polyester dyeing industry wastewater. Although the textile plant effluent was treated by a biological treatment process, the quality was not sufficient to reuse it on site. The membrane process (RO and NF) was successfully used to obtain a permeate quality which allowed water reuse in the dyeing process, but this process required a physico-chemical pretreatment. After physico-chemical treatment higher retention rates were achieved in NF and RO membranes. Although the permeate quality of NF was lower than RO, it was acceptable for reuse in the dyeing process [80]. In a recent study, Capar et al. (2006) investigated the treatability of the print dying process of a carpet manufacturing industry wastewater using a combined process including chemical precipitation and membrane processes. They reported that chemical precipitation with NF process provided very high separation performance for COD, color, turbidity, total solids and total hardness [81]. Mo et al. (2006) investigated the treatment of different kinds of dye artificial dye solutions with NF polyamide composite membranes to obtain basic information on the dyeing wastewater reuse. NF-membranes with MWCO 500 are good enough to separate several different dyes, producing colorless water. The separation efficiency turned out to be good, especially when one of the chemical coagulants, alum, was used for the pretreatment of the artificial dyeing wastewater. About 20% of improvement of flux was obtained by the pretreatment of the wastewater [82].

Membrane separation technology has emerged as a feasible alternative in the treatment of textile effluents due to major advantages of reusable water production and reducing the consumption of freshwater. The methodology required for water management using membrane technology in a textile industry depends largely on the nature of the operations employed and consequently on the composition of the wastewater [72, 3]. Processes using membranes provide very interesting possibilities of separating hydrolyzed dyestuffs and dyeing auxiliaries, thus simultaneously reducing coloration and the BOD/COD of the wastewater. In the current studies, it is difficult to recommend a particular membrane process (MF, UF, NF and RO), and the choice is guided by the desired quality of the permeation results [10].

MF membranes are suitable for removing colloidal dyes from the exhausted dye bath and the subsequent rinses and the chemicals remain in permeate [3]. MF can also be used as a pretreatment for NF or RO in the textile effluent treatment [19, 77]. Fersi et al. (2005) have found MF as a realistic pretreatment method for the treatment of a textile effluent. They reported that MF pretreatment increased the permeate quality and fluxes of further NF membranes [77].

UF membranes also have been successfully applied for recycling high molecular weight and insoluble dyes, auxiliary chemicals (polyvinyl alcohol) and water. The permeate of UF was of a quality allowing wastewater reuse in the minor processes (rinsing, washing) of the textile industry, but it did not possess the requirement to be reused in delicate processes as dyeing light-colored yarns. UF does not remove low molecular weight and soluble dyes (acid, reactive, basic, etc.) and the UF permeate is therefore not suitable for reuse for all processes [14, 77]. The most important criteria for reuse of process water in the textile industry are the absence of hardness, the salt concentration, and the total color. These criteria can be reached by NF or RO membranes [3, 14].

NF membranes retain organic compounds of low molecular weight, divalent ions or large monovalent ions, such as hydrolyzed dyes as well as dyeing auxiliaries [10]. Jiraratananon et al. (2000) investigated the application of NF membranes for the treatment of textile effluents containing reactive dyes and salt, and obtained that NF is effective in retaining color and producing permeate with reuse possibility [83]. In another study, Chakraborty et al. (2002) used NF process to treat the effluent from a textile plant including reactive dyeing plant and reported high reduction in COD, up to 94% and complete removal of dyes were achieved [15]. In a recent study, Qin et al. (2007) investigated the feasibility for recovering the wastewater of a specific dyeing facility using two NF membranes and obtained over 99% color removal. The quality of the treated water in terms of TOC, hardness and turbidity met the requirements of dyeing process [16].

RO membranes which are suitable for removing ions and larger species [3], permit the removal of all mineral salts, hydrolyzed reactive dyes and other chemical auxiliaries from the dye bath effluents. RO membranes have a retention rate of 90% or more for most types of ionic compounds and produce a high quality of permeate. Decolorization and the elimination of chemical auxiliaries in dye house wastewater can be carried out in a single step. The problem involved is that the higher the concentration of salt, the more important the osmotic pressure becomes and therefore the greater the energy required [10]. Nandy et al. (2007) investigated the applicability of the application of UF and RO processes to produce treated effluent as boiler feed water which requires high quality water. The results revealed that reusable effluent characteristics with concentrations of SS, BOD and COD below detectable limits and TDS concentration of 40 mg/L were obtained [84]. Kim et al.

(2005) investigated the applicability of combined process of NF and RO membranes, not only to improve the rejection efficiencies and flux recovery, but also to recycle the permeate back into the process from desalination and purification process of reactive dye manufacturing industry. COD, color and salt concentrations of permeate were 5.0 mg/L, 3.0 Pt-Co and 0.08%, respectively. This treated wastewater can be reused as refrigerating water, a washing water and a process water for the dye synthesis such as blending or scrubbing processes. The permeate was found as to be recycled back into the process, thus offering economical benefits by reducing the water consumption and wastewater treatment cost [85].

On the other side, the progressive worsening of the quality and permeation rate of permeate produced is also one of the most recurring problems in membrane filtration of textile effluents. The flow reduction has to be ascribed to a reversible (concentration polarization) or irreversible (fouling) increased resistance of the membrane to the permeate flow. The permeate flux decline due to the accumulation of molecules on the nearby membrane surface, known as concentration polarization, may lead to membrane fouling [86].

Membrane characteristics are very important to understand the phenomenon of fouling. Membrane properties, which are important to explain inorganic and colloidal fouling, are the MWCO, the hydrophobicity, the surface roughness and the surface charge. A hydrophilic, smooth and strongly negatively charged membrane seems to be favorable to reduce the fouling tendency of the membrane [87]. Akbari et al. (2006) investigated the influence of the interactions between a polyamide membrane and seven dyes (basic, acidic, disperse, direct and reactive), on the transport properties in NF. Although high removal efficiencies were obtained for all dyes tested the membrane suffered from flux decline due to its sensitivity to fouling. In the presence of salt, the osmotic pressure resulted in a further decrease in flux [44]. Koyuncu (2002), have investigated the treatment of dye baths containing salt and three reactive dyes using NF membranes. According to the results of this study, the dye concentration had a significant effect on permeate fluxes and membrane separation performance. Permeate fluxes decreased with increasing dye concentration and color removals were higher in low salt concentrations [88].

The textile dyes are reactive towards the chemical functions present at the fiber surface. These same chemical functions are found in the polymer surface used for the preparation of membranes. For example, most NF membranes are composite membranes, the active surface of which is polyamide. Polyamide fibres can be dyed by most classes of dyes. Acid, disperse, direct and reactive dyes are classic examples but basic dye can also be used by changing pH. Thus, it is reasonable to think that NF of textile dyes with polyamide membranes could be problematic, heavy fouling is very probable because the dyes will be fixed to the fibres by chemical bonds; and it is highly probable that this fouling will be irreversible [44].

Because of limitations of single separation unit operations, hybrid processes have been suggested: integrating two unit operations with different separation principles may have a synergetic effect, and the resulting separation may be better than the separation obtained with either unit operation alone. Combinations of pressure-driven membrane processes (MF/UF/NF/RO) may yield product water with sufficient quality for discharge or reuse. Membrane technology may offer a realistic solution: NF of the effluent provides a permeate water claimed to have a sufficiently good quality for reuse in the process However, methods of coupling the membrane units are still unclear. The methodology required for integrated water management in a textile finishing company depends largely on the nature of the finishing operations and, consequently, on the composition of the finishing baths and waste water [3]. As noted by Van der Bruggen et al. (2001) the results of lab scale membrane filtration experiments should be confirmed in full-scale experiments and a technical economical evaluation is necessary to differentiate between membrane types [79].

4.3. Reuse Criteria for the Textile Effluents

It is quite difficult to define a general quality standard for textile water reuse because of the different requirements of each raw material used and the textile process applied and because of the different quality required for the final product. The quality of the recovered water shows great variations from one industry to another and each textile industry needs to establish its own reuse water criteria. A few basic conditions are related to water turbidity, which should be less than the turbidity of the ground water that is used as fresh water, and of course, all colors should be removed before reuse [3]

In the literature there is a wide range of studies for different types of textile wastewaters performed to obtain reusable water using membrane technologies. These studies report different quality criteria for water reuse. In Table 4.1, a summary of the quality criteria to be met is presented.

Though, in permeates from NF and RO treatment of textile wastewaters, due to of high salt concentration, it is difficult to meet the required quality. In most of the cases direct reuse of permeate water can not be possible and often it is used after mixing with fresh waters. In the reuse of permeate form NF/RO treatment of textile wastewaters, the following alternatives should be considered:

- reuse of permeate pure or mixed with fresh water,
- use of permeate merely for rinsing or both for dyeing and rinsing,
- need to adapt the salt dosage in case permeate is used for dyeing of cotton since the electrolyte concentration in the permeate can be substantial,
- necessity to carry out the last rinsing bath with fresh water [92].

Table 4.1. The characteristics of reusable water in textile industries given in literature

Parameters	**Li and Zhao, (1999)***	**Rozi et al., (1999)****	**Goodman and Porter, (1980),*****
pH	6.5-8.0	7.8	6-7
COD (mg/L)	0-160	30	178-218
TSS (mg/L)	0-50	-	-
TDS (mg/L)	100-1000	-	-
Total Hardness (mg $CaCO_3$/L)	0-100	270	1-3
Conductivity (µS/cm)	800-2200	1800	1650-2200
Alkalinity (mg $CaCO_3$/L)	50-200	-	32-73
Color	0-2 Lovibond unit	0.01 (426 nm absorption)	20-30 Pt-Co

* the effluent of reactive and acid dyeing wastewaters reused in the dyeing process [89]

** dyeing type not mentioned [90]

***the product water was reused to dye % 100 cotton fabric with reactive dyes [91]

CHAPTER 5

MATERIALS AND METHODS

5.1. Wastewater Characterization

Throughout the study, mainly four different wastewater samples were taken from the indigo dyeing unit of the plant. The first three were for the treatability of the first post-rinsing tank effluent and the last one was for the treatability of the composite wastewater from all post-rinsing stages.

From the first post-rinsing tank effluent, the first three samples that were collected were with the volumes of 100 L, 150 L and 300L. These wastewater samples were pre-filtered thru a 0.8 mm metal filter, analyzed for their constituents and then stored in plastic containers in a temperature controlled room at $4^{o}C$. The wastewater samples were highly variable in composition with excessive amount of pollutants as presented in Table 5.1. The first wastewater sample (Sample 1) was used for MF and coagulation experiments. The second sample (Sample 2) was utilized for UF tests. The third sample (Sample 3) was used in NF and RO experiments. Particle size distribution of wastewater samples utilized in experiments is given in Appendix A.

Table 5.1. Characterization of the first post-rinsing tank wastewaters of the indigo dyeing process

Parameter	**Sample 1**	**Sample 2**	**Sample 3**
pH	11.8-12.5	11.2-11.3	11.2-11.3
COD (mg/L)	1718-1874	1300-1554	1547-1635
Conductivity (mS/cm)	12.3-12.4	12.2-12.3	11.0-11.3
Color (Pt-Co)	3450-3710	3132-4190	4824-4950
Total Suspended Solids (TSS) (mg/L)	-	-	200-400
Alkalinity (mg/L $CaCO_3$)	-	-	4000-4200

For the investigation of the treatability of the composite post-ring tank wastewater, only one single sample, including equal volumes (12.5L) of wastewater from each post-rinsing tank effluent with the total volume of 50 L was taken. This wastewater was also filtered thru 0.8 mm coarse filtration and stored at 4^0C before use. The characterization of this composite wastewater is given in Table 5.2.

Table 5.2. Characterization of the composite post-rinsing tank wastewaters of the indigo dyeing process

Parameter	**Sample 4**
pH	12.1-12.2
COD (mg/L)	853-870
Conductivity (mS/cm)	8.5-8.6
Color (Pt-Co)	2980-3100

5.2. Analytical Methods

The performance of the filtration tests was followed in terms of color, COD, conductivity and pH parameters. These parameters were measured both in the influent (feed) and effluent (permeate) samples. Color measurements were performed by a HACH DR-2000 Model spectrophotometer following USEPA approved HACH Method #8000. For color measurements this device was calibrated at a wavelength of 455 nm with Pt-Co standard solution. Alkalinity measurements were conducted according to Standard Methods (2320 B-titrimetric method) [93]. Conductivity and pH measurements were conducted using a Hach Sension 378 pH, Conductivity, Dissolved Oxygen meter. Particle size distribution of the indigo dyeing wastewater was determined by laser diffraction method using a Mastersizer 2000 instrument (Malvern Instruments Ltd. UK) in TUBITAK Marmara Research Center Labaratories. The measurement size range of the particles was between 0.02 to 2000 μm. Zeta potential measurements were done using a Zeta Potential Meter (Malvern Instruments, Malvern, UK).

5.3. Experimental Methods

5.3.1. Coagulation Experiments

Batch coagulation tests were conducted in 500 mL glass beakers using a conventional jar-test apparatus (Aqua Lytic, Germany). $Al_2SO_4.18H_20$ and $FeCl_3.6H_2O$ of analytical grade were used as coagulants. To initiate an experiment, a total amount of 500 mL wastewater was transferred to a beaker and coagulant was added at the desired dose. After coagulant addition, the suspensions were rapidly mixed at 110 rpm for 1 min, followed by 30 min of slow mixing at 30 rpm. Then the flocs were allowed to settle for 1 h, before samples were taken for residual color, COD and pH measurements. The tests were carried out at room temperature (20±2°C). For each coagulant, optimum pH and optimum coagulant doses were determined by running jar tests at different coagulant concentrations (25 to 1000 mg/L) and pH values (3-10). In adjusting the initial pH of wastewater samples to the desired value; NaOH and HNO_3 solutions were utilized.

5.3.2. Dead-end MF Experiments

In dead-end MF experiments, a conventional filtration apparatus equipped with a vacuum pump (GE, USA) was used at 0.85 bar pressure with an effective membrane area of 1.7×10^{-3} m^2. The temperature was kept constant at 20±2°C for all dead-end MF experiments. Filtration fluxes were calculated based on the amount of filtrate collected in a known time interval. COD, color, conductivity and pH parameters were measured both in the wastewater and in the filtrate.

Dead-end MF experiments were run in two parts. In the first part; filtration performance was evaluated for the first 100 mL and for the last 400 mL of the filtrate samples representing initial and final stages of filtration, respectively. In this part of the study; 8 µm, 5 µm, 1.2 µm, 0.45 µm, 0.22 µm and 0.1 µm membranes were tested and the effect of pH was evaluated at two pH values (original wastewater pH of 12.5±0.5 and pH of 7.0±02). In the second part of the dead-end MF experiments, collected filtrate volume was monitored on a continuous basis by a computerized system (Figure 5.1). Two series of dead-end MF experiments were carried out using this system; single and sequential stage tests.

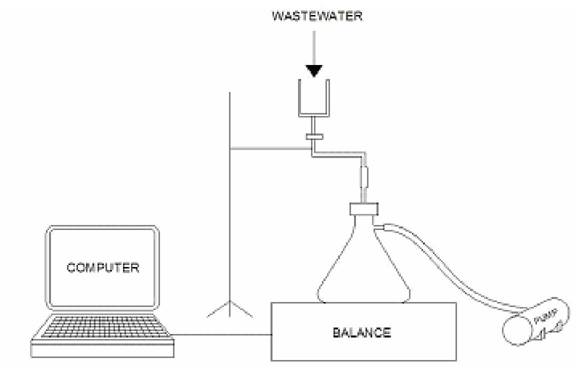


Figure 5.1. Filtration test apparatus used in dead-end MF experiments

In single stage tests, 20-25 µm, 8 µm, 5 µm, 1.2 µm, 0.45 µm membranes were utilized. In the application of sequential MF, the target was to improve the performance of dead-end MF. In this MF application, a coarse MF filtration was followed by a relatively fine MF and the improvement in performance was followed. It was expected that a fine membrane after a coarse one would increase the flux and removals in further membrane applications. In these sequential dead-end MF experiments, the following alternatives were tested: 20-25 µm +1.2 µm, 20-25 µm +0.45 µm and 5 µm +1.2 µm, and 5 µm +0.45 µm. All the experiments of the second part were repeated at least two times until a reproducible data was gathered. Thus, the experimental data represent the arithmetic average of these results.

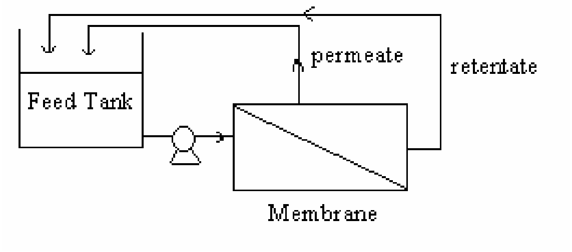
5.3.3. Cross-flow Experiments

Cross-flow membrane filtration experiments were carried out in two modes; a) total recycle b) concentration mode. Schematics of operation modes of membrane filtration experiments are given in Figure 5.2. In the total recycle mode of filtration (TRMF) both retentate and permeate are returned to the feed vessel, in order to obtain a constant feed composition. This is done to evaluate the performance of the membrane under stable conditions. The second mode of cross-flow tests were in concentration mode at which the retentate is returned to the feed vessel but permeate is withdrawn from the system (Figure 5.2).

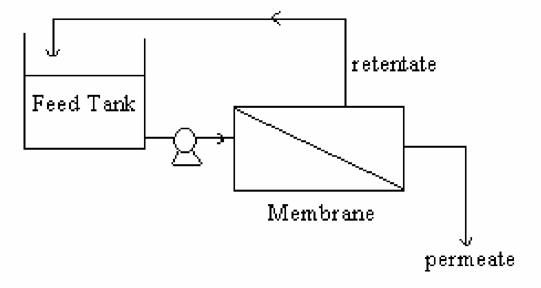
CFV, (ν) is calculated from the retentate flow according to the following equation;

$$\nu = \left(\frac{dV}{dt}\right)\frac{1}{A} \qquad (1)$$

where V is the volume of retentate collected during filtration at time t, and A is the cross-sectional area of the membrane.



(a)



(b)

Figure 5.2. Schematics of operation modes of membrane filtration experiments a) total recycle mode and b) continuous concentration mode

TMP was calculated as the average of the feed pressure (P_f) and retentate pressure (P_r) minus the permeate pressure (P_p, atmospheric pressure) as shown in the following equation:

$$\mathrm{TMP} = \left(\frac{P_f + P_r}{2}\right) - P_p \qquad (2)$$

Percentage removal efficiency or percentage retention for any constituent of the wastewater filtered is determined using the equation;

$$R\ \% = 1 - (C_p/C_f) * 100 \qquad (3)$$

where; C_p: permeate concentration, C_f: feed concentration

Cross-flow experiments were performed in a cross-flow plate and frame module (DSS LabStak M20) equipped with a circular flat membrane giving a total membrane surface area of 0.036 m^2 (Figure 5.3). The membrane module was equipped with a temperature control system and the temperature was kept at 18 ± 2^0C. The volume of the feed solution was 6-6.5 L, including 2.5 L in the tubes of the installation.

Figure 5.3. Photo of DSS LabStak M20 plate and frame membrane module

In cross-flow membrane filtration experiments, permeate flux was monitored by measuring the time at which a known amount of permeate was collected in a graduated cylinder. Permeate flux measurements were periodically done till steady state by simply measuring the volume of filtrate collected per unit time and dividing it by the membrane surface area. COD, color, conductivity and pH parameters were measured in each timely taken filtrate samples.

5.3.3.1. Cross-flow MF Experiments

Based on the results obtained in dead-end MF experiments; firstly, cross-flow MF experiments were performed. In all cross-flow MF experiments, the feed wastewater pH was adjusted to 7.0± 0.2 using HNO_3 and NaOH solutions. The feed and permeate samples were taken with volumes of 100 mL and 250 mL, respectively.

Cross-flow MF experiments were run in two parts. In the first part of the cross-flow MF study, experiments were performed using 0.45 µm membrane after a coarse MF membrane which is 5 µm. The effect of pH, TMP and CFV on the performance of cross-flow MF of 0.45 µm membrane were investigated. For 0.45 µm membrane, investigated CFVs were 0.42 m/s, 0.64 m/s, 1.06 m/s and TMPs were 0.47 bar, 1.02 bar and 1.47 bar.

In the second part, according to the results obtained in previous sequential cross-flow MF studies with 0.45 µm, additional alternatives were evaluated. In this part, the first filtration step was a coarse filtration using 5 µm membrane in dead-end mode and permeate of this step was fed to 1.2 µm, and 0.22 µm membranes and the performances of these three second stage membranes were compared. For 1.2 µm and 0.22 µm membranes; experiments were performed under 1.02 bar TMP and 1.06 m/s CFV and 0.47 bar TMP and 1.06 m/s CFV, respectively.

The effect of TMP and CFV on the performance of cross-flow MF was investigated for only 0.45 µm membrane after 5 µm dead-end MF at TRMF. Concentration mode of filtration tests were performed only with 0.45 µm membrane after 5 µm prefiltration at 1.02 bar TMP and 1.06 m/s CFV conditions till the feed volume decreased to 10% of its initial volume.

5.3.3.2. Cross-flow UF Experiments

As in cross-flow MF tests, UF experiments were performed in the continuous membrane filtration unit (DSS LabStak M20) described in Section 5.3.3. UF experiments were performed after prefiltration with single 5 µm dead-end MF and sequential 5 µm+0.45 µm MF of the wastewater. The preliminary filtration using the single 5 µm MF and sequential 5 µm +0.45 µm MF membranes were intended to reduce the suspended solids fractions and improve the performance of UF membranes.

In single stage MF (5 µm) followed by UF experiments, 100 kDa, 50 kDa, 20 kDa, 2 kDa and 1 kDa membranes were examined. In sequential MF (5 µm+0.45 µm) followed by UF experiments, 100 kDa, 50 kDa membranes were tested. In sequential MF application; 5 µm experiments were performed under dead-end mode (0.85 bar) and 0.45 µm experiments were performed under cross-flow mode of operation at 1.02 bar TMP and 1.06 m/s feed velocity conditions. After dead-end MF, the wastewater pH adjusted to 7.2± 0.4 and then given to further filtrations. UF experiments were performed at 1.87 bar TMP and 1.29 m/s feed velocity conditions for 100 kDa, 50 kDa and 20 kDa membranes and for 2 kDa and 1 kDa membranes, operation conditions of the system were 3.07 bar TMP and 0.98 m/s feed velocity conditions at TRMF. Concentration mode of operation was performed only with 100 kDa membrane at 1.87 bar TMP and 1.29 m/s feed velocity conditions till the feed volume decreased to 10% of its initial volume.

Permeate flux was periodically followed till reaching to steady values which lasted approximately 10-15 h. Color, COD, conductivity and pH values of permeate and feed were measured during the experiments. Feed and permeate were regularly sampled to study the evolution of retention and permeate fluxes as a function of time. The permeate and feed sample volumes were 50 mL, which is negligible as compared to the total feed volume.

5.3.3.3. NF and RO Experiments

As in MF and UF tests, NF and RO tests were performed for the first post-rinsing tank wastewaters and with the same crossflow module described in Section 5.3.3. Two alternative pretreatment methods were evaluated in order to decrease the fouling in NF applications. The first alternative was single stage 5 µm dead-end MF and the second alternative was sequential stage pre-filtration with 5 µm dead-end MF followed by 100 kDa UF. In this second alternative, after 5 µm dead-end MF following the pH adjustment to pH 7.2±0.4 the wastewater was filtered thru 100 kDa UF membranes. The performances of three different NF membranes (NF 270 and NF 90, Dow Film Tech, USA and NF 99, Alfa Laval, Denmark) and two different RO (HR 98 PP and CA 995 PE, Alfa Laval, Denmark) membranes were investigated. The two prefiltration alternatives mentioned above were evaluated for one type of NF membrane (NF 270). For the other NF and RO membranes, only 5 µm dead-end MF was employed as pretreatment.

After single stage NF/RO experiments, sequential NF experiments consisting of two stages of NF were conducted for NF 270 membrane for the treatment of the first post-rinsing tank wastewaters. In this test, the permeate of the first stage NF 270 membrane was the feed of the second stage NF 270 membrane. In order to evaluate the effect of pH, NF experiments were also performed at pH 9.7±0.2 after 5 µm dead-end MF.

Lastly, NF experiments were performed for the treatment of composite effluent from the all post-rinsing tanks to see the effect of concentration on NF performance. The wastewaters from four sequential post-rinsing tanks were mixed equally and the NF performance was evaluated after 5 µm dead-end MF.

All NF and RO experiments were conducted at TRMF at 5.07 bar TMP and 0.62 m/s CFV conditions except the last NF test which is performed at concentration mode. Concentration mode of filtration tests were also performed under the same hydraulic conditions. All NF and RO experiments at TRMF lasted about 10-15 h till the permeate flux was steady and the experiments at concentration mode lasted when the feed volume decreased to 10% of its initial volume. Meanwhile feed and permeate were sampled regularly for color, COD, conductivity and pH measurements. Sample volumes of feed and permeate were 50 mL.

5.4. Membranes

In this part, membranes and their characteristics used in the experiments are described.

5.4.1. MF Membranes

Throughout the study different MF membranes were used in dead-end and cross-flow MF tests. These were selected on the basis of their pore size range. Table 5.3 presents, the specifications of the membranes used in dead-end MF experiments. As seen, the coarser ones are made of cellulose acetate, the tightest one (0.1 µm) is polyvinyldene fluoride and the others are nitrocellulose.

Table 5.3. Specifications of membranes used in dead-end MF experiments

Membrane Code	**Characteristic**	**Pore Size**	**Effective Surface Area**
Whatman 41	Cellulose acetate	20-25 µm	$1.7*10^{-3}$ m^2
SCWP04700	Nitrocellulose	8 µm	$1.7*10^{-3}$ m^2
SMWP04700	Nitrocellulose	5 µm	$1.7*10^{-3}$ m^2
RAWP04700	Nitrocellulose	1.2 µm	$1.7*10^{-3}$ m^2
HAWG04700	Nitrocellulose	0.45 µm	$1.7*10^{-3}$ m^2
HOJN82855	Nitrocellulose	0.22µm	$1.7*10^{-3}$ m^2
VVLP04700	Polyvinyldene fluoride	0.1 µm	$1.7*10^{-3}$ m^2

The specifications of the membranes used in cross-flow MF experiments are presented in Table 5.4. As presented, membranes are of different construction material.

Table 5.4. Specifications of the membranes used in cross-flow MF experiments

Membrane Code	**Characteristic**	**Pore Size**	**Effective Surface Area**
RAWP29325	Nitrocellulose	1.2 μm	$3.6*10^{-2}$ m^2
FSM0.45PP	Fluoropolymer	0.45 μm	$3.6*10^{-2}$ m^2
GRM0.2PP	Polysulphone	0.2 μm	$3.6*10^{-2}$ m^2

5.4.2. UF Membranes

All membranes used in cross-flow UF experiments are commercially available UF membranes which were selected on the basis of their molecular cut-offs to cover the wide range of operation for UF. Table 5.5 summarizes the most important specifications of membranes given by the manufacturer used in UF experiments. All membranes are based on a unique construction of propylene support material.

Table 5.5. Specifications of membranes used in cross-flow UF experiments

Membrane Code	**Membrane Characteristic**	**MWCO**	**Temperature**	**pH Range**
GR40PP	Polysulphone	100 kDa	0-75^{0}C	1-13
GR51PP	Polysulphone	50 kDa	0-75^{0}C	1-13
GR61PP	Polysulphone	20 kDa	0-75^{0}C	1-13
GR95PP	Polysulphone	2 kDa	0-75^{0}C	1-13
ETNA01PP	Composite Fluoro Polymer	1 kDa	0-60^{0}C	1-11

5.4.3. NF and RO Membranes

All membranes used in the NF and RO experiments are also commercially available membranes. The most important specifications of the membranes given by the manufacturer are summarized in Table 5.6. NF 99 membrane is reported in literature as having a sulfonated polyamide skin layer on top of a polyether support [94]. The membrane NF 270, made from piperazine and benzenetricarbonyl trichloride, and benzenetricarbonyl trichloride is a starting material for the membrane NF 90. However, instead of piperazine, 1.3 phenylene diamine is used to complete the interfacial polymerisation [87]. Boussu et al. (2006) reported that, NF 270 membrane is a negatively charged, hydrophilic and has a smooth surface. On the contrary, NF 90 membrane is a hydrophobic and has a rougher surface than NF 270 membrane [87]. CA 995 PE membrane made from cellulose triacetate/diacetate blend on polyester and HR 98 PP membrane was made from thin film composite on polypropylene [95].

Table 5.6. Specifications of membranes used in NF and RO experiments

Membrane Code	**Manufacturer**	**pH range (20^oC)**	**Temperature Resistance**	**Pore size**
NF 270	Dow-Filmtec, (USA)	3-10	45	200-300 Da, 0.84 nm [96, 97]
NF 90		2-11	45	100 Da, 0.68 nm [87, 96]
NF 99	Alfa Laval, (Denmark)	2-10	50	159 Da [94]
CA 995 PE		5-6.5	30	NaCl rejection ≥ 95%
HR 98 PP		2-11	60	NaCl rejection ≥ 85%

5.5. Evaluation of Filtration Performance

The primary performance parameter used in the evaluation of the membranes during membrane filtration experiments was the flux. For each membrane tested; the following flux values were determined.

1) Initial clean water flux (J_{cwi}): This is the first flux determined with the virgin or clean membrane,
2) Wastewater flux (J_{ww}): This is the wastewater flux monitored as a function of time during filtration,
3) Clean water flux of the cleaned membrane (J_{cwc}): This is the last flux measured with clean water after the membrane had been subjected to chemical cleaning/ultra pure water cleaning.

The flux declines and recovery values were calculated based on the equations given in Table 5.7.

Table 5.7. Flux decline calculations used in membrane studies

Formula	**Type/Cause of flux**
$\frac{J_{cwi} - J_{ww}}{J_{cwi}}$	Total flux decline
$\frac{J_{cwi} - J_{cwc}}{J_{cwi}}$	Irreversible fouling
J_{cwc}/J_{cwi}	Flux recovery

5.6. Cleaning and Preparation of Membranes

The experimental protocol followed for cleaning and preparation of membranes were almost the same for all of the membranes tested. In the cleaning and preparation of cross-flow MF membrane pairs, in order to minimize membrane compaction during the experiments, 8-10 h compaction was employed at 3.0 bar pressure. After compaction, membranes were wetted in ultrapure water for 24 hours. For the chemical cleaning of membranes, each membrane pair were waited in an alkaline solution having a pH value of 9 (adjusted with NaOH) for 8 hours and in an acidic solution having a pH of 3 (adjusted with HNO_3) for 8 hours sequentially. After chemical cleaning, membranes were again wetted in ultrapure water for 8 hours to remove cleaning chemicals on the surface of the membrane. This compaction and cleaning procedure with chemicals was applied only before the first usage of membrane pairs. After compaction and chemical cleaning, water fluxes were measured before wastewater application till reaching to steady state (J_{cwi}). The wastewater fluxes were also measured till steady state (J_{ww}). The membrane module was rinsed with approximately 20-30 L distilled water for 30 min after the wastewater applications. After water cleaning by distilled water the water flux of the membrane module was measured using ultrapure water and if the clean water flux was more than 10% lower than its first value (J_{cwi}) chemical cleaning as described above was applied and then the clean water flux (J_{cwc}) was measured using ultrapure water.

In the cleaning and preparation of UF membranes, in order to minimize membrane compaction during the experiments, firstly 10 h compaction was applied under 5.0 bar TMP. After compaction chemical cleaning was applied to each UF membrane pair rinsing with a solution having a pH value of 3 ± 0.2 (adjusted with HNO_3) for 20-30 min and with a solution having a pH of 9 ± 0.2 (adjusted with NaOH) for 20-30 min sequentially under low feed and retentate pressures of 2 bar with clean-in-place method. The membranes were kept in the filtration module while the cleaning solutions were circulated through the system and permeate and retentate being continuously discarded. After the chemical cleaning, UF membranes were rinsed with ultrapure water to remove cleaning chemicals on the surface of the membrane and clean water fluxes were measured till reaching to steady state values (J_{cwi}). The membrane clean water fluxes were measured before (J_{cwi}) and after (J_{cwc}) wastewater application to evaluate the filtration performance of the membrane. Chemical cleaning was repeated after the wastewater applications if the J_{cwc} decreased more than 10% of the J_{cwi}.

The cleaning and preparation of NF and RO membranes were carried out according to the procedure followed in the preparation of UF membranes as described above but the compaction pressure was increased to 7.0 bar for these membranes.

CHAPTER 6

Pretreatment of Indigo Dyeing Wastewaters

In membrane filtration systems, flux decline is the major problem to be solved and the most effective solution is usually found in providing an effective pretreatment as a part of an integrated membrane system. For NF and RO processes, physicochemical pretreatment and/or MF/UF pretreatment alternatives which offer a number of benefits to NF and RO by way of increased flux and membrane life decreased cleaning frequency and energy consumption are considered. Besides the advantages of physicochemical and MF/UF processes as a pretreatment, they also individually remove some part of the pollutants and selected as one of the units of the treatment scheme identified in wastewater treatment studies. Accordingly, in the present study, as described in Chapter 5, coagulation and MF and/or UF pretreatments were applied to indigo dyeing wastewater. In the proceeding sections, the findings from i) MF, ii) UF and iii) coagulation experiments are presented.

6.1. MF

MF experiments were designed and carried out to decrease solids loading to further membrane processes to improve the final effluent quality and also to increase the overall permeate flux. The alternatives considered are given in Figure 6.1.

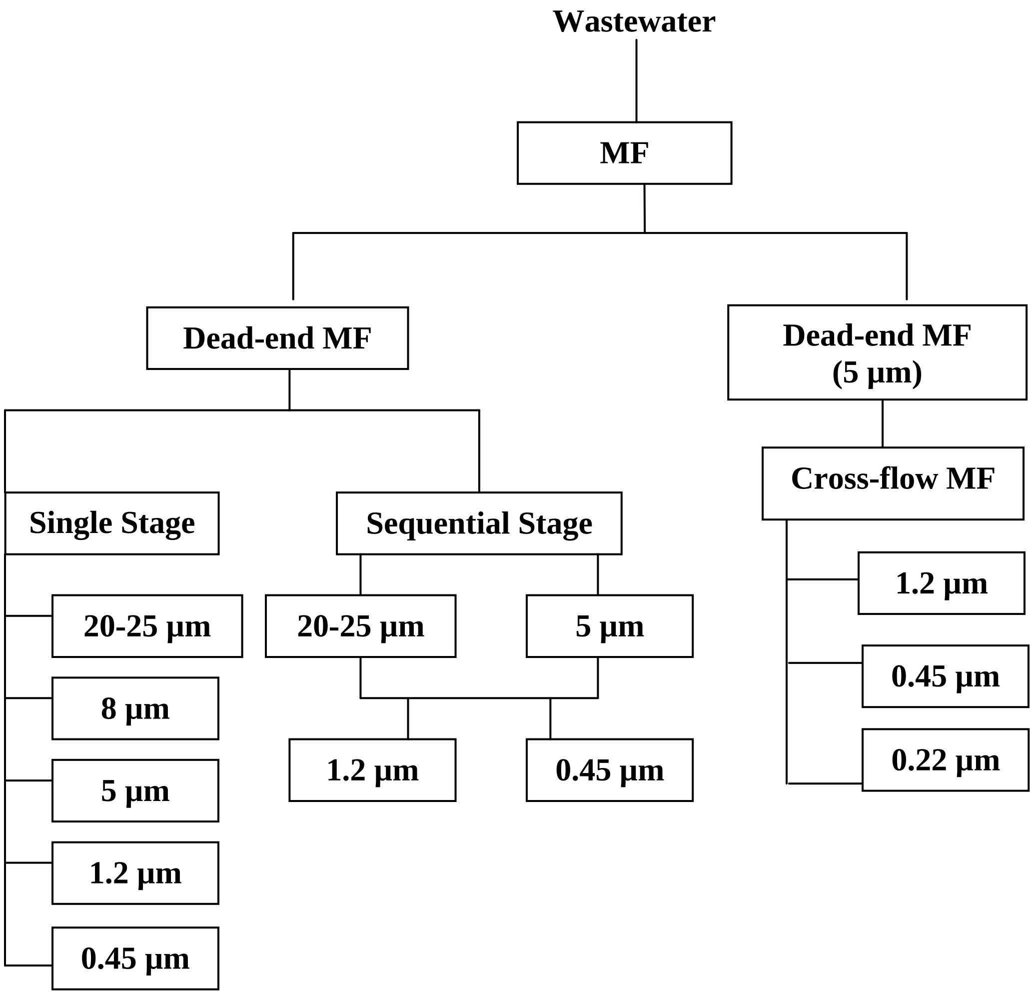


Figure 6.1. MF alternatives tested for the indigo dyeing wastewater

As seen in Figure 6.1, MF studies were run in two parts; dead-end MF and cross-flow MF. In dead-end MF studies, MF membranes with indicated pore sizes were tested in single and sequential modes to achieve the highest performance in terms of retentions and permeate flux. In dead-end MF tests, the best MF membrane sequence and the effect of pH was determined; and based on the results obtained, cross-flow tests were conducted to compare the performances of dead-end and cross-flow MF systems. In cross-flow MF tests, the effect of CFV, TMP and pH of the feed wastewater were also evaluated in terms of color and COD retentions and permeate fluxes. The alternatives specified in the MF tests were evaluated in the further UF tests. In the following sections, results of dead-end and cross-flow MF experiments for the pretreatment of indigo dyeing wastewater are presented.

6.1.1. Dead-end MF

Dead-end MF experiments were carried out in two phases. Firstly, the effect of wastewater pH and membrane pore size on the performance of MF was investigated. Secondly, the effect of MF filtration sequence (single and sequential filtration) on the performance of MF with different pore sized MF membranes was investigated.

6.1.1.1. Single Stage MF

In single stage dead-end MF experiments, two different pH alternatives were evaluated as the original wastewater pH of 12.5±0.5 and the neutral pH of 7.0±02; and the comparison was made on the basis of permeate flux, color and COD retentions.

The particle size distribution of the first post-rinsing tank wastewater used in this part of the study is given in Figure A.1. As seen from this figure, particles size of solids in wastewater was highly variable and the average pore size was 2.67 µm. With this wastewater sample, six different MF membranes (8, 5, 1.2, 0.45, 0.22 and 0.1 µm) were tested and color and COD retentions and also permeate fluxes corresponding to 100 mL and 400 mL filtrate volumes as presented in Table 6.1 were measured. The measurements for 100 mL and 400 mL permeate volumes are thought to represent the flux corresponding to the initial and final stages of filtration, respectively.

As presented in Table 6.1, at both pHs, initial and final COD retentions were similar and low at around 4-18% and 5-20%, respectively (Table 6.1). Fersi et al. (2005) reported similar low COD retentions in the pretreatment of textile wastewaters as 14% for 5 µm MF membrane [77]. Membranes with pore sizes greater than 1.2 µm appeared to provide lower COD removals than tighter ones. This difference was decreased for the final stage of filtration and similar COD retentions obtained for all membranes tested. Nevertheless, COD retentions were low and never above 20%. In MF, decrease in COD is only obtained when a significant organic fraction is associated with particles larger than the pore size. Thus, the membranes with large pore sizes could remove less COD than the tighter ones [19]. As expected in dead-end MF studies, no significant COD retention was obtained [98]. Due to low COD retention in single stage MF experiments, permeate COD was not followed in later MF experiments. As contrary to COD retention, color retentions were quite high reaching to 95% with MF media smaller than 0.45 µm for both of the pH values investigated.

Table 6.1. Dead-end MF results for 100 mL and 400mL at pH 12.5±0.5 and at pH 7.0±0.2 [98]

pH	**Filter**	**COD Retention (%)**		**Color Retention (%)**		**Flux (10^3 L/m2/h)**	
		100 mL	**400 mL**	**100 mL**	**400 mL**	**100 mL**	**400 mL**
12.5±0.5	8 µm	4	5	80	87	3.1	0.4
	5 µm	8	10	81	88	3.2	0.4
	1.2 µm	9	9	87	90	1.5	0.4
	0.45 µm	13	10	92	93	1.2	0.4
	0.22 µm	14	13	94	94	0.9	0.2
	0.1 µm	14	12	94	95	0.8	0.2
7.0±0.2	8 µm	6	11	43	81	69	0.5
	5 µm	5	12	40	76	51	0.4
	1.2 µm	18	18	59	85	9	0.4
	0.45 µm	18	20	95	95	1	0.3
	0.22 µm	18	13	95	95	0.8	0.3
	0.1 µm	16	18	95	96	0.6	0.2

As presented in Table 6.1, for coarse MF membranes, at the initial stage of the MF tests, higher fluxes were obtained at neutral pH than at the original wastewater pH. Ohmori and Glatz (1999), also reported higher fluxes at lower pH values for the MF of *Corynebacterium glutamicum* particles [99]. Nevertheless, at the final stage of filtration, no significant change was measured in permeate flux with a change in pH. For fine membranes however, pH of 12.5±0.5 appeared to provide slightly higher initial permeate flux. Furthermore, although initial percentage COD and color retentions were higher at pH 12.5±0.5 than at 7.0±0.2 with 8, 5, 1.2 µm MF membranes, at final stages there were no effect of pH on COD and color retention. Therefore it was decided that there is no benefit of decreasing the pH of the wastewater and the wastewater pH should not be adjusted.

After identifying the original wastewater pH as a better value than the neutral pH, single stage MF tests were repeated using a Buchner funnel filtration system that provides the opportunity to monitor filtrate volume on a continuous basis on a computer in order to analyze flux decline better. In these MF experiments, 20-25, 8, 5, 1.2, and 0.45 µm pore sized membranes were examined individually; and along with flux variation, final color retentions were also determined.

As can be seen from Figure 6.2, clean water fluxes for 20-25, 8, 5 µm membranes were nearly the same. However, for 0.45 µm membrane there was a significant decrease in clean water flux. Surprisingly, clean water flux of 5 µm membrane was higher than those of the 20-25 µm and 8 µm membranes tested. This anomaly may be attributed to the nature and pore size distribution of the membrane. The 0.45 µm membrane showed the lowest wastewater flux compared to other membranes used in the experiments.

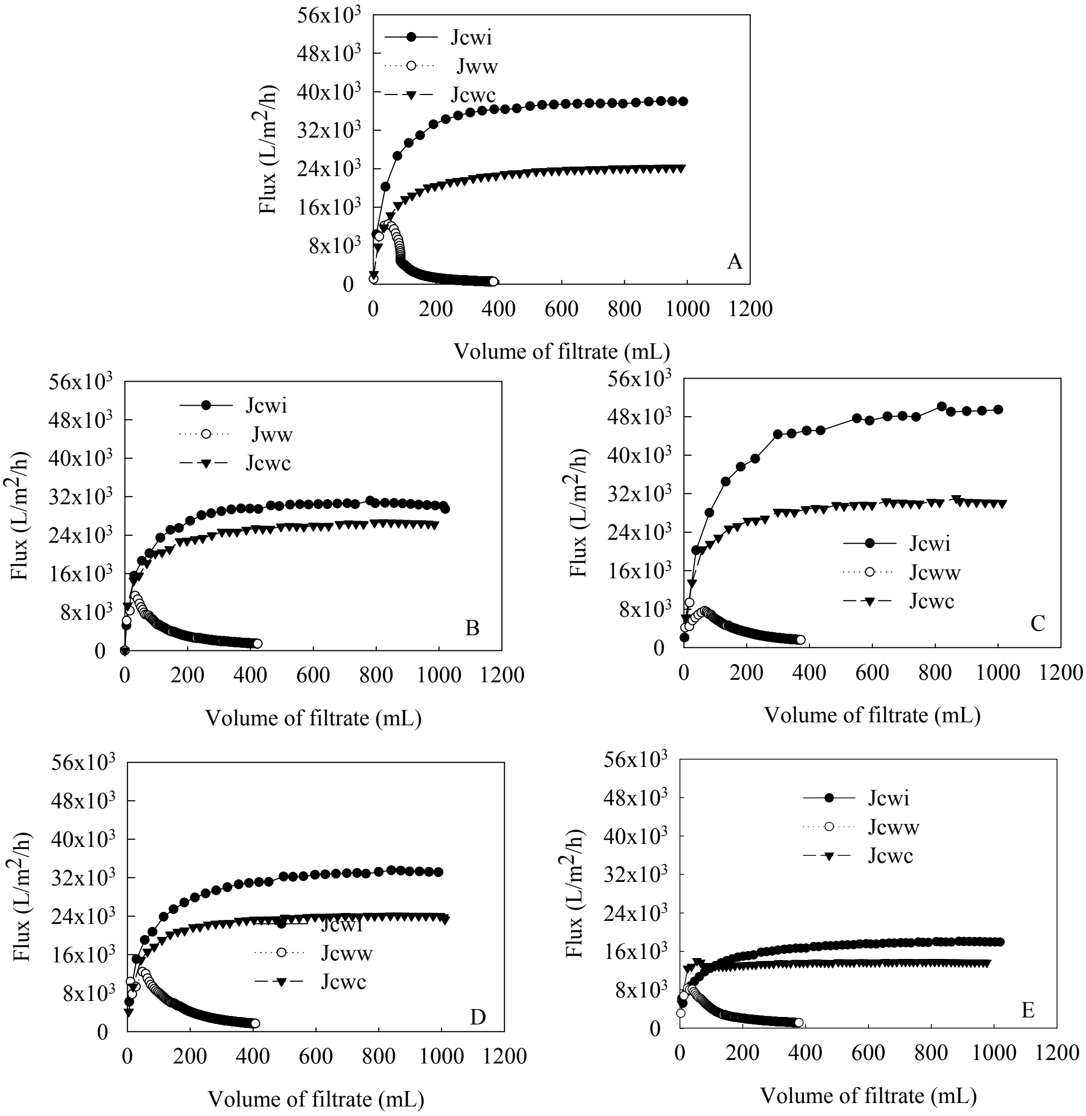


Figure 6.2. Single stage dead-end MF flux results of A) 20-25 μm, B) 8 μm, C) 5 μm, D) 1.2 μm, E) 0.45 μm membranes (J_{cwi}: clean water flux of virgin membrane, J_{ww}: wastewater flux, J_{cwc}: clean water flux of washed membrane)

Flux decline, flux recovery and irreversible fouling of each membrane tested are presented in Table 6.2. As seen, although there were no significant differences in total flux decline, the lowest flux decline was obtained for 1.2 μm and 0.45 μm membranes. On the other side, the highest flux decline was observed for 20-25 μm membrane among all the membranes tested (Table 6.2).

Table 6.2. Flux decline, recovery and irreversible fouling measurements of single stage dead-end MF experiments

Membrane	Flux Decline (%)	Flux Recovery (%)	Irreversible Fouling (%)
20-25 μm	96	56	44
8 μm	89	85	15
5 μm	92	70	30
1.2 μm	85	77	23
0.45 μm	86	88	12

Although the highest flux recovery and the lowest irreversible fouling was obtained for 0.45 μm membrane (as 88% and 12%, respectively), clean water and wastewater fluxes were low for this membrane (Figure 6.2). High flux recovery and low irreversible fouling (gel layer formation) with this membrane was probably due to accumulation of the particles on the membrane surface instead of complete pore blocking. On the other side, the lowest flux recovery and the highest irreversible fouling were observed for 20-25 μm membrane (as 56% and 44%, respectively). Higher fouling observed for 20-25 μm than those for with smaller pore sizes may be attributed to the difference in the nature of the membrane. As can be seen from Table 5.3, 20-25 μm membrane is cellulose acetate while the other membranes are nitrocellulose.

The important advantage of using MF was reported as that these membranes generally have a much higher filtration rate per unit area than UF membranes and require much less membrane surface. Because of this the membrane cost may be much less in many applications [100]. Thus, in the selection of the optimum MF membrane, permeate flux is the most significant paremeter to be considered. Accordingly, findings from single stage dead-end MF experiments have revealed that, 5 µm membrane is the best MF membrane among the membranes tested as its wastewater flux is high as compared to smaller pore size membranes along with a low permeates color.

6.1.1.2. Sequential MF

In the application of sequential MF, the target was to improve the performance of single stage MF. To this purpose, coarse dead-end MF filtration was followed by a relatively finer MF and the improvement in performance was followed. It was expected that a fine membrane after a coarse one would increase flux and color retention in further NF/ RO processes.

In sequential dead-end MF experiments, as preceding stages, 20-25 and 5 µm MF were selected as coarse membranes and applied before both 0.45 and 1.2 µm filtration. Hence, the alternatives tested were as follows: 20-25+1.2 µm, 20-25+0.45 µm, 5+1.2 µm, and 5+0.45 µm (Figure 6.3).

Water fluxes of sequential dead-end MF schemes of 20-25+1.2 µm, 20-25+0.45 µm, 5+1.2 µm and 5+0.45 µm are presented in Figure 6.3. Wastewater flux corresponding to the first 200 mL filtrate volume for the single stage 1.2 µm MF was 4152 $L/m^2/h$ (Figure 6.2). However, when 20-25 µm and 5 µm MF were applied as prefiltration, the flux was found to increase to 11648 $L/m^2/h$ and 19156 $L/m^2/h$, respectively (Figure 6.3, A and C). Similarly, the wastewater flux of 2097 $L/m^2/h$ (for the first 200 mL filtrate) of the single stage 0.45 µm MF increased to 5931 $L/m^2/h$ and 15347 $L/m^2/h$, respectively, when 20-25 µm and 5 µm MF were applied as prefiltration. As seen in Figure 6.3 B and D, the application of coarse MF before a finer one increased the wastewater fluxes significantly.

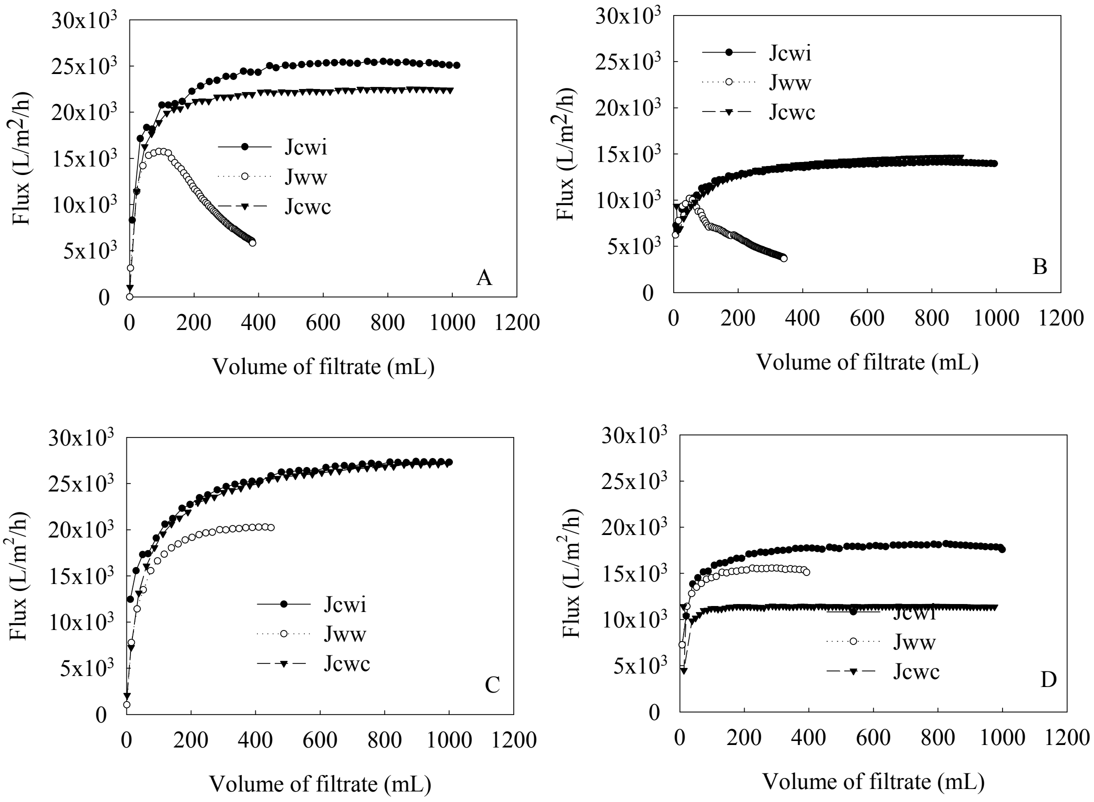


Figure 6.3. Sequential stage dead-end MF flux results of A) 20-25+1.2 µm, B) 20-25+0.45 µm, C) 5+1.2 µm, D) 5+0.45 µm (J_{cwi}: clean water flux of virgin membrane, J_{ww}: wastewater flux, J_{cwc}: clean water flux of washed membrane)

In order to evaluate the effect of sequential MF on initial wastewater flux in a comparative way, flux decline, flux recovery and irreversible fouling of each membrane tested were determined and the results shown in Table 6.3 were obtained. As the pore size of the coarse membrane used as a pre-filter was decreased, the flux decline of the fine membranes also decreased (Table 6.3). As can be depicted from Table 6.3, in sequential dead-end MF tests, the highest flux decline was obtained for both 1.2 µm and 0.45 µm membranes after 20-25 µm prefiltration. However, in both cases flux recovery was above 95 %. Flux declines after 5 μm prefiltration were lower than those after 20-25 μm filtration which imply that 5 μm MF is better in performance than 20-25 μm MF.

Table 6.3. Flux decline, recovery and irreversible fouling measurements of sequential stage dead-end MF experiments

Membrane	**Flux Decline (%)**	**Flux Recovery (%)**	**Irreversible Fouling (%)**
1.2 μm	85	77	23
5+1.2 μm	16	96	4
20-25+1.2μm	48	95	5
0.45 μm	86	88	12
5+0.45 μm	8	68	32
20-25+0.45 μm	53	100	0

As contrary to the improvement in flux decline, there was no improvement in color retention with the application of a coarse MF before a finer one. Color retention of 90 % obtained for 1.2 μm filtration has not improved with sequential applications of 20-25+1.2 μm and 5+1.2 μm MF (Table 6.1 and 6.4). Similarly, for single and sequential (20-25+0.45 μm and 5+0.45 μm) dead-end MF applications of 0.45 μm membrane, color retentions were also not changed and found to be 93%. These findings revealed that in the first stage of coarse MF (20-25 μm and 5 μm) color causing substances that are bigger than membrane pore size were completely removed and remaining color causing substances in the permeate of these coarse MF membranes were smaller than the fine MF membranes tested.

As regards permeate conductivity and pH; it was observed that these values did not change after sequential dead-end MF (Table 6.4). All these findings which indicate no improvement in color retentions by a coarse MF before a finer one are in fact expected, as coarse MF could not remove dissolved constituents. However, in terms of flux decline, coarse MF was beneficial and provided a decrease in it. From all above dead-end MF tests, 5µm MF appeared to be the most suitable coarse MF stage before 0.45 µm and 1.2 µm, hence further cross-flow MF tests were carried out for this scheme.

Table 6.4. pH, conductivity, and color measurements of sequential stage dead-end MF experiments

Parameter	**pH**	**Conductivity (mS/cm)**	**Color Retention (%)**	**Cumulative Color Retention (%)**
Original wastewater	12.0	12.3	na	na
20-25 µm	11.7	12.2	71	na
5 µm	11.8	12.2	92	na
20-25+1.2 µm	11.6	12	75	93
25+0.45 µm	11.7	12.1	75	93
5+1.2 µm	11.7	12.1	23	92
5+0.45 µm	11.7	12.1	9	93

na: not applicable

6.1.2. Cross-flow MF

Based on the results obtained from the previous sequential dead-end MF tests cross-flow MF experiments were run for 0.45 µm membrane after 5 µm dead-end MF and the effect of TMP and CFV on the performance of the second stage of sequential MF was investigated. As alternatives to 0.45 µm; 1.2 µm, and 0.22 µm MFs were also tested and the permeate from 5 µm dead-end MF was fed to these membranes in TRMF. Based on the results obtained from these experiments, concentration mode of filtration experiments were performed for only 0.45 µm MF after 5 µm dead-end MF.

6.1.2.1. 0.45 µm cross-flow MF after 5 µm MF

6.1.2.1.1. Effect of TMP

Three different TMPs (0.48 bar, 1.02 bar and 1.47 bar) were examined at the same CFV of 1.06 m/s and color retentions presented in Figure 6.4 were obtained. Color retentions for 1.02 and 1.47 bar TMP were similar and in the range of 20-28%, and 19-28%, respectively (Figure 6.4). However at the TMP of 0.48 bar, color retention was higher and more stable at about 30%. For all TMP tested, color retentions reached to steady state at about 4 h of operation.

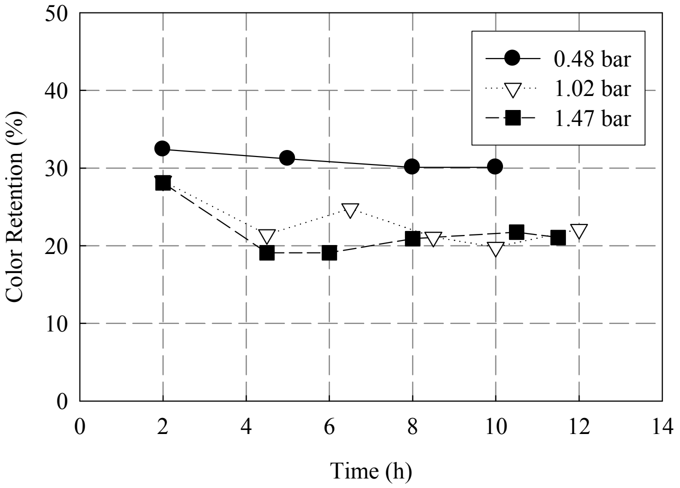


Figure 6.4. Effect of TMP on color retentions of 0.45 µm cross-flow MF after 5 µm prefiltration

As can be seen from Figure 6.5, TMP was effective on permeate fluxes of 0.45 µm cross-flow MF after 5 µm dead-end prefiltration. At steady state, permeate fluxes were 115 L/m^2/h at 0.48 bar TMP, 150 L/m^2/h at 1.02 bar TMP and 148 L/m^2/h at 1.47 bar TMP. Thus the permeate fluxes at 1.02 and 1.47 bar were nearly the same and higher than that at 0.48 bar. Thus, to conclude one can state that, the increase in TMP resulted as an increase in permeate flux and a decrease in color retention for a given CFV. Thomassen et al. (2005) also reported that the permeate flux increase with the increase in TMP for the transmission of dextrin and BSA solutions using cross-flow MF [101].

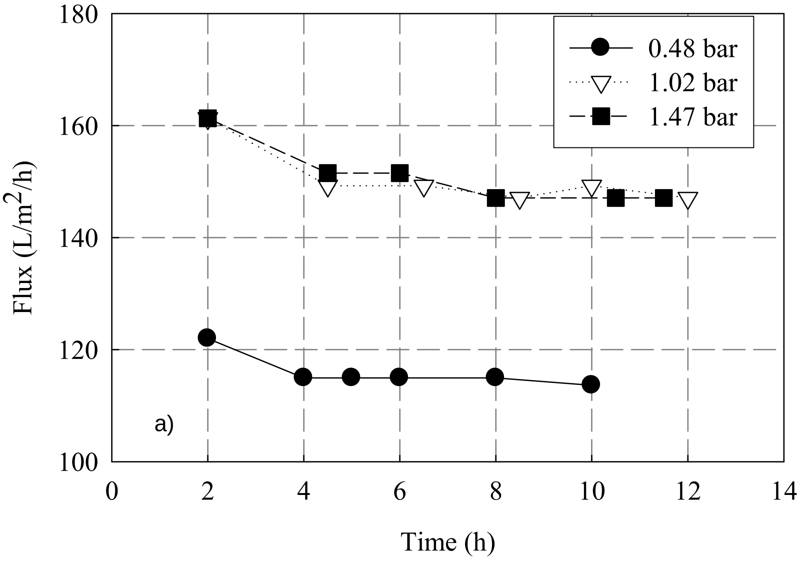


Figure 6.5. Effect of TMP on permeate fluxes of 0.45 µm cross-flow MF after 5 µm prefiltration

Water flux, flux decline and flux recovery and irreversible fouling for 0.45 µm cross-flow MF after 5 µm dead-end prefiltration for three different TMPs at a CFV of 1.06 m/s are presented in Table 6.5. As can be depicted, the increase in TMP resulted as an increase in flux decline and irreversible fouling. The highest flux decline and irreversible fouling were obtained for 1.47 bar TMP condition as 38% and 20 %, respectively. On the other hand, the total flux decline for 0.48 bar and 1.02 bar TMPs were same as 31 % and also lower than the flux decline for 1.47 bar TMP which is 38%. The highest flux recovery and lowest irreversible fouling were obtained for 0.48 bar TMP as 100% and 0%, respectively.

Table 6.5. Water flux, flux decline, recovery and irreversible fouling of 0.45 μm cross-flow MF after 5 μm prefiltration for different TMPs (CFV: 1.06 m/s)

Membrane	**0.48 bar**	**1.02 bar**	**1.47 bar**
Water flux *(L/m^2/h)	164	214	236
Wastewater flux (L/m^2/h)	114	147	147
Water flux **(L/m^2/h)	168	180	188
Flux Recovery (%)	102	84	80
Flux Decline (%)	31	31	38
Irreversible Fouling (%)	0	16	20

*clean water flux with ultra pure water of virgin membrane
**water flux of fouled membrane after cleaning

As presented above, for 0.48 bar TMP, color retention was higher than 1.02 bar and 1.47 bar TMPs due to the insufficient driving force and cake layer formation on the surface of the membrane. For 1.02 bar and 1.47 bar TMPs, permeate fluxes were nearly the same. Consequently, considering color retention and fouling behavior at different TMPs, 1.02 bar was selected as the optimum TMP at a CFV of 1.06 m/s for 0.45 μm membrane after 5 μm prefiltration.

6.1.2.1.2. Effect of CFV

The effect of CFV on the performance of permeate flux from 0.45 μm cross-flow MF (after 5 μm dead-end prefiltration) was investigated at three different CFVs

(0.42 m/s, 0.64 m/s and 1.06 m/s) and the results given in Figures 6.6 and 6.7 were obtained. During these tests a constant TMP of 0.48 bar was maintained and the tests were performed at TRMF.

The effect of CFV on color retentions and permeate fluxes by 0.45 μm cross-flow MF after 5 μm dead-end prefiltration is given in Figures 6.6 and 6.7. As clearly seen, an increase in CFV resulted as an increase in color retention and steady state retentions were achieved after a short operation time of 4 h.

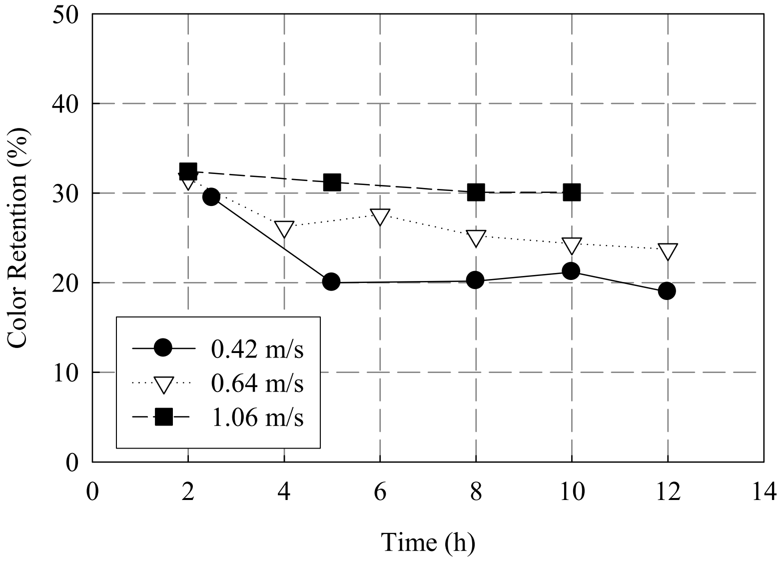


Figure 6.6. Effect of CFV on color retentions of 0.45 μm cross-flow MF with 5 μm prefiltration

As can be depicted from Figure 6.7, CFV was influential on permeate flux. At steady state, the permeate flux was 95 L/m^2/h, 104 L/m^2/h and 114 L/m^2/h at 0.42, 0.64 and 1.06 m/s CFV, respectively; indicating a considerable increase in flux with an increase in CFV. At the begining of the filtration, the permeate fluxes declined sharply due to cake formation for all CFVs tested. As time progressed, the system reached a steady state with a constant permate flux. Lin et al. (2004) also reported similar trend for the permeate fluxes [102]. As in color retentions steady fluxes were achieved at about 4 h of operation.

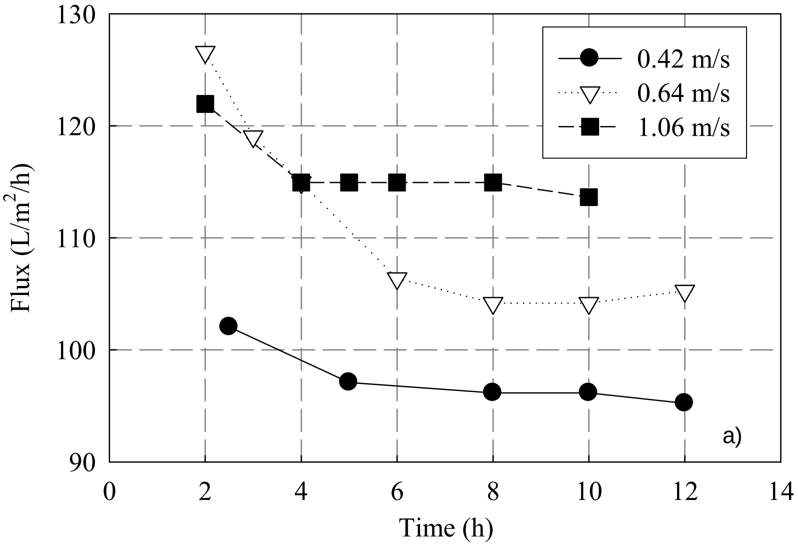


Figure 6.7. Effect of CFV on permeate flux of 0.45 µm cross-flow MF after 5 µm prefiltration

In addition to color retention and flux evaluations, fouling of 0.45 µm membrane was also evaluated for different CFVs and the results given in Table 6.6 were obtained. The lowest flux decline was obtained at 1.06 m/s CFV. As the CFV increased, flux decline and fouling decreased and flux recovery increased. A greater CFV provides a higher shear flow to reduce the concentration polarization and also increases the turbulence on the feed side of membrane to reduce solute precipitation, thus reducing fouling. At steady conditions, increase in CFV resulted in a decrease in flux decline and irreversible fouling which may be attributed to the decrease in mass and thickness of the cake layer formed in cross-flow MF of indigo dyeing wastewaters [102]. All above findings have indicated that, 1.02 bar TMP and 1.06 m/s CFV were the optimum conditions for the sequential 5 µm+0.45 µm MF application.

Table 6.6. Water flux, flux decline, recovery and irreversible fouling of 0.45 µm cross-flow MF after 5 µm prefiltration for three different CFVs (TMP: 0.48 bar)

Membrane	**0.42 m/s**	**0.64 m/s**	**1.06 m/s**
Water flux *(L/m^2/h)	191	167	164
Wastewater flux (L/m^2/h)	95	105	114
Water flux **(L/m^2/h)	171	170	168
Flux Recovery (%)	90	102	102
Flux Decline (%)	50	37	31
Irreversible Fouling (%)	10	0	0

*clean water flux with ultra pure water of virgin membrane
**water flux of fouled membrane after cleaning

6.1.2.2. Effect of Membrane Pore Size on Cross-flow MF after 5 µm MF

After determining the optimum CFV and TMP for 0.45 µm cross-flow MF after 5 µm dead-end prefiltration; additionally, the performances of 0.22 µm and 1.2 µm cross-flow MF alternatives as a sequential MF stage were assessed and compared with that of 0.45 µm membrane at a CFV of 1.06 m/s and a TMP of 0.48 bar.

Comparison of color retentions and fluxes of 0.45 µm and 0.22 µm membranes after 5 µm dead-end prefiltration (at a CFV of 106 m/s and TMP of 0.48 bar) is given in Figure 6.8 and 6.9. Color retention of 0.22 µm membrane was about 50% while that of 0.45 µm membrane was 30% at steady state.

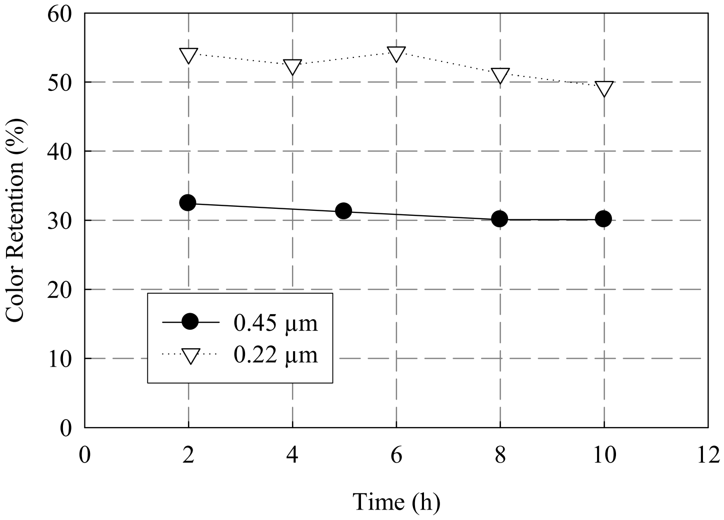


Figure 6.8. Comparison of color retentions of 0.45 µm and 0.22 µm cross-flow MF after 5 µm prefiltration

In Figure 6.9, comparison of wastewater and normalized fluxes of 0.45 µm and 0.22 µm cross-flow MF after 5 µm dead-end prefiltration are given. As can be seen, wastewater flux of 0.45 µm membrane at steady state was 114 L/m^2/h and twice that of 0.22 µm. In parallel with the permeate flux, normalized flux of 0.45 µm was higher than that of 0.22 µm membrane. The flux decline was higher in 0.22 µm membrane than that those for 0.45 µm membrane at 1.06 m/s CFV and 0.48 bar TMP conditions (Figure 6.9 b).

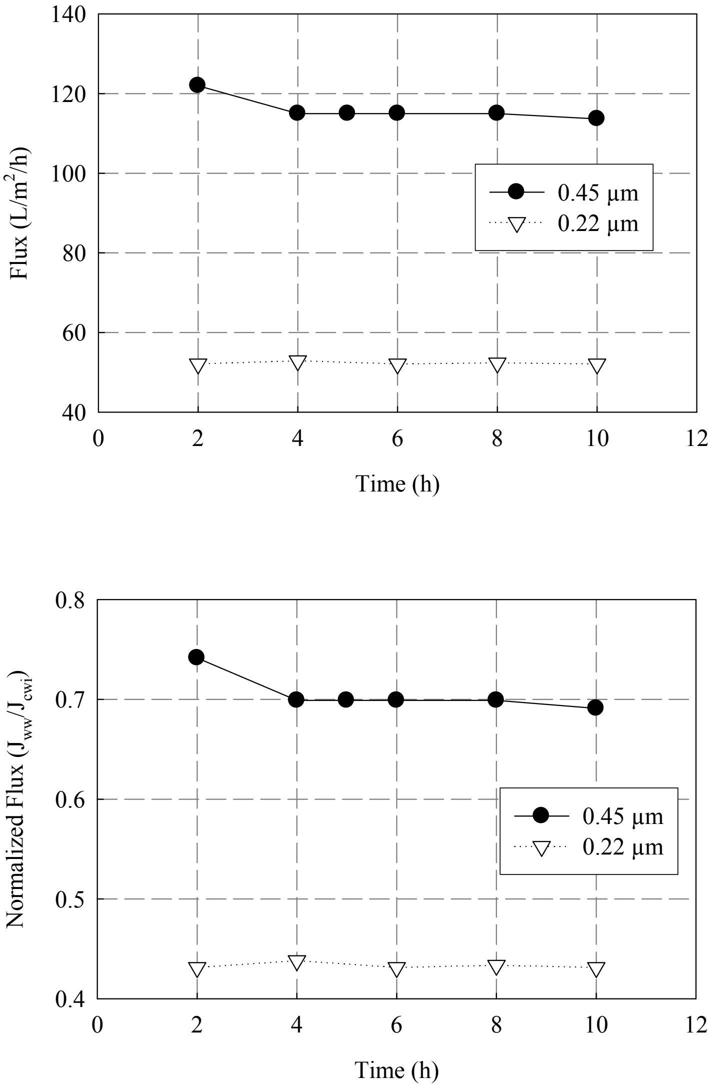


Figure 6.9. Comparison of a) permeate and b) normalized fluxes of 0.45 µm and 0.22 µm cross-flow MF after 5 µm prefiltration

Water flux, flux decline and flux recovery and irreversible fouling of 0.45 µm and 0.22 µm membranes after 5 µm dead-end prefiltration are given in Table 6.7. Total flux decline and irreversible fouling of 0.22 µm membrane were higher than those of 0.45 µm membrane but not significantly. Flux recoveries of the two membranes were quite high and over 90%.

Table 6.7. Comparison of water fluxes and flux decline, recovery and irreversible fouling of 0.45 μm and 0.22 μm membranes after 5 μm prefiltration

Membrane	**0.45 μm**	**0.22 μm**
Water flux *(L/m^2/h)	164	121
Wastewater flux (L/m^2/h)	114	52
Water flux **(L/m^2/h)	168	110
Flux Recovery (%)	100	91
Flux Decline (%)	31	57
Irreversible Fouling (%)	0	9

*clean water flux with ultra pure water of virgin membrane
**water flux of fouled membrane after cleaning

According to the results obtained in the comparison of 0.45 μm and 0.22 μm membranes after 5 μm dead-end prefiltration, 0.22 μm membrane was better in terms of color retention, and 0.45 μm membrane was better in terms of permeate flux and fouling behavior.

After determining that the 0.45 μm was superior to 0.22 μm MF in terms of permeate flux and flux recovery but not in terms of color retention, performances of 0.45 μm and 1.2 μm membranes were also compared. Comparison of color retention of 0.45 μm and 1.2 μm membranes after 5 μm dead-end prefiltration at a CFV of 106 m/s and TMP of 1.02 bar is given in Figure 6.10. Color retention of 1.2 μm membrane was quite lower than that of 0.45 μm membrane. Color retention of 0.45 μm membrane was in the range of 20-28% while that of 1.2 μm membrane was in the range of 0-5%. As can be seen from Figure 6.10, color retention for 1.2 μm was quite low and nearly no color retention was obtained.

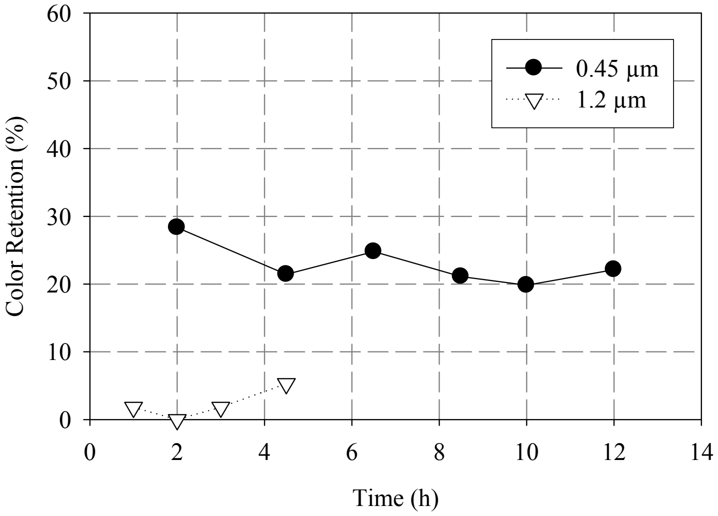


Figure 6.10. Comparison of color retentions of 0.45 µm and 1.2 µm cross-flow MF after 5 µm prefiltration

In Figure 6.11 a and b, comparison of permeate and normalized fluxes of 0.45 µm and 1.2 µm cross-flow MF after 5 µm dead-end prefiltration at a CFV of 1.06 m/s, and a TMP of 1.02 bar is given. As can be seen, wastewater flux of 0.45 µm at steady state was 147 L/m^2/h and lower than that of 1.2 µm. In parallel with the permeate flux, normalized flux of 1.2 µm was higher than that of 0.45 µm membrane. The flux decline was higher for 0.45 µm membrane at 1.06 m/s CFV and 1.02 bar TMP conditions than for 1.2 µm membrane (Figure 6.11 b).

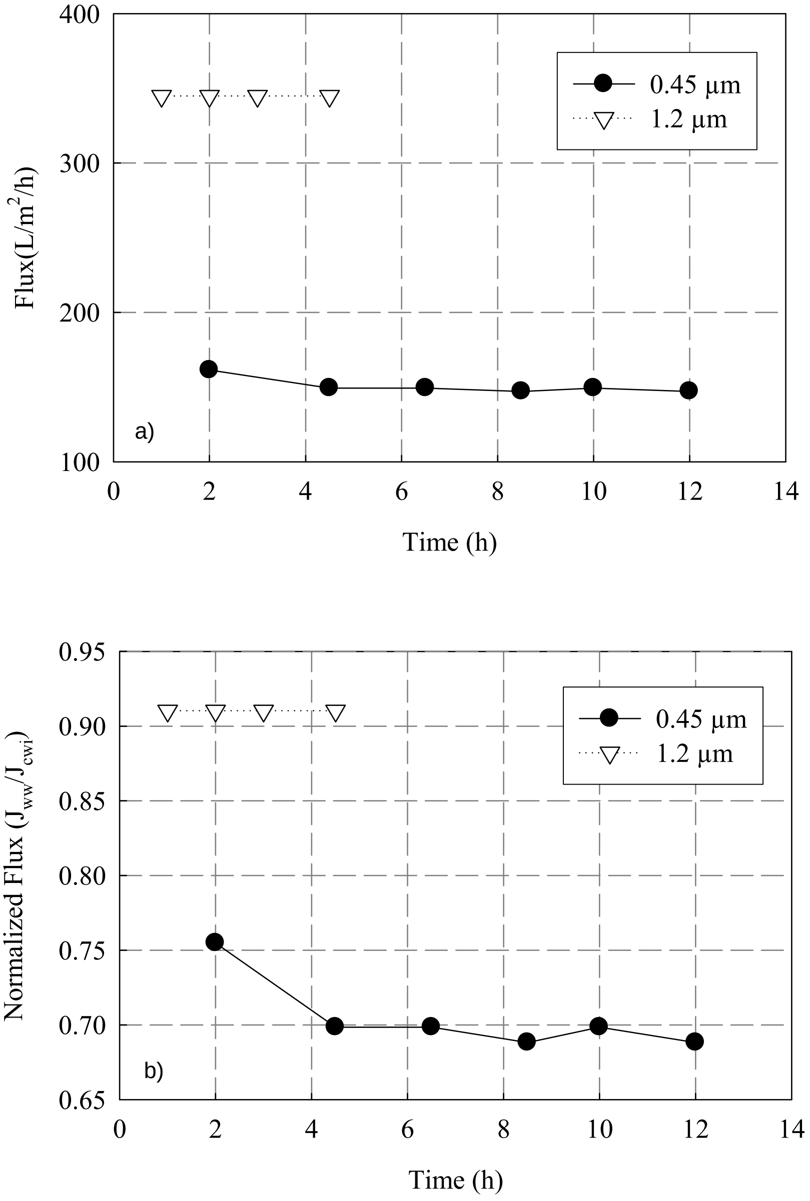


Figure 6.11. Comparison of a) permeate and b) normalized fluxes of 0.45 µm and 1.2 µm cross-flow MF after 5 µm prefiltration

In addition to permeate flux evaluation as a function of time, fouling of 0.45 µm and 1.2 µm membranes after 5 µm dead-end prefiltration was also evaluated and the results given in Table 6.8 were obtained. Total flux decline and irreversible fouling of 0.45 μm membrane was higher than 1.2 μm membrane. Flux recovery for 1.2 μm membrane was quite higher than that for 0.45 μm membrane.

Table 6.8. Water fluxes, flux decline and flux recovery and irreversible fouling of 0.45 μm and 1.2 μm membranes after 5 μm prefiltration

Membrane	**0.45 μm**	**1.2 μm**
Water flux *(L/m^2/h)	214	379
Wastewater flux (L/m^2/h)	147	345
Water flux **(L/m^2/h)	180	373
Flux Recovery (%)	84	99
Flux Decline (%)	31	9
Irreversible Fouling (%)	16	1

*clean water flux with ultra pure water of virgin membrane
**water flux of fouled membrane after cleaning

Although water fluxes and flux recovery for 1.2 μm MF membrane were higher than those for the 0.45 μm membrane, 0.45 μm MF membrane was found to be more effective in terms of permeate color and color retention (Table 6.8). In addition, no substantial increase in color retention was observed for 1.2 μm MF membrane after 5 μm dead-end MF.

6.1.2.3. Concentration Mode of 0.45 μm MF after 5 μm MF

Concentration mode of filtration tests were performed to achieve water recovery and to understand membrane performance under the conditions of worsening feed quality with time due to increased volume recovery fraction. In concentration mode of 0.45 μm cross-flow MF tests, wastewater pH was adjusted to 7.0±0.2 after 5 μm dead-end MF and 30 L of wastewater was filtered thru 0.45 μm MF. The flux decline was monitored and the results given in Figure 6.12 were obtained. The experiment was continued till the volume of the feed decreased to 10% of the initial feed volume. The permeate flux which was 152 L/m^{2}h after 1 h decreased to 95 L/m^{2}h in the end. As can bee seen, normalized flux decreased in parallel to wastewater flux. The decline in flux was similar to the levels in total recycle mode of filtration.

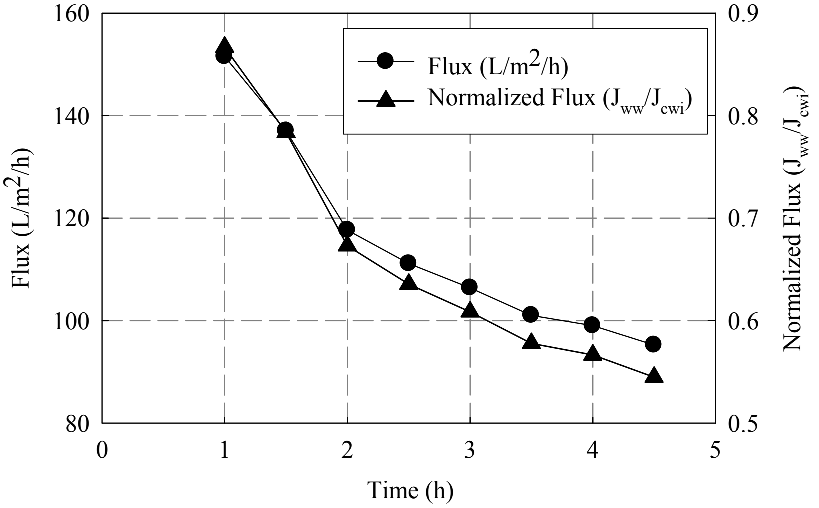


Figure 6.12. Wastewater flux and normalized flux of concentration mode of 0.45 μm filtration as a function of time after 5 μm prefiltration

In Figure 6.13, feed and permeate color values and the corresponding color retention for 0.45 μm MF in concentration mode are given. As seen, although the feed color was increased with time, permeate color and color retentions were nearly constant during the filtration period. As the feed solution increases no significant change was observed in permeate color was found as independent from the feed solution concentration.

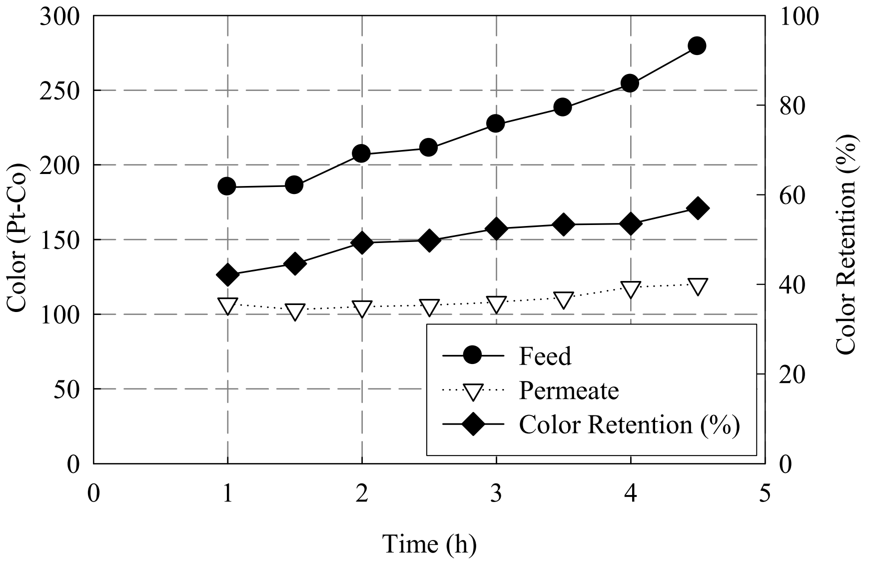


Figure 6.13. Feed and permeate color and retention of concentration mode of 0.45 μm filtration as a function of time after 5 μm prefiltration

6.1.3. Coagulation

The subsequent set of experiments were conducted to investigate the effectiveness of coagulation as pretreatment and also to find the optimal conditions, i.e. pH and coagulant ($FeCl_3.6H_2O$ and $Al_2SO_4.18H_2O$) dose, for maximum color and COD removal which will cause fouling of the further membrane/s (UF/NF/RO) from the indigo dyeing wastewater.

Destabilization of wastewater was examined at pH 3-10 for both coagulants at a dose range of 25-1000 mg/L and the results presented in Table 6.9 were obtained. As can be seen, with the increasing concentration of $FeCl_3.6H_2O$ coagulant, color and COD retentions increased. The maximum color and COD retentions were 83% and 12%, respectively, at the dose of 100 mg/L $FeCl_3.6H_2O$. As for the $Al_2SO_4.18H_2O$ coagulant, the maximum color and COD retentions were 68% and

12%, respectively, at the 1000 mg/L $Al_2SO_4.18H_2O$ concentration. Hence, $FeCl_3.6H_2O$ appeared to be a better coagulant than $Al_2SO_4.18H_2O$, as its optimum concentration is ten folds lower than that of alum, along with much higher color retention. For $FeCl_3.6H_2O$, the coagulant dose increased from 100 to 1000 mg/L but no significant increase was obtained in color retentions. One can say that over 100 mg/L $FeCl_3.6H_2O$ dose, color retentions were independent from the dose of the coagulant.

Table 6.9 Optimum coagulant dose determination experiment results of $FeCl_3.6$ H_2O and $Al_2SO_4.18$ H_2O

Type	**Coagulant dose (mg/L)**	**Parameters**		
		pH*	**Color Retention (%)**	**COD Retention (%)**
$FeCl_3.6$ H_2O	Original wastewater	12.0	na	na
	25	12.0	54	8
	50	12.0	72	11
	75	12.0	80	12
	100	12.0	83	12
	150	12.0	82	15
	250	11.9	83	13
	500	11.8	82	16
	750	11.7	84	18
	1000	11.5	86	19
$Al_2SO_4.18$ H_2O	Original wastewater	12.0	na	na
	25	12.0	3	<dl
	50	12.0	8	<dl
	75	12.0	5	<dl
	100	12.0	7	<dl
	150	11.9	5	<dl
	250	11.9	7	<dl
	500	11.9	10	<dl
	750	11.7	38	6
	1000	11.5	68	12

* pH values measured at the end of the experiments,

na:not applicable, <dl: under detection limit

As can be depicted from Table 6.9, for both coagulants (and at all the coagulant concentrations examined), no significant decrease was observed in pH after coagulation. For the highest coagulant concentration (1000 mg/L), wastewater pH decreased from 12.0 (original pH of the wastewater) to only 11.5 for both of the coagulants as the alkalinity of the wastewater is sufficiently high. Also no significant change was observed in the conductivity of the wastewater after coagulation for both of the coagulants tested.

Table 6.10. Optimum pH determination experiment results of $FeCl_3.6\ H_2O$ and $Al_2SO_4.18\ H_2O$

		Parameters		
Type	**Initial pH**	**pH ***	**Conductivity (mS/cm)**	**Color Retention (%)**
$FeCl_3.6\ H_2O$ (100mg/L)	Original wastewater	12.0	11.7	na
	pH12.0	12.0	11.4	80
	pH 10.0	9.9	10.0	55
	pH 9.0	8.7	10.1	63
	pH 8.0	8.0	10.1	3
	pH 7.0	7.1	10.3	8
	pH 6.0	6.1	10.5	5
	pH 3.0	3.1	11.1	6
$Al_2SO_4.18\ H_2O$ (500mg/L)	Original Wastewater	12.0	11.7	na
	pH12.0	11.8	10.4	9
	pH 10.0	9.0	9.7	30
	pH 9.0	9.0	9.8	62
	pH 8.0	7.5	9.8	70
	pH 7.0	6.9	9.9	73
	pH 6.0	5.8	10.2	89
	pH 3.0	3.2	10.8	31

*pH values measured at the end of the experiments, na: not applicable

On the other side, the optimum pH which provides maximum color retention was obtained as 6 for $Al_2SO_4.18H_2O$ and as 12 for $FeCl_3.6H_2O$ (Table 6.10) From a comparison of Tables 9 and 10, it is evident that $FeCl_3.6H_2O$ is a better coagulant than $Al_2SO_4.18H_2O$, as the execution of coagulation at the original wastewater pH gives an opportunity to eliminate acid addition to reduce the pH of the indigo dyeing rinsing wastewaters. Golob and Ojstrsek (2005), also reported higher dye removals with $FeCl_3.6H_2O$ coagulant than $Al_2SO_4.18H_2O$ in the removal of three vat dyes, that indigo is a sub dye of this dye class [103]. In an attempt to explain the precipitation mechanism, zeta potential measurements were performed for samples coagulated with $FeCl_3.6H_2O$ at the dose 100mg/L. The original wastewater zeta potential which is -32.57 mV has not changed at all after coagulation and determined as -34.04 mV. This observation has probably indicated that coagulation is not by charge neutralization. At pH values higher than pH 6.5, the ferric flocs became negatively charged and at these high pH values Fe $(OH)^{4-}$ becomes the dominant species. The prevailing mechanism was though to be sweep floc as at higher pHs Fe exists as $Fe(OH)_3$ precipitate.

6.1.4 UF

As to investigate the possible improvement in the quality of the permeate from MF before NF and RO processes UF experiments were carried out. The alternatives considered in UF experiments are given in Figure 6.14. After MF of raw indigo dyeing wastewater, two different feed solutions for UF alternatives were obtained and named as F1 and F2 as given in Figure 6.14. In UF experiments, different pore sized UF membranes (100, 50, 20, 2, 1 kDa) were tested in terms of permeate flux, color and COD retention at TRMF and F1 was used as a feed water at this stage of the study. F2 feed water was tested for only 100 kDa and 50 kDa membranes.

The effects of fouling on the UF membrane separation efficiency was also examined by comparing the permeate flux, color and COD retentions of clean and fouled 100 kDa and 50 kDa UF membranes again at TRMF. Based on the results obtained in UF tests described above, concentration mode of filtration experiments were carried out only with 100 kDa membrane. In the following sections, findings from UF experiments are presented.

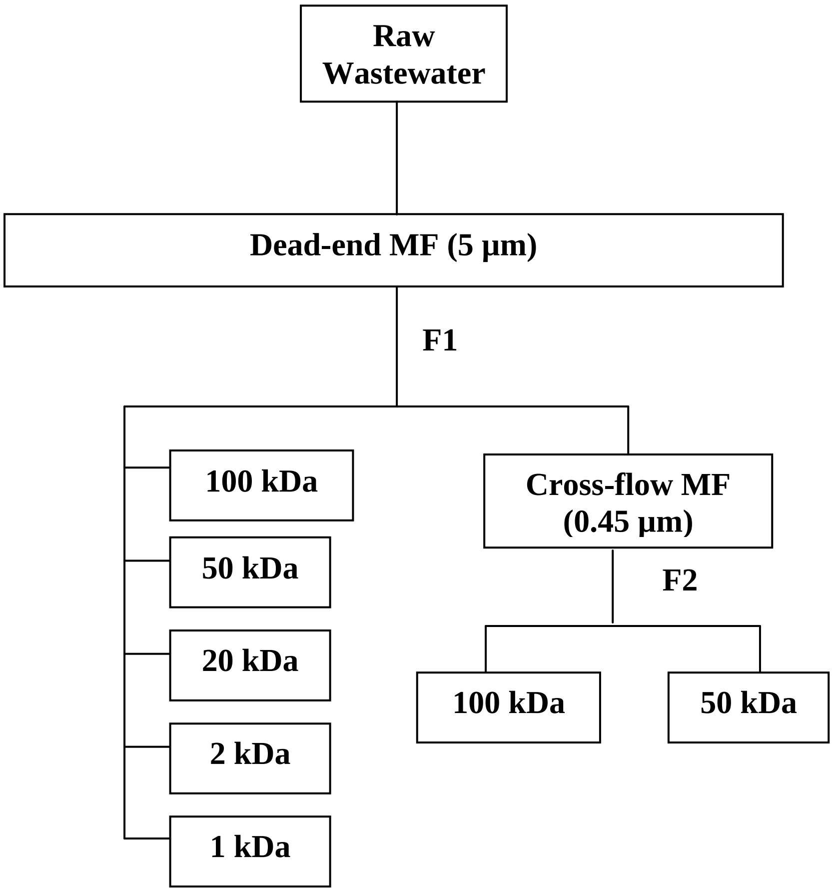


Figure 6.14. MF/UF alternatives tested for the indigo dyeing wastewater

6.1.4.1. Single MF followed by UF

In this series of experiments, 5 µm dead-end MF was followed by 100, 50, 20, 2 and 1 kDa UF at TRMF and the time dependent color retentions presented in Figure 6.15 were obtained. As can be seen, color retentions by UF were steady after 2h of filtration, and in general, there was a reduction in color removal with an increase in membrane MWCO. This finding was in agreement with Alves and Pinho (2000), who reported that the tightest membranes present high color rejections of the wastewater coming from tannery industry [104]. As can be depicted from Figure 6.15, the highest color retention of about 71-76 % was obtained for UF with 2 kDa membrane while the lowest of 36-52% was for UF with 50 kDa membrane. Unexpectedly, color removal by 100 kDa membrane was higher than that by 1 kDa membrane; possibly due to different chemical structures and not homogenous pore size distributions.

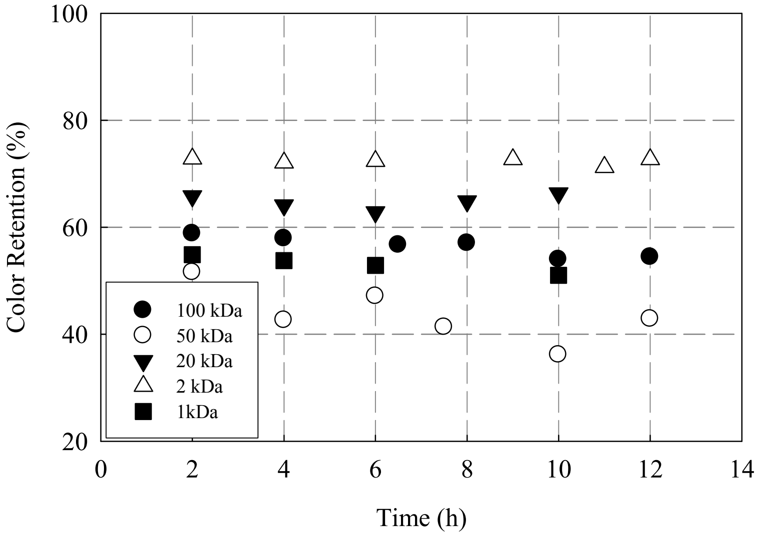


Figure 6.15. Time dependent color retention in UF using F1 as feed

As for the comparison of UF membrane performances after 5 µm MF at steady conditions, the results presented in Table 6.11 were obtained. All UF membranes provided a high cumulative color retention of about 98-99 % and the permeates' color were found at around 37-68 Pt-Co. The highest permeate color was obtained for 50 kDa as 68 Pt-Co and the lowest for 2 kDa membrane as 37 Pt-Co. In UF experiments, permeate color values and color retentions (Table 6.11) achieved were comparable to those obtained with NF membranes [95, 105]. Lopes et al. (2005) reported 99% color retention for the two different NF membranes in the treatment of textile wastewaters [105]. In addition to this, Petrinic et al. (2002) also reported over 99 % color retentions for the treatment for four different reactive dyes with NF membranes [95].

On the other side, cumulative COD retentions by all the UF membranes were also similar but not as high as color retentions. COD retentions were observed to be at around 45-59% (Table 6.11). The highest COD retention was obtained for 100 kDa membrane as 59% and the lowest for 1 kDa membrane as 45%. This finding is in fact expected as UF membranes are known with their suitability for the retention of particles and macromolecules but not dissolved organic matter [77, 106]. As presented in Table 6.11 no significant conductivity retention was obtained in UF experiments. There was only a slight decrease in permeate conductivity with decreasing membrane MWCO. In literature UF membranes were reported as their suitability for extensively removing suspended solid content, but it had difficulty in removing dissolved solids [106].

Table 6.11. Comparison of UF membrane performances using F1 as feed at steady state conditions

Membrane	Final Permeate Quality			Cumulative Retention (%)		
	COD (mg/L)	Color (Pt-Co)	Conductivity (mS/cm)	COD	Color	Conductivity
100 kDa	726	57	11.1	59	98	9
50 kDa	772	68	11.2	56	98	9
20 kDa	759	37	9.7	51	99	10
2 kDa	882	38	10.8	47	99	11
1 kDa	859	48	9.7	45	99	15

In an attempt to investigate the flux performances of UF membranes after 5 µm MF, flux data presented in Figure 6.16 was collected. As expected, the highest permeation rates were obtained for coarse membranes; 100 kDa and 50 kDa, and the lowest for 2 kDa membrane. In essence, the wastewater permeabilities of 20, 2 and 1 kDa membranes were nearly the same and quite lower than those for 100 kDa and 50 kDa membranes.

In opposition to permeabilities, normalized fluxes of 100 kDa and 50 kDa membranes were lower than those of the other UF membranes tested. Normalized fluxes of 20, 2 and 1 kDa membranes were quite similar to each other and higher than those of 100 kDa and 50 kDa membranes (Figure 6.16 b). This observation has indicated that, the particles in the wastewater applied to UF are in the size range of 50 and 100 kDa membranes.

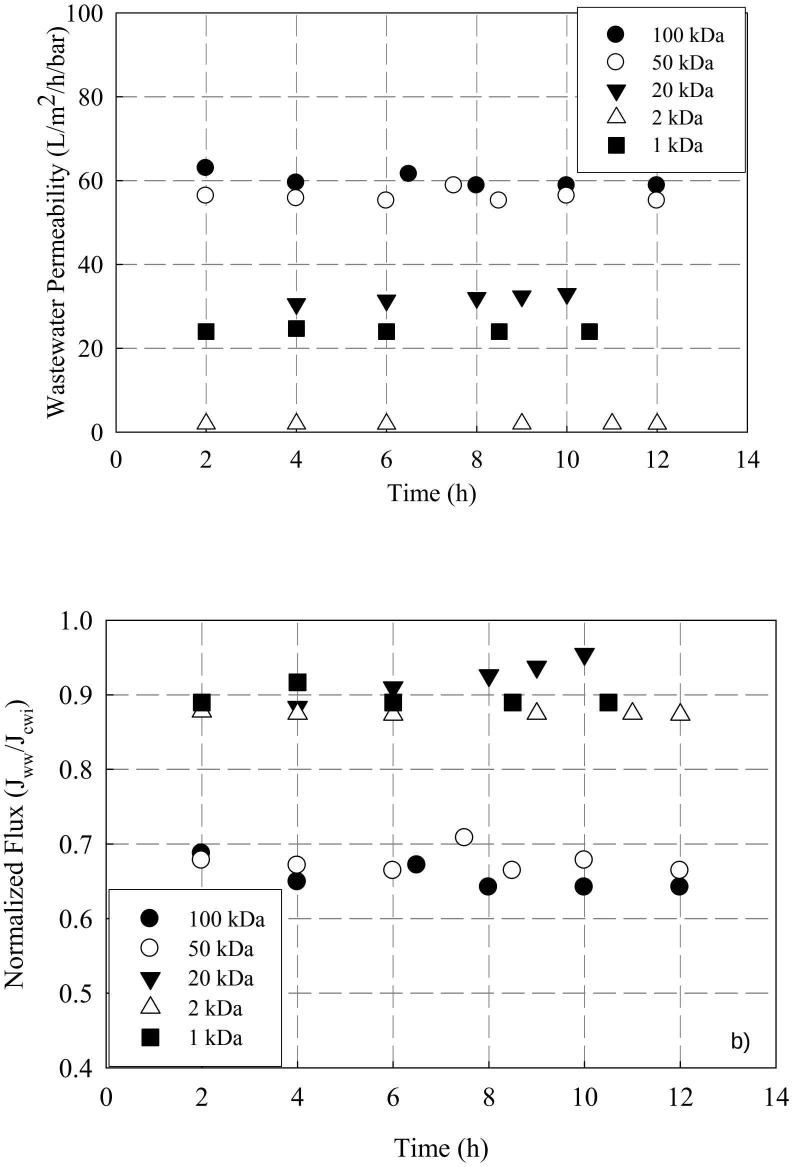


Figure 6.16. Comparison of a) wastewater permeability and b) normalized fluxes as a function of time for UF membranes using F1 as feed

Table 6.12, presents the steady state wastewater permeability measurements and fouling tendencies of all UF membranes tested in a comparative way. As expected, the clean water permeability decreased with the decrease in molecular cut-off of the membranes. However surprisingly, the clean water permeability for 1 kDa was higher than 2 kDa membrane. This anomaly may be attributed to the nature of the 1 kDa membrane. Four of the UF membranes used in experiments are made of PS except 1 kDa membrane, which is made of a composite fluoro polymer (Table 5.6). In parallel with clean water permeability, permeate permeability of coarser UF membranes (100 kDa and 50 kDa) was higher than those of the finer (20 kDa, 2 kDa and 1 kDa) UF membranes.

Although pure water and wastewater permeability for 100 kDa and 50 kDa membranes were similar and much higher than those for the other membranes tested, flux decline for these two membranes were severe (Table 6.12). The flux decline was thought to be mainly caused by the dyes and other chemicals used in dyeing operations. This flux decline was partly reversible because of the osmotic pressure of the feed mixture, and partly irreversible because of pore blocking and adsorption of organic compounds on the membrane surface [95].

Table 6.12. Water permeability, flux decline, recovery and irreversible fouling of the UF membranes using F1 as feed

Membrane	**100 kDa**	**50 kDa**	**20 kDa**	**2 kDa**	**1 kDa**
Water permeability * ($L/m^2/h/bar$)	91	83	35	2	27
Wastewater permeability ($L/m^2/h/bar$)	59	55	33	2	24
Water permeability ** ($L/m^2/h/bar$)	60	59	35	2	27
Flux Recovery (%)	66	71	100	100	100
Flux Decline (%)	36	34	5	14	11
Irreversible Fouling (%)	34	29	0	0	0

*clean water permeability with ultra pure water of virgin membrane
**water permeability of fouled membrane after cleaning

The highest irreversible fouling and lowest flux recovery were obtained for 100 kDa and 50 kDa membranes. However, for 20 kDa, 2 kDa and 1 kDa membranes no irreversible fouling and complete flux recovery were obtained (Table 6.12). Irreversible fouling of the 100 kDa and 50 kDa membranes were determined as 34% and 29%, respectively and explained as pore blocking and adsorption of organic materials.

Total flux declines for 20, 2 and 1 kDa membranes were quite low as compared to 100 kDa and 50 kDa membranes. Flux decline for these membranes were thought to be due to concentration polarization and found to be completely reversible.

As it is highlighted above, in UF experiments after 5 µm dead-end MF, the best performance was achieved for 50 and 100 kDa UF membranes in terms of permeation rate, color and COD retentions. However, with these membranes, fouling was much more severe as compared to tighter ones.

Based on all these findings, 50 and 100 kDa membranes were selected as the most suitable UF membranes after 5 µm MF. Nevertheless, considering the serious flux decline with these membranes, it was proposed that the fouling observed with these membranes should somehow be reduced. It was thought that this could be achieved by a sequential MF application and a tighter MF of 0.45 µm was chosen as a sequential MF step after 5 µm.

6.1.4.2. Sequential MF followed by UF

At this phase of the experimental studies, as pointed out before, the permeation rates of 100 kDa and 50 kDa membranes were tried to be increased by sequential MF application. Permeate from 5 µm MF was sequentially filtered through 0.45 µm MF before 50 and 100 kDa UF. Fig 6.17 and Table 6.13 present the retentions and permeate quality achieved.

As can be seen in Figure 6.17, color retentions by both UF membranes were quite similar and at around 36-38% for 50 kDa and 32-34% for 100 kDa membrane, respectively and essentially not much different than obtained without 0.45 µm MF (Table 6.11).

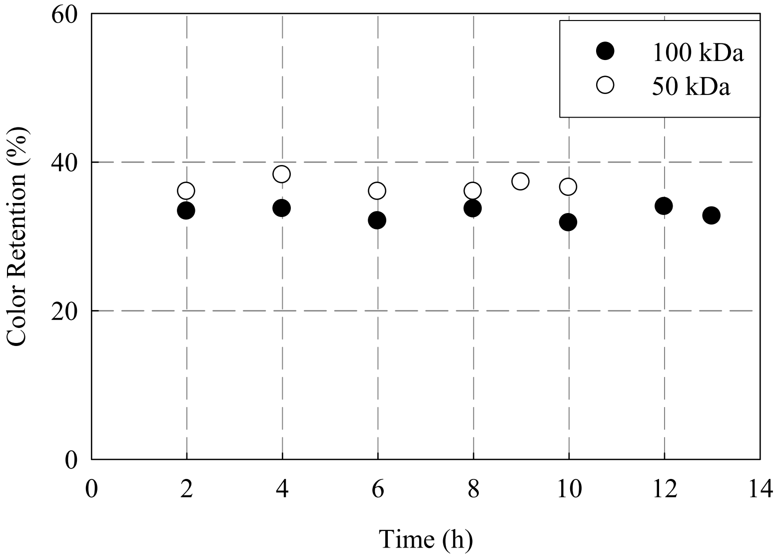


Figure 6.17. Comparison of color retentions as a function of time for 100 kDa and 50 kDa UF membranes using F2 as feed

Further, comparison of performances of 100 kDa and 50 kDa UF membranes that used F2 as feed water at steady conditions is presented in Table 6.13. The permeate color of 100 kDa was 70 Pt-Co and higher than 50 kDa membrane which was 66 Pt-Co. When there is single stage MF using 5 µm membrane, the corresponding final permeate's color values were 57 and 68 Pt-Co (Table 6.11).

Therefore, there was no improvement in color retention by the application of 0.45 µm MF after 5 µm. This finding was not surprising as 5 µm membrane alone removed almost all color in the wastewater. Also, the retentions achieved in COD with and without 0.45 µm MF were not different (Table 6.11 and 6.13).

Table 6.13. Comparison of performances of 100 kDa and 50 kDa UF membranes using F2 as feed at steady state conditions

Membrane	**Final Permeate Quality**			**Cumulative Retention (%)**		
	COD (mg/L)	**Color (Pt-Co)**	**Conductivity (mS/cm)**	**COD**	**Color**	**Conductivity**
100 kDa	850	70	11.0	61	98	10
50 kDa	802	66	11.2	54	98	9

In Figure 6.18, time variation of wastewater permeability was given for UF membranes using F2 as feed water. As seen, for both of the UF membranes, steady permeabilities were reached at around 6 h, and at that time for 100 kDa membrane the wastewater permeability was at around 71 L/m^2/h/bar, and for 50 kDa it was 51 L/m^2/h/bar. In contrast, normalized fluxes of 50 kDa were slightly higher than 100 kDa membranes (Figure 6.18).

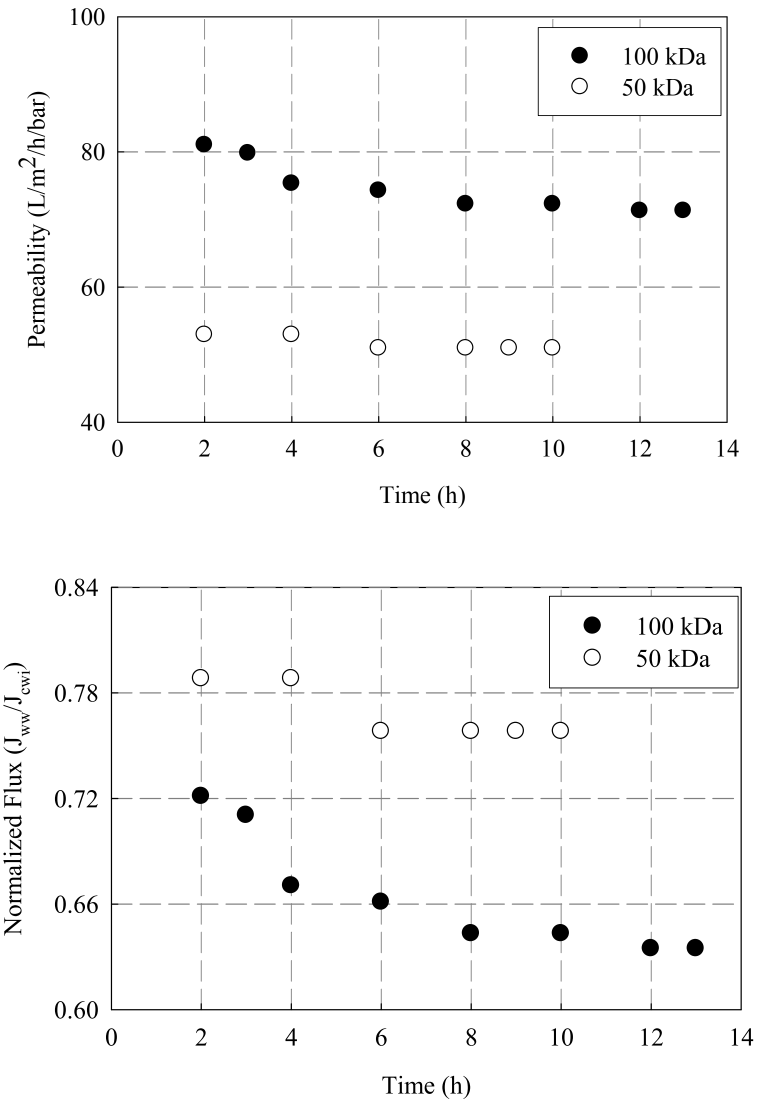


Figure 6.18. Comparison of a) wastewater permeability and b) normalized fluxes as a function of time for 100 kDa and 50 kDa UF membranes using F2 as feed

After 5 µm+0.45 µm prefiltration, total flux decline and irreversible fouling of 100 kDa was higher than those of 50 kDa membrane (Table 6.14). In addition, flux recovery of 100 kDa was lower than that of 50 kDa membrane.

Table 6.14. Water permeability, flux decline and recovery and irreversible fouling of the UF membranes measured using F2 as feed

Membrane	**100 kDa**	**50 kDa**
Water permeability *(L/m2/h/bar)	112	67
Wastewater permeability (L/m2/h/bar)	71	51
Water permeability **(L/m2/h/bar)	67	53
Flux Recovery (%)	60	79
Flux Decline (%)	37	24
Irreversible Fouling (%)	40	21

*water permeability with clean water of virgin membrane
**water permeability of fouled membrane after cleaning

In order to highlight the effect of MF on UF performance, Table 6.15 that presents information on color, COD and conductivity retentions by 100 kDa and 50 kDa UF membranes was prepared. As can be seen, for 100 kDa UF membrane for both of the MF prefiltration alternatives; color, COD and conductivity retentions were nearly the same. Although the wastewater permeabilites of 100 kDa membrane that used F2 as feed water was higher than the that used F1 as feed water, additional 0.45 µm MF has provided no additional color, COD and conductivity removals. F2 feed water had lower concentration of solids in the wastewater than F1 feed water and this is resulted as higher permeation rates of 100 kDa membrane which is used F2 as feed water. Permeation rates and retentions of 50 kDa membrane for both of the prefiltration alternatives were similar and as seen, there was no clear effect of additional 0.45 µm MF before UF.

Table 6.15. Comparison of the effect of feed water (F1 and F2) on the performance of 100 kDa and 50 kDa UF membranes

Membrane	**Wastewater Permeability ($L/m^2/h/bar$)**	**Total Flux Decline (%)**	**Irreversible Fouling (%)**	**Cumulative Retention (%)**		
				Color	**COD**	**Conductivity**
F1+100 kDa	59	36	34	98	59	9
F2+100 kDa	71	37	40	98	61	10
F1+50 kDa	55	34	29	98	56	9
F2+50 kDa	51	24	21	98	54	9

Coming to the effect of sequential MF application, one can easily depict that there was no net favorable effect of 0.45 µm MF on UF performance, especially on the performance of 100 kDa membrane. With and without 0.45 µm MF, the total flux decline for 100 kDa membrane was the same. Likewise, irreversible fouling observed in these two cases was also quite comparable. On the other hand, in case of 50 kDa UF, there was a benefit of having 0.45 µm MF after 5 µm MF. Total flux decline has reduced from 34 % down to 24 % with the sequential MF application.

When these benefits of having 0.45 µm MF after 5µm are considered jointly with the color and COD retentions achieved; it was decided that it would not be feasible to have a secondary MF step, just for an average 10 % improvement in irreversible fouling. It was thought that secondary MF before UF will bring additional investment and operational costs when this process is applied at field scale.

After all investigations, it was decided that 5 µm+100 kDa (MF+UF) sequence is the optimum pretreatment sequence, therefore forthcoming NF/RO tests should be carried out with the permeate from this sequence.

6.1.4.3. Concentration Mode of 100 kDa UF after 5µm MF

Considering to the results obtained in UF experiments using F1 and F2 feed water alternatives, to evaluate the performance of the system under the conditions of worsening feed quality, concentration mode of 100 kDa experiment using F1 as feed water was performed. Concentration mode of 100 kDa UF test was performed under 1.87 bar TMP and 1.29 m/s CFV conditions.

Wastewater to be fed to concentration mode of 100 kDa UF was prepared by passing 30 L wastewater sample thru 5 µm dead-end MF and adjusting its pH to 7.0±0.2. In Figure 6.19, feed and permeate color values and color retentions of concentration mode of 100 kDa UF membrane as a function of time is given. As can be seen, feed color has increased with time. At the beginning of the experiment feed color was 149 Pt-Co and at the end it increased to 306 Pt-Co. However, permeate color values and color retention did not change significantly.

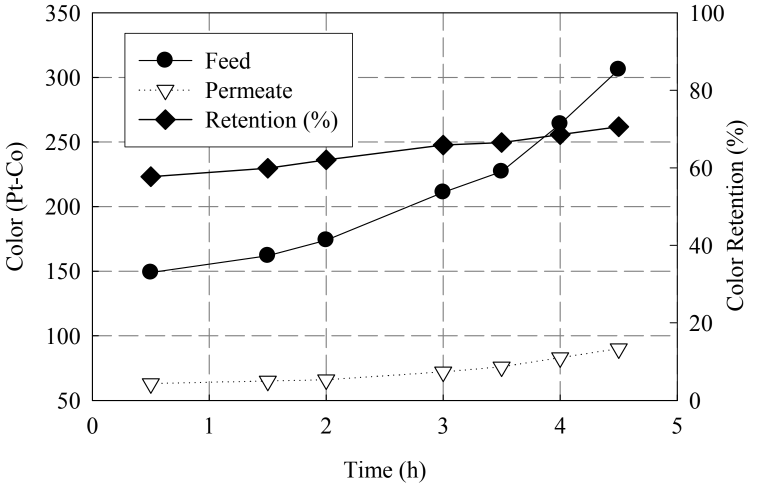


Figure 6.19. Feed and permeate color and color retentions of concentration mode of 100 kDa UF membrane using F1 as feed

In Figure 6.20, time dependent feed and permeate COD values and COD retentions by 100 kDa membrane at concentration mode is given. As can be seen, feed COD also increased with time but not as much as feed color. At the beginning of the experiments feed COD was 1273 mg/L and at the end it increased to 1593 mg/L while permeate COD and retention of COD did not changed significantly. All COD and color retention results revealed that although the feed quality worsened the retentions did not changed significantly as in concentration mode of 0.45 μm filtration tests.

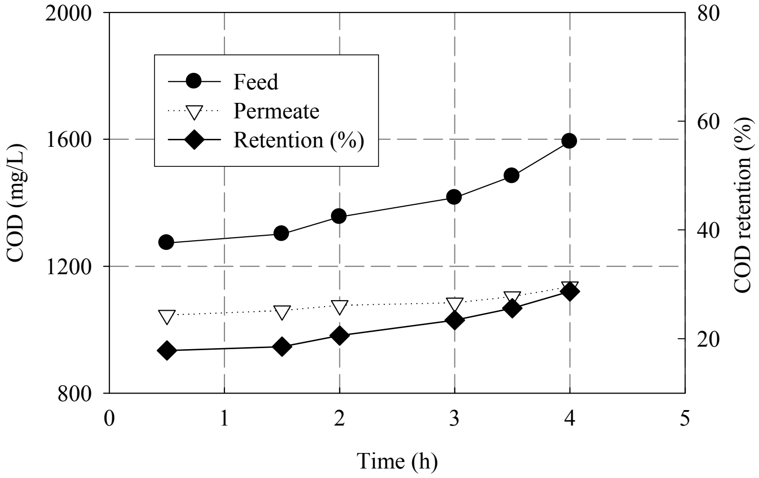


Figure 6.20. Feed and permeate COD and COD retentions of concentration mode of 100 kDa UF membrane using F1 as feed

In addition to color and COD retentions, the changes in permeate and normalized fluxes were monitored (Figure 6.21). As can be seen from Figure 6.21, permeate flux was steady after 4th hour and thus the test was ended at 4.5th hour. At this time, permeate flux was 95 L/m^2/h; at about 24% less than the original value of 124 L/m^2/h. At the end of the experiment, the volume of the feed was decreased to 10% of its beginning volume.

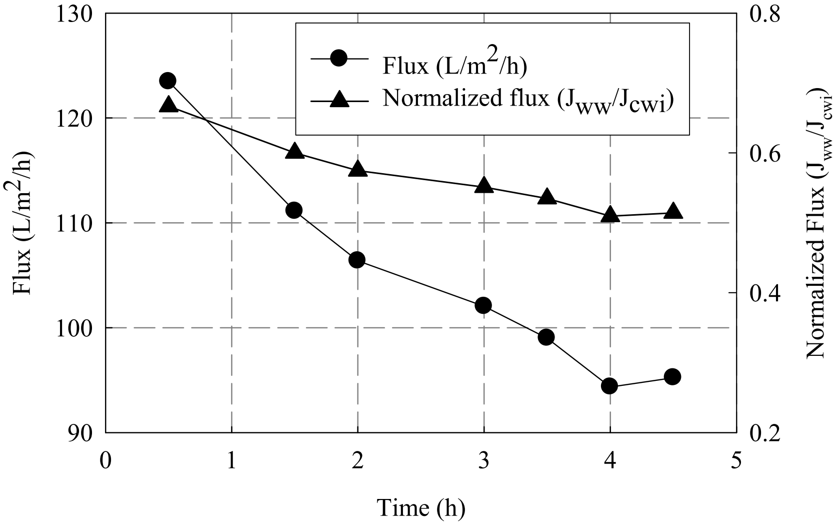


Figure 6.21. Wastewater fluxes and normalized fluxes of concentration mode of 100 kDa UF membrane using F1 as feed

CHAPTER 7

Reclamation and Reuse of Indigo Dyeing Wastewaters

7.1. NF

In this chapter, experimental findings from NF and RO experiments are presented. NF and RO experiments were performed as an additional stage to MF and UF processes to determine the best membrane treatment scheme for reusable water production. The effect of prefiltration, membrane type, pH and concentration on the performance of NF was investigated. Single and sequential stage NF and RO membrane performances were tested and evaluated in accordance with reuse criteria. The schematic representation of the experimental methodology followed in NF and RO experiments is given in Figure 7.1.

As indicated in section 7.1.2 and 7.2, three NF (NF 270, NF 90, Dow Filmtec USA; and NF 99, Alfa Laval, Denmark) and two RO (HR 98 PP ve CA 995 PE, Alfa Laval, Denmark) membranes were tested in this part of the experimental studies.

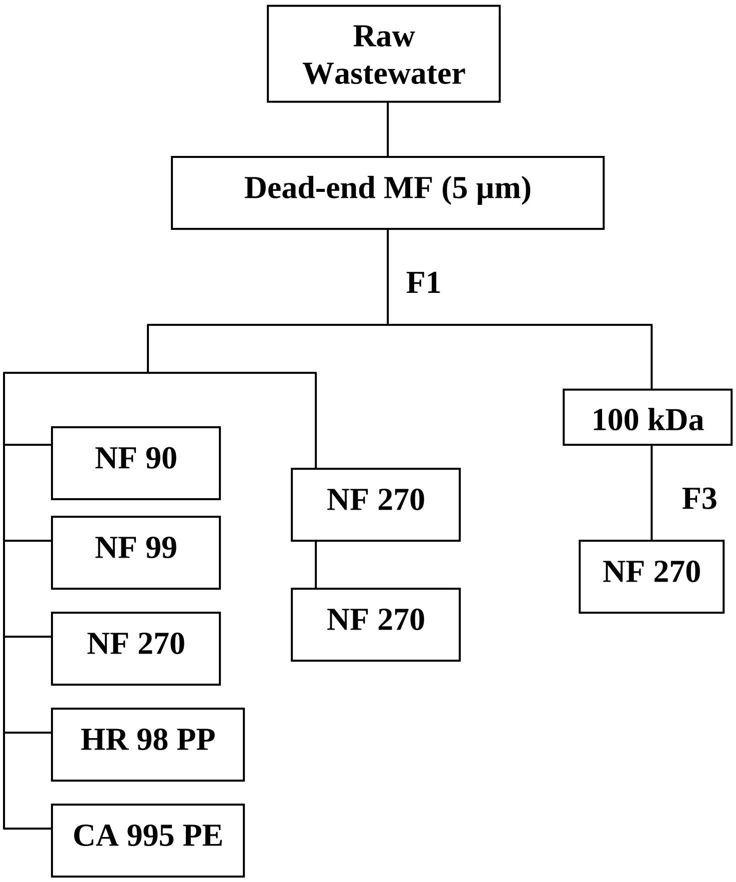


Figure 7.1. Schematic representation of experimental methodology followed in NF/RO experiments

7.1.1. Effect of Pretreatment

As presented in the preceding sections , single stage 5 µm MF and sequential stage 5 µm MF followed by 100 kDa UF prefiltration alternatives were determined as the optimum. These two prefiltration alternatives were considered for only NF 270 membrane and the best pretreatment alternative was selected for NF 270 membrane. This alternative was used as a prefiltration for the other NF and RO membranes tested.

Color, COD and conductivity retentions and permeate flux of NF 270 membrane after above mentioned prefiltration alternatives were evaluated in TRMF and the results at steady state conditions presented in Table 7.1 were obtained. (The time dependent color, COD and conductivity retentions and permeate flux are given in Appendix B in Figure B.1, B.2 and B.3).

For both of the prefiltration alternatives, the color retention of NF 270 membrane was over 90% (Table 7.1). For the first and second prefiltration alternatives, cumulative color retentions were 93% and 96%, respectively. As can be clearly seen, no significant difference was observed in color retention among the two prefiltration alternatives evaluated. COD retention of NF 270 using F1 as the feed was at around 92%, and higher than that of using F3 as the feed with 87%.

The overall findings indicated that, the application of F3 as the feed, did not provide any significant improvement in terms of color and COD retentions over F1 feed. Permeate conductivities for the two feed water alternatives were also quite similar. With an additional prefiltration thru 100 kDa UF membrane, no improvement was obtained in permeate conductivity of NF 270 membrane (Table 7.1).

Table 7.1. Comparison of NF 270 performance using F1 and F3 wastewaters as feed at steady state conditions

Membrane	**Flux ($L/m^2/h$)**	**Final Permeate Quality**			**Cumulative Retention (%)**		
		COD (mg/L)	**Color (Pt-Co)**	**Conductivity (mS/cm)**	**COD**	**Color**	**Conductivity**
F1+ NF 270	31	87	8	4.3	92	93	60
F3+ NF 270	37	115	2	4.4	87	96	59

In addition to the color, conductivity and COD retentions of NF 270 membrane, the permeate fluxes for these two prefiltration alternatives at steady state conditions were also evaluated (Table 7.1). The permeate flux of NF 270 membrane using F3 as the feed water was higher than that of using F1 as the feed. However, the improvement was not so much and at around 10%.

In Table 7.2, fouling behavior of NF 270 membrane after two prefiltration alternatives is presented. Although the wastewater flux of NF 270 membrane using F3 wastewater as feed was higher than that of using F1 wastewater, the flux decline and irreversible fouling were quite similar for both of the feed wastewater alternatives evaluated. The flux decline was thought to be due to concentration polarization, which was found to be completely reversible for both of the feed water alternatives tested (Table 7.2).

Table 7.2. Water flux, flux decline, flux recovery and irreversible fouling of NF 270 membrane using F1 and F3 wastewaters as feed

Membrane	**Prefiltration**	
	F1	**F3**
Water flux * (L/m^2/h)	64	70
Wastewater flux (L/m^2/h)	31	37
Water flux ** (L/m^2/h)	63	73
Flux Recovery (%)	98	104
Flux Decline (%)	52	47
Irreversible Fouling (%)	2	0

*water flux with clean water of virgin membrane
**water flux of fouled membrane after cleaning

All of the results given above revealed that, using an additional 100 kDa UF membrane as a second stage after 5 μm MF membrane did not result in a significant improvement in color and COD retentions and also in permeate flux by NF 270 membrane. Based on these findings, further NF and RO tests were carried out with 5 µm MF prefiltration only without 100 kDa UF.

7.1.2. Effect of Membrane Type

In this series of experiments, the performances of three different commercially available NF membranes (NF 99, NF 90 and NF 270) were evaluated in order to highlight the effect of NF membrane type on performance. For all NF membranes tested, F1 wastewater was used as the feed (Figure 7.1). Permeate quality and permeate flux achieved for these NF membranes are given in Table 7.3. As seen, color retentions were quite high and not significantly different from each other for the three NF membranes tested. The lowest color retention was obtained for NF 99 membrane (91%) with a permeate color of 15 Pt-Co. The color retention by NF 270 and NF 90 membranes was same (93%) resulting in a permeate value of 8 Pt-Co. Chakraborty et al. (2003) reported similar high color retentions with NF membranes from dye effluents. They investigated the treatability of two reactive dyes and obtained 92-94% dye retentions [17]. Color values decreased to 8 Pt-Co for NF 270 and NF 90 membranes. So quality of permeates from these NF membranes in terms of color were low and acceptable for reuse when compared with the reuse criteria given in Table 4.1.

In addition to high color retention, NF 270 and NF 90 membranes also provided high COD retentions (Table 7.3). The COD retention of NF 270 and NF 90 membranes were at around 92 and 94%, respectively while that of NF 90 was 88%. In the literature, similar retention values were reported for COD with NF membranes. Lopes et al. (2005) reported 87% COD retention of for the treatment of textile wastewaters [105]. In another study, Chakraborty et. al. obtained COD retentions up to 94% using NF for the treatment of dyeing wastewaters [17]. As color parameter, permeate COD of all NF membranes tested were within the limits of reuse criteria given in Table 4.1.

Table 7.3. Comparison of performances of NF membranes at steady state conditions using F1 wastewater as feed

Membrane	**Flux ($L/m^2/h$)**	**Final Permeate Quality**			**Cumulative Retention (%)**		
		COD (mg/L)	**Color (Pt-Co)**	**Conductivity (mS/cm)**	**COD**	**Color**	**Conductivity**
NF 270	31	87	8	4.3	92	93	60
NF 90	8	67	8	1.0	94	93	91
NF 99	2	113	15	4.9	88	91	55

NF membranes have the potential to remove dissolved solids causing conductivity. However, their complete removal was not achieved with the NF membranes tested. As seen in Table 7.3, the lowest permeate conductivity was obtained for NF 90 membrane as 1.0 mS/cm which is satisfactory in meeting the reuse criteria given in Table 4.1. Permeate conductivity of NF 99 and NF 270 membranes were quite similar to each other (4.9 mS/cm and 4.3 mS/cm, respectively) and higher than that of NF 90 membrane. Similar results were also reported by Nghiem et al. (2007) whom reported higher conductivity retention with NF 90 membrane than NF 270 membrane in the treatment of pharmaceutically active compounds [96].

Permeate fluxes of the three NF membranes were also measured and the results given in Table 7.3 were obtained. The permeate fluxes of NF 99 and NF 90 membranes were close to each other and quite lower than that of NF 270 membrane. As can be seen, the highest permeate flux was obtained for NF 270 membrane. The permeate flux of NF 270 membrane was significantly high and about 4 to 6 times higher than those of two other alternative membranes.

In order to highlight the fouling behavior of NF membranes used in experiments, the water and wastewater flux are presented in Table 7.4. As can be seen, water and wastewater flux of NF 270 membrane were quite higher than those of NF 99 and

NF 90 membranes. On the other hand, NF 99 and NF 270 membranes presented similar and lower flux decline and irreversible fouling than that of NF 90 membrane. In literature, contact angles of NF 270 and NF 90 membranes were reported as 27° and 54°, respectively [87, 96]. This implies that NF 90 is more hydrophobic than NF 270 membrane. Flux decline was severe with NF 90 membrane possibly due to hydrophobic nature of this membrane. Another reason was speculated as NF 90 is a relatively tight NF membrane with an average pore diameter of only 0.68 nm while NF 270 can be considered as a loose NF membrane with an average pore diameter of 0.85 nm (Table 5.6) [96]. As presented previously in Table 5.6, all three NF membranes tested in this study also differ from each other in their characteristics. As can be seen in Table 5.6 molecular cut off of membranes is in the increasing order: NF 90 < NF 99 < NF 270, which is fully in agreement with water fluxes given in Table 7.4.

Table 7.4. Water flux, flux decline, recovery and irreversible fouling of NF membranes using F1 wastewater as feed

Membrane	**NF 99**	**NF 90**	**NF 270**
Water flux * (L/m^2/h)	3	31	64
Wastewater flux (L/m^2/h)	2	8	31
Water flux ** (L/m^2/h)	3	28	63
Flux Recovery (%)	99	90	98
Flux Decline (%)	48	76	52
Irreversible Fouling (%)	1	10	2

*water flux with clean water of virgin membrane
**water flux of fouled membrane after cleaning

As it is known, fouling occurs in large time scales (days, hours), however the more temporary phenomenon of concentration polarization is built up in minutes or seconds. While the increased concentration of the rejected particles in the boundary layer is not itself a type of fouling it promotes adsorption, pore blocking and cake/gel layer formation and hence often is a fouling precursor. Membrane lifetime is mostly limited by irreversible fouling. Irreversible fouling of NF 270 and NF 99 membranes were quite low, 2% and 1%, respectively and thought to be due to concentration polarization as it was almost completely reversible [96]. Irreversible fouling of 10% observed for NF 90 is in fact not noticeable as this degree of fouling is low when compared to the fouling data given in the literature [94]. Irreversible fouling observed with NF 90 was possibly arising from pore blockage or adsorption to the surface. The higher flux decline could also be attributed to the hydrophobic nature of the NF 90 membrane. In a study, Van der Bruggen et al. (2004) reported that the most hydrophobic membranes showed the highest fouling, whereas no significant effect was measured with the most hydrophilic membrane [107].

All above results from the comparison of three NF membranes tested indicated that in terms of flux NF 270 membrane is better in performance than the other two membranes and comparable to those in terms of COD and color retentions. In essence, tested three NF membranes have all met the reuse criteria given in Table 4.1 in terms of COD, color and pH parameters, but not in terms of conductivity. Only the permeate from NF 90 membrane was satisfactory in meeting the reuse criteria.

However, still NF 270 membrane was selected as the best NF membrane as its permeate flux is definitely high. It was speculated that alternative water reuse approaches could be considered as described in Section 4.3. For example, the effluent of NF 270 membrane could be used in the first post-rinsing stage/s but not in the last post-rinsing tank. Final stage of post-rinsing could be carried out with fresh water as already practiced in the process.

7.1.3. Effect of pH

Besides the importance of filter medium used, wastewater pH is also an important factor in the determination of best filtration scheme. As aforementioned, NF 270 was found to be the best membrane among the tested ones. Therefore, in this series of experiments, the effect of wastewater pH in NF was investigated using NF 270 membrane. To this purpose, two pH alternatives were evaluated; pH 7.2±0.4 and pH 9.7±0.2 and the color, COD and conductivity values and retentions and permeate flux presented in Table 7.5 were achieved. (Time dependent color, COD and conductivity values and retentions and permeate flux are given in Appendix B in Figure B.9, B. 10 and B.11). Permeate color values were same for both of the pHs evaluated. As in color, no significant effect of pH was obtained in COD retention. COD retention at pH 7.2±0.4 was 92% and slightly higher than at pH 9.7±0.2 (89%). In literature, Chen et al. (2007) reported higher COD retention for high pHs in opposite to the present study. However, in that study, the major chemical in the textile wastewater was starch and it is more hydrolysable at acidic conditions [108]. On the contrary, indigo dye is the major chemical in the present study and it is a water insoluble dye. Indigo dye is soluble with the help of a reducing agent and at high pH (pH 12-13 or more) [109]. As the solubility of indigo dye is low at low pHs, it was natural to have higher color and COD retentions at pH 7.2±0.4 than pH 9.7±0.2.

Table 7.5. Performance of NF 270 membrane for pH 7.2±0.4 and pH 9.7±0.2 at steady state conditions

Membrane	**Flux ($L/m^2/h$)**	**Final Permeate Quality**			**Cumulative Retention (%)**		
		COD (mg/L)	**Color (Pt-Co)**	**Conductivity (mS/cm)**	**COD**	**Color**	**Conductivity**
pH 7.2±0.4	31	87	8	4.3	92	93	60
pH 9.7±0.2	32	130	8	2.9	89	94	73

As presented in Table 7.5, a considerable difference was obtained in permeate conductivity and retention for the two pH alternatives evaluated. Increase in pH of the wastewater resulted as a decrease in permeate conductivity. This was consistent with the results reported by Nghiem et al. (2007) who indicated that NF 270 membrane is a charged membrane at high pH and become negatively charged as the solution pH increases [96]. They also reported that the conductivity retention drops with a decrease in pH of the solution.

As to better understand the effect of wastewater pH on NF, permeate flux of NF 270 at these two pHs was followed (Table 7.5. and 7.6). The permeate flux of NF 270 at pH 9.7±0.2 was slightly higher than that at pH 7.2±0.4. A comparison of the permeate conductivity with the reuse criteria reveals that the permeate of the two pHs were not appropriate for reuse. To improve the permeate quality in terms of conductivity; sequential NF and RO experiments were conducted at pH 7.2±0.4.

In addition to permeate flux, the effect of pH on the fouling of NF 270 membrane was evaluated and the results in Table 7.6 were obtained. As can be seen from the table, water and wastewater fluxes were similar for both of the pHs tested.

Table 7.6. Water flux, flux decline, recovery and irreversible fouling of NF 270 membrane at pH 7.2±0.4 and pH 9.7±0.2

	pH 7.2±0.4	**pH 9.7±0.2**
Water flux * (L/m^2/h)	64	64
Wastewater flux (L/m^2/h)	31	32
Water flux ** (L/m^2/h)	63	67
Flux Recovery (%)	98	105
Flux Decline (%)	52	51
Irreversible Fouling (%)	2	0

*water flux with clean water of virgin membrane
**water flux of fouled membrane after cleaning

The flux decline and irreversible fouling were also similar. As discussed previously, the flux decline could be due to concentration polarization and it was completely reversible. Although the solubility of indigo was higher at pH 9.7±0.2 than at pH 7.2±0.4 no significant differences were obtained in terms of flux decline, recovery and irreversible fouling for these two pHs.

All these findings revealed that, there is no significant effect of pH on the performance of NF 270 membrane except conductivity retention. Although the permeate conductivity at pH 9.7±0.2 was slightly lower than that at pH 7.2±0.4, the quality of the permeate in terms of conductivity was not acceptable for reuse (Table 4.1).

7.1.4. Effect of Concentration

The aim of the last stage of NF studies was to come up with a generic approach to the reclamation of indigo dyeing wastewater. In the first phase of the study, as presented, wastewater from the first stage of post-rinsing after indigo dyeing was utilized and the optimum treatment scheme was identified for it. However, as textile dyeing wastewaters are highly variable in composition, it was decided that the aforementioned optimum reclamation scheme (5 µm + NF 270) would be tested for a dilute indigo dyeing wastewater and the results obtained till now will be generalized. To this purpose, the composite effluent from all post-rinsing tanks of the indigo dyeing process was utilized. Evidently, the first post-rinsing tank effluent is the most heavily polluted one while the composite post-rinsing sample is much lower in pollution load. The characteristics of these wastewaters are given in Table 5.1 and 5.2.

Table 7.7 represents steady state color, COD and conductivity retention and permeate flux of NF 270 membrane used for the treatment of the composite indigo dyeing wastewater along with those for the 1st stage post rinsing tank wastewater. (Time dependent permeate color, COD and conductivity values and flux are presented in Appendix B). Color and COD retentions by NF 270 membrane from the composite wastewater were slightly higher than the retentions from the first post-rinsing tank wastewater. For the composite wastewater, the permeate color and COD were at around 3 Pt-Co and 40 mg/L, respectively.

Table 7.7. Comparison of NF 270 membrane performance at steady state conditions for the treatment of composite post-rinsing and first post-rinsing tank wastewaters

Effluent	**Flux ($L/m^2/h$)**	**Final Permeate Quality**			**Cumulative Retention (%)**		
		COD (mg/L)	**Color (Pt-Co)**	**Conductivity (mS/cm)**	**COD**	**Color**	**Conductivity**
1st post-rinsing	31	87	8	4.3	92	93	60
Composite post-rinsing	40	40	3	3.5	93	98	51

Permeate conductivity for the first post-rinsing tank wastewater was higher than that for the composite post-rinsing tank wastewater. However, permeate flux from the first post-rinsing tank wastewater was lower than that from the composite post-rinsing tank wastewater. As can be seen from Table 5.1, the first post-rinsing tank effluent is the most polluted wastewater stream in the dyeing process.

In Table 7.8, the water and wastewater flux and fouling behavior of NF 270 membrane used for the treatment of two different wastewaters; first post-rinsing tank wastewater and composite post-rinsing tank wastewaters is presented. Due to this, flux decline of NF 270 membrane used for the treatment of mixture of post-rinsing wastewaters was lower than the NF 270 membrane used for the treatment of first post-rinsing tank wastewaters. Although the flux decline was higher for the NF membrane used for the treatment of first post-rinsing tank effluents, irreversible fouling was lower than the NF 270 membrane used for the treatment of composite wastewaters. Irreversible fouling of NF 270 membrane could be mainly explained by the pore blockage mechanism.

Table 7.8. Water flux, flux decline, recovery and irreversible fouling of NF 270 membrane for the treatment of composite post-rinsing and first post-rinsing tank wastewaters

	1st post-rinsing tank wastewaters	**Composite post-rinsing tank wastewaters**
Water flux * (L/m^2/h)	64	73
Wastewater flux (L/m^2/h)	31	40
Water flux ** (L/m^2/h)	63	63
Flux Recovery (%)	98	86
Flux Decline (%)	52	45
Irreversible Fouling (%)	2	14

*water flux with clean water of virgin membrane
**water flux of fouled membrane after cleaning

All above findings have revealed that the composite wastewaters of indigo dyeing process which is relatively low in pollutant concentration as compared to the first post-rinsing tank effluent could be treated effectively using the same membrane sequence (5µm+NF 270) used for the most polluted first post-rinsing tank effluent. This result indicates that, the membrane filtration sequence including NF 270 membrane after 5 µm MF could be adopted for all type of indigo dyeing wastewaters. Thus, one can identify this membrane treatment scheme as a generic scheme for the treatment of indigo dyeing wastewaters.

7.1.5. Concentration Mode of NF 270 after 5 µm MF

In order to better assess the performance of the predetermined filtration scheme and to approach to the field scale behavior of NF 270 membrane, concentration mode of NF test was carried out using the permeate from 5 µm prefiltration which was performed under 5.07 bar TMP and 0.62 m/s CFV conditions. The experiment was ended when the volume of the feed was decreased to 10% of the beginning feed volume. A sample of first stage post-rinsing tank wastewater of the volume 25 L was taken and passed thru 5 µm dead-end MF. Then its pH was adjusted to pH 7±0.2 and used in the concentration mode of NF experiment. In Figure 7.2, time dependent feed and permeate color values and color retention by NF 270 membrane in concentration mode filtration are given.

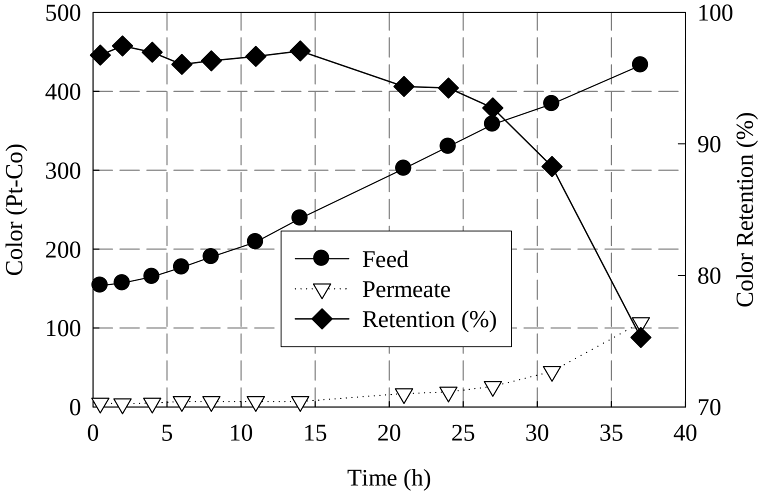


Figure 7.2. Feed and permeate color and color retention of concentration mode of NF 270 membrane

As can be seen, at the beginning of the experiment, the feed color was 154 Pt-Co and at the end it increased, three fold to 433 Pt-Co. At the beginning of the filtration, permeate color was 5 Pt-Co and at the end it increased to 107 Pt-Co.

After 15 hours of operation, a sharp decrease was observed in the color retentions as a result of worsening feed quality.

Figure 7.3 depicts the feed and permeate COD and also COD retention of NF 270 membrane at concentration mode of filtration. As can be seen, the feed COD level increased drastically with time while there is a gradual increase in the permeate COD. At the beginning of the experiments, the feed COD was 1023 mg/L and at the end it increased to 2868 mg/L. In parallel, at the beginning of the experiment, the permeate COD was 150 mg/L and at the end it increased to 1152 mg/L (Figure 7.3). But still COD retention was never below 65%.

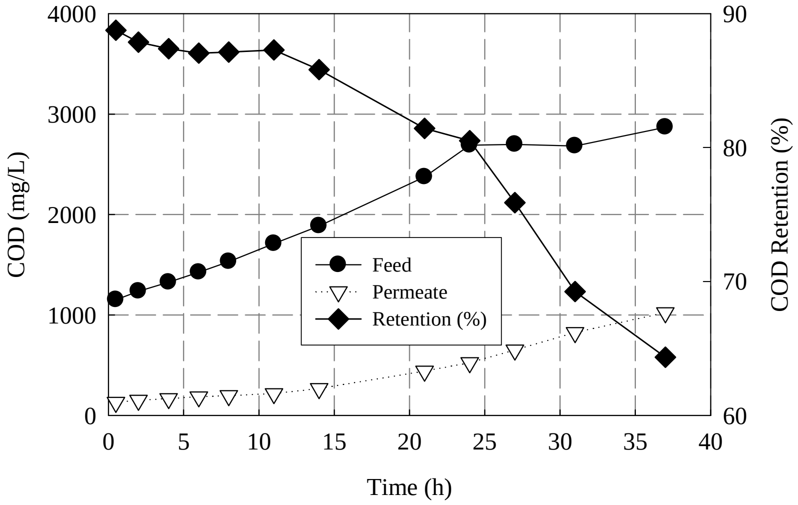


Figure 7.3. Feed and permeate COD and COD retentions of concentration mode of NF 270 membrane

In addition to color and COD retentions, the feed and permeate conductivity values were monitored and the results presented in Figure 7.4 were obtained. As the feed conductivity level increased with time due to continuous removal of permeate, the permeate conductivity was also increased. At the beginning of the experiment, the feed conductivity was 11.4 mS/cm and at the end, it increased two fold to 22.9 mS/cm. On the other side, at the beginning of the experiments, the permeate conductivity was 4.38 mS/cm and at the end it increased two fold to 9.91 mS/cm (Figure 7.4).

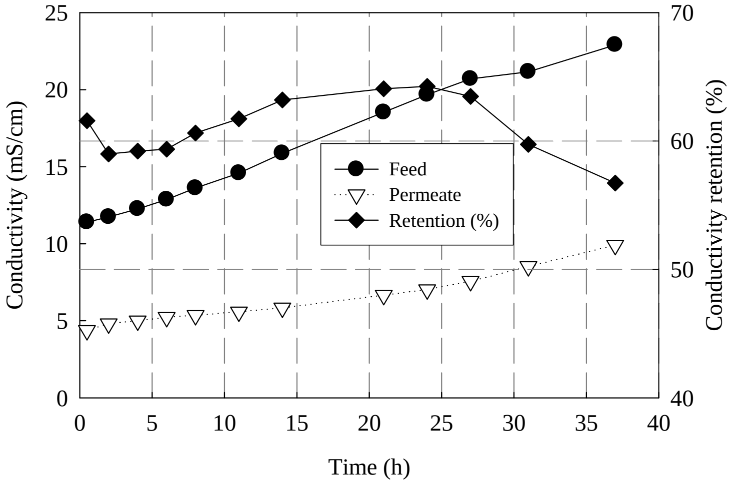


Figure 7.4. Feed and permeate conductivity and conductivity retentions of concentration mode of NF 270 membrane

Membrane properties (charge, pore size, etc) and the feed solution characteristics can influence the retention in NF applications. For all color and COD parameters followed during the concentration mode of NF 270 membrane, after at about 15 h of operation due to the worsening feed quality permeate quality and retentions were decreased. Denyer et al. (2007) also reported the decrease in the retention of dyes with increasing duration of the experiment [111]. In another study, Akbari et al. (2002) found that the dye retention decreased with the increase in conductivity [112]. Conductivity values of feed and permeate were also increased during the experiments (Figure7.4). Donnan exclusion and diffusion play an important role in the salt retention mechanism. Donnan forces especially have a significant effect on salt retentions. NF 270 membrane is a negatively charged membrane and due to Donnan potential counter ions are transported to the membrane surface and co ions are transported to the solution phase [113]. The main salt used in the indigo dyeing process considered in this study is $Na_2S_2O_4$. For the first 20-25 h of operation, conductivity retentions were nearly constant however with an increase in salt concentration in the feed solution and a decrease of the fixed membrane charge Donnan exclusion becomes less or negligible [112]. Donnan potential effect is greatest at low to mid salinities (1000 mg/L < TDS < 3000 mg/ L). In our study, the salinity of feed wastewater is so high and during the concentration mode experiments it continued to increase. Increasing the feed salinity weakens the Donnan potential and leads to a decrease in membrane retention. The theory behind this phenomenon suggests that along with increasing feed concentration, comes an increase in the cations at the membrane surface and thus a shielding of the Donnan potential [114]. At increasing concentrations, more diffusion can also take place as a consequence of a higher driving force, so that a decrease in retention is observed [113].

Figure 7.5 depicts the changes in permeate and normalized fluxes in this experiment. Experiment duration was 37 h and flux decline continued till this point. At the beginning of the experiment, permeate flux was 28 $L/m^2/h$ and at the end of the experiment it decreased to 2 $L/m^2/h$. The flux decline was clearly due to continuous gel layer formation on the surface of the membrane.

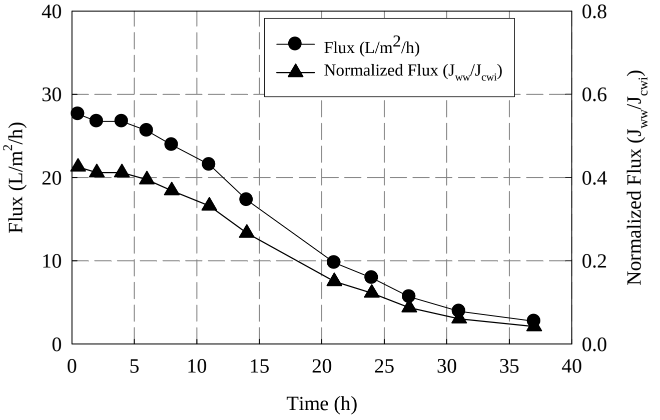


Figure 7.5. Wastewater and normalized flux of concentration mode of NF 270 membrane

In Table 7.9, water fluxes and flux decline, recovery and irreversible fouling of NF 270 membrane for concentration mode of operation is given. As can be seen from the table, the flux decline was higher than the values obtained at TRMF. However, the flux recovery and irreversible fouling was similar. As indicated, no irreversible fouling was obtained and flux was recovered completely.

Table 7.9. Water flux, flux decline, recovery and irreversible fouling of NF 270 membrane for concentration mode of operation

Membrane	**NF 270**
Water flux * (L/m^2/h)	65
Wastewater flux (L/m^2/h)	3
Water flux ** (L/m^2/h)	66
Flux Recovery (%)	100
Total Flux Decline (%)	96
Irreversible Fouling (%)	0

*water flux with clean water of virgin membrane
**water flux of fouled membrane after cleaning

7.1.6. Sequential NF

NF membranes sometimes do not satisfy the reuse criteria, due to high salt concentrations as seen in previous single NF tests performed with NF 270 and NF 99 membranes. Considering the permeate quality from single NF (NF 270) experiments, sequential NF experiments were performed to improve the permeate quality for reuse purposes. The first stage NF experiment were performed in concentration mode of operation, permeate of this system was collected and was fed to the second stage NF. The results of concentration mode of NF experiments are given in Section 7.1.5 above.

Table 7.10 and 7.11, represents permeate quality and fouling performances of sequential NF and single stage NF experiments using F1 as the feed water. Color retention of single NF was at around 93% and with sequential NF application, color retention increased to 99%. The permeate color for single NF 270 at steady state condition was 8 Pt-Co, and for sequential NF 270 it decreased to 1 Pt-Co. The improvement in color retention was not considerably high with sequential NF application. The COD retention for single NF 270 was between 92% and for sequential NF 270 COD retention was increased 97 %. The permeate COD concentrations for single NF 270 was 87 mg/L, and for sequential NF 270 it was 39 mg/L.

Table 7.10. Performance of NF 270 membrane for single and sequential stage applications at steady state conditions

Membrane	**Flux ($L/m^2/h$)**	**Final Permeate Quality**			**Cumulative Retention (%)**		
		COD (mg/L)	**Color (Pt-Co)**	**Conductivity (mS/cm)**	**COD**	**Color**	**Conductivity**
Single NF 270	31	87	8	4.3	92	93	60
Sequential NF 270	54*	39	1	2.8	97	99	74

* permeate flux of second stage NF 270 membrane

In addition to color and COD retentions, the permeate conductivity 2.8 mS/cm of sequential NF was lower than that 4.3 mS/cm of single NF. With sequential NF application, although 35% improvement was obtained, permeate conductivity was still not satisfactory in meeting the reuse limit given in Table 4.1.

In Table 7.11, fouling tendency of NF 270 membrane in single and sequential applications is presented. As seen permeate flux of sequential NF were higher than single NF. The flux decline was quite higher in single NF when compared to sequential NF. For single NF 270, flux declines were around 52% and for sequential NF 270 this value decreased to 22%. Although the flux decline of single NF application was higher than that of sequential NF application, nearly no irreversible fouling was obtained for both of the NF applications and the fouling was completely reversible. All these findings indicate that using a second stage NF should be evaluated based on its economic feasibility during which permeate flux data should be considered.

Table 7.11. Water flux, flux decline, recovery and irreversible fouling for single and sequential application of NF 270 membrane

	Single NF	**Sequential NF**
Water flux * (L/m^2/h)	64	70
Wastewater flux (L/m^2/h)	31	54
Water flux ** (L/m^2/h)	63	70
Flux Recovery (%)	98	100
Flux Decline (%)	52	22
Irreversible Fouling (%)	2	0

*water flux with clean water of virgin membrane
**water flux of fouled membrane after cleaning

7.2. RO

In textile wastewater reuse or reclamation, RO processes generally preferred when salt concentrations are considerably high and NF permeate quality was not enough to be reused in the process as in this present study. RO experiments were performed using two different RO membranes; CA 995 PE and HR 98 PP (Alfa Laval, Denmark) to improve the quality of water recovered from indigo dyeing process. The performance of these two RO membranes were evaluated in terms of flux, color COD and conductivity retention at 5.07 bar TMP and 0.62 m/s CFV conditions after 5 µm MF prefiltration. Color, COD and conductivity values and retentions and permeate fluxes of two RO membranes (HR 98 PP and CA 995 PE) tested are given in Table 7.12. Color retentions of RO membranes were not significantly different from each other and 94 % for CA 995 PE and 97 % for HR 98PP. The COD retention of HR 98 PP was 96 % and higher than that of CA 995 PE which is 90%. Thus, HR 98 PP membrane showed slightly better performance than CA 995 PE membrane in terms of COD and color retentions. (Time dependent color, COD and conductivity retentions and permeate fluxes of RO membranes are given in Appendix B in Figure B.18, B.19 and B.20).

Table 7.12. Comparison of performances of RO membranes at steady state conditions

Membrane	**Flux ($L/m^2/h$)**	**Final Permeate Quality**			**Cumulative Retention (%)**		
		COD (mg/L)	**Color (Pt-Co)**	**Conductivity (mS/cm)**	**COD**	**Color**	**Conductivity**
CA 995 PE	3	115	7	3.2	90	94	71
HR 98 PP	5	46	3	0.9	96	97	92

As presented in section 7.1.2., in NF experiments, the reuse criteria in terms of color, COD and pH was satisfied however permeate conductivity was not proper to be directly reused in the process. Even in the sequential NF application, the permeate was not within an acceptable quality in terms of conductivity. However, RO process was much better in performance and the permeate conductivity of HR 98 PP was 0.9 mS/cm and met the reuse criteria given in Table 4.1. On the other hand, CA 995 PE membrane was not satisfactory with an effluent conductivity of 3.2 mS/cm. In parallel with retentions, the permeate flux of HR 98 PP membrane was higher than that of CA 995 PE membrane.

In Table 7.13 the water and wastewater flux and fouling tendency of RO membranes are presented. Water and wastewater flux of HR 98 PP membrane were quite higher than CA 995 PE membrane. The highest flux decline was obtained for HR 98 PP membrane as 74%. Flux recovery and irreversible fouling of HR 98 PP and CA 995 PE membranes were quite similar. As in NF membranes very low irreversible fouling values were measured and the fouling was completely reversible.

Table 7.13. Water flux, flux decline, recovery and irreversible fouling of RO membranes at steady state conditions

Membrane	**CA 995 PE**	**HR 98 PP**
Water flux * (L/m^2/h)	8	18
Wastewater flux (L/m^2/h)	3	5
Water flux ** (L/m^2/h)	7	17
Flux Recovery (%)	96	97
Flux Decline (%)	57	74
Irreversible Fouling (%)	4	3

*water flux with clean water of virgin membrane
**water flux of fouled membrane after cleaning

7.3. Comparison of RO and NF Experiments

The comparison of performances of NR and RO membranes is given Table 7.14. Color retention of all membranes was at or above 90 % and was not significantly different from each other. Moreover, all membranes meet the reuse criteria in terms of permeate color. The highest COD retention of over 95% was obtained for the sequential NF 270 and HR 98 PP membranes. As can be clearly seen, all NF and RO membranes tested meet the reuse criteria in terms of permeate color and COD.

The lowest permeate color and COD was obtained for sequential NF 270 application. The highest permeate color was obtained for NF 99 membrane and the highest permeate COD was for CA 995 PE and NF 99 membranes.

Table 7.14. Comparison of performances of NF and RO membranes at steady state conditions

Membrane	Flux ($L/m^2/h$)	Final Permeate Quality			Cumulative Retention (%)		
		COD (mg/L)	Color (Pt-Co)	Conductivity (mS/cm)	COD	Color	Conductivity
NF 270	31	87	8	4.3	92	93	60
NF 90	8	67	8	1.0	94	93	91
NF 99	2	113	15	4.9	88	91	55
Sequential NF 270	54	39	1	2.8	97	99	74
CA 995 PE	3	115	7	3.2	90	94	71
HR 98 PP	5	46	3	0.9	96	97	92

The most important quality parameter that should be considered in comparing NF and RO tests performances is conductivity. As presented before, the lowest and similar permeate conductivities (highest permeate retention) were obtained for NF 90 and HR 98 PP membranes as 1.0 mS/cm and 0.9 mS/cm, respectively. Among the NF and RO membranes tested only these two membranes satisfied the reuse criteria given in Table 4.1. Permeate conductivity values of NF 99 and NF 270 membranes were also similar and highest among all NF and RO membranes tested. All these results indicated that, in terms of conductivity parameter, the best performances were obtained with NF 90 and HR 98PP membranes. However, in terms of permeate flux, flux recovery and fouling NF 270 membrane was the best alternative for the treatment of indigo dyeing post rinsing wastewaters. The permeate flux of NF 270 was quite higher than those of the other NF and RO membranes tested (Table 7.15). Flux recovery for all NF and RO membranes was quite high and similar. The highest flux decline and irreversible fouling was measured for NF 90 membrane and the lowest flux decline was measured for NF 99 membrane.

Table 7.15. Water flux, flux decline, recovery and irreversible fouling of NF and RO membranes at steady state conditions

Membrane	**NF 99**	**NF 90**	**NF 270**	**Sequential NF 270**	**CA 995 PE**	**HR 98 PP**
Water flux * (L/m^2/h)	3.2	31.1	64.1	69.4	7.6	17.9
Wastewater flux (L/m^2/h)	1.7	7.5	30.7	54.3	3.3	4.7
Water flux ** (L/m^2/h)	3.2	27.9	62.50	69.4	7.4	17.4
Flux Recovery (%)	99	90	98	100	96	97
Flux Decline (%)	48	76	52	22	57	74
Irreversible Fouling (%)	1	10	2	0	4	3

*water flux with clean water of virgin membrane
**water flux of fouled membrane after cleaning

Based on all results given above, NF 270 membrane appeared to be the best alternative in terms of permeate flux and fouling. It was also comparable in terms of color and COD retention with the other NF and RO membranes tested. For NF 270 membrane, color and COD retentions were over 90%. However, permeate conductivity of this membrane was 4.3 mS/cm which is not satisfactory in meeting the reuse quality criteria given in Table 4.1. Nevertheless, the criteria given in this table in fact may not be valid for the indigo dyeing plant in consideration. As the plant from which wastewater samples were taken can not define reuse criteria and all comparisons in the present study has been on the basis of Table 4.1. Another issue to be considered here is the rinsing stage at which recycled water to be reused. If this permeate water with a conductivity of 4.3 mS/cm is attempted to be used in the initial rinsing stages after dyeing it may be acceptable. This option could be investigated when full scale application of NF 270 is practiced. During these investigations, possibility of using treated wastewater from NF could be evaluated by simply observing the effectiveness of rinsing using this permeate.

CHAPTER 8

CONCLUSIONS

In this study, a generic treatment scheme targeting at water reuse for indigo dyeing wastewaters was developed. As indigo dyeing requires good quality colorless water with less than 2.2 mS/cm conductivity, the membrane filtration processes were investigated. With the purpose of decreasing possible fouling in NF and RO, firstly pretreatment tests were carried out and to this purpose MF and coagulation tests were applied. Then after, for the possible improvement in the feed quality of NF/RO, UF was investigated. Finally NF/RO tests aiming at reusable water production were run. The main conclusions that can be drawn from this study can be summarized as follows:

1. In the pretreatment of indigo dyeing rinsing waters by MF, two alternatives were evaluated; single and sequential stage MF. In single stage MF; the optimum pretreatment process appeared to be 5 µm MF providing 93% color removal with a high permeate flux. In sequential dead-end MF tests, 5 µm + 0.45 µm was obtained as the optimum with the highest color removal and lower flux decline.

2. Coagulation tests with alum and ferric chloride revealed that coagulation is not an effective pretreatment process for the retention of color from indigo dyeing wastewater when compared with MF alternative.

3. The optimum MF alternatives; single stage 5 µm and sequential 5 µm+0.45 µm MF were evaluated in UF tests. Sequential MF application (5 µm+0.45 µm) before UF was found not to have any improvement in UF performance. 5 µm MF prefiltration showed the best performance as a prefiltration alternative for the UF of rinsing waters of indigo dyeing process.

4. All UF membranes tested having pore sizes ranging from 1 to 100 kDa provided a high color retention (98-99%) and the membrane having 100 kDa MWCO was found to be the most suitable UF membrane for the prefiltration to NF considering its high flux, and COD and conductivity retentions.

5. Single stage 5 µm MF and sequential stage 5 µm MF followed by 100 kDa UF prefiltration alternatives were determined as the optimum pretreatment alternatives and their performances were evaluated in NF tests. The results revealed that, using an additional 100 kDa UF membrane as a second stage after 5 µm MF membrane did not result in a significant improvement in color and COD retentions and also in permeate flux in NF. Based on these findings further NF and RO tests were carried out with 5 µm MF prefiltration only without 100 kDa UF.

6. The effectiveness of three different commercially available NF membranes; NF 99, NF 90 and NF 270 were evaluated for the water recovery from the pretreated indigo dyeing wastewaters after 5 µm dead-end MF. NF 270 membrane showed better performances than other NF 99 and NF 90 membranes. However, the permeate from NF 270 membrane did not satisfy the conductivity criteria for reuse in the process.

7. It was observed that pH of the indigo dyeing wastewater, for the pH values studied (nominally pH 7 and 10), is not significantly effective on the performance of NF 270 membrane.

8. In order to determine the effect of feed quality on the performance of the predetermined filtration scheme (5 µm + NF 270), composite wastewaters of indigo dyeing process which is relatively low in pollutant concentration was compared to the first post-rinsing tank effluent. It was observed that, composite wastewaters could also be treated effectively using the same membrane sequence (5µm+NF) used for the most polluted first post-rinsing tank effluent. This membrane filtration sequence including NF after 5 µm MF could be adopted for all type of indigo dyeing wastewaters. Thus, one can identify this membrane treatment scheme as a generic scheme for the treatment of indigo dyeing wastewaters.

9. In addition to three different NF membranes, the effectiveness of two different commercially available RO membranes; CA995PE, HR98 PP were evaluated. HR 98 PP membrane showed a better performance than the CA 995 PE membrane in terms of flux, color and COD retentions.

10. As a result of all the NF and RO experiments, NF 90 and RO HR 98 PP membranes were found to be most effective in conductivity retention for the treatment of indigo dyeing wastewaters. However, in terms of permeate flux, flux recovery and fouling NF 270 membrane was the best alternative for the treatment of indigo dyeing post-rinsing wastewaters.

CHAPTER 9

RECOMMENDATIONS

In addition to all conclusions drawn above, further investigations are needed on membrane based treatment of indigo dyeing rinsing wastewaters. The developed process train for this wastewater should be evaluated from an economic point of view. In membrane processes, final destination of the concentrate stream is still unclear. Membrane concentrate stream of the treatment scheme developed in this study should be characterized first and environmental fate of this stream prior to discharge should be studied aiming zero liquid discharge. Treatability and reuse potential of indigo dye bath effluents, that are high in concentration than the rinsing waters considered in this study, should also be evaluated.

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APPENDIX A

A. 1. Particle size distribution analysis

Particle size distribution (PSD) analysis was performed for three samples taken at different times from the first post-rinsing tanks of indigo dyeing process. The first one was for the wastewater used in MF and coagulation experiments (Sample 1) and the second was for the wastewater used in UF experiments (Sample 2) and the last one was for the wastewater used in NF experiments (Sample 3). Another PSD analysis was performed for the composite wastewaters of the post rinsing tanks (Sample 4) used in NF experiments. To observe the effect of prefiltration on the PSD of the wastewater, PSD was also performed for the first post rinsing tank wastewaters and for the composite wastewaters after 5 µm dead end MF.

PSD of the first sample (Sample 1) taken from the post-rinsing tank wastewater is given in Figure A.1. As seen, the particles are mainly in the size range of 1-10 µm. Meanwhile, there are particles in the range of 0.04-0.2 µm and also in the range of 9-50 µm. From this analysis volume based average particle size appeared to be 2.67 µm.

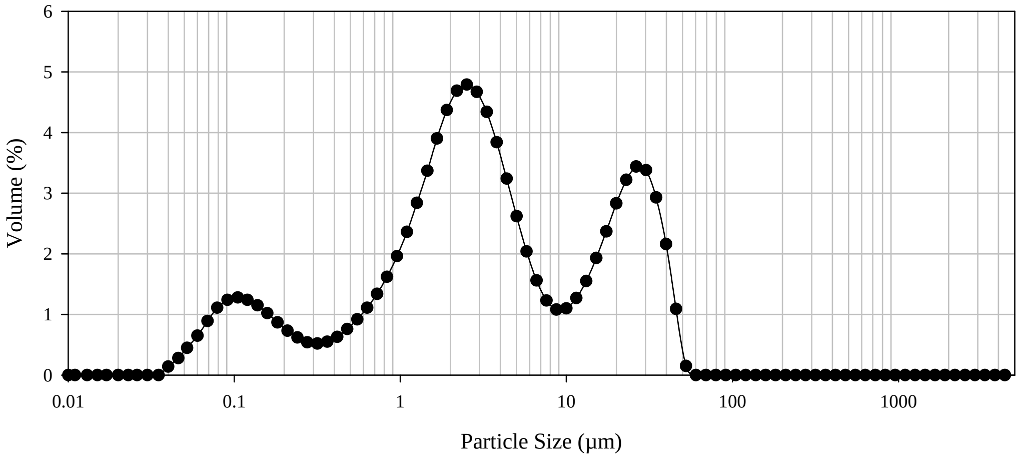


Figure A.1. PSD of Sample 1

The PSD of the second sample (Sample 2) is given in Figure A.2. As seen, the particles are mainly in the size range of 0.3-11 µm. Meanwhile, there are particles in the range of 0.03-0.2 µm. From this analysis volume based average particle size appeared to be 2.57 µm.

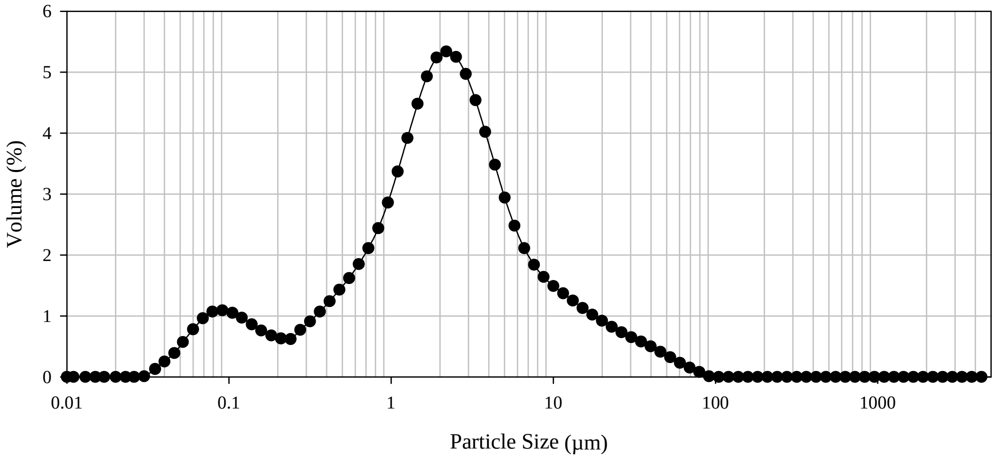


Figure A.2. PSD of Sample 2

The PSD of the third wastewater sample (Sample 3) is given in Figure 5.3. As seen from figure, the particles are mainly in the size range of 0.4-10 µm. Meanwhile, there are also particles in the range of 0.04-0.2 µm and 25-60 µm. And the average particle size was 1.69 µm. The PSD curves showed that the wastewater was highly variable and the PSD curve of the Sample 1 and Sample 3 showed nearly the same variance (Figure A.1 and A.3).

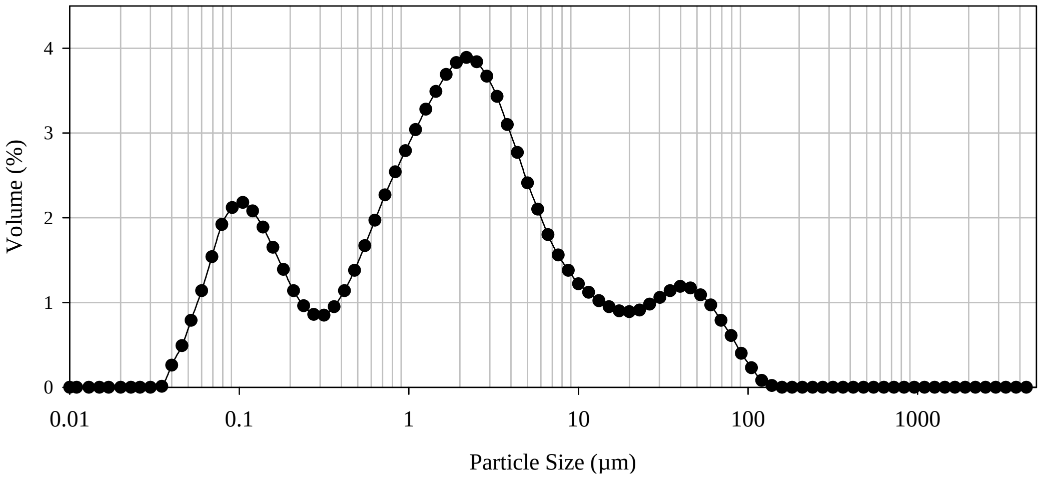


Figure A.3. PSD of Sample 3

PSD of composite wastewaters from indigo dyeing post-rinsing tanks (Sample 4) used in nanofiltration experiments is given in Figure A.4. As seen from figure, the particles are mainly in the size range of 0.04-0.4 µm. Meanwhile, there are also particles in the range of 1-100 µm. And the average particle size was 1.29µm.

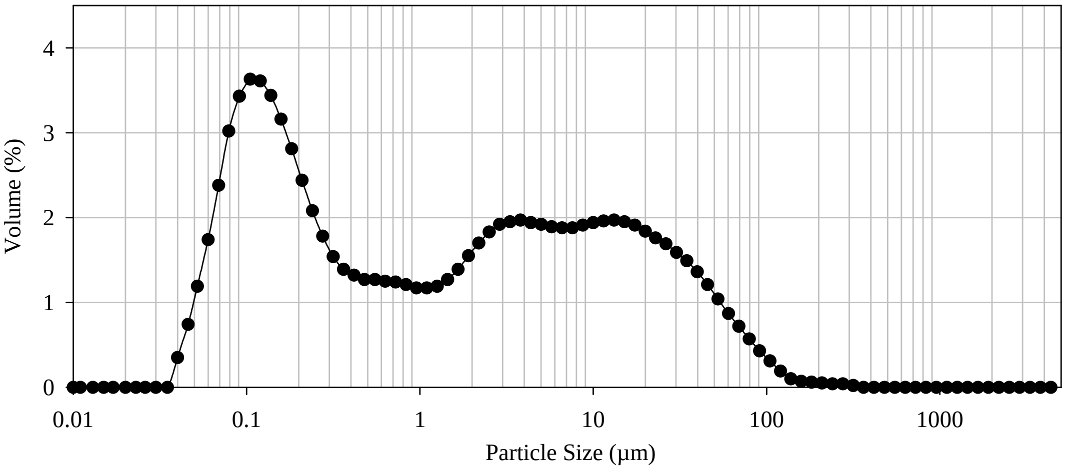


Figure A.4. PSD of Sample 4

PSD of Sample 3 after 5 µm prefiltration is given in Figure A.5. As seen from figure, the particles are mainly in the size range of 200-500 nm. Meanwhile, there are also particles in the range of 600-1500 nm. And the average particle size was 504.28 nm.

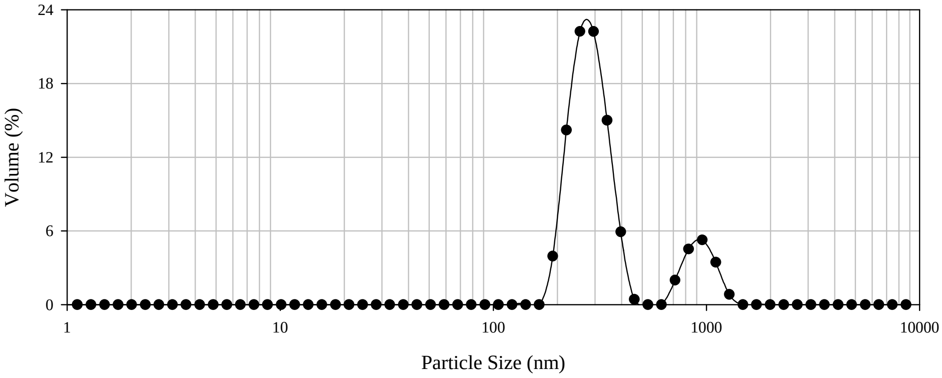


Figure A.5. PSD of Sample 3 after 5 µm prefiltration

PSD of Sample 4 after 5 µm prefiltration used in nanofiltration experiments is given in Figure A.6. As seen from figure, the particles are mainly in the size range of 100-600 nm. Meanwhile, there are also particles with small peaks was observed but it could be defined as a noise and it is negligible. And the average particle size was 263.07 nm.

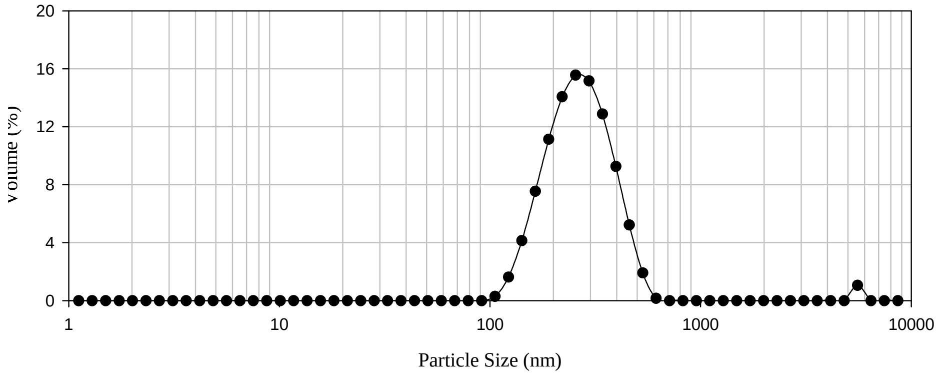


Figure A.6. PSD of Sample 4 after 5 µm prefiltration

Sample 3 and 4 after 5 µm prefiltration showed similar PSD’s. For these two wastewaters, main size range of particles was quite similar to each other.

APPENDIX B

B.1.NF

B.1.1. Effect of pretreatment

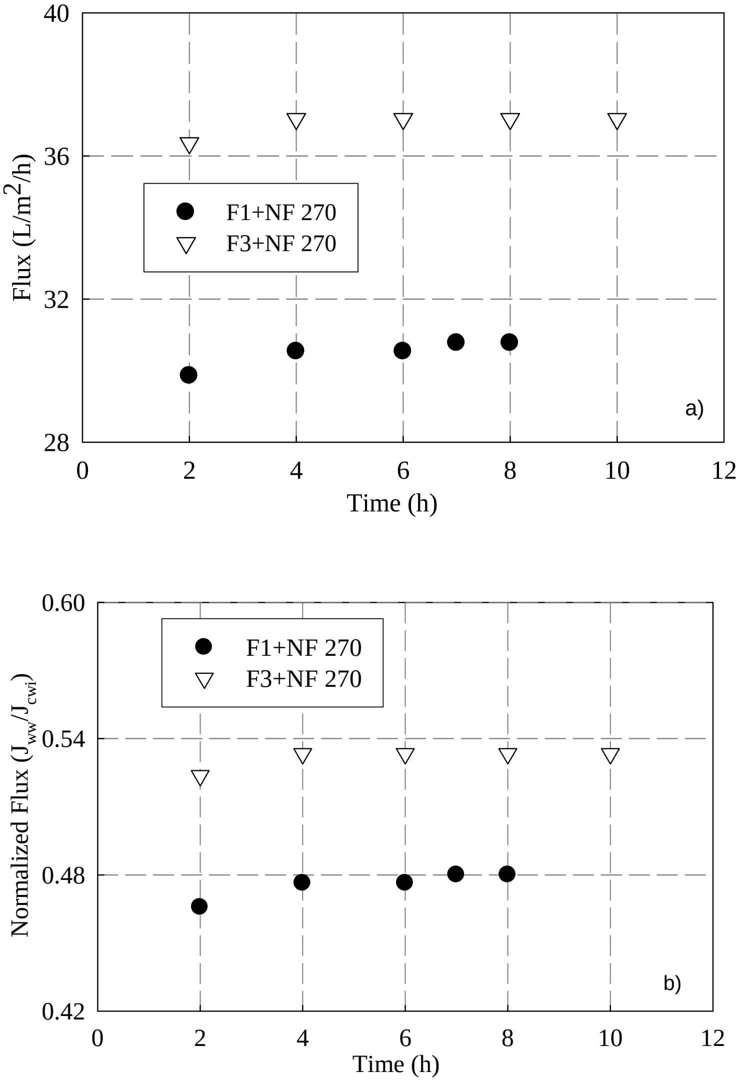


Figure B.1. Comparison of a) permeate flux and b) normalized flux of NF 270 membrane using F1 and F3 as feed

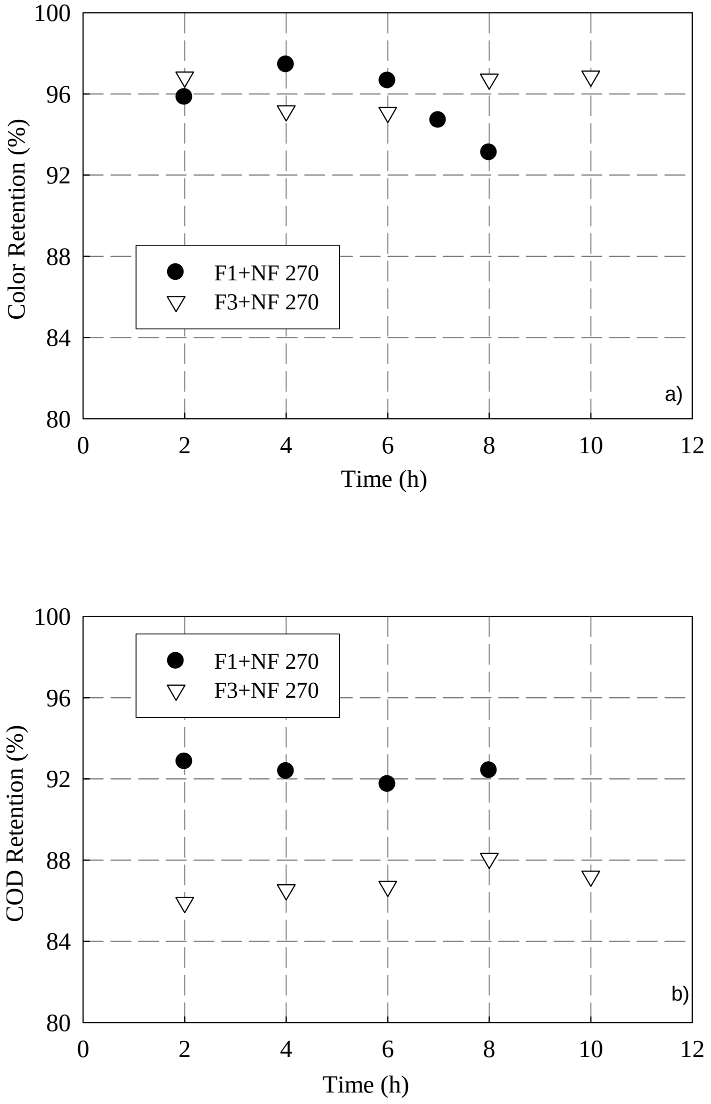


Figure B.2. Comparison of a) color and b) COD retentions for NF 270 membrane using F1 and F3 as feed

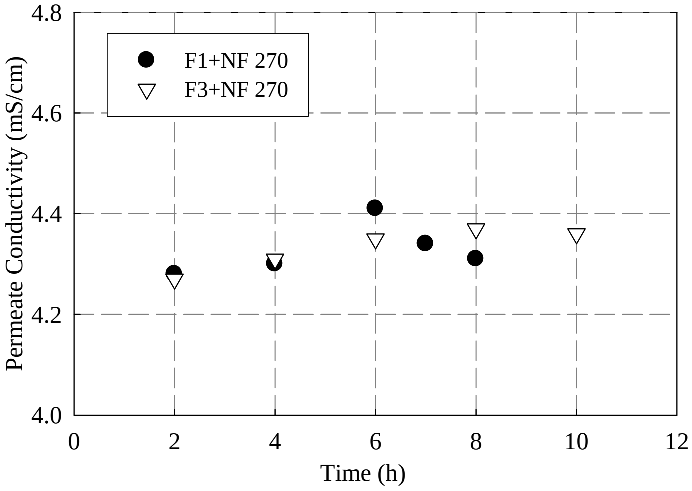


Figure B.3. Comparison of permeate conductivity of NF 270 membrane using F1 and F3 as feed

B.1.2. Effect of membrane type

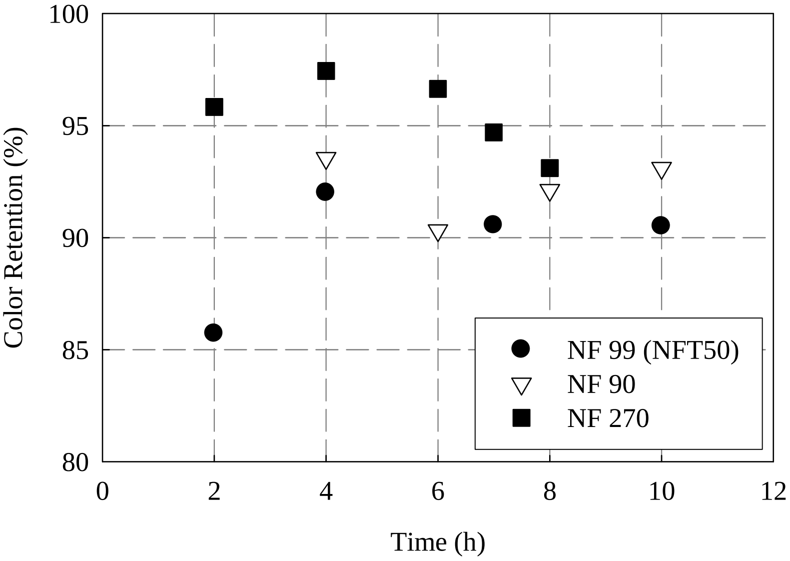


Figure B.4. Comparison of color retentions of NF membranes using F1 as feed

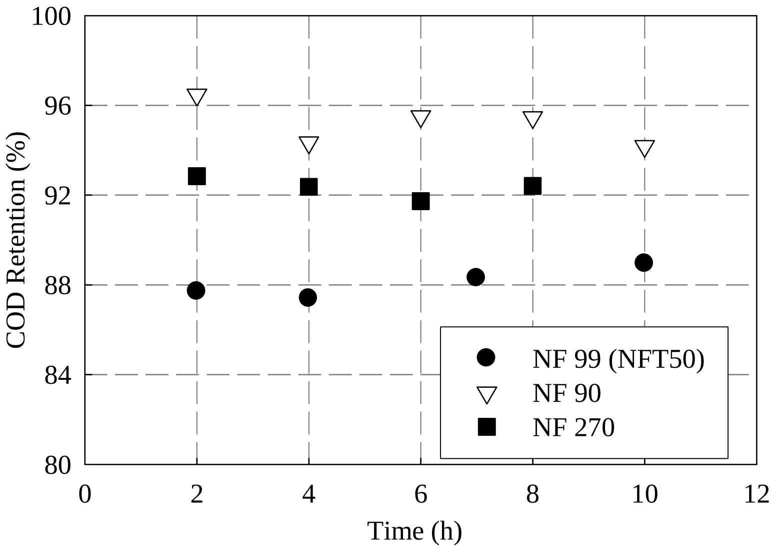


Figure B.5. Comparison of COD retention of NF membranes using F1 as feed

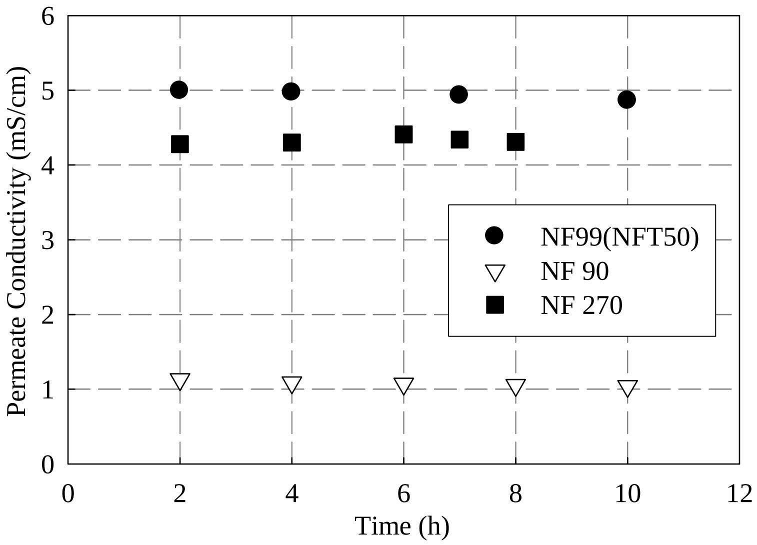


Figure B.6. Comparison of permeate conductivity of NF membranes using F1 as feed

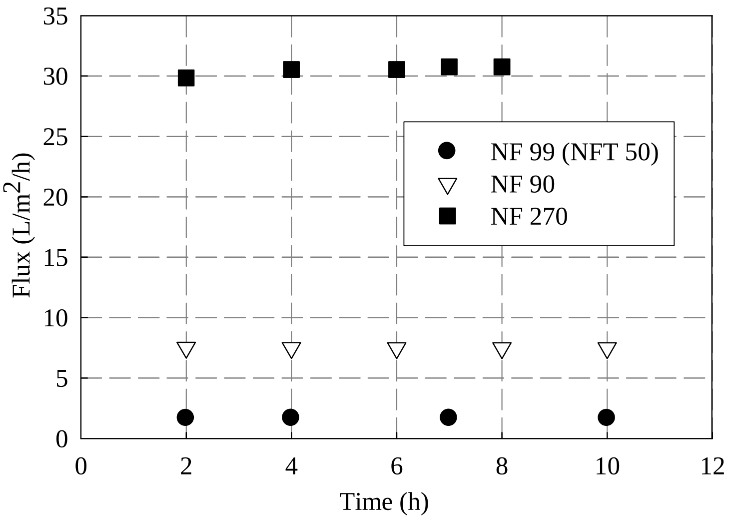


Figure B.7. Comparison of permeate fluxes of NF membranes (NF99, NF90 and NF 270) using F1 as feed

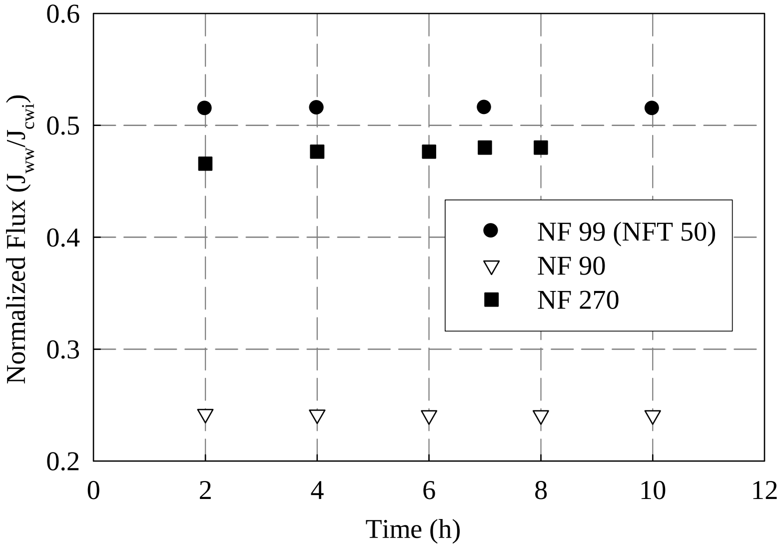


Figure B.8. Comparison of normalized fluxes of NF membranes (NF99, NF90 and NF 270) using F1 as feed

B.1.3. Effect of pH

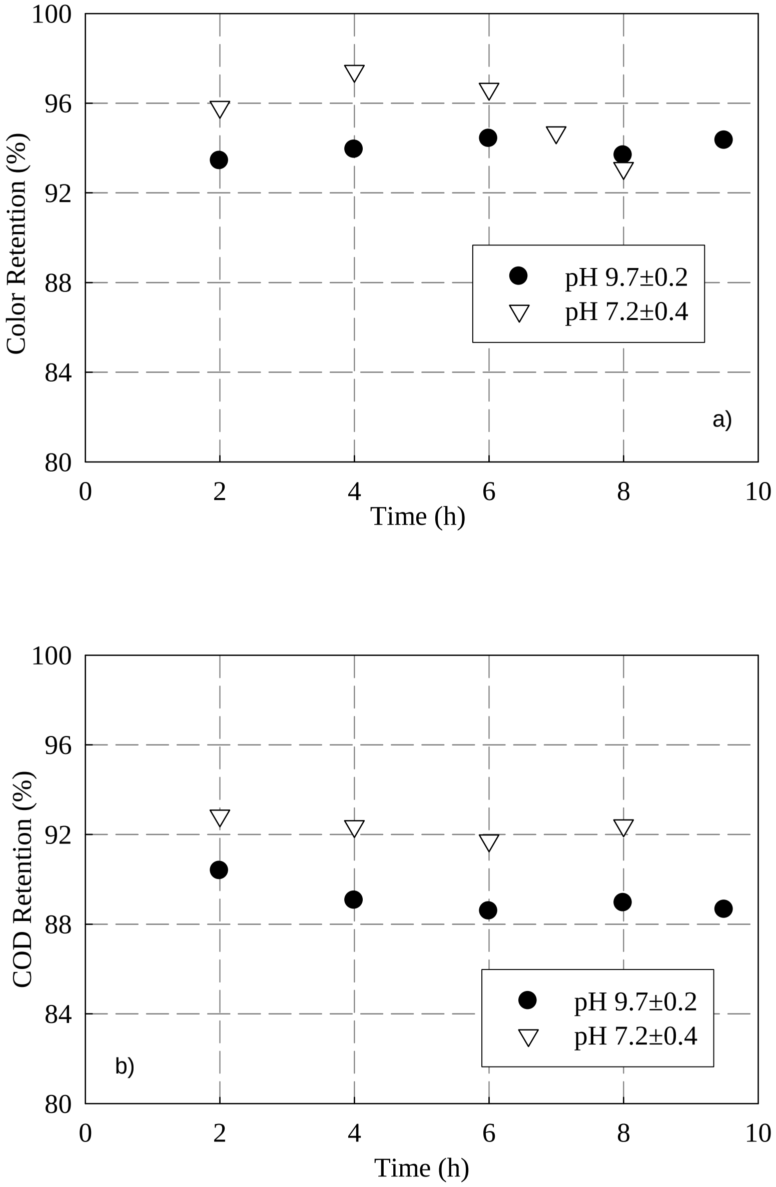


Figure B.9. Comparison of a) color and b) COD retention of NF 270 membrane as a function of time at pH 7.2±0.4 and pH 9.7±0.2 using F1 as feed

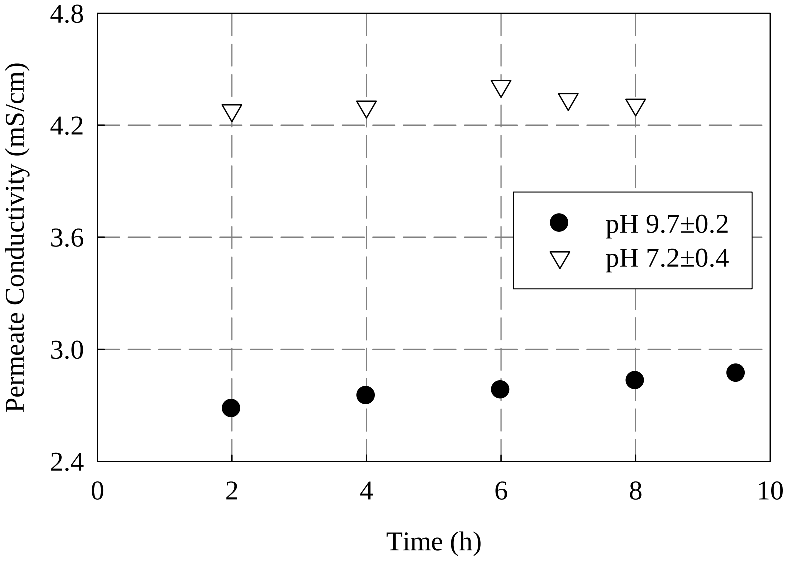


Figure B.10. Comparison of permeate conductivity of NF 270 membrane at pH 7.2±0.4 and pH 9.7±0.2 using F1 as feed

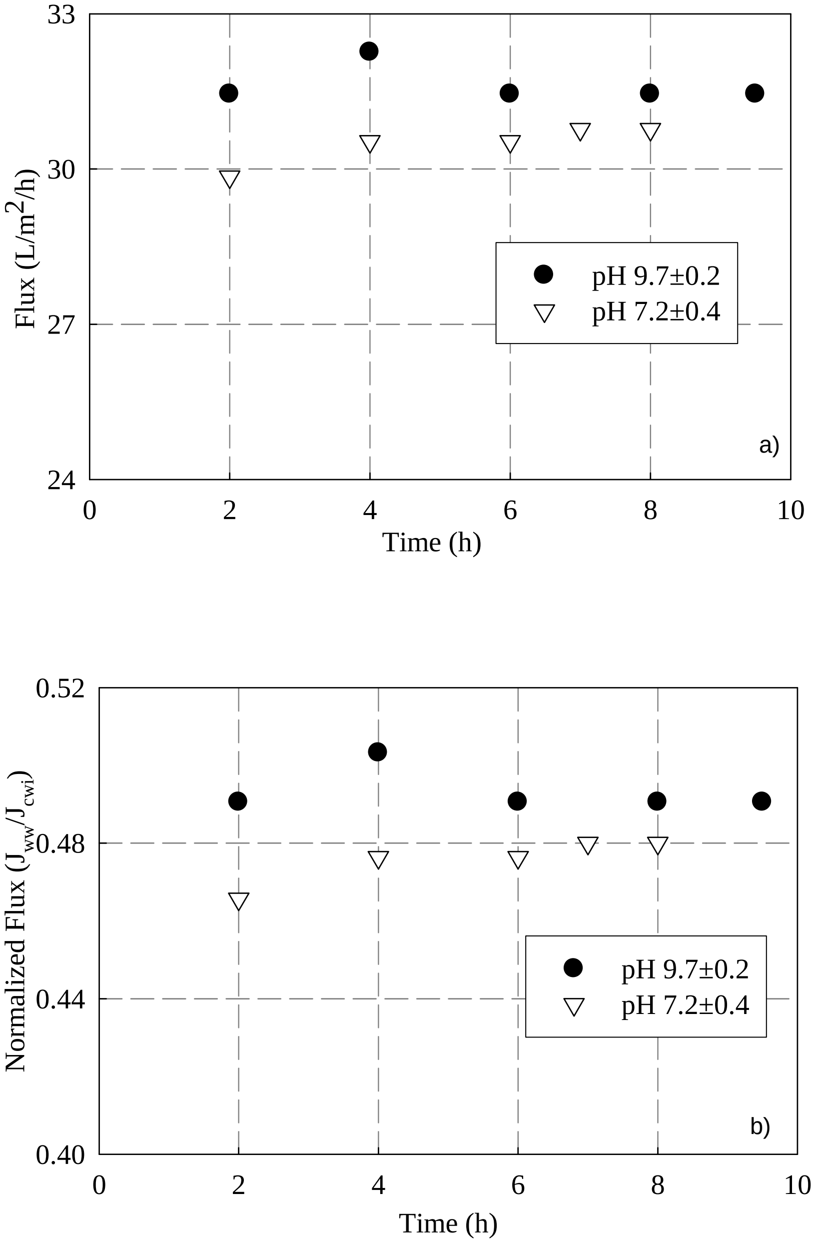


Figure B.11. Comparison of a) permeate flux and b) normalized flux of NF 270 membrane at pH 7.2±0.4 and pH 9.7±0.2 using F1 as feed

B.1.4. Effect of concentration

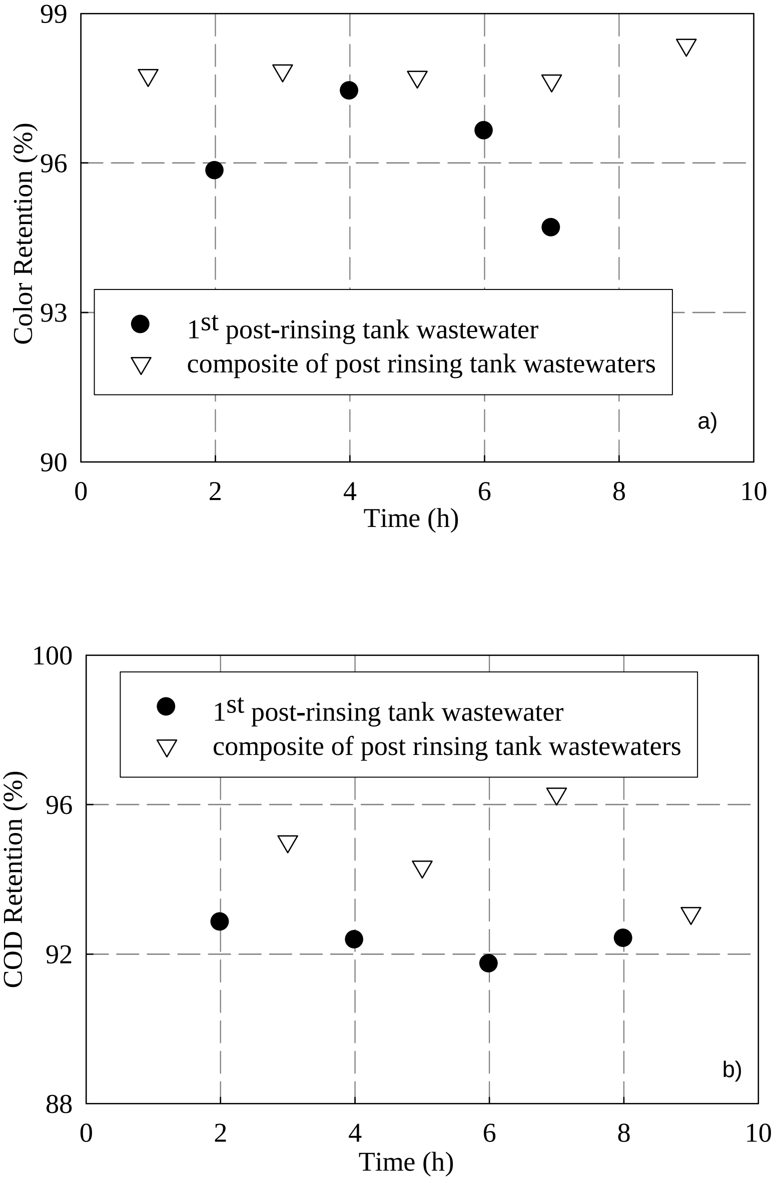


Figure B.12. Comparison of a) color and b) COD retention of NF 270 membrane used for the treatment of different concentrations of rinsing waters of indigo dyeing process

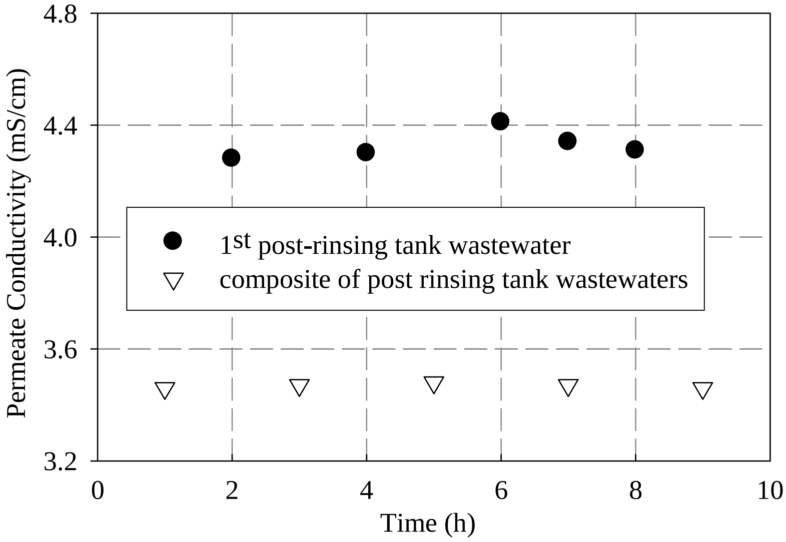


Figure B.13. Permeate conductivity of NF 270 membrane used for the treatment of different concentrations of rinsing waters of indigo dyeing process using F1 as feed

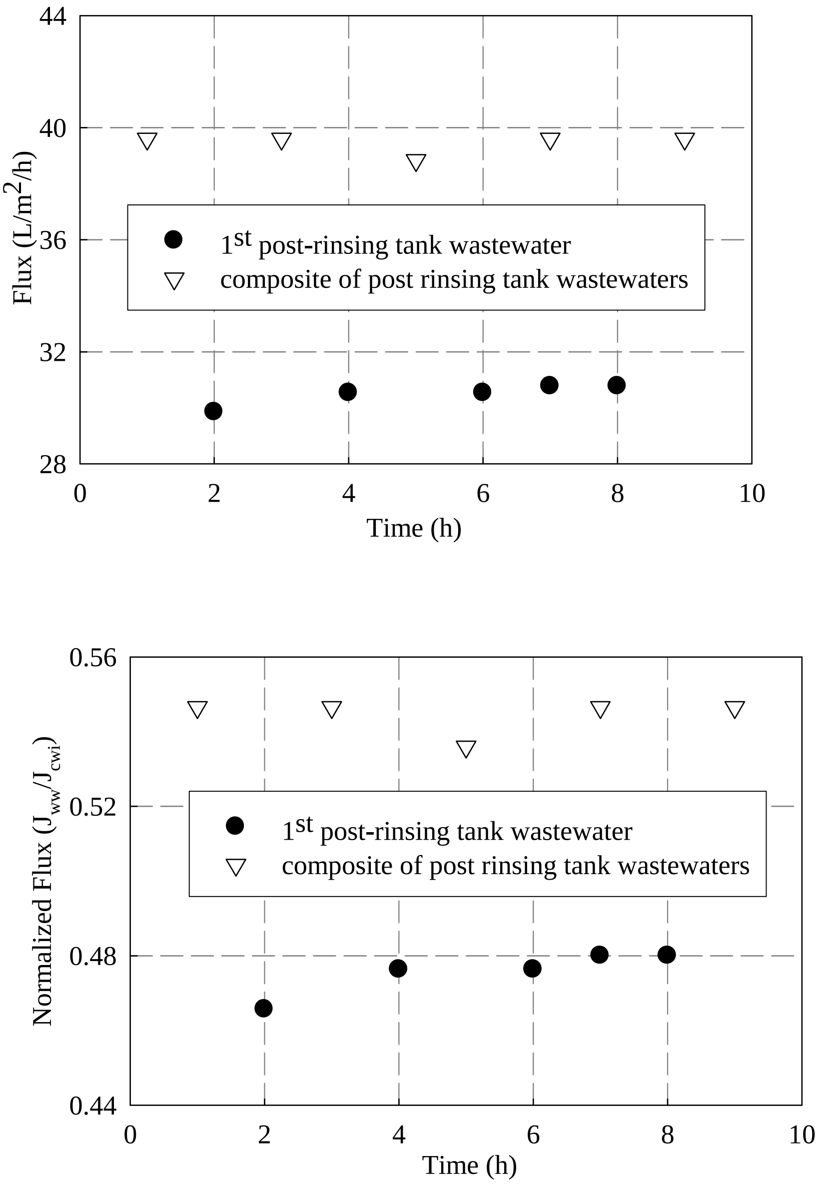
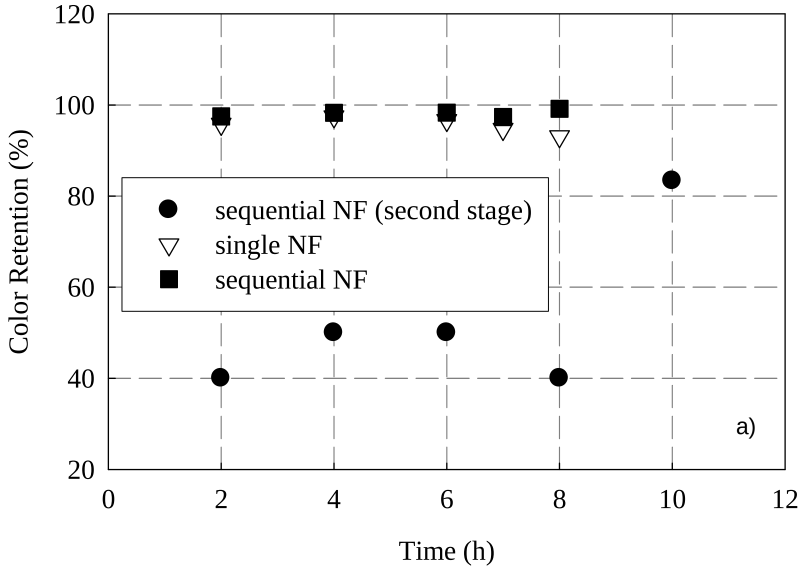


Figure B.14. Comparison of a) permeate and b) normalized flux of NF 270 membrane used for the treatment of different concentrations of rinsing waters of indigo dyeing process

B.1.5. Sequential NF



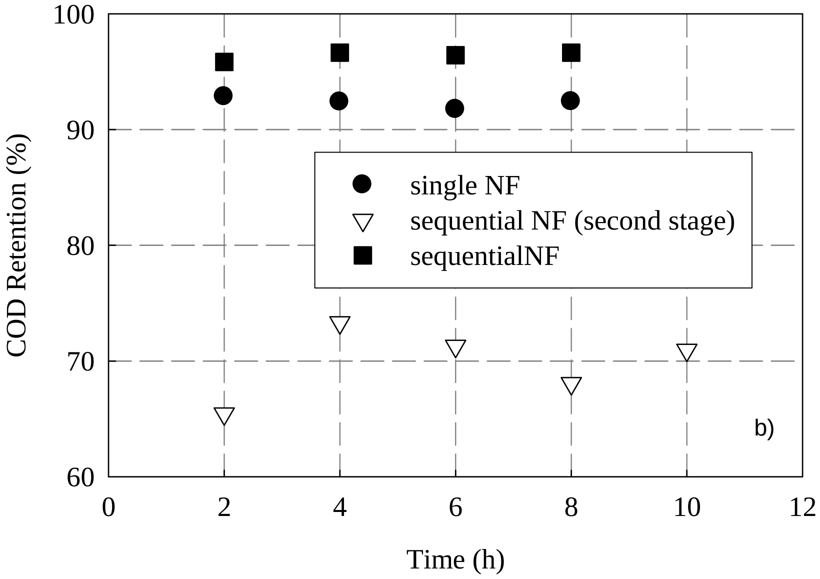


Figure B.15. Comparison of a) color and b) COD retention of single and sequential application of NF 270 membrane using F1 as feed

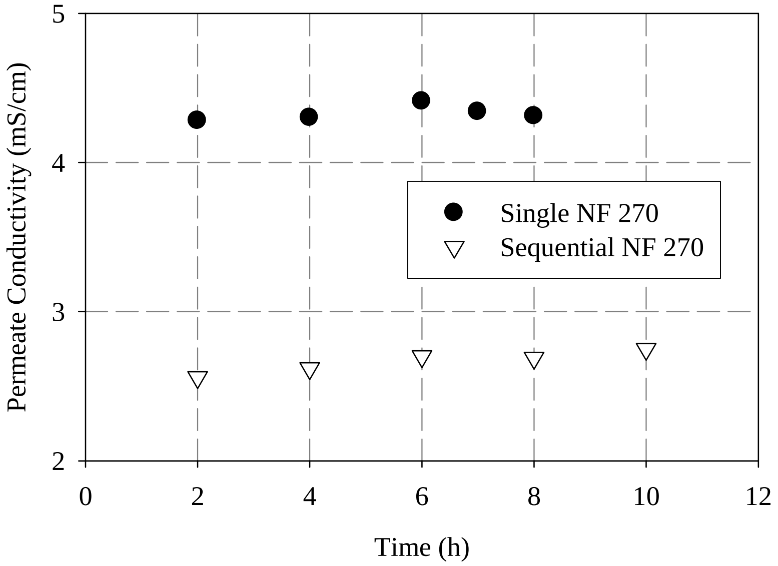


Figure B.16. Comparison of permeate conductivity of single and sequential application of NF 270 membrane using F1 as feed

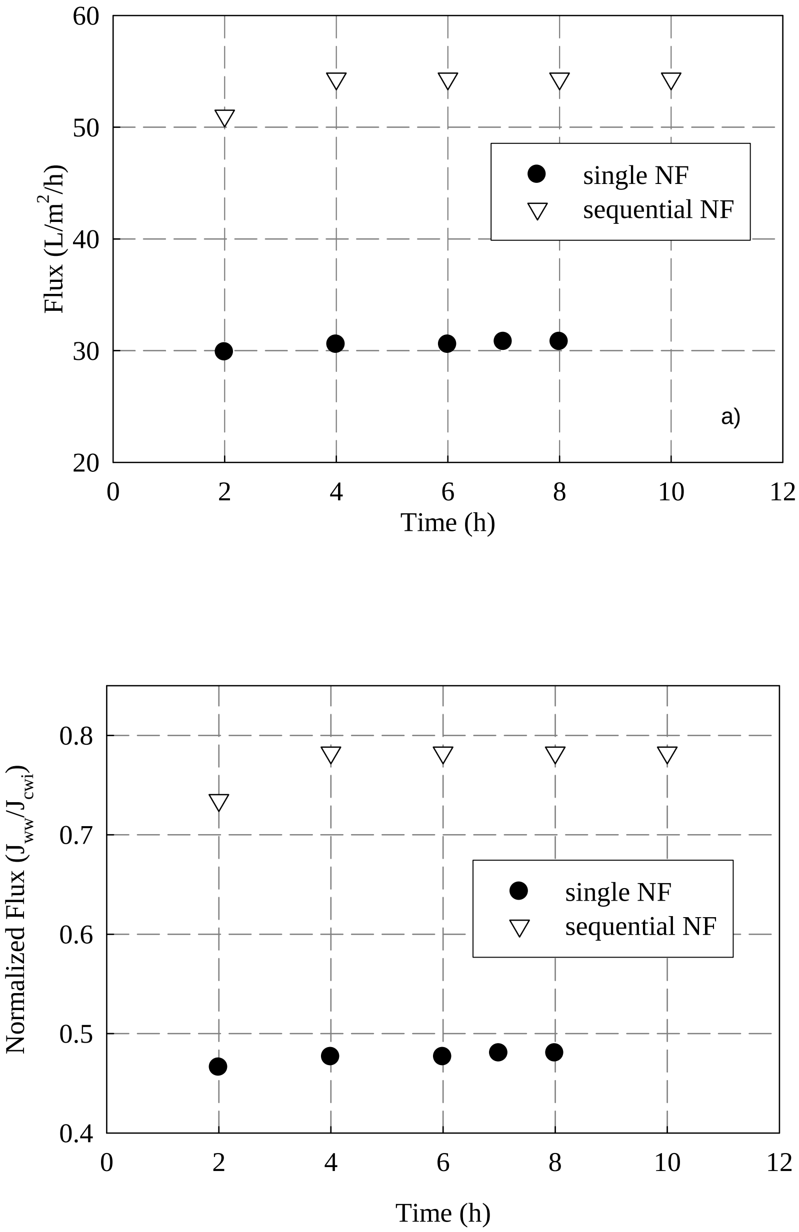


Figure B.17. Comparison of a) permeate flux and b) normalized flux for single and sequential application of NF 270 membrane using F1 as feed

B.2. RO

B.2.1. Effect of membrane type

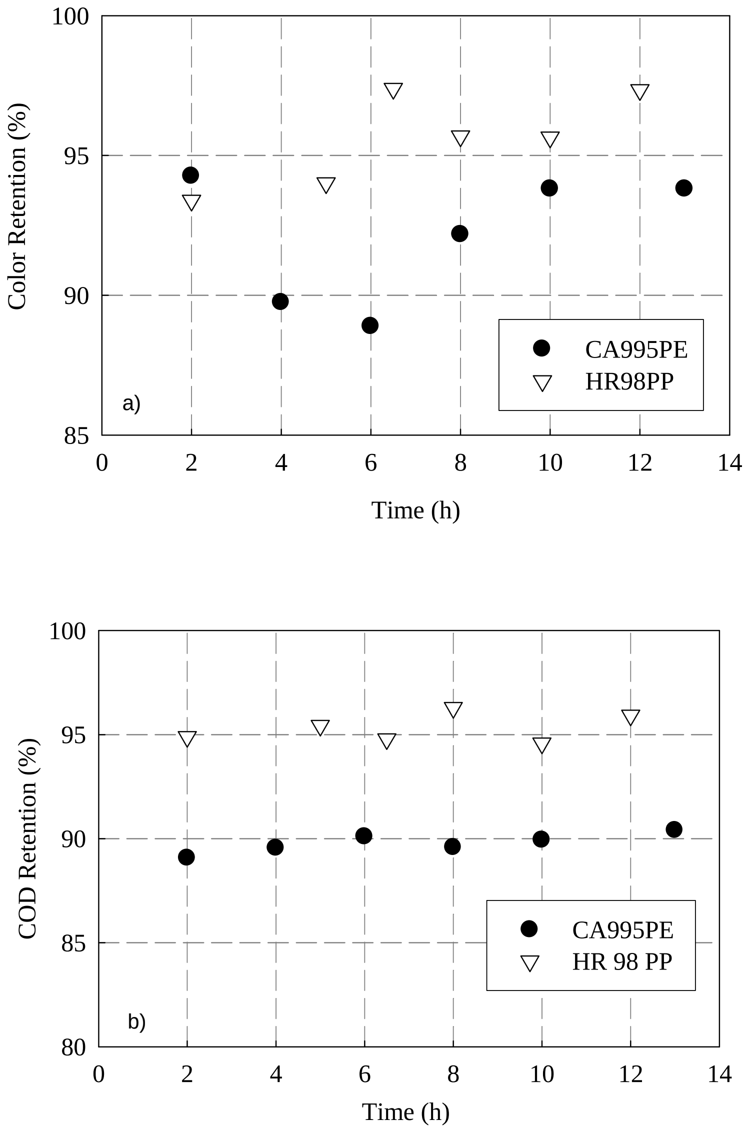


Figure B.18. Comparison of a) color and b) COD retentions of RO membranes (HR98PP, CA995PE) using F1 as feed

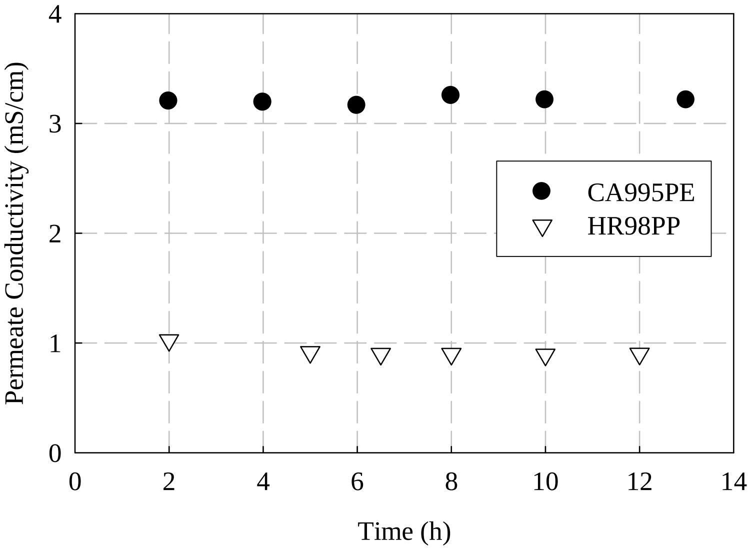
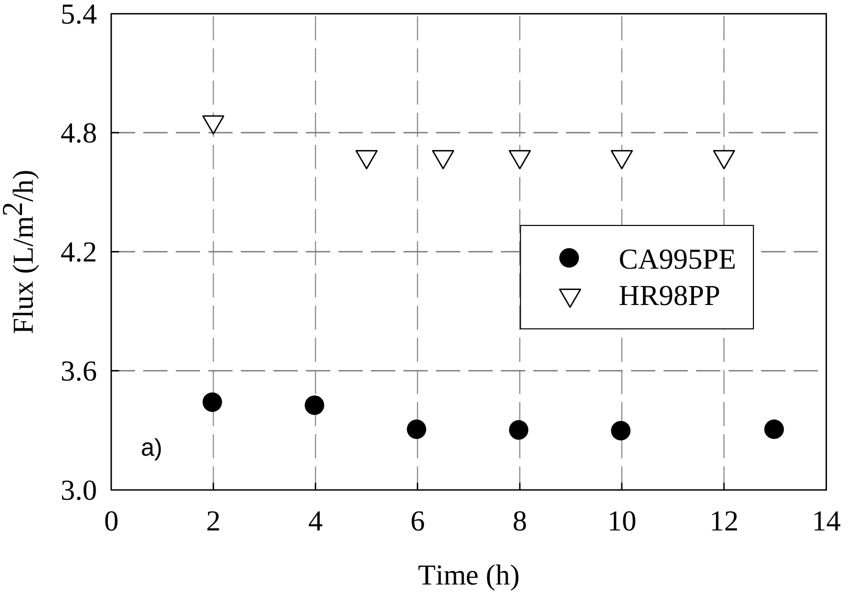


Figure B.19. Comparison of permeate conductivity values of RO membranes (HR98PP, CA995PE) using F1 as feed



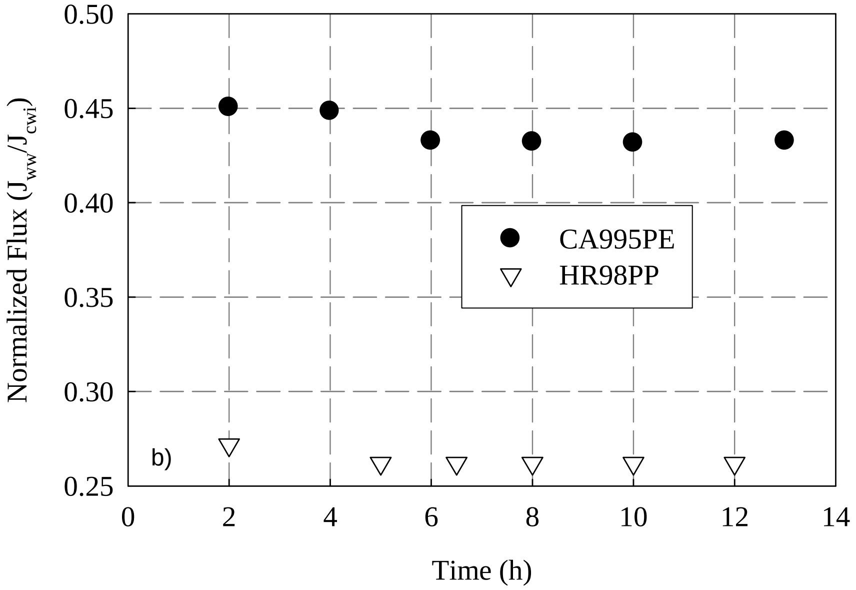


Figure B.20. Comparison of a) permeate and b) normalized flux of RO membranes (HR98PP, CA995PE) using F1 as feed

B.3. Comparison of RO-NF Experiments

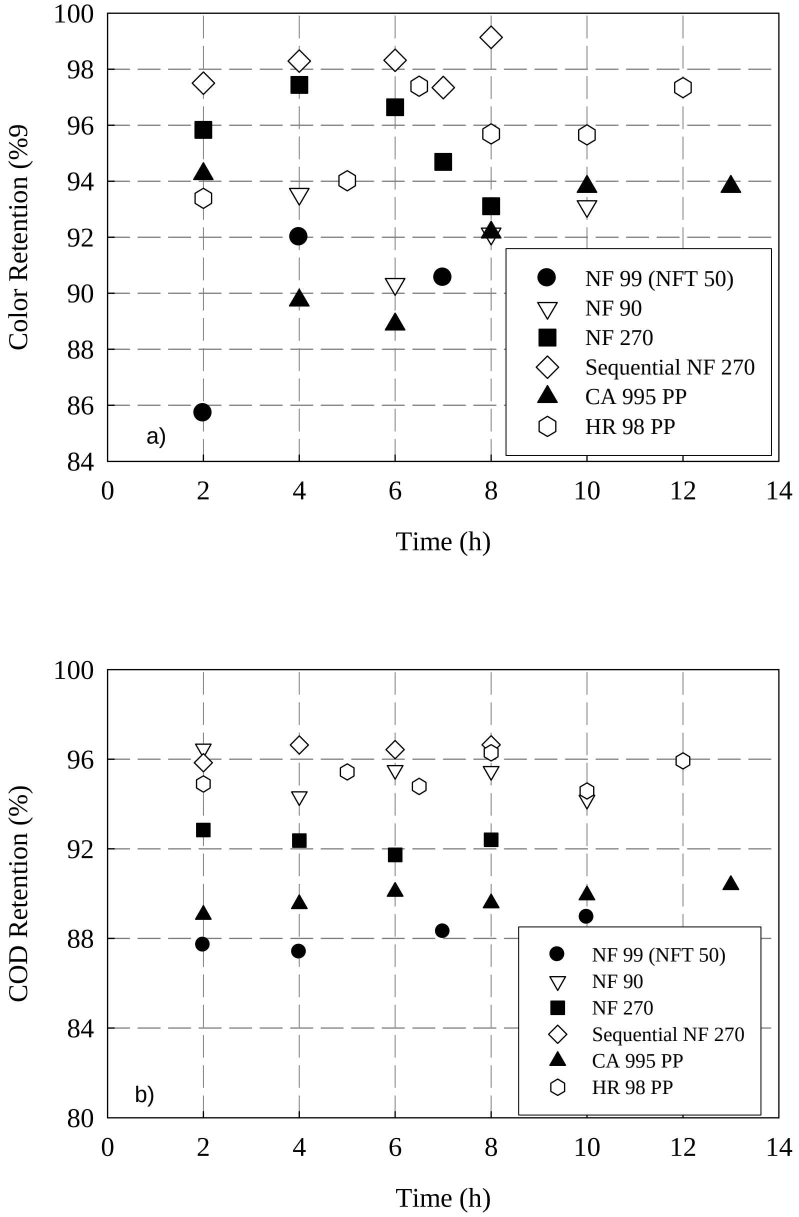


Figure B.21. Comparison of a) color and b) COD retentions of NF and RO membranes using F1 as feed

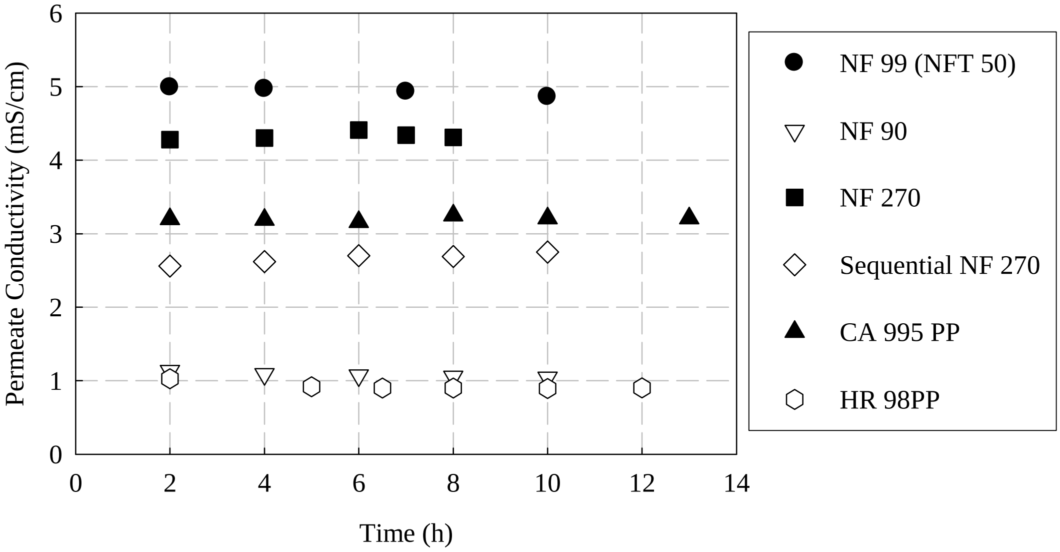
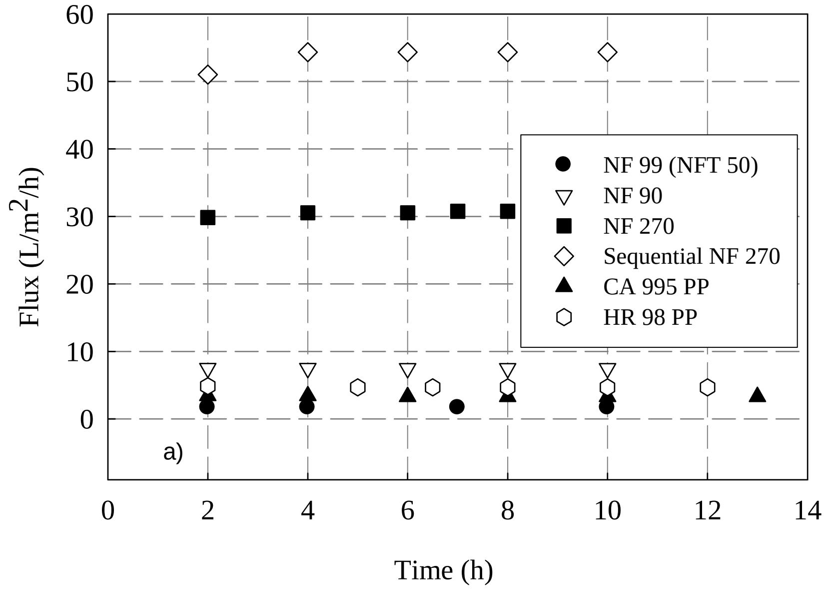


Figure B.22. Comparison of permeate conductivity values of NF and RO membranes using F1 as feed



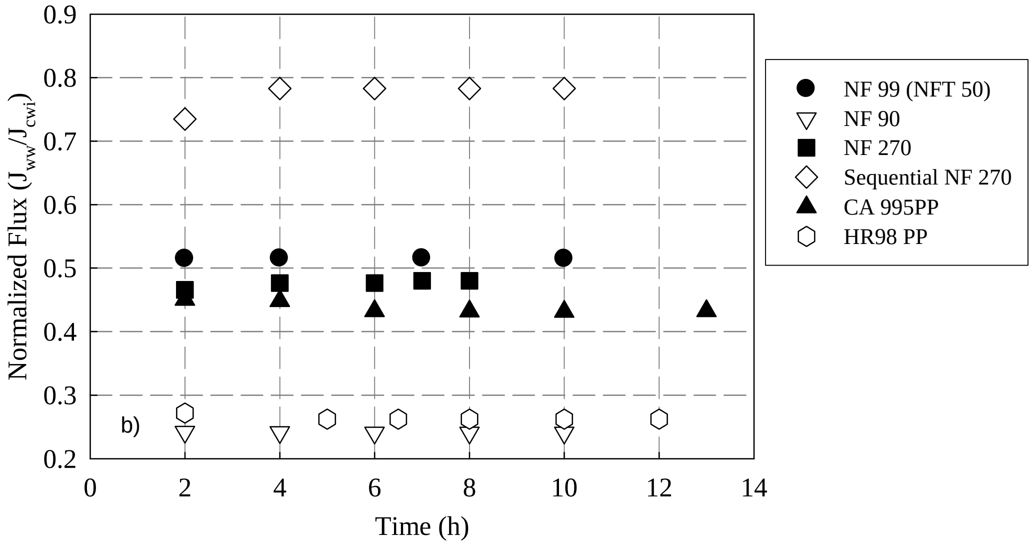


Figure B.23. Comparison of a) permeate and b) normalized fluxes of NF and RO membranes using F1 as feed

CURRICULUM VITAE

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Marital Status : Married
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EDUCATION

- **Ph.D.** Middle East Technical University, Department of Environmental Engineering, Ankara, Turkey, 2001-. Academic Advisor: Dr. Ülkü Yetiş, Academic Co-Advisor: Dr. Levent Yılmaz, Thesis Title: "Recovery and Reuse of Indigo Dyeing Wastewater Using Membrane Technology".

- **M.Sc.** Middle East Technical University, Department of Environmental Engineering, Ankara, Turkey. 1999-2001. Academic Advisor: Dr. Göksel. N. Demirer, Academic Co-Advisor: Dr. Celal F. Gökcay, Thesis Title: "Sequential Biological (Anaerobic/Aerobic) Treatment of Malt Whisky Wastewater".

- **B.Sc.** Mersin University, Department of Environmental Engineering, Mersin, Turkey. 1993-1997.

WORK EXPERIENCE

Teaching and Research Assistant, Department of Environmental Engineering, Middle East Technical University, Ankara/Turkey, 1999-

Organization Committee Member, UNESCO-IHE – UN/DOALOS - UNEP/GPA Train-Sea-Coast training on “Improving Municipal Wastewater Management in Coastal Cities”, 12-16 September 2006, Trabzon, Turkey

Organization Committee Member, UNESCO-IHE – UN/DOALOS - UNEP/GPA Train-Sea-Coast training on “Improving Municipal Wastewater Management in Coastal Cities”, 29 November-3December 2005, Ankara, Turkey

Researcher, Development of Tools and Guidelines for the Promotion of the Sustainable Urban Wastewater Treatment and Reuse in the Agricultural Production in the Mediterranean Countries, European Union - MEDAWARE, October 2003 – 2005

Organization Committee Member, II. National Environmental Pollution Control Symposium, METU, October 2003, Ankara

ASSISTED COURSES

Enve 102 Environmental Chemistry
Enve 201 Fundamentals of Environmental Engineering Processes
Enve 202 Environmental Microbiology Laboratory
Enve 208 Environmental Chemistry Laboratory
Enve 304 Unit Operations and Processes of Wastewater Treatment
Enve 409 Wastewater Engineering

CERTIFICATES

Advanced Seminar on “The Clean Development Mechanism (CDM) projects and the development of renewable energies in the Mediterranean Region”, 2006, from the 12- 14 September, 2006, Tangier, Morocco

XXIII EMS Summer School on Membranes, “SMART MATERIALS”, Institute of Macromolecular Chemistry, September 3-6, 2006, Prague

STaR City of the Future, TC 1, Sector C, “Waste-Changing Problems into Possibilities”, February 26th-March 3rd, 2006, Palma de Mallorca, Spain.

Network Young Membrains 6, 22-24 September 2004, Hamburg, Germany

PUBLICATIONS

1. Sahinkaya E., Uzal N., Yetis U. and Dilek F. B., “Biological treatment and nanofiltration of denim textile wastewater for reuse” *Journal of Hazardous Materials*, In press

2. Yukseler H., Uzal N., Unlu M., Varol C., Sahinkaya E., Yigit N. O., Yilmaz L., Kitis M., Demirer G. N., Dilek F. B. and Yetis U., 2007, “Integrated Wastewater Management in a Denim Manufacturing Textile Mill-Implementation of EU’s IPPC Directive”, 6th IWA Specialist Conference on Wastewater Reclamation and Reuse for Sustainability, 09-12 October, Antwerp, Belgium(oral presentation)

3. Uzal N., Yilmaz L., Yetis U., 2007, “Microfiltration/Ultrafiltration As Pretreatment For Reclamation Of Rinsing Waters Of Indigo Dyeing”, Membrane Science and Technology Conference of Visegrad Countries, 2-6 September, Siofok, Hungary (oral presentation)

4. Yigit N.O., Uzal N., Koseoglu H., Harman I., Yukseler H., Yetis U., Civelekoglu G., Kitis M., 2007, “Treatment of A Denim Producing Textile Industry Wastewater Using Pilot-Scale Membrane Bioreactor”, Membrane Science and Technology Conference of Visegrad Countries, 2-6 September, Siofok, Hungary (oral presentation)

5. Varol C., Uzal N., Dilek F. B., Kitis M., Yetis U., 2007, “Caustic Recovery From Highly Alkaline Denim Finishing Wastewaters Using Membrane Technology”, Membrane Science and Technology Conference of Visegrad Countries, 2-6 September, Siofok, Hungary (poster presentation)

6. Yiğit N. Ö., Harman İ., Uzal N., Yükseler H., Yetiş Ü., Civelekoğlu G., Kitis M., 2007, “Treatment of textile industry wastewater using pilotscale membrane bıoreactor”, National Environmental Symposium, 18-21 April 2007, Icel, Turkey

7. Uzal N., Yukseler H., Unlu M., Yılmaz O., Varol C., Demirer G.N., Dilek F. B., Yetis U., 2006, “Water Reuse and Recycling opportunities in dyeing process of a denim producing factory”, IWA, The Seventh International Symposium on Waste Management Problems in Agro-Industries, 27-29 September 2006, Amsterdam RAI, The Netherlands. (oral presentation)

8. Yükseler H., Uzal N., Ünlü M., Yılmaz Ö., Varol C., Demirer G.N., Dilek F. B., Yetiş Ü., “Adoption Of EU’s IPPC Directive: Determining BAT In A Turkish Denim Manufacturing Plant”, The Seventh International Symposium On Waste Management Problems In Agro-Industries, 27 – 29 September 2006, Amsterdam RAI, The Netherlands. (poster presentation)

9. Uzal N., Yılmaz L, Yetiş U, 2006,”Microfiltration: A Pretreatment Alternative for Indigo Dyeing Textile Wastewater”, *Desalination*, vol 199, pp, 515–517, (presented in Euromembrane 2006, September 24-28, Giardini Naxos, Taormina, Italy)

10. Uzal N, Yılmaz L, Yetis Ü., 2006," Microfiltration: A Pretreatment Alternative for Indigo Dyeing Textile Wastewater" Tenth Industrial Pollution Control Symposium, Istanbul Technical University, 07-09 June 2006, Istanbul, Turkey, (in Turkish), (oral presentation)

11. Uzal N., Yılmaz L., Yetis U., 2005, "Pretreatment of Indigo Dyeing Wastewater: Comparison of Chemical Coagulation and Prefiltration Processes", Sixth National Environmental Engineering Congress, UCTEA Chamber of Environmental Engineers, October 2005, Istanbul, Turkey. (in Turkish)

12. Uzal N., Gökçay C.F., and Demirer G.N., 2005, "Evaluation of the performance of UASB reactor system for malt whisky wastewater treatment", 3'rd European Bioremediation Conference, 4-7 July 2005, Chania, Greece.

13. Uzal N., Network Young Membrains 6, "Pretreatment of indigo dyeing wastewater using microfiltration", 22-24 September 2004, Hamburg, Germany

14. Uzal N., Gökçay C.F., and Demirer G.N., 2003. "Sequential (anaerobic/aerobic) biological treatment of malt whisky wastewater", *Process Biochemistry*, Volume 39, Issue 3, Pages 279-286.

15. Uzal N., Ergüder T.H., Tezel U., İmamoğlu İ., Demirer G.N., 2003, "Use of natural zeolites in environmental pollution control and a case-study on Cu(II) removal" II. National Environmental Pollution Control Symposium, 22-24 October 2003, METU, Ankara, Turkey (in Turkish)

16. Arıkan Y., Uzal N., Oğuz M., Demirer G. N., 2004, "Characterization of the Mamak municipal solid waste dump site leachate and its effects on the Imrahor creek", Environment Science and Technology, Volume 2 Issue 1. (in Turkish)

17. Varolan N., Gökçay C.F., and Demirer G.N., 2001, “Sequential biological (anaerobic/aerobic) treatment of whisky production wastewater”, Fourth National Environmental Engineering Congress, UCTEA Chamber of Environmental Engineers, 443-450, 7-10 November 2001, İçel, Turkey. (in Turkish)

18. Bayrakçi F., Sentörengil S., Ayvaz-Kahramantekin T., Atalay Ç., Karakurt B., Sen S., Varolan N. and Demirer G.N., 2001, “Treatment of sunflower oil production wastewater in batch anaerobic reactors”, Fourth National Environmental Engineering Congress, UCTEA Chamber of Environmental Engineers, 600-603, 7-10 November 2001, İçel, Turkey. (in Turkish)

19. Demirer G.N., Duran M., Güven E., Ugurlu Ö., Ergüder T.H., Tezel U., Sen S., Korkusuz E.A., and Varolan N., 2001, "Biogas production from organic wastes by anaerobic methods: applicability in Turkey", Renewable Energy Symposium, Chamber of Electrical Engineers, 18-20 January 2001, İzmir, Turkey, 99-105. (in Turkish)

20. Demirer G.N., Duran M., Güven E., Ugurlu Ö., Ergüder T.H., Tezel U., Sen S., Korkusuz E.A., Varolan N., Demirci G., Çapar G., Acuner E., and Sahinkaya E., 2000, "An example for biomass energy: Biogas production from organic wastes by anaerobic methods", Third National Clean Energy Symposium, İstanbul Technical University and Clean Energy Foundation, 15-17 November 2000, İstanbul, Turkey, 467-474. (in Turkish)

RESEARCH PROJECTS

1. Researcher, Demirer G. N., Duran M., R. E. Speece, A. Atimtay, Güven E., Ergüder T.H., Ugurlu Ö., Tezel U., Sen S. and Varolan N. “Application of Anaerobic Technologies for the Management of Industrial Wastewaters” State Planning Organization of Turkey, AFP-03-11DPT.98K122800, Budget: 50,000 USD, METU, Ankara, Turkey, 1998-2001.

2. Researcher, İmamoğlu İ., Demirer G. N., Tezel U., Ergüder T.H., Uzal N., “Use of Natural Zeolites in Environmental Pollution Prevention”, BAP, METU, Ankara, 2003-2004.

3. Researcher, Yetiş Ü., Dilek F.B., Demirer G.N., Kitiş M., Yılmaz L., Kerestecioğlu M., Uzal N., Yükseler H., Sahinkaya E., “Studies on Adopting the EU IPPC Directive in Textile Sector: BAT Applications”, The Scientific and Technical Research Council of Turkey, ÇAYDAG-105Y088, Budget: $332,700 METU, Ankara, Turkey, 2005-.