DEVELOPMENT OF A MEMBRANE BASED TREATMENT SCHEME FOR WATER RECOVERY FROM TEXTILE EFFLUENTS

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
OF
MIDDLE EAST TECHNICAL UNIVERSITY

BY

GÖKŞEN ÇAPAR

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY
IN
ENVIRONMENTAL ENGINEERING

JANUARY 2005

Approval of the Graduate School of Natural and Applied Sciences

Prof. Dr. Canan Özgen
Director

I certify that this thesis satisfies all the requirements as a thesis for the degree of Doctor of Philosophy.

Prof. Dr. Filiz B. Dilek
Head of Department

This is to certify that we have read this thesis and that in our opinion it is fully adequate, in scope and quality, as a thesis for the degree of Doctor of Philosophy.

Prof. Dr. Levent Yılmaz Co-Supervisor	Prof. Dr. Ülkü Yetiş Supervisor

Examining Committee Members

Prof. Dr. Celal F. Gökçay	(METU, ENVE)	
Prof. Dr. Ülkü Yetiş	(METU, ENVE)	
Prof. Dr. Filiz B. Dilek	(METU, ENVE)	
Prof. Dr. Türker Gürkan	(METU, CHE)	
Prof. Dr. Veysel Eroğlu	(ITU, ENVE)	

I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

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ABSTRACT

DEVELOPMENT OF A MEMBRANE BASED TREATMENT SCHEME FOR WATER RECOVERY FROM TEXTILE EFFLUENTS

Çapar, Gökşen

Ph. D., Department of Environmental Engineering
Supervisor: Prof. Dr. Ülkü Yetiş
Co-Supervisor: Prof. Dr. Levent Yılmaz

January 2005, 245 pages

A membrane based treatment scheme was developed for the recovery of the print dyeing wastewaters (PDWs) and the acid dye bath wastewaters (ADBWs) of carpet manufacturing industry. The treatment schemes were developed by selecting the best pre-treatment and treatment processes among the alternatives of chemical precipitation (CP), microfiltration (MF), ultrafiltration (UF) and nanofiltration (NF). The best process train for PDW was CP+NF, where organic matter, color, turbidity and total hardness were removed at >95%. The alternative process train CP+UF also removed color and turbidity almost completely, however organic matter rejection was low, being 25% at highest. The quality of NF permeates were suitable for dyeing of light colors whereas UF permeates were suggested for washing of the printed carpets or dyeing of the dark colors.

The best process train for ADBW was MF (1.0 μm)+NF, where organic matter rejection increased from 65% to 97% due to pH neutralization. Alternatively, sequential NF was required up to three stages in order to achieve similarly high rejections at the acidic pH of ADBW. Therefore, pH neutralization was realized to be a very important operational parameter affecting the treatment scheme. Although pH neutralization increased the flux declines by almost 5%, chemical cleaning was very effective to restore the original fluxes.

Finally, ADBW was mixed with PDW, which already had a pH around neutral, so that the pH of ADBW would rise towards neutral without chemical consumption. The results suggested that these wastewaters could be treated together as long as they were mixed up to equal volumes at pH around neutral. Therefore, a final treatment scheme, which involved single NF for the mixture of PDW and ADBW, following their individual pre-treatment stages, was proposed as the most efficient process train.

Keywords: Carpet Dyeing Wastewater, Color, Flux, Membrane, Recovery

ÖZ

TEKSTİL ATIKSULARINDAN SU GERİ KAZANIMI İÇİN MEMBRAN ESASLI BİR ARITMA SÜRECİ GELİŞTİRİLMESİ

Çapar, Gökşen

Doktora, Çevre Mühendisliği Bölümü
Tez Yöneticisi: Prof. Dr. Ülkü Yetiş
Ortak Tez Yöneticisi: Prof.Dr. Levent Yılmaz

Ocak 2005, 245 sayfa

Halı üretim endüstrisine ait baskı boyama atıksuları (BBA) ile asit boya banyosu atıksularının (ABBA) geri kazanımı için membran esaslı bir arıtma süreci geliştirilmiştir. Arıtma süreçleri, ön arıtma ve arıtma aşamalarında test edilen kimyasal çöktürme (KÇ), mikrofiltrasyon (MF), ultrafiltrasyon (UF) ve nanofiltrasyon (NF) alternatifleri arasından en iyi ön-arıtma ve arıtma proseslerinin seçilmesi sonucunda belirlenmiştir. BBA için en iyi arıtma süreci, %95'in üzerinde organik madde, renk, bulanıklık ve toplam sertlik giderimi ile CP+NF olmuştur. CP+UF'in denendiği alternatif süreçte renk ve bulanıklığın benzer olarak yaklaşık tamamı tutulurken, organik madde giderimi en çok %25 ile sınırlı kalmıştır. NF süzüntü suyunun kalitesi, açık renkli halıların dahi boyanmasında kullanıma uygunken, UF süzüntü sularının baskı yoluyla boyanan halıların yıkanmasına veya koyu renklerin boyanmasına uygun olduğu sonucuna varılmıştır.

ABBA için en uygun arıtma sürecinin MF (1.0 μm)+NF olduğu tespit edilmiş, asidik pH'da %65 olan organik madde giderimi, pH nötralizasyonu ile %97'ye çıkarılmıştır. ABBA'nın orijinal asidik pH'sında benzer şekilde yüksek giderimler elde etmek için üç aşamalı seri NF uygulaması gerektiği bulunmuştur. Bunun sonucunda, pH nötralizasyonunun arıtma sürecini etkileyen çok önemli bir işletim parametresi olduğu ortaya çıkmıştır. Akı azalmaları, pH nötralizasyonu nedeniyle % 5 kadar artmış olmasına rağmen, kimyasal yıkama ile akılar geri kazanılmıştır.

Ek bir kimyasal harcamadan ABBA'nın pH'sının nötralize edilmesi amacıyla, ABBA ile hali hazırda yaklaşık nötr pH'ya sahip olan BBA'nın karıştırılarak arıtılmaları denenmiştir. Elde edilen sonuçlar bu iki atıksuyun nötr pH'da eşit hacimlere kadar karıştırıldıkları sürece birlikte arıtılabileceklerini göstermiştir. Böylece, BBA ve ABBA'nın kendi ön-arıtma proseslerinden geçtikten sonra karıştırılmaları ve birlikte tek NF ünitesinden nötr pH'da geçirilerek arıtılmaları, en etkin proses süreci olarak önerilmiştir.

Anahtar Kelimeler: Halı Boyama Atıksuyu, Akı, Geri Kazanım, Membran, Renk

To all those waters wasted by us…

ACKNOWLEDGMENTS

I would like to express my deepest gratitude to my supervisor Prof. Dr. Ülkü Yetiş for her guidance, trust, care and encouragement, which have never been limited to the time periods of our research studies.

I wish to express my deep gratitute to my co-supervisor Prof. Dr. Levent Yılmaz for his excitement, guidance and constant support throughout this research.

I would like to thank the Supervising Committee Members, Prof. Dr. Filiz B. Dilek and Prof. Dr. Türker Gürkan for their valuable suggestions and constructive criticism.

TÜBİTAK is gratefully acknowledged for the financial support via grant no MİSAG-214.

Thanks to Samur Carpet Factory personnel for providing hundreds of liters of wastewaters with pleasure, especially Arzu Deveci for her kind help.

Many thanks go to all the Environmental and Chemical Engineering Department staff for their help and cooperation, especially Cemalettin Akın for driving me to Samur Carpet Factory several times.

My sincere thanks go to my family for their endless support, especially Gülten Kesiktaş for being a devoted mother.

And I owe very special thanks to my twin star Muzaffer Çapar for being by my side in all the hard times.

Lastly, I wish to thank my lovely daughter, Öykü Buke Çapar for crowning my life with joy and happiness.

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ABBREVIATIONS

ADBW : Acid Dye Bath Wastewater
BOD : Biochemical Oxygen Demand
BTTG : British Textile Technology Group
CA : Cellulose Acetate
CIP : Cleaning in Place
CMF : Concentration Mode of Filtration
COD : Chemical Oxygen Demand
CP : Chemical Precipitation
Da : Dalton
DW : Distilled Water
EPA : Environmental Protection Agency
EU : European Union
GCGO : German Consumer Goods Ordinance
GG : Grey G
HDCP : High Dose Chemical Precipitation
J_{cw} : Clean Water Flux
J_{ww} : Wastewater Flux
LC_{50} : Lethal Concentration
LDCP : Low Dose Chemical Precipitation
MF : Microfiltration
MWCO : Molecular Weight Cut Off
NF : Nanofiltration
NPOC : Non-purgeable Organic Carbon
NTU : Nephelometric Turbidity Unit
P : Pressure

PA	: Polyamide
PDW	: Print Dyeing Wastewater
PTFE	: Polytetrafluoroethylene
R	: Retention
Red G	: Red G
RO	: Reverse Osmosis
rpm	: Revolution Per Minute
T	: Temperature
TMP	: Trans Membrane Pressure
TOC	: Total Organic Carbon
TRMF	: Total Recycle Mode of Filtration
UF	: Ultrafiltration
UVA	: Ultraviolet Absorbance
WPCR	: Water Pollution Control Regulation
Y2R	: Yellow 2R

CHAPTER 1

INTRODUCTION

1.1. Textile Wastewaters

The potential scarcity of water supplies on earth has become one of the most challenging problems of human beings. The world population is ever increasing, creating the need for more production of goods, leading to more industrialization, and hence more water consumption through the industrial processes. Today, approximately half of the available water is being used for domestic purposes, and the other half is consumed by the industrial and agricultural activities (Tang and Chen, 2002). In addition to fresh water shortage, industrial activities lead to the most severe environmental pollution problems via discharge of wastewaters into the receiving water bodies. Although treatment of these wastewaters before discharging is obligatory by the relevant environmental protection legislations, neither all the industrial facilities in the world have treatment plants nor do the existing ones have adequate treatment efficiencies. As a result, the water quality in the receiving environments rapidly deteriorates. The shortage of water supplies also forces the industrialists to pay even more for their fresh water consumption and wastewater generation. All these facts force the industrialists to consider the recovery and reuse of their wastewaters, at least to a certain extent.

Textile industry is one of the oldest and heaviest polluters in the world. Textile effluents have been subjected to a considerable extent of research for many years due to the fact that they are generated in huge volumes in addition to being quite complex in nature due to the presence of several dyes and auxiliary chemicals.

The textile industry consists of a number of processes employed for converting fibers of natural origin such as cotton, silk and wool, and of synthetic origin such as nylon; first into fabrics by weaving and knitting and then into the final products by applying wet processes such as dyeing, sizing, printing, and finishing. These stages involve treating the fabric with chemical baths including dispersing agents, salts, emulsifiers, leveling agents, and in some cases heavy metals, and often require additional washing, rinsing, and drying steps, and hence they imply a large consumption of fresh water, energy, chemicals and a large production of waste streams. In terms of waste generation and environmental impacts, wet processing is the most significant textile operation.

The wastewaters originating from dyeing processes are generally characterized by the high content of color caused by the dyestuffs; salts; chemical oxygen demand (COD) deriving from additives such as acetic acid, detergents and complexing agents; suspended solids including fibers; high temperature and broadly fluctuating pH. Textile industries typically generate 200-500 L of wastewater per kg of finished product (Marcucci et al., 2001) resulting in an average pollution of 0.1 kg COD per kg of fabric (Jekel, 1997).

Dyes are aromatic organic compounds, and based fundamentally on the structure of benzene, toluene or naphthalene as they are typically derived from coal tar and petroleum-based intermediates. Through chemical processes such as nitration and sulfonation, these chemicals are processed into dye intermediates such as aniline, which are processed further by special operations like diazotization to give the final product - a dry chemical powder. There are many types of dyes, which are most commonly classified according to their structure or their dyeing properties. According to the dyeing properties the dye classes are; acid, basic, direct, disperse, mordant, reactive, sulfur and vat dyes. Each dye class is suitable to a specific type of fiber and hence the fixation rate of each class of dye is different. The highest and lowest fixation rates belong to basic dyes (97-98%) and sulfur dyes (60-70%), respectively (USEPA, 1997). In general, approximately 20-40% of the input dye remains in the wastewater (Wu et al., 1998). Their concentrations in dye-baths range from 10 to 1000 mg/L (İnce and Tezcanlı, 1999). The inefficiency of the conventional biological treatment methods for decolorizing the textile effluents leads to the discharge of highly colored wastewaters into the receiving environment. Accumulation of dyes in certain forms of aquatic life is suspected of leading to toxic and carcinogenic degradation products. Moreover, dyes limit aquatic plant growth by reducing light transmittance, and prohibiting the photosynthetic activity in the receiving water bodies (Buckley, 1992).

There are many subcategories of the textile industry, where different types and concentrations of dyes and chemicals are used in a number of processes for the production of a wide variety of fabrics. The diversity of the textile production schemes leads to the generation of wastewaters of highly varying concentrations; such that, 50-5000 mg/L of COD, 50-500 mg/L of suspended solids, and a highly variable range of color (Marcucci et al., 2003). This fact makes the treatment of textile wastewaters a difficult task, and necessitates the examination of each factory individually for the determination of the best treatment method.

1.2. Treatment Alternatives

There are several conventional methods used to treat the textile wastewaters in order to meet the effluent standards set for the industry. These methods are mainly biological treatment (aerobic, anaerobic or both), physico-chemical treatment (precipitation and coagulation followed by flocculation and sedimentation), adsorption, ion exchange, chemical oxidation (with oxidizing agents like ozone and hydrogen peroxide) and membrane separation. Each treatment method has its own advantages and disadvantages, and the selection of the method mainly depends on the treatment target to be achieved. The basic advantages and disadvantages of each method are discussed in the following paragraphs.

Biological methods, especially the traditional activated sludge process have been widely used for the treatment of textile wastewaters due to their low operational costs (Naim and El Abd, 2002). These systems offer high efficiencies in COD removal, but cannot provide a complete color removal because most textile dyes have complex aromatic molecular structures that resist degradation. Moreover, biological systems need constant attention to maintain the correct operational conditions like pH, temperature, oxygen and nutrient concentrations. The bacteria are extremely intolerant to the toxicity of the waste, and the problem of sludge bulking is often observed (Lin and Peng, 1996; Ahn et al., 1999).

Physico-chemical treatment has the advantage of being flexible and tolerant to the wide variations in wastewater quality provided that the chemical dosages are adjusted accordingly. Alum, ferric sulfate or ferric chloride is used as coagulant, together with lime or sulfuric acid for pH control. The efficiency of the coagulation and flocculation processes vary with the changing properties of the wastewaters and the color removal may not be sufficient for each case. Therefore, the drawbacks of the chemical methods are generally the excess chemical usage, increased sludge production, and often unsatisfactory dye removal (Machenbach, 1998).

Activated carbon is a very good adsorbent for removing dissolved organic material from water, especially solvents and low levels of dyestuff or toxic products. However, the degree of color removal is dye-specific and the adsorption capacity can be as low as 20%. In addition, regeneration results in a performance reduction up to 70-80% of that of the virgin carbon and the efficiency becomes dependent on high carbon dosages (Naim and Yehia, 2002).

The oxidation methods are usually successful in treating the dyes that are resistant to biodegradation. In oxidative processes it is aimed to break the dye molecule and destroy the chromophore, or convert it into a readily biodegradable form. Ozonation can achieve high color removal, reduce the level of organic compounds, improve biodegradability, destroy phenols, and insure disinfection. One of the drawbacks of ozonation is the cost (Gahr et al., 1994). Moreover, even high doses of ozone do not completely convert the organics to carbon dioxide and water, particularly for dye wastes containing surfactants and suspended matter (Lin and Lui, 1994). Problems in oxidative treatment can be the formation of toxic intermediates like aromatic amines or elevated heavy metal concentrations in the case of metal-complex azo dyes. If ozonated effluent is reused in the dyeing process, degradation products are likely to accumulate in the recycled liquor and interfere in the dyeing process (Erswell et al., 1988).

All these treatment methods mentioned above are basically applied as end-of-pipe processes to comply with the limits imposed by legislation for discharge. However, the recalcitrance and biotoxicity of most of the compounds together with their fluctuating concentrations and flow rates makes the conventional processes quite insufficient for the treatment of textile wastewaters, especially for color (Shu and Huang, 1995; Marmargne and Coste, 1996). As a feasible alternative to the conventional methods there is the membrane separation technology, a quite promising process-integrated method allowing not only advanced treatment but also recovery of valuable materials like water, dyes and chemicals (Wu et al., 1998; Noel et al., 2000; Akbari et al., 2002).

The need for the minimization of water consumption due to the potential shortage of earth's water supplies and the increased rates paid by the manufacturers for fresh water has lead to a growing interest in water reuse. Textile factories are large consumers of groundwater for quality reasons and therefore, water reclamation has become a key topic in the textile industry. There have been an extensively growing number of studies performed on the purification of the complex textile wastewaters using membrane separation processes in the last decade (Nelson, 1994; Chen et al., 1997; van't Hull et al., 1997; Wu et al., 1998; Sojka-Ledakowicz, 1998; Dhale and Mahajani, 2000; Ciardelli et al., 2000; Jirarantananon et al., 2000; Noel at al., 2000). Almost all the researchers have obtained high removal efficiencies for color and organic matter (%80-100) and also achieved high rates of water recovery (%70-100).

The major problem with the application of membrane technology is the flux decline, which is defined as the reduction in the volume of the fluid passing through the membrane per unit time and area. Flux decline is a natural consequence of filtration since the concentration of the retained materials accumulating reversibly and/or irreversibly at the membrane surface, increase with time. Flux decline occurs as a result of two phenomena; concentration polarization and fouling. Concentration polarization is totally reversible and diminishes by the release of the driving force, whereas fouling can either be reversible or irreversible due to adsorption, precipitation, pore blocking and cake formation. Reduction in flux means decreased productivity, therefore a proper pre-treatment stage is often necessary in order to minimize it. Choosing a suitable membrane and the correct module type as well as the optimized operational conditions is also important for achieving the most efficient membrane operation. Reduced fluxes can be restored by cleaning, however cleaning procedures are generally more effective in removing foulants accumulated on the membrane surface rather than within its pores, which may lead to the occurrence of an irreversible fraction of fouling. Therefore, monitoring the time dependent behaviour of flux and the determination of the reversible and irreversible fractions of flux decline are important for evaluating the performance of the membrane systems.

There have been several approaches consisting of two or more step processes for textile wastewater reclamation, where more conventional methods like coagulation, flocculation and clarification are used as well as microfiltration (MF) and ultrafiltration (UF) in the pre-treatment stages. After passing through one or more of these stages, the wastewater is further purified in other pressure-driven membrane processes, i.e., nanofiltration (NF) or reverse osmosis (RO) to the degree of reuse quality. There has been a shift in trend to MF in the pre-treatment stage as it is economically more attractive as compared to conventional methods (Vedavyasan, 2000). Depending on the requirement of the final permeate quality, the process combinations vary, making the best treatment scheme quite specific to the particular effluent. Therefore, each particular textile effluent needs to be handled individually. In addition, the requirement of more than one unit in the process train points out the disadvantage of increased treatment costs. To this end, production of the final permeates having adequate quality for reuse via the most simple and energy efficient membrane process combinations is of great value.

Although most of the textile subcategories use groundwater for dyeing processes, wide variations in the acceptable quality of the recovered process waters have been reported in literature (Groves et al., 1979; Comodo et al., 1993; Sojka-Ledakowics et al., 1998; Rozzi et al., 1999; Ciardelli et al., 2001; Marcucci et al., 2001; Bottino et al., 2000; van der Bruggen et al., 2001; British Textile Technology Group, 1999). Therefore it seems that each textile manufacturing subcategory needs to establish its own reuse criteria.

1.3. Aim and Scope of the Study

The objective of this thesis is to develop the most suitable membrane based treatment scheme for the dyeing wastewaters of a carpet manufacturing industry, generated by the printing and the acid dyeing processes, aiming at waste treatment, water reuse and chemical usage minimization.

Carpet manufacturing industry is one of the textile subcategories, where mostly carpets made of polyamide (namely nylon) fibers are dyed using mostly acid dyes (EPA, 1997). The wastewater generation rate of this subcategory is high like other textile industries. The color and turbidity contents of wastewaters are comparably low due to the high fixation rates of the dyes on the synthetic fiber. The wastewaters samples used in this study were provided by the Samur Carpet Factory. The reason to choose the carpet manufacturing industry as a textile subcategory in this study is that acid and metal-complex dyes are used in the carpet dyeing process, on which limited literature background is available regarding their treatment by membrane processes. Much of the efforts of the membrane researchers have been spent on the treatment of wastewaters generated by the other textile subcategories, with a special attention on the reactive type of dyes, whose fixation rates on the fabric is one of the lowest (60-90%) (Tegtmeyer, 1993; Rautenbach and Mellis, 1994; Uygur, 1995; Guo and Yang, 1996; Wenzel et al., 1996; vant Hull et al., 1997; Jirarantananon et al., 2000; van der Bruggen et al., 2001). In the current literature, there are few studies on the treatment of acid dyes, and these studies have been performed mainly for the purpose of treatment but not for the recovery of water (Beltran de Heredia et al., 1990; Farag et al., 1994; Shi and Li, 1997; Walker and Weatherley, 1997, 2001).

Another reason for studying the acid dyeing wastewaters is that some acid dyes are among the azo dyes that release carcinogenic amines. The production and import of consumer goods produced with these dyes have been recently banned

(EU, 2002) where textiles, including synthetic carpets, are the majority of these goods. In this regard, acid dye bath wastewaters need special attention for their proper treatment and recovery.

Following the characterization of the print dyeing wastewaters (PDW) and the acid dye bath wastewaters (ADBW) of the Samur Carpet Factory in Ankara, in terms of the parameters as COD, ultra violet absorbance (UVA), turbidity, color, total solids, total hardness, chloride, pH and conductivity, the determination of the optimum pre-treatment processes for PDW and ADBW was undertaken separately. This part of the research covers the comparison of the performances of a variety of processes like chemical precipitation, MF and UF via the application of parallel and sequential filtration alternatives.

In the second part of the study, the determination of the treatment stage(s), which covers the comparison of the performances of a variety of UF and NF membranes with different molecular weight cut off (MWCO) values was carried out. The evaluation of the membranes was based on the removal performances and also the flux declines. The removal performances were evaluated in terms of agreement with the reuse criteria set for the process water quality. The fouling of the membranes were evaluated in terms of the extent of flux decline and the efficiency of the membrane cleaning procedures for flux recovery.

The study also covers the investigation of the effect of pH on the selection and development of the most efficient process train. Since color removal is of particular interest in this study, testing of the developed process train for its capability to handle highly colored wastewaters via spiking of the wastewaters by varying doses of dye solutions and monitoring of the permeate quality under worsening feed conditions was also undertaken.

CHAPTER 2

CARPET DYEING WASTEWATERS

The characteristics and the environmental impacts of carpet dyeing wastewaters are discussed here followed by the legislations for their discharge as well as the reuse requirements for their recovery. Carpet dyeing methods are also summarized to aid in developing a better understanding of the characteristics of carpet dyeing wastewaters in terms of their complexity and variability.

2.1. Carpet Dyeing Methods

There are two classifications of dyeing carpets: pre-dyed yarns and post- dyed yarns. As the name implies, pre-dyed yarns are dyed before the fiber is tufted into a tufting blanket. Post-dyed yarns are dyed after the tufting blanket is stitched. Since this study deals with the wastewaters generated from the carpet dyeing process, post-dyeing methods are considered here. All carpet fiber that is to be post-dyed is extruded as “white” fiber or fiber that is extruded without color pigment added. This white fiber is spun, twisted, heat set and tufted into a blanket. After tufting the blanket, dyeing is performed, generally, in one of three fashions, beck or piece dyeing, continuous dyeing and printing (Michael Hilton, 2004).

Beck dyeing is primarily for solid colors in limited runs. In this method, the carpet is dyed "in a piece" after tufting but before other finishing processes such as attaching the secondary backing. Large rolls in rope form of uncolored carpet are placed in a large vat of dye solution (dye beck) and heated to high temperatures to open the dye sites of the fiber. The pH of the dyeing solution is also lowered to around 5 as required by the process. The negatively charged dye molecules attach to the positively charged dye sites and the dye adheres to the fiber. The carpet moves over a rail onto a reel, which immerses it into the dye and then draws the carpet up and forward to the front of the machine, providing continuous agitation. It is then removed, washed, and dried. Beck dyeing a roll of carpet usually takes between three to six hours, depending on the color and the amount of carpet to be dyed. This is the most expensive method, however, achieves excellent color uniformity on the carpet.

Continuous dyeing is a process in which the carpet is dyed on a continuous dye range. The carpet is rinsed and then passed under a dye applicator, which spreads or sprays dyes evenly across the entire width of the carpet. The carpet then enters a steam chamber, where the dyes are "set" into the fibers. This method is for longer runs of both solid and multi-color applications. Several hundred feet of dyed carpet can be produced per hour, which significantly reduces the cost.

Print dyeing is similar to continuous dyeing in that printing is a continuous operation. Generally, a multicolored pattern is produced on carpets with screen-printing, roller equipment, or ink jet printers. The carpets are dyed by a computer-controlled system using a print paste, which is prepared by mixing the desired dyes with the required chemicals at acidic pH. After printing, the carpet is steamed to fix the dye on it, followed by vacuuming to separate the excess print paste left on the carpet. Then the carpet is immersed into a water tank to wash away the residual color and print paste.

2.2. Dyes Used in Carpet Manufacturing

The suitable class of dye for carpet dyeing process changes according to the type of the fiber used to make the carpet. There are five basic types of fibers used in carpet manufacturing: wool, polyamide (nylon), polypropylene, polyester and acrylic. Among these, only wool is natural and the rest are synthetic. Table 2.1 gives all the dye classes for all types of fibers used in textile industry (USEPA, 1997). As seen, acid, basic and disperse dyes are the ones suitable for carpet dyeing. Today, approximately 97% of all carpets are produced using synthetic fibers due to the advantages such as the lower cost and the ability to withstand stains, wear, and soiling. Among the synthetic fibers, polyamide is the most resilient one, accounting for over 55% of all carpets made today (Dalton Carpet Mill, 2003). Therefore, more than half of the carpet dyeing wastewaters contain unfixed acid dyes. As the recovery of the wastewaters generated by the polyamide carpet dyeing processes are investigated in this study, only the associated dyes will be mentioned here, namely the acid dyes and their metallized complexes.

Table 2.1. Typical Characteristics of Dyes Used in Textile Dyeing Operations

Dye Class	Description	Method	Fibers	Typical Fixation (%)
Acid	Water-soluble anionic compounds	Exhaust Beck Continuous (carpet)	Wool, Nylon	80-93
Basic	Water-soluble, applied in weakly acidic dyebaths; very bright dyes	Exhaust Beck	Acrylic, Some polyesters	97-98
Direct	Water-soluble, anionic compounds; can be applied directly to cellulosics without mordants (or metals like chromium and copper)	Exhaust Beck Continuous	Cotton, Rayon, Other cellulosics	70-95
Disperse	Not water-soluble	High temperature Exhaust Continuous	Polyester, Acetate, Other synthetics	80-92
Reactive	Water-soluble, anionic compounds; largest dye class	Exhaust Beck Cold pad batch Continuous	Cotton, Other cellulosics, Wool	60-90
Sulfur	Organic compounds containing sulfur or sodium sulfide	Continuous	Cotton, Other cellulosics	60-70
Vat	Oldest dyes; more chemically complex; water-insoluble	Exhaust Package Continuous	Cotton, Other cellulosics	80-95

2.2.1. Acid Dyes

Acid dyes are synthetic dyes that react with basic groups in the polyamide. They possess an acidic group as part of their structure which confers water solubility upon the dye but are so named because in textile dyeing they are used with some sulfuric or acetic acid in the water solution. This is required to protonate the amino groups of polyamide fibers. The acid dye ionizes (dissociates) to a negatively charged anion in water, which can bond to the positively charged protonated amino groups of fibers by salt linkages, which are intermediate in strength (Figure 2.1). In addition to the salt linkages, hydrogen, dipole and van der Waals bonds are also formed between the dye and the fiber polymer (Timar-Balazsy and Eastop, 1998). These dyes are typically applied in beck dyeing process at pH values ranging from strongly acidic to neutral, and usually at temperatures approaching boiling.

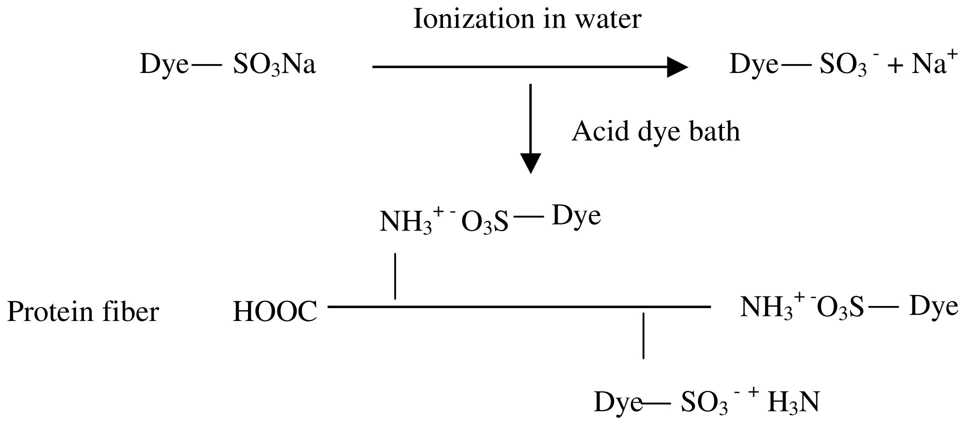
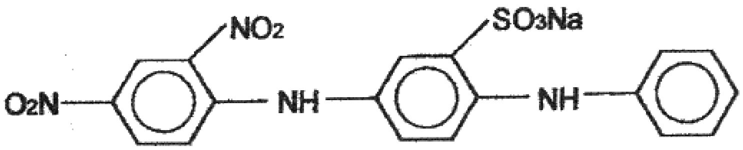


Figure 2.1. Salt Linkages Between a Protein Fiber and an Acid Dye

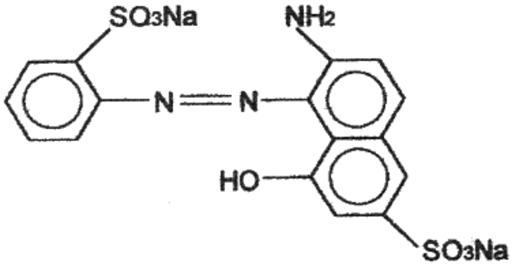
There are three common acid dyeing methods. Equalizing acid dyes have good migration properties and are applied from a strong acid dye bath (made with sulphuric acid) containing sodium sulphate, which controls the levelling (equal distribution) of the dye. Intermediate acid dyes have poor migration properties in strong acid solutions, and they are therefore applied under weak acid conditions (made with acetic acid). Milling acid dyes are applied from a dye bath containing ammonium sulphate or ammonium acetate at an almost neutral pH, which turns into acid on evaporation of the ammonia (Clipson, 1990).

Acid dyes range from dull tones to brilliant shades (Doug Wilson, 2004) and they possess average to very good light fastness (Table 2.2), which means that they are resistant to the destroying effect of light on colored objects due to the breakage of electronic bonding within the molecule (A dye that does not fade when the material it was applied to is exposed to conditions associated with its intended use is called a fast dye. Some of the conditions that could cause such a change in the properties of a dye include exposure to acids, sunlight, or excessive heat as well as various washing and cleaning procedures). The chemical structures of some acid dyes are depicted in Figure 2.1. The general characteristics of acid dyes are as follows:

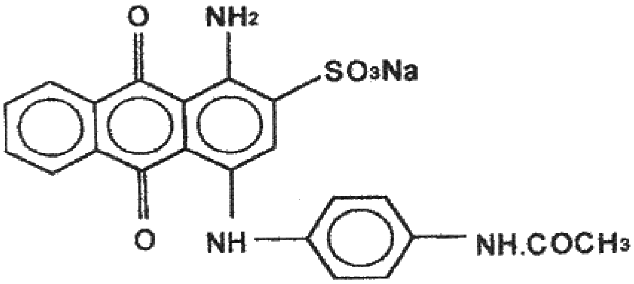
- Sodium salts of organic acids,
- Water-soluble anionic compounds,
- Typical fixation rates: 80-93%,
- Negatively charged, bind to positively charged tissue,
- Staining mechanism is ionic bonding,
- Suitable for reuse, no chemical change.



(a) Acid Orange 156



(b) Acid Red 361



(c) Acid Blue 277:1

Figure 2.2. Chemical Structures of Some Acid Dyes

2.2.2. Metal-Complex Dyes

A metal-complex dye, also called a pre-metallized dye or mordant dye, is a complex of dye molecules with a metal ion. The term “pre-metallized” is used primarily to refer to the classes of acid dyes, but is also applicable to some reactive dyes. There are 1:1 metallized dyes, having one dye molecule per metal atom (applied in very strong acid dye baths), and 2:1 types, having two dye molecules per metal atom (applied from almost neutral dye bath). The metal helps the dye attach to the fiber, providing excellent wash fastness due to the strong bond created between the dye and the fiber by the metal ion and the formation of a large complex molecule (Timar-Balazsy and Eastop, 1998). Being comprised of electromagnetic radiation, light can have a destructive effect on dyes. An inorganic molecule such as iron oxide has very stable, strong molecular forces, which hold the atoms in the molecule together. The energy in sunlight is not sufficient to break these bonds. Conversely, the bonds that hold an organic dye molecule together are much weaker and sunlight is ultimately able to break the bonding arrangement, which causes the color to fade. Some dyes are more light fast than others and the best performance can be expected from the metallized dyes (Table 2.2). Acid dyes can be improved from a light fastness standpoint by incorporating a metal ion into the molecule. The metal most commonly used is chromium, although cobalt and copper are also used.

Table 2.2. Suitability of Acid and Pre-metallized Dyes For Polyamide (Nylon) (Zimmer Maschinenbau GmbH, 2004)

Specification	**Acid dyes**	**Pre-metallized dyes**
Light fastness	+ + +	+ + +
Wash fastness	+ / -	+ +
Brilliancy	+ + +	+ / -
Ecological aspects	+ + + / -	- -

2.3. Characteristics of Carpet Dyeing Wastewaters

Like all textile wastewaters, carpet dyeing wastewaters are complex and highly variable in nature. The complexity of these wastewaters is due to the usage of several auxiliary chemicals in addition to the variable classes of dyes. Carpet dyeing wastewaters generally contain acids, uniformity agents, thickeners, antifoaming agents, and penetrants, most of which are classified as surfactants. Although the dyes are fixed on the carpet up to 90%, the auxiliary chemicals are not consumed during the dyeing process and end up in the wastewater stream. The high variability in the characteristics of carpet dyeing wastewaters is basically due to the changing color and carpet properties from one piece to another.

In terms of volumes of wastewaters generated, carpet dyeing process, as a subcategory, is ranked one of the lowest (Table 2.3). As seen from Table 2.3, wool and felted fabrics processes are more water intensive than other processing subcategories such as wovens, knits, stock, and carpet. However, in terms of unit processes, beck dyeing and print afterwashing, having water use rates of around 230 and 110 L/kg, respectively, are among the most water demanding ones (Horning, 1981; Wagner, 1993).

The characteristics of some textile wastewaters including carpet mills are presented in Table 2.4 (BTTG, 1999). As seen, the textile wastewater characteristics are highly variable, especially in terms of their COD and BOD levels, which is most significant for wool scouring. According to this data, the carpet dyeing wastewaters have considerably high polluting potential with COD as high as 4000 mg/L.

Table 2.3. Water Use in Textile Subcategories (Smith, 1986)

Processing Subcategory	Water Use (L per kg of production)		
	Minimum	Median	Maximum
Wool	111	285	659
Woven	5	114	508
Knit	20	84	377
Carpet	8	47	163
Stock yarn	3	100	558
Nonwoven	3	40	83
Felted fabric	33	213	933

Table 2.4. Characteristics of Some Textile Wastewaters (BTTG, 1999)

Parameter	Value			
	Carpet Mill	Wool Scouring	Woven/Knitted Fabric Finishing	Stock and Yarn Dyeing
COD (mg/L)	1-4000	5-35000	100-1000	800
BOD (mg/L)	300-1200	20-60000	50-400	250
SS* (mg/L)	120-180	1-20000	50-150	100
Temperature (°C)	30-40	30-40	30-40	25-50
pH	6-8	8-10	7-9	5-9

* SS: Suspended Solids

Color, resulting from the unfixed dyes in spent dye baths and wash waters, is a widely recognized problem in textile effluents. Although it is an aesthetic pollutant in the first place, extremely high doses of color may interrupt photosynthesis activity in the receiving waters. The reactive type of dyes has the highest color causing potential as they have the lowest fixation rates onto the fabric. Therefore, cotton and wool dyeing processes where reactive dyes are commonly used are said to generate highly colored wastewaters as compared to the synthetic dyeing processes. However, the relatively less colored effluents generated by the synthetic dyeing processes including carpets may indicate a more severe problem, that is the toxicity and carcinogenicity of the dyes used in these processes.

In addition to color, the presence of unfixed dyes in the textile wastewaters addresses to another problem, which is the aquatic toxicity. The aquatic toxicity of textile industry wastewaters varies considerably among production facilities. In a study carried out in North Carolina, out of 75 mills tested, effluent from about one-half showed no toxicity (USEPA, 1996). Similarly, Little and Lamp (1972) realized that 63% out of 46 dyes from all classes had low aquatic toxicity with lethal concentration (LC_{50}) of greater than 180 ppm. They also observed that the basic dyes showed significantly higher toxicity (Table 2.5). According to their study, acid dyes correspond to a relatively high toxic class of dyes. The LC_{50} values of some dyes are given in Table 2.6. As seen, one of the acid type of dyes, Acid Black 52, is among the most toxic dyes listed. Out of the 3000 dyes commonly used, 98% are reported to have an LC_{50} value in excess of 1 mg/L. Among the different dyes examined, fish toxicity levels vary from less than 1 to more than 500 mg/L LC value. Among the dye classes, reactive dyes are the least harmful since none of these dyes had appeared in the list of banned dyes. These figures are good indications for the complexity of textile wastewaters, as the adverse effect of any one dye cannot be expected to be similar to any other even under the same class.

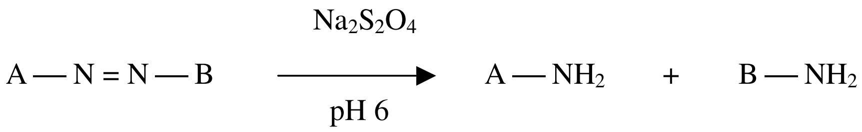
Table 2.5. Toxicity of Dye Classes (Little and Lamp, 1972)

Dye Class	Number Tested	Percent Toxic (%)
Disperse	6	33
Acid	12	66.7
Direct	14	7.1
Basic	5	100
Vat	7	0

Table 2.6. LC_{50} Values of Some Dyes/Substances (UNEP, 1996)

Dye/Substance	LC_{50}
Acid Red 52	>500
Acid Yellow 17	180
Acid Blue 7	1-100
Acid Black 52	7
Copper Suphate	1.8
DDT	0.006

Carcinogenicity is another adverse effect of the presence of dyes in textile wastewaters. The aromatic amines associated with the production of azo type of dyes are often bladder carcinogens but may also attack the liver and spleen (Ward et al., 1991; Garner et al., 1984). Azo dyes, having -N=N- bond in their structure, make up 60-80% of all dyes used in the textile industry, and the greatest fraction belong to the direct dyes. Among the 112 dyes, which can be cleaved to release carcinogenic amines defined by the German Consumer Goods Ordinance (GCGO, 1997), only 17 are acid type of dyes, and the majority are the direct dyes. The potentially carcinogenic aromatic amines are aniline, toluidine, benzidine and naphthalene groups. The reductive cleavage of azo dyes into amines is schematically shown in Figure 2.3 (Puntener and Page, 2003).



$$\mathrm{A - N = N - B} \xrightarrow[\mathrm{pH\ 6}]{\mathrm{Na_2S_2O_4}} \mathrm{A - NH_2} + \mathrm{B - NH_2}$$

Figure 2.3. Reductive Cleavage of Azo Dye to Form Amines

The European Union as well as many individual countries have regulations to ban the production or import of consumer goods dyed with those azo dyes which may release the carcinogenic amines for health reasons (EU, 2002). The majority of these consumer goods are textiles in regular contact with human body including the carpets apart from hand-made oriental ones. Fortunately, it has been estimated that only 4% of the known azo dye structures would release the corresponding amines and in the last years all the reputable dye manufacturers have stopped manufacturing such azo dyes (Puntener and Page, 2003). The Turkish regulations also contain a list of 119 generic names of dyestuffs that can release the mentioned amines.

The surfactants are used as auxiliary chemicals in the carpet dyeing process and they cause serious environmental problems such as increasing the organic content and the toxicity of the wastewaters and also foaming. These surfactants are mostly anionic or non-ionic. The non-ionic surfactants dissolve in water without forming ions, while anionic surfactants form negative ions when dissolved in water. Non-ionic surfactants can be acutely toxic to aquatic life at levels as low as 1 ppm and can cause chronic effects in the 0.1 to 1 ppm range. The concentrations of surfactants in textile effluents were reported to be 50-200 ppm (Kravetz et al., 1986).

Turbidity, being one of the pollution parameters in textile wastewaters originates from two different sources in carpet dyeing wastewaters. First one is the fiber itself escaping from the carpet surface during the dyeing process, and the second one is the residual surfactants like thickeners left in the print after wash waters. The turbidity levels of beck dyeing wastewaters are generally very low as compared to printing wastewaters. This is due to the excess usage of print paste, some portion of which ends up in the print after wash water. The turbidity of carpet dyeing wastewaters may be considered low as compared to some other textile subcategories such as the wool processing, where natural fiber preparation contributes high levels of solids into the wastewaters. Similarly, carpet dyeing wastewaters do not contain high levels of salts as the carpet dyeing process does not particularly necessitate the use of salts. However, acid dyes used in carpet dyeing processes contain salts in their structures, but their high fixation rates avoid high levels ending up in the waste streams.

Most of the carpet effluents contain few or no metals, and whenever metals are present, they may contain metals such as copper, chromium and cobalt, which are mostly originating from the structure of the acid dyes (Wagner, 1993). These metals are either functional as fastness improvers or simply impurities generated during dye manufacture. Among the metals mentioned, the copper content of the acid dyes has been reported to be the highest (ADMI, 1972), however high concentrations of metals are not expected in the carpet wastewaters due to the high fixation rates of the dyes on to polyamide fiber.

It is obvious that the pollutants mentioned above result in the generation of highly complicated carpet wastewaters with high volumes, which make their treatment a difficult task. Today, most of the conventional treatment methods are found to be insufficient to provide adequate treatment efficiency for the parameters regulated under environmental legislations. Although biological treatment has been the most widely applied method for the removal of all textile effluents including carpets, it has often been found ineffective in decolorization (Shu and Huang, 1995; Law et al., 1996; Perkowski et al., 1996; Marmargne and Coste, 1996). Adsorption, being the most common technique for color removal, is a slow process and its performance is limited by the equilibrium (Chakraborty et al., 2003).

The discharge regulations are becoming more stringent, and there is a growing tendency and interest in the advanced treatment methods like ozonation, photo catalysis, and membrane filtration for a better treatment of the textile wastewaters (Tang and Chen, 2002). Combination of several processes like chemical coagulation, Fenton's oxidation, activated carbon adsorption and activated sludge has also been suggested (Lin and Peng, 1996; Ahn et al., 1999). Nevertheless, all these conventional methods either applied individually or in sequence, are basically aimed to meet the discharge regulations. When it is aimed to recover and reuse the valuable materials from waste streams, membrane technology, with its unique separation performance holds great promise in this field (Erswell et al., 1988; Marcucci et al., 2001). To this end, membrane processes would perfectly meet the target of water recycling in the carpet manufacturing industry to save the groundwater supplies.

2.4. Environmental Legislation for Carpet Dyeing Wastewaters

In Turkey the textile effluents are regulated under the Water Pollution Control Regulation (WPCR, 1988). The Turkish effluent limitations for carpet finishing are listed in Table 2.7. Although textile effluents are highly colored and have adverse effects on aquatic life, color is not listed yet among the parameters regulated by most countries' legislations. However the German Standards (Federal Ministry, 2001) have recently set some limits for color, where a spectral absorption coefficient of 7 m^{-1} (426 nm), 5 m^{-1} (525 nm) and 3 m^{-1} (620 nm) are required at the point of discharge.

Table 2.7. Carpet Finishing Industry Effluent Limitations (WPCR, 1988)

Parameter	**2 hours Composite Sample (mg/L)**	**24 hours Composite Sample (mg/L)**
BOD_5	120	100
COD	300	200
TSS	160	120
Ammonium Nitrogen (NH_4-N)	5	
Free Chlorine	0.3	
Oil and Grease	10	
Total Chromium	2	1
Sulfide (S^{-2})	0.1	
Sulfite	1	
Phenol	1	0.5
pH	6-9	6-9

The European guidelines for urban and industrial wastewater mention a maximal COD of 125 mg/L and a maximal BOD of 25 mg/L, however the limits may be different in some countries (European Commission, 1991). In Belgium for instance, although the limit for BOD is the same, it is as high as 400 mg/L for COD.

In USA, EPA promulgated effluent guidelines for the textile manufacturing point source category. Among nine subcategories, the effluent limitations for the Carpet Finishing Subcategory (Subpart F) are given in Table 2.8, representing the degree of effluent reduction attainable by the application of the best practicable control technology currently available (BPT) (USEPA, 1982).

Table 2.8. USEPA Carpet Finishing Subcategory Effluent Limitations

Pollutant or Pollutant property	BPT* Limitations	
	Maximum for any 1 day	Average of daily values for 30 consecutive days
	Kg/kkg (or pounds per 1000 lb) of product	
BOD_5	7.8	3.9
COD	70.2	35.1
TSS	11.0	5.5
Sulfide	0.08	0.04
Phenol	0.04	0.02
Total Chromium	0.04	0.02
pH	6.0-9.0	6.0-9.0

* Best practicable control technology currently available

2.5. Water Reuse Requirements

It is quite difficult to define a general standard for water reuse in textile industry because of the different requirements of each fiber (wool, silk, cotton, polyester, etc.) and because of the different quality required for the final fabric. Low hardness water is usually needed for scouring, dyeing and for preparing printing pastes but softening is not necessary for all the washing cycles. A high salt content may interfere with the dyeing process and with the detergent action of the surfactants used in washing the dyed fabric. Chemical reduction of the chromophores in the dye molecules by ammonia, nitrite and sulphide may alter the color and therefore spoil the dyeing process. Organic substances, and particularly surfactants and traces of dyes, may interfere with bleaching, dyeing and printing by causing differences in hues and tones (Rozzi et al., 1999).

The recovery and reuse of textile wastewaters have been studied extensively by membrane researchers (Comodo et al., 1993; Sojka-Ledakowicz et al., 1998; Rozzi et al., 1999; Ciardelli et al., 2001; Marcucci et al., 2001; Bottino et al., 2001). Wide variations in the quality of the recovered waters have been reported and their adequacy differs from one process to another (Tables 2.9 and 2.10). Therefore it seems that each textile manufacturing factory needs to establish its own reuse criteria. However, there are a few basic conditions such as the water turbidity, which should be comparable to the groundwater that is used as freshwater, and the water hardness, which should be in the normal range for relatively soft groundwater (not higher than 40 mg/L Ca or 10 °Fr). Of course, all color should be removed before reuse. Furthermore no concentration of other components such as heavy metals can be allowed in the water cycle (van der Bruggen et al., 2001).

Table 2.9. Water Reuse Criteria in Textile Industry

Textile Process	Removal Performance/ Produced Water Quality	Reuse Criteria Set/Remark	Ref.
Wool, polyester and silk	TOC = 40-300 mg/L Color = 50-427 ADMI Conductivity = 1300-8000 µS/cm	Unacceptable results obtained when dyeing with very light colors, and when the effluent conductivity was > 3000 µS/cm	Groves et al., 1979
Low quality wool	Hardness = 300 mg/L $CaCO_3$ Conductivity = 2000 µS/cm COD = 40 mg/L UVA $_{426}$ = 0.02 Anionic surfactants = 0.21 mg/L Non-ionic surfactants = 0.26 mg/L		Comodo et al., 1993
Dyeing of synthetic fibers	COD = 31-42 mg/L Hardness = 1.4-29 mg/L $CaCO_3$ Conductivity = 1740-2050 µS/cm UVA $_{426}$ = 0.001-0.003 pH = 7.52-8.10	COD = 30 mg/L Hardness = 270 mg/L $CaCO_3$ Conductivity = 1800 µS/cm UVA $_{426}$ = 0.01, pH = 7-8 TSS = 10 mg/L Anionic surfactants = 0.025 mg/L Non-ionic surfactants = 0.5 mg/L	Rozzi et al., 1999

Table 2.9. Water Reuse Criteria in Textile Industry (continued)

Textile Process	**Removal Performance/ Produced Water Quality**	**Reuse Criteria Set/Remark**	**Ref.**
	COD < 10 mg/L Conductivity < 40 µS/cm No color	Reports that it is feasible to reuse this water in textile mills.	Rozzi et al., 1999
Dyeing and finishing of fabrics made of natural and synthetic origin	COD = 34 mg/L Conductivity = 35 µS/cm UVA 420 = 0.002 pH = 6.3 Cl- = 42 mg/L Fe = 0.07 mg/L Sulphates = 7 mg/L Potassium = 1.1 mg/L Magnesium = 4.2 mg/L	Produced water by RO is reported to be better than the original process water drained from wells and softened (with a conductivity of 800 µS/cm, no COD and no color). This water is said to be suitable for all the processes of textile factories, even the most demanding such as dyeing yarns or light colors.	Ciardelli et al., 2001
Natural and synthetic yarn dyeing	COD =8-10 mg/L Conductivity =330-2350 µS/cm Total hardness <1-3.5 °F TSS < 5 mg/L	The water produced by NF had conductivity and total hardness so the quality did not match the requirements of reuse in delicate processes such as dyeing with very light colors. This water can be used for washing and dyeing of light colors. Yarn dyeing with RO water had excellent results, even with light shades.	Marcucci et al., 2001
	COD = 21-39 mg/L Conductivity = 59-797 µS/cm $UVA_{420} < 0.005$ Cl^{-} = 17-199 mg/L pH = 7.5 Surfactants < 0.05 mg/L $SO4^{-2}$ = 1-5 mgL	NF and RO water have enough quality to be reused in all wet textile processes including the most demanding concerning water quality.	Bottino et al., 2001
Wool dyeing	Removal: COD = 76-95% Conductivity = 70-90% Color = 96-99 Turbidity = 98-99%	Reuse Criteria: No turbidity No color Hardness < 40 mg/L Ca It is stated that the permeate quality appeared to be good enough to make reuse as a process water possible.	Van der Bruggen et al., 2001

Table 2.10. Water Reuse Criteria Set by the British Textile Technology Group (BTTG, 1999)

Process	**Hardness (mg/L)**	**Color (AU)***	**Turbidity (FTU)**	**Dissolved Solids (mg/L)**	**Fe: Cu: Mn (mg/L)****
Acrylic Yarn (Package)	1	10	1	300	0.01
Nylon Yarn	**60**	**5**	**15**	**500**	**0.01**
Polyester Fabric	80	5	5	250	0.01
Cotton Fabric	75	17	5	150	0.10
Knitted Cotton	30	5	1	470	0.01
Worsted (Package)	75	4	7	180	0.03
Woolen Loose Stock	65	30	85	220	0.10

* AU: Absorbance units in 10 mm cell

** This figure is the maximum allowable concentration for each of the metals.

CHAPTER 3

MEMBRANE SEPARATION PROCESSES

The first membranes produced in Germany in 1920 were used for the filtration of bacteria at laboratory scale. Later in 1960s, the development of the synthetic asymmetric membrane at the University of California, Los Angeles, by Loeb and Sourirajan (1962) for the separation of salt from seawater has lead to a significant development of the membrane technology. Since then, the application areas have been widely spread in many industries, among which beverage, food, pharmaceutical, electronics, paper and textile are only a few. In addition to being used in several industrial production stages, membranes have been widely used in the treatment of wastes and the recovery of valuable materials like dyes, metals, and water. Drinking water treatment is another area where membrane separation processes have recently been introduced (Singh, 1998; Fusaoka et al., 2001). The popularity of the membrane technology in environmental applications has emerged due to the potential scarcity of fresh water supplies and the stringent environmental regulations. Meanwhile, the rapid development of the membrane material science over the recent years has also helped the widespread use of membrane technology due to the availability of membranes from a wide range of materials of different structures, including synthetic polymers, cellulose-based natural products and others like inorganic, ceramic and metals (Scott and Hughes, 1996).

3.1. Definitions and Basic Principles

A membrane can be defined as an interphase that separates components according to their structure. Some components can be transported more readily than others due to the differences in physical and chemical properties between the membrane and the permeating components (Mulder, 1996). Another definition states that a membrane is a permeable or semi-permeable barrier through which fluids and solutes are selectively transported when a driving force is applied across it. The driving force can be a gradient of concentration, temperature, pressure or electrical potential. It can be inferred from these definitions that the application of conventional filtration of solids and particles from liquid or gaseous streams is further extended by the membrane filtration to include the separation of dissolved solutes in liquid streams and the separation of gas mixtures (Cheryan, 1986). The membrane discussion in this chapter is limited to the pressure-driven membranes since this study is based on their performances for textile wastewater treatment and recovery.

Although membrane separation process is an extension of the conventional filtration in a way, there are some differences that make the membrane separation one of the most promising new technologies today. The basic difference that distinguishes the membrane separation process from conventional filtration is the flow pattern. In conventional filtration, particles are simply collected on a filter media under an applied pressure, where the liquid flowing perpendicular to the filter media causes the accumulation of the retained particles, leading to the formation of a cake layer at the surface (Figure 3.1a). This is called the *dead-end* filtration. The thickness of the cake increases with filtration time and causes an increase in the pressure drop or a decrease in the filtration rate. When the pressure drop becomes too high, or the filtration rate becomes too low, the cake is removed and the filter media is cleaned. However, in most practical cases, the filter media is simply replaced. Dead-end filtration is generally suitable for concentrated suspensions, and not appropriate for the filtration of very fine and dilute suspensions or production of very pure filtrates (Murkes and Carlsson, 1988).

Where dead-end filtration is not appropriate, *cross-flow* filtration is an alternative technique, especially in cases of high purity filtrate requirement. In cross-flow filtration the feed water is recycled under an applied pressure, where the feed flow is parallel to the filter media (Figure 3.1b). The purpose of this flow is to control the thickness of the cake. As the speed of the flow enables the suspended solids to be carried away, the retained particles accumulate on the surface to a low extent, providing longer service lives for the filter media before cleaning or replacing. Cross-flow filtration and membrane filtration has become synonymous, although they are not, in principle, as the term "membrane filtration" implies nothing about the flow pattern and the term "cross-flow" does not mean anything for the filter media. However, in practice, cross-flow filtration overlaps membrane filtration almost completely. In other words, membrane filtration is almost always carried out by cross-flow, as dead-end filtration through a membrane would end very rapidly due to total clogging (Murkes and Carlsson, 1988).

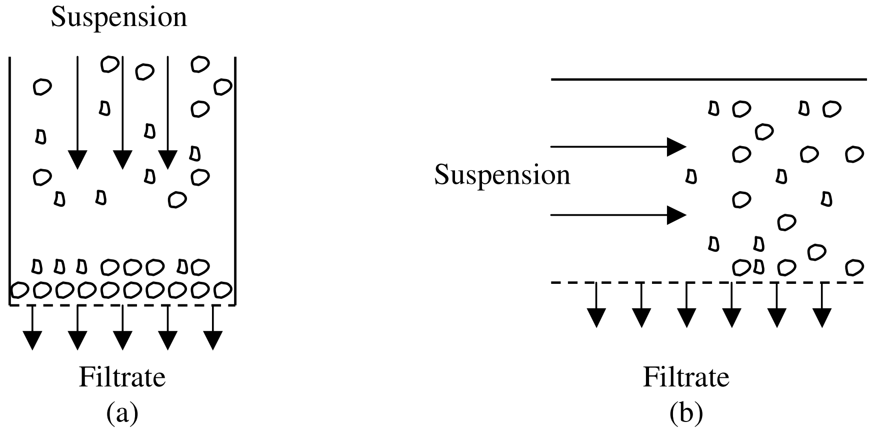


Figure 3.1. (a) Dead-end Filtration with Cake Formation **(b)** Cross-flow Filtration

Two streams are produced in a membrane separation process; one stream, called the *permeate*, is depleted in certain components and a second stream, called the *retentate*, is concentrated in them. The term *permeate* is used in membrane technology instead of *filtrate,* representing the portion of the feed solution passing through the membrane. The term *retentate,* which is used interchangeably with the term *concentrate,* represents the portion of the feed solution that is retained on the high-pressure side of the membrane (Figure 3.2).

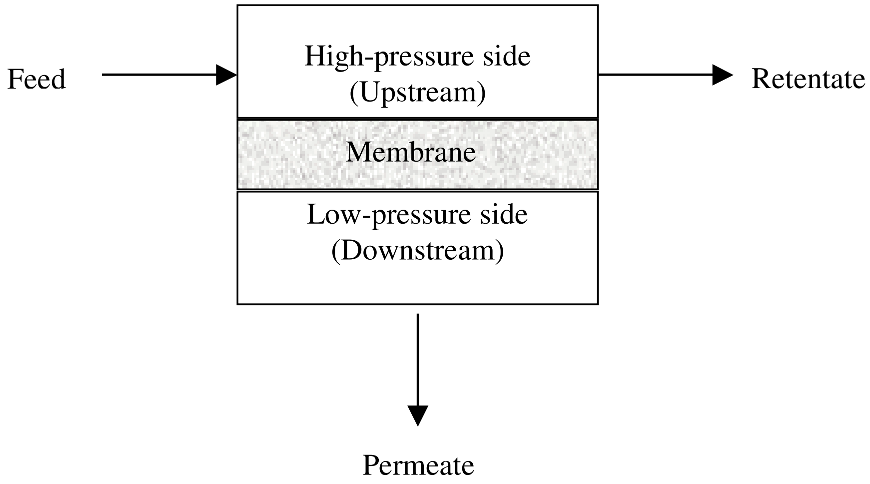


Figure 3.2. Schematic Presentation of a Pressure Driven Membrane Process

The performance of a membrane is defined in terms of two factors, *flux* and *selectivity* (Mulder, 1996). The term *flux* describes the amount of fluid passing through the membrane, i.e., the volumetric flowrate of the permeate, which is usually given in terms of volume per unit membrane area per unit time as follows:

$$J = \frac{1}{A}\frac{dV}{dt}$$

where,

J : flux (L/m^2/h)
dV/dt : permeate flowrate (L/h)
A : effective membrane area (m^2)

The flux of a membrane basically defines its productivity and the *selectivity* of the membrane defines whether it will be useful or not as it is an indication of how pure the product stream is and how much of it is recovered at the desired purity. Selectivity is generally expressed by one of the two parameters: *retention* or *separation factor.* For dilute aqeous mixtures, consisting of a solvent (mostly water) and a solute, it is more convient to express the selectivity in terms of retention towards the solute (Mulder, 1996). The solute is partly retained while the solvent (water) molecules pass freely through the membrane. The retention is given by:

$$R = \frac{C_f - C_p}{C_f} = 1 - \frac{C_P}{C_f}$$

where,

R : retention
C_p : solute concentration in the permeate
C_f : solute concentration in the feed

The value of R varies between 1, which means complete retention of the solute, and 0, which means the solute and the solvent pass through the membrane freely. Membrane selectivity towards gas mixtures and mixtures of organic liquids is usually expressed in terms of the separation factor:

$$\alpha_{A/B} = \frac{y_A / y_B}{x_A / x_B}$$

where,

$\alpha_{A/B}$: the separation factor
y_A, y_B : the concentrations of components A and B in the permeate
x_A, x_B : the concentrations of components A and B in the feed

If the permeation rate of component A through the membrane is greater than that of component B, the separation factor is denoted by $\alpha_{A/B}$, otherwise by $\alpha_{B/A}$. The selectivity is desired to be greater than unity because $\alpha_{A/B} = \alpha_{B/A} = 1$ means no separation is achieved through the membrane (Mulder, 1996). Ideally a membrane with a high selectivity and permeability is required although typically attempts to maximise one factor are compromised by a reduction in the other (Scott and Hughes, 1996). The flux and selectivity of membranes differ significantly, due to the varying types of materials used in membrane manufacturing and also the methods of fabrication. Therefore, the nature of the membrane is the principal factor that determines the type of the application, ranging from the separation of microscopic particles to the separation of molecules of an identical size and shape (Mulder, 1996).

One of the major problems in the operation of the membrane separation processes is the flux decline, which occurs as a result of two phenomena; c*oncentration polarization* and *fouling*. *Concentration polarization* is the build-up of solutes close to or on the membrane surface. Solute is brought to the membrane surface by convective transport; solutes larger than the MWCO of the membrane are retained by the membrane, while solutes smaller than the pores will freely or partially permeate through the membrane. Solutes not passing through the membrane will accumulate on the membrane surface, causing either an increased resistance to solvent transport or an increase in local osmotic pressure, either of which may decrease flux, and possibly a change in the sieving characteristics of the membrane (Cheryan, 1986). *Fouling* is a phenomenon in which the membrane adsorbs or interacts in some manner with solutes in the feed stream, resulting in a decrease in membrane performance, i.e., lowering of the flux and/or increase in rejection of solutes by time. Fouling is usually irreversible, by which it is distinguished from concentration polarization. While concentration polarization is affected by operating parameters such as velocity, pressure, temperature and feed concentration, fouling is primarily time-dependent and also partially concentration-dependent. Fouling effects can only be overcome by shutting down the system and cleaning the membrane by chemical means (Cheryan, 1986).

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

Dead-end filtration	Cross-flow filtration
$TMP = P_{in} - P_p$	$TMP = \left(\frac{P_{in} + P_{out}}{2}\right) - P_p$

where,

P_{in} : inlet pressure (feed side)
P_{out} : outlet pressure (retentate side)
P_p : permeate pressure (permeate side)

In many cases the permeate flux is proportional to the pressure difference across the membrane, where the proportionality is expressed by:

$$J = P\frac{(\Delta p - \Delta \pi)}{l}$$

where,

P : permeability coefficient
Δp : hydrostatic pressure difference
$\Delta \pi$: osmotic pressure difference between the feed and the permeate
l : membrane thickness

The applied hydraulic pressure must first overcome the *osmotic pressure,* which is the natural force that seeks to pull water from the permeate side of the membrane to equilibrate the solute concentration on each side. For any solute, the osmotic pressure is higher for higher concentrations, higher specific ion's activity, and smaller organic molecules.

3.2. Pressure-Driven Membrane Separation Processes

Membranes are generally classified in broad categories by their ability to remove particles, ions and other substances in certain size ranges. The type of the driving force applied across the membrane leads to a basic classification of membrane separation processes, as shown in Table 3.1. As seen, there are four commonly accepted pressure-driven membrane separation processes, defined based on the size of the material they will remove from the solvent. Ranking from the largest to the smallest pore size, these are microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). As the pore size gets smaller, the hydrodynamic resistance of the membranes increases, which necessitates the application of higher pressures across the membranes.

MF is well understood as the fine end of the particle filtration, with pore sizes ranging from 0.05 to 10 μm, which are visible under a microscope. UF, NF and RO membranes do not have holes as such, but rely on higher pressures to defuse a liquid or gas through the molecular structure of the medium. The molecular spacing can be controlled during manufacturing to permit the creation of membranes having any desired molecular weight cut-off (MWCO) level, which is a means of determining the size of the largest molecule able to permeate a UF, NF or RO membrane. Table 3.2 shows the ranges of material sizes retained, the pressures required, the typical fluxes obtained and the separation mechanisms used by each membrane separation process.

Table 3.1. Membrane Processes According to Their Driving Forces (Mulder, 1991)

Membrane process	Driving force
Microfiltration Ultrafiltration Nanofiltration Reverse Osmosis	Pressure difference
Pervaporation Gas separation Dialysis Liquid membranes	Concentration difference
Thermoosmosis Membrane distillation	Temperature difference
Electodialysis Electroosmosis	Electrical potential difference

Table 3.2. Specifications of Pressure Driven Membrane Processes (Mulder, 1996; Ho and Sirkar, 1992)

Process	**Size of Materials Retained**	**TMP (Bar)**	**Permeability ($L/m^2/h/bar$)**	**Separation Mechanism**
MF	0.05-10 µm (microparticles)	0.1-2	> 50	Sieving
UF	1-100 nm (macromolecules)	1-10	10-50	Sieving
NF	0.5-5 nm (molecules)	5-20	1.4-12	Solution-diffusion
RO	< 1 nm (molecules)	10-100	0.05-1.4	Solution-diffusion

MF

When pressure-driven flow through a membrane or other filter medium is used to separate micron-sized particles from fluids, the process is called MF. The MF process is used in a wide variety of industrial applications where particles of a size greater than 0.1 μm can be retained. However, the irregular nature of the membrane pores and the irregular shape of the particles to be filtered point out the difficulty in defining sharp cut-off of size during filtration (Scott, 1996).

The separation in MF process is achieved by sieving mechanism when the particle sizes are greater than the pore size, that they are collected on the surface of the membrane rather than inside the pores, thus forming a cake layer. This sieving mechanism is sometimes called *surface filtration.* In case the particle sizes are smaller than the pore sizes then they can enter the interior of the filter medium, which is called the *in-depth filtration* (Davis, 1992). In both types of filtration, the particle build up results in an increased resistance to flow, and the permeate flux decreases if the TMP is kept constant.

As the sizes of the particles retained by MF are larger than the sizes of solutes retained by NF or RO, the osmotic pressure for MF process is negligible, and the required TMP is relatively small, generally less than 2 bar. The permeate flux is typically larger for MF than for other membrane processes as the pore sizes are much more larger. MF is often applied in dead-end filtration mode in the analytical laboratories, which is one of the most important application areas of MF process today. On the other hand, cross-flow application is preferred for larger scale applications to ensure longer media life. Sterilisation and clarification are the main applications of MF processes in food and pharmaceutical industries. Removal of particles for ultra pure water production in semiconductor industry and cell harvesting in biotechnology are among the other applications (Mulder, 1996).

UF

UF is primarily a size-exclusion based pressure-driven separation process. UF membranes have typically pore sizes ranging from 1 to 100 nm, and are capable of retaining medium to large size dissolved molecules in the molecular weight range of 300 to 300000 Da. These MWCO values are only approximate because the same molecules can have different sizes depending on the solution properties like pH and ionic strength. In addition, physico-chemical interactions between the solute, solvent and the membrane surface would also affect the retention performance (Scott, 1996). Typical species rejected by UF are sugar, biomolecules, polymers, and colloidal particles, where the separation mechanism is sieving (Kulkarni et al., 1992). UF is similar to MF based on the separation principle, however UF membranes have a much higher hydrodynamic resistance due to their structure. Since UF membranes do not typically reject salts, osmotic pressure differentials are small as compared to RO membranes. UF operates at TMP of 1-10 bars, and typical permeate fluxes are lower than those of MF.

UF processes are widely used for feed clarification, concentration of rejected solutes and fractionation of solutes. Some applications may require the separation of high molecular weight components from low molecular weight ones. Typical examples of applications are the food and dairy, pharmaceutical, textile, chemical, metallurgy, paper and leather industries. The applications of UF process in food and dairy industry are highly diverse, such as the concentration of milk, cheese making, recovery of whey proteins, concentration of egg products and the clarification of fruit juices and alcoholic beverages (Mulder, 1996).

RO

Reverse osmosis gets its name from the osmosis phenomenon, where a pressure difference greater than the osmotic pressure difference must be applied so that separation of water from solutions becomes possible. In RO process the separation of ions and microsolutes from the aqueous streams is aimed. The separation mechanism for RO membranes is different than that of MF, and it is not just a physical process based on the size differences of solute and solvent. Such species are of similar molecular size and of a size comparable to the wide range of pore spaces in the polymeric RO membrane (Scott, 1996). The typical RO membrane pore size is less than 1 nm and they can essentially separate all solutes with molar masses greater than 300 Da completely from the solution. Water, having a molecular size nearly one tenth of the RO pore size, can pass through the membrane freely (Matsuura, 1994).

In RO, the mechanism of separation is based on processes relating to their size and shape, their ionic charge and the interactions with the membrane itself. This separation principle is called the *solution-diffusion model*, where solvent and solute dissolve and diffuse. In order to overcome the molecular friction between permeates and membrane polymer, during diffusion, large operating pressures are applied, in the range of 10-100 bar (Scott, 1996).

RO membranes were originally developed for the purpose of seawater and brackish water desalination. Today, RO process can be used for a wide range of applications, most of which are in the purification of water, mainly the desalination of brackish and seawater to produce potable water. In these applications, the salt content of brackish water and seawater can be as high as 1000-5000 ppm and 35000 ppm, respectively. Production of ultra pure water for semiconductor industry, the concentration of fruit juice, sugar and coffee in food industry and reclamation of process waters and wastewaters are some of the other RO applications (Mulder, 1996).

NF

The term NF was first used nearly a decade ago to define the membranes which had already been referred to as “loose RO” due to their more open network structure. Therefore, NF is said to be in the area between the separation capabilities of RO and UF membranes. The typical pore size of NF membranes is 0.5-5 nm, and the applied pressures are typically 5-20 bar, which are lower than the RO process, but yield higher fluxes (Mulder, 1996; Scott, 1996).

NF membranes can retain low molecular weight solutes such as inorganic salts or small organic molecules such as glucose and pollutants such as pesticides, and dyes. NF typically has partial salt retention and rejects molecules from 500 to a few thousands Da. The retention of divalent ions (Ca^{2+}, Mg^{2+}) by NF process is generally higher than the retention of monovalent ions (Na^+, K^+, Cl^-). This is because most NF polymers have formal charges, which exclude higher valence ions more than monovalent ions from passing through the membrane (Paulson, 1995). The application of NF and RO are obviously different, NF is the preferred process when a high retention is not required for NaCl (Mulder, 1996). The typical rejections of NF are 60% for NaCl, 80% for calcium bicarbonate and 98% for magnesium sulphate, glucose and sucrose (Scott, 1996). Among the widely spreading application areas of NF process are the water softening, removal of trihalomethanes and natural organic matter, retention of dyes and metals, and wastewater treatment and recovery. NF process has recently emerged as a feasible alternative to the conventional treatment methods in the environmental engineering field due to its unique separation ability and possibility of valuable material recovery.

3.3. Membrane Fouling and Cleaning

The membrane performance often changes significantly with time during an actual operation, and a typical flux-time behaviour is observed, i.e., the flux through the membrane decreases over time. This behaviour is mainly due to the concentration polarisation and fouling, which occur as a result of the build-up of retained components in the boundary layer of the membrane-solution interface. Concentration polarisation is a reversible phenomenon, while fouling is irreversible and can be caused by several mechanisms: adsorption, pore blocking and/or formation of a gel layer on the membrane. The two phenomena are not completely independent of each other since fouling can also result from concentration polarisation. The extent of fouling is strongly dependent on the type of the membrane processes involved and the feed employed. The flux decline is most severe in MF and UF membranes.

There are many factors affecting membrane fouling. Fouling depends on the membrane material, bulk concentration, solution conditions (pH, ionic strength), and operating parameters (transmembrane pressure, cross-flow velocity, temperature) (Jones and O’Melia, 2000). The fouling causing components of the feed solutions are the soluble inorganic compounds, colloidal or particulate matter, dissolved organics, chemical reactants and microorganisms. When fouling occurs, the membrane requires cleaning to restore the membrane properties. The degree of membrane fouling determines the frequency of cleaning, lifetime of the membrane, and the membrane area needed, and this will have a significant effect on the cost, design and operation of membrane plants (Speth et al., 1998). The following measures can be taken to reduce fouling for the most economical membrane operation:

- Pre-treatment of the feed solution to remove or change the properties of foulants by methods such as heat treatment, pH adjustment, chlorination, activated carbon adsorption, chemical clarification, pre-microfiltration and pre-ultrafiltration,

- Choosing the correct membrane such as using hydrophilic rather than hydrophobic membrane as fouling is more severe with the latter, and use of negatively charged membranes in the presence of negatively charged colloids in the feed,
- Choosing the appropriate module configuration and optimising the flow conditions such as the use of turbulent promoters, ultrasonic vibration and rotating modules,
- Cleaning of the membranes.

In order to understand the membrane fouling and cleaning, it is essential to understand the interactions between a) fouling materials and membrane, b) cleaning chemicals and fouling materials, c) cleaning chemicals and membrane, and d) the fouling materials. It has been recognized that electrostatic interaction and hydrophobic/hydrophilic interaction between the membranes and the fouling materials have a significant effect on membrane fouling. Electrostatic interactions occur among functional groups of membranes, fouling materials, and water primarily through dissociation, which strongly depend on the pH, ionic strength, and concentrations of multivalent cations in the solution. Hydrophobic-hydrophilic interactions are functions of structure similarities between membranes and fouling materials, the types and density of functional groups on both membrane surfaces and fouling materials, and solubility of molecules of fouling materials (Liu et al., 2004).

Surface charge of membrane media is the results of ionization of particular functional groups existed on the membrane surface (e.g., carboxyl and amine). Because ionization of a functional group depends on pH, surface charge of a particular membrane is also pH-dependent. In pH range of typical natural waters, most membranes appear to have a neutral to negative net surface charge. On the other hand, colloids, particles, and dissolved organic matters typically carry negative charges at the pH of natural water. Therefore, there is a tendency of electrostatic repulsion between membranes and those constituents.

Conditions other than pH may also affect the interactions between fouling materials and membranes. For example, high ion strength of a solution can compress "double electric layer" of colloids, which could reduce their repulsion to negatively charged membranes. Another example is divalent cations, which can act as "salt bridge" between a negatively charged membrane and other negatively charged species in the fluid by charge neutralization. It has been reported that high ion strength and high calcium concentration increased the tendency of membrane fouling (Clark and Junker, 1993; Hong, 1996).

As discussed above, membranes and most fouling materials are likely to carry negative charges. Therefore, electrostatic repulsion is a major force to keep membrane and fouling materials apart. Hence, increasing the electrostatic repulsion is expected to enhance the membrane cleaning by increasing the charge density of fouling materials. The balance between hydrophobic attraction and electrostatic repulsion essentially determines if a membrane is being fouled or being cleaned. As molecular weight and mass/charge ratio of solutes, ionic strength, and the concentration of divalent cations increases, hydrophobic attraction tends to increase, so does the potential of membrane fouling. On the other hand, increases in charge density and polarity of solutes, and pH will increase electrostatic repulsion between the membrane and solutes, which reduces the adhesion between membrane and fouling materials and enhances the cleaning efficiency (Liu et al., 2004).

Membrane cleaning is an essential step in maintaining the permeability and selectivity of a membrane process. The cleaning process must remove deposits and restore the normal capacity and separation characteristics of the system. The choice of cleaning method depends on the module configuration, membrane resistance and nature of the foulants. The type of cleaner required depends on the nature of the foulant and membrane material. Cleaning techniques for membrane restoration could be broadly categorized into three types: physical, chemical and physico-chemical methods. Physical cleaning based on mechanical treatment dislodges and removes foulants from the membrane surface. Chemical cleaning depends purely on chemical reactions to remove foulants from membrane surfaces. Chemicals react with deposits, scales, corrosion products and other foulants. The chemicals should loosen and dissolve the foulants, keep the foulant in dispersion and solution, avoid new fouling and not attack the membrane (Madaeni and Mansourpanah, 2004).

Each type of foulant requires certain types of chemical agents. A large number of chemicals are available for removing deposits. Table 3.3 lists the major classes of chemicals used for membrane cleaning. The important factors for selection of a cleaning agent are: the cleaning ability, the ease with which it can be suspended and rinsed away, its chemical stability during use, cost and safety (Madaeni and Mansourpanah, 2004).

Table 3.3. Classes of Membrane Cleaning Chemicals

Class	Function	Typical Chemical
Caustic	Hydrolysis, Solubilization	NaOH
Oxidants, Disinfectants	Oxidation, Disinfection	NaOCl, H_2O_2, Peroxyacetic acid
Acids	Solubilization	Citric acid, Nitric acid
Chelating Agents	Chelation	Citric acid, EDTA
Surfactants	Emulsifying, Dispersion, Surface conditioning	Surfactants, Detergents

CHAPTER 4

LITERATURE REVIEW

Reclamation of textile wastewaters have become a widespread application of membrane technology since the environmental regulations for wastewater discharge are getting more stringent and the scarcity of fresh water supplies on earth are increasing, which in turn, have been forcing textile manufacturers to focus on water recycling. Although membrane technology requires an initial high setup cost, it is outweighed by the significant cost savings achieved through the reuse of chemicals, dyes and water. The costs can be reduced by the implementation of pre-treatment processes and regular cleaning to eliminate fouling problems and by choosing the most appropriate membrane system (Tang and Chen, 2002). Several approaches consisting of individual or combined membrane processes have been offered for advanced treatment of textile wastewaters, including microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). The recyclable effluents are reported to be produced by RO, after biological treatment and flocculation, and NF, after physico-chemical treatment (Tinelli, 1997). However, a systematic approach to investigate the most suitable solution for the textile industry seems to be lacking in terms of the kind of effluent to treat, the type of the membrane to use, and the process combinations to use (Bottino et al., 2000). In an attempt to contribute to the existing efforts for filling this gap, this study involves the development of the most suitable combinations of membrane processes for the reclamation of the effluents of a carpet manufacturing industry, which was handled as a sample textile subcategory.

MF membranes comprise the largest fraction of total membrane production due to their increasing usage in recent years (Porter and Gomes, 2000). MF provides a simple clarification of the effluent by removing suspended solids (Bottino et al., 2000) and colloidal dyes (Buckley, 1992). Therefore, its application alone has been reported to be inadequate for water recycling, making it more generally adopted in pre-treatment for further membrane processes (Bottino et al., 2000). MF has been gaining a wider acceptance for the pretreatment stage since it is economically more competitive than conventional methods such as coagulation, flocculation, sedimentation and filtration (Vedavyasan, 2000).

UF is generally applied in the separation of macromolecules with a molecular weight of 1000 Da or above (Erswell et al., 1988). Although UF has been successfully applied in many industries, its use in textile industry has been limited due to the variability of rejection performances, which makes direct reuse impossible (Watters et al., 1991). UF performance is highly dependent on the type of membrane material and the feed composition as well as the shape and size of the macromolecules. In UF process, the removal of polluting substances is never complete, i.e., 21-77% COD, 31-76% color, and 32-94% surfactants. However, even in the best case, the permeate quality cannot meet the reuse requirements for the dyeing of light colors. Hence, the UF permeates have been accepted only for minor processes in textile industry when salinity is not a problem (Bottino et al., 2000). On the other hand, several applications of the UF process have been reported for the separation of certain dyes, such as indigo, direct, disperse and reactive dyes (Nowak et al., 1986; Porter J. J., 1990; Townsend et al., 1992). Dye rejection performances as high as 90-100% had been obtained in these studies, whereas UF performance was shown to be significantly variable, i.e., 34-93%%, for total waste streams from dyehouse (Watters et al., 1991). Therefore, further filtration by either NF or RO would be required in the case of water recovery (Tang and Chen, 2002).

The use of effective pre-treatment processes such as coagulation, sand filtration, disinfection, flotation, or other membrane processes (MF and/or UF) is fundamental to guarantee a good and constant performance of the NF and RO systems (Coste et al., 1996; Marcucci et al., 2003). Ciardelli et al. (2001) have applied a process train consisting of sand filtration, UF and RO for treating the dyeing and finishing effluents of a textile plant, which were pre-treated in an activated sludge system. The sand filtration achieved a satisfactory reduction of suspended solids and slight reduction of color. The quality of UF permeate was realized to be adequate for feeding the RO membranes. Finally, the RO step produced a permeate with much better quality with respect to the process water quality currently in use. Therefore, they have concluded that the permeate could be reused in all production steps, including the most demanding ones concerning water quality such as dyeing of light colors.

In order to determine the most suitable kind of membrane for the production of permeate with the desired quality for reuse, Marcucci et al. (2003) chose two approaches for the textile effluents downstream of a biological activated sludge process, i.e., UF+RO and MF+NF, which were tested alternatively after the pre-treatment stage of sand filtration. In the first case, sand filtration and UF stages made it possible to achieve a turbidity-free effluent, as required to minimize RO membrane fouling. Sand filtration and UF removed COD partially (less than 30%), and color poorly (5%). The RO permeate was of excellent quality where 95% COD removal was achieved. The dyeing tests revealed very high quality of the dyeings with RO permeate, which achieved better results than the well water currently used as the process water. In the second case, sand filtration and MF removed 99% of suspended solids and 80% of turbidity, whereas only 36% of COD and 13% of color were removed. The NF membrane achieved complete removal of the COD left, and a very high fraction of the remaining color. The dyeing tests performed with NF permeate gave satisfactory results even if the water quality was worse than RO permeate in terms of salt content and chlorides.

They finally concluded that both permeates from the two-stage membrane systems could be used as process water for the textile industry, and about 60-65% of the plant effluents could be recycled using this kind of advanced treatment systems.

Similarly, Van der Bruggen et al. (2001) tested two options for textile wastewater recovery, i.e., direct NF, which was performed with simulated dye baths, and sand filtration followed by NF, which was performed with biologically treated effluent. In the first case, they observed problems with high osmotic pressures and hence the need for a membrane configuration with double pass was reported. In the second case where a biological treatment and sand filtration preceded NF, acceptable water flux was obtained and the salt concentrations were low enough to avoid the problems with build-up of an osmotic pressure. Furthermore, the tested process train allowed the retentions to be sufficiently high to make the recirculation of the permeate possible.

Another investigation performed with the biologically treated textile effluents belongs to Bes-Pia et al. (2004), where ozonation was further tested in the pre-treatment stage for NF. A COD removal efficiency of 43% was accomplished with low ozone doses at 60 min ozonation period, which in turn, resulted in an increase of NF membrane life.

Implementation of UF alone as an alternative to NF or RO has been proven to be insufficient to achieve the desired permeate quality for reuse (Bes-Pia et al, 2002; Sostar-Turk et al. (2005). Bes-Pia et al. (2002) have tested UF against NF after chemical precipitation for the reclamation of wastewaters of a printing, dyeing and finishing textile industry. A COD reduction of 50% in the chemical precipitation stage was reported where 200 mg/L of coagulant and 1 mg/L of anionic flocculant were used. None of the UF membranes with MWCO ranging from 5000 to 100000 Da could effectively reduce COD. On the other hand, the NF membranes produced permeates almost free of organic matter, which were suitable for reuse in the industry. Similarly, Sostar-Turk et al. (2005) tested UF against RO for the recovery of a textile printing wastewater containing reactive dyes. The UF membrane, which removed 42% of COD and 30-37% of color could not even meet the discharge limits, and further treatment was required. When the UF permeate was used as the RO feed, which was pre-filtered through a ceramic membrane of 0.1 μm before the RO unit, the COD and color rejections increased to 94% and 99%, respectively, making it possible to reuse the recovered water in the washing process of printed textiles.

Improvement of UF performance by a suitable pre-treatment process was also investigated (Marcucci et al., 2002). In this work, the performance of the physico-chemical processes (clariflocculation and ozonation) followed by UF treatment, which was applied directly to the textile wastewater was compared to another process train composed of sand filtration and MF followed by NF, which was applied to the biologically treated effluent. The configuration with UF as the final membrane process revealed good performance of the clariflocculation and ozonation steps where a turbidity removal of 49% and a color removal of 71% were achieved, respectively. In the UF step, 27% of turbidity and 30% of total solids were achieved. In addition, a satisfactory COD removal of 66% was accomplished and the total color removal reached 93%. The dyeing tests performed with 50% UF permeate and 50% well water provided successful results, suggesting a limit of 50% for the contribution of recycled water into the process water. In the second configuration with NF as the final membrane process, the sand filtration and MF steps removed suspended solids completely and turbidity at 78%, whereas COD was removed partially at 30%. The NF membrane removed the remaining COD and color almost completely. The results of the dyeing tests conducted with 100% NF permeate suggested that NF permeate was reusable in all dyeing cycles, even for light colors.

In another study with similar approach, Rozzi et al. (1999) tested two different process combinations for the reclamation of a textile effluent subjected to biological treatment. The first combination was MF coupled with NF and the second one was clariflocculation plus multimedia filtration coupled with low-pressure RO. They observed that the qualities of the final permeates produced by both treatment schemes were acceptable for water reuse. However, the requirement of an additional pre-treatment step consisting of coagulant addition to the first treatment scheme was reported in order to assure acceptable duration of filtration cycles.

As seen from all the studies summarized here, pre-treatment step is very important for the development of the best process train for a given textile effluent, and therefore the pre-treatment process must be optimized to ensure minimized flux decline. In a study performed by Dhale and Mahajani (2000), NF was tested after pre-filtration through a 50 μm membrane for the recovery of a highly colored disperse dye bath waste and a drastic flux decline of 80% was observed accompanied with 98% color and 70% COD rejection efficiencies. Although the selected process train produced a permeate which had suitable quality for recycling into the process, the severe flux decline makes this process train unfeasible, thereby necessitating the implementation of alternative pre-treatment processes to ensure better permeate flux.

Most of the studies mentioned above have shown that the recovery of textile wastewaters with membrane technology currently proposes two or more-step processes and hence the costs involved have caused a limitation of the wide application of the technique (Bottino et al., 2000). Furthermore, the presence of several applications downstream of an already existing biological treatment would rise the question of whether there is a limitation of the applicability of membrane technology for the textile plants, which possess a biological treatment plant. To this end, achievement of the reclamation of the textile effluents with good permeate qualities and minimized flux declines in the most simple and energy efficient integrated process combinations would be of great value for spreading the membrane applications.

In an attempt to achieve this target, Bottino et al. (2000) performed a screening of a number of approaches consisting of MF, UF, NF and RO for the treatment of several streams generated in different textile processes and at different purification stages. According to their results, NF and RO produced high quality permeates, with a very high removal of COD, i.e., 79-81% by NF and 89-91% by RO. Similarly, color was removed at greater than 96% by both processes. They considered that the degree of removal was good enough for the NF permeate to be reused in all wet textile processes, including the most demanding ones. Moreover, they observed that the removal performances were only slightly dependent on the quality of the feed concerning flows (prior to or after biological treatment), and suggested the viability of a single-step membrane process as nanofiltration for the specific application, which allows for significant reduction of treatment costs. On the other hand, Rautenbach et al. (2000) reports the requirement of cascaded, all membrane processes for the achievement of high water recovery rates, which should be around 100% for most industries. To this end, it is obvious that each particular textile effluent should be handled individually for the development of the most suitable process or process combinations for its recovery to the degree of quality required for the dyeing process.

There are many factors affecting the membrane performance, which can be grouped into four: the membrane characteristics such as the MWCO, porosity, morphology, surface charge and membrane hydrophobicity; the solute characteristics such as the molecular weight (MW), molecular size, charge and hydrophobicity; the solution chemistry such as pH, ionic strength, hardness, and organic matter; and the system operating conditions such as the applied pressure, temperature, cross flow velocity and recovery ratio. The membrane literature involves many studies investigating the effects of the above mentioned factors on the membrane separation performance (Childress and Elimelech, 1996; Yen et al., 2002; Tay et al., 2002; Akbari et al., 2002; Koyuncu, 2002; Qin et al., 2004; Bellona and Drewes, 2005).

In membrane studies concerning the rejection of organic solutes, some interactions are well understood; for example, the major mechanism of solute rejection by NF is physical sieving of solutes larger than the membrane MWCO. However, other mechanisms of rejection such as electrostatic exclusion and hydrophobic-hydrophilic interactions between membrane and solute are not as well understood. In addition, solution chemistry and membrane fouling may considerably influence the rejection of organic solutes (Bellona et al., 2004).

Several attempts have been made to predict the performance of membrane processes in order to optimise membrane applications. Due to the complexity of membrane systems, researchers have been trying to formulate and apply modeling approaches that can describe the retention of solutes at membrane pores through steric exclusion, electrostatic exclusion, solution-diffusion and adsorption (Kargol, 2001; Van der Bruggen and Vadecasteele, 2001; Mohammed and Ali, 2002). Although, the present modeling approaches have shown promise in describing the separation of components during specific membrane processes, the urgent need for a truly predictive model based on membrane and solute property is reported (Bellona et al., 2004).

It has been proposed that rejection of non-charged compounds can be predicted based on their MW (Ozaki and Li, 2002). In addition, it has been confirmed that the MW is a poor predictor of rejection for compounds other than non-charged and hydrophilic (Kiso et al., 2001). Indeed, a quantification of the molecular size (and geometry) of a solute coupled with the pore size of a membrane is suggested as a better descriptor of rejection than MWCO or MW (Bellona et al., 2004).

In case of charged compounds, electrostatic interactions between the solute and a porous membrane have been reported to be an important rejection mechanism (Tsuru et al., 1991; Wang et al., 1997; Bowen and Mohammed, 1998; Xu and Lebrun, 1999; Mohammed and Ali, 2002; Childress and Elimelech, 2000). The skin layer (surface) of NF membranes mostly carries a negative charge to minimize the adsorption of negatively charged foulants present in membrane feed waters and increase the rejection of dissolved salts (DiGiano et al., 2001; Deshmukh and Childress, 2001; Shim et al., 2002). The negative charge on the membrane surface is usually caused by sulfonic and/or carboxylic acid groups that are deprotonated at neutral pH.

Studies have determined that pH had an effect on the charge of a membrane due to the disassociation of functional groups (Deshmukh and Childress, 2001; Childress and Elimelech, 2000; Xu and Lebrun, 1999; Tanninen and Nystrom, 2002). Zeta potential, which is used to quantify the membrane surface charge, have been observed to become increasingly more negative for most membranes as pH is increased (Hagmeyer and Gimbel, 1998; Lee at al., 2002). Accordingly, increasing the surface charge of the membrane results in increased electrostatic repulsion between a negatively charged solute and membrane. On the other hand, the presence of counter ions such as Ca^{2+}, Na^{+}, Mg^{2+} and K^{+} in feed water was reported to reduce the negative zeta potential of a membrane (Deshmukh and Childress, 2001; Ariza et al., 2002; Shim et al., 2002).

Berg et al. (1997) have determined that charged organics were rejected at higher levels than non-charged organics of the same size. Similarly, Ozaki and Li (2002) performed a rejection experiment utilizing urea and acetic acid, both having the same MW, at different pH ranges using a low pressure RO membrane. Acetic acid is negatively charged at a pH of 4.8 while urea remains non-charged throughout the pH range of 3-9, which was tested in the study. They observed that the rejection of urea decreased slightly from 35% to 28% whereas the rejection of acetic acid increased from 32% in the non-charged form at pH 3 to 100% in the negatively charged form at pH 9, which is most likely due to electrostatic repulsion at the membrane surface. The increase in the rejection of acetic acid at pH values above the pK_a was most likely caused by the increasing negative charge of the membrane repulsing the negatively charged acetic acid (Ozaki and Li, 2002).

The adsorption of hydrophobic compounds onto the membranes is reported to be an important factor in the rejection of micropollutants during membrane applications (Bellona et al., 2004). The hydrophobicity of membranes is determined by their contact angle measurements. Recently, it has been reported that membranes with higher contact angles could reject and adsorb more mass per unit area of a hydrophobic compound than a membrane having smaller contact angle (Kimura et al., 2003; Wintgens et al., 2003). The rejection of compounds by MF having MWCO, which is much larger than the MW of the compound, has been explained by adsorption (Chang et al., 2002). According to the results of these studies, hydrophobic-hydrophobic interactions between the solute and the membrane play an important role in the rejection of hydrophobic compounds.

The influence of operating parameters on the membrane performance was also reported (Yen et al., 2002; Koyuncu, 2002; Majewska-Novak et al., 1989). The study conducted by Yen et al. (2002) aimed to investigate the effect of temperature, pressure and solute concentration on the treatment of a textile effluent by RO. Their results have shown that both the water flux and the solute rejection increased with an increase in applied pressure in the range of 50-200 psi. The water flux increased and solute rejection decreased with an increase in temperature in the range of 15-45°C). On the other hand, the water flux decreased and the solute rejection increased with an increase in solute concentration in the feed. Moeover, the water flux was proportional to the applied pressure whereas the solute rejection was found to be a nonlinear function of the applied pressure and temperature.

Among the dye classes used in textile industry, the reactive dyes attracted the highest attention in membrane research field since they are removed less efficiently as compared to other dye classes by biological treatment methods (Pierce, 1994). Moreover, the fixation of the reactive dyes on the fabric is low as compared to other dye classes, resulting in the generation of highly colored effluents. Due to these reasons, there has been an extensive research conducted on the removal of reactive dye wastewaters by membrane processes (Brandon et al., 1981; Treffrey Goatley et al., 1983; Porter and Goodman, 1984; Erswell et al., 1988; Gaeta and Fedele, 1991; Buckley, 1992; Tegtmeyer, 1993; Fritsch, 1993; Mishra and Tripathy, 1993; Rautenbach and Mellis, 1994; Wenzel et al., 1996; Kornmuller, 1997; van’t Hull et al., 1997; Jiraratananon et al., 2000).

Another class of dyes, namely the acid dyes have high fixation rates (80-93%) on to the fabric and hence result in relatively less colored effluents. This may be one reason for the relatively less interest for the reclamation of acid dye bath wastewaters, as they seem to impose less threat on the environment. However, some acid dyes are among the most hazardous azo dyes due to the release of carcinogenic amines defined by the German Consumer Goods Ordinance (GCGO, 1997) and hence the production or import of consumer goods dyed with those azo dyes were banned for health reasons (EU, 2002). The majority of these consumer goods are textiles in regular contact with human body including the synthetic carpets. Based on their toxicity in addition to carcinogenicity, the discharge of these azo dyes into the receiving water bodies would adversely affect the aquatic life. In this regard, reactive dyes are among the least harmful ones since they do not appear in the list of banned azo dyes.

One of the application areas of acid dyes is the carpet manufacturing process where carpets made of synthetic fiber are dyed with non-metallized or metallized acid dyes. The literature lacks information about the reclamation of carpet dyeing wastewaters by membrane processes, which is an important subcategory of textile industry for Turkey. To this end, this thesis aimed to develop a treatment scheme for the reclamation of acid dye bath wastewaters and print dyeing wastewaters of a carpet manufacturing industry, where the treatment scheme for each wastewater stream was optimised towards the simplest one by choosing the most suitable pre-treatment and treatment processes among several alternatives. The effect of wastewater pH on the membrane performance was also studied, results of which significantly influenced the selection of the best process train to be implemented and the operational conditions to be provided for the recovery of the carpet dye house effluents.

CHAPTER 5

MATERIALS AND METHODS

5.1. Sampling

The print dyeing wastewaters (PDW) and the acid dye bath wastewaters (ADBW) were collected from the dyehouse of the Samur Carpet Factory (SCF). The details of the dyeing processes are described in Appendix A for a better understanding of the wastewater characteristics. The PDWs were taken from the print afterwash tank into which fresh water is continuously added to keep the water level constant while the dyed carpet moves in and out of the tank in order to wash away the residue of the print paste left on it. The PDW has neutral pH and the wastewater characteristics is subject to high fluctuations due to the varying colors of the carpets.

The PDW stream was sampled four times throughout the experimental study and a total of 20 bottles with volumes of about 30 L each were collected. Three composite mixtures were prepared from these bottles and the experiments were performed with the composite mixtures in order to compensate for the high fluctuations in wastewater characteristics. The first sampling was done for characterization purpose only and no composite mixtures were obtained. The characteristics of individual samples are given in Tables B.1-B.4 (Appendix B) whereas the characteristics of PDW mixtures are given in Table 5.1. The pre-treatment and treatment studies were carried out with Mixtures 1, 2 and 3.

Table 5.1. The Characteristics of PDW Mixtures

Parameter	**Measured Value ± Standard Deviation**		
	Mixture 1	**Mixture 2**	**Mixture 3**
COD (mg/L)	391 ± 10	846 ± 10	852 ± 10
UVA_{195}	3.12 ± 0.03	3.78 ± 0.05	3.51 ± 0.06
Color (Pt-Co)	301 ± 3	576 ± 6	706 ± 0
Turbidity (NTU)	41 ± 1.4	58 ± 0	71.6 ± 0.7
T. Solids (mg/L)	603 ± 13	713 ± 16	678 ± 9
T. Hardness (mg/L as $CaCO_3$)	20 ± 0	13 ± 1.4	33 ± 1.4
Conductivity (µS/cm)	700 ± 0	785	697
Chloride (mg/L)	15 ± 0	21 ± 0	15.5 ± 0.7
pH	7.60 ± 0	7.32 ± 0.01	7.16 ± 0.01

The ADBWs are generated in a batch process where the wastewater characteristics are also subject to fluctuations from one carpet to the other. Besides, their characteristics differ significantly from those of PDW such that ADBWs have much higher COD and much lower color and turbidity. Moreover, the ADBWs have acidic pH and their temperature is around 90-100 °C. Another difference between the two types of wastewaters is their volumes of generation. With the production capacities of the SCF during the experimental study of this thesis, the ADBW was generated at only one-third to one-fourth of the PDW volume. This ratio is even smaller now due to the extension of the print dyeing process line to twice of its original capacity.

The ADBW stream was sampled for 8 times throughout the experimental study and a total of 42 bottles were collected. The individual wastewaters collected at each sampling program were mixed to obtain composite mixtures. The reason for this stream to be sampled more frequently than the PDW stream was the fungal and/or bacterial growth observed in the ADBW samples due to their acetic acid contents, which in turn, changed the wastewater characteristics significantly, especially in terms of color and turbidity. Therefore, not all the bottles were used during the experimental study but most of them were used for the characterization purpose only. The characteristics of individual wastewaters are given in Tables B.5-B.12 (Appendix B) and the characteristics of the composite mixtures obtained with these wastewaters are shown in Table 5.2. As seen, four composite mixtures were prepared and one individual sample was used during the experimental study.

Table 5.2. The Characteristics of ADBW Mixtures

Parameter	**Measured Value ± Standard Deviation**				
	Mixture 1	**Mixture 2**	**Mixture 3**	**Mixture 4**	**Sample 42**
COD (mg/L)	1163 ± 21	1494 ± 4	1014 ± 2	1462 ± 22	1925 ± 30
UVA_{200}	3.28 ± 0	3.15 ± 0	3.09 ± 0	2.99 ± 0	3.25 ± 0
Color (Pt-Co)	112 ± 9	23 ± 1	102 ± 0.7	8 ± 0	50 ± 0
Turbidity (NTU)	12 ± 0	2.9 ± 0.1	11 ± 0	1 ± 0	3.3 ± 0
T. Solids (mg/L)	703 ± 13	894 ± 20	818 ± 14	899 ± 4	1326 ± 23
T. Hardness (mg/L as $CaCO_3$)	-	26 ± 2.8	24 ± 0	44 ± 0	18 ± 0
Conductivity (µS/cm)	600	615 ± 7	635	732	837
Chloride (mg/L)	9.5 ± 0.7	13.5 ± 0.7	10 ± 0	13 ± 0	15 ± 0
pH	4.71	4.74 ± 0	5.08 ± 0	4.73 ± 0	5.30 ± 0

The composite mixtures 1 and 2 were used for the pre-treatment studies only and then discarded due to fungal/bacterial growth. The wastewaters collected in Sampling 3, 4 and 5 were used for characterization purpose only and no mixtures were obtained with them. Mixture 3 was obtained by the samples collected in sampling 6 program, and only the pre-treatment studies were performed. Mixture 4 was obtained by mixing the wastewaters collected in sampling 7 program, with which the membrane experiments were carried out. Finally the last wastewater sample was collected from the ADBW stream, the Sample 42, and it was also used in the membrane experiments.

In order to preserve the samples, sodium azide (NaN_3) was tried to be used as an inhibitor, however NaN_3 was observed to cause some additional COD. In order to determine the COD contribution by NaN_3, a COD test was performed by dosing 1 g/L of NaN_3 to the sample mix and to a standard solution having a COD of 1000 mg/L (Table 5.3). The increase in the COD's of the two samples was 6% for the sample mix and 12% for the standard solution, which was not a constant value. Therefore, the use of NaN_3 was eliminated and the wastewater samples were only kept at +4 °C for preservation.

Table 5.3. Effect of Sodium Azide on COD Readings

Sample	**COD (mg/L)**
Distilled water + NaN_3	248 ± 42
Standard solution (1000 mg/L COD)	1069 ± 9
Standard solution+ NaN_3	1194 ± 26
Sample mix	1104 ± 24
Sample mix + NaN_3	1166 ± 13

5.2. Experimental Methods

5.2.1. Chemical Precipitation (CP)

A conventional jar test apparatus equipped with six mixers and six jars each having a capacity of 0.8-2.0 L was used. $Al_2SO_4.18H_2O$ (Merck) was used as the coagulant and a stock solution of 25 g/L was added into the samples at doses varying from 50 to 600 mg/L. PDW samples were mixed rapidly for 1 min at 100 rpm in order to distribute the chemical homogeneously, and then mixed slowly for 30 min at 30 rpm in order to promote floc formation. Then, sedimentation was provided for 1 h for the settlement of the flocs formed. The clear supernatant was taken and analysed for the parameters given in Table 5.6.

5.2.2. Microfiltration (MF)

The applicability of dead-end microfiltration (MF) was tested for both PDW and ADBW in the pre-treatment stage. A conventional vacuum filtration apparatus (Millipore) providing dead-end filtration was used to simulate sand filtration. The filter media having pore sizes ranging from 11 μm to 0.2 μm were first washed with 1 L of distilled water and then used under a vacuum of 550 mm Hg (gauge). The specifications of microfilters are given in Table 5.5. The filtrate were collected and analysed for their color and turbidity contents. The filtration rates were determined by dividing the total volume of the filtrates by the time periods of filtration. The calculated values represent cumulative filtration rates since the filtration rates decreased with time of filtration due to the accumulation of material on the filter media.

5.2.3. Ultrafiltration/Nanofiltration (UF/NF)

The UF and NF experiments were mainly carried out by a lab-scale plate and frame module, LabStak M20 (DSS Company) in cross-flow mode of filtration. In this system, up to ten pairs of flat sheet circular membranes, each pair having an effective membrane area of 0.036 m^2 can be installed into the module simultaneously. The membrane sheets have to be mounted in even numbers, making pairs, due to the configuration of the system. To make one pair, two membrane sheets are mounted on to both sides of a plastic support plate. The support plate is composed of two perforated halves forming an inside cavity where the permeate flow, passing through the membranes is collected and directed towards a cannular outlet pipe located at the plate periphery. Two opposite lock rings mounted at the center hole of the support plate position the two membranes. The feed, coming from the main feed stream is distributed among the membranes via plastic spacer plates, which have on both sides a set of radial cross flow channel beads connected to a number of through holes close to the periphery to distribute the flow.

A few UF experiments were performed with another module, Osmonics SEPA CF Module, which is also used with flat sheet membranes and provides cross-flow filtration. The membranes are rectangular in shape and have the dimensions of 10 x 15.5 cm, providing an effective filtration area of 0.0155 m^2. However, only one membrane can be installed into the module at one time, yielding single membrane surface for filtration.

In LabStak M20 Module, the UF membranes were tested under an inlet pressure of 2 or 6 bars (gauge) and the NF membranes were tested under an inlet pressure of 6 bar (gauge). In SEPA CF Module, the inlet pressure was kept at 3-4 bars (gauge), whereas the pressure on the retentate side was 1 bar (gauge). The trans membrane pressures (TMP) across the membranes were calculated by taking the arithmetic average of the pressures measured on the feed side and the retentate side, where the permeate side is open to atmosphere. The samples were fed to the system at a flow rate of 6 L/min for LabStak M20 Module and at a flowrate of 0.9 L/min for Sepa CF Module.

The membrane experiments were carried out in two different modes of filtration; namely the total recycle mode of filtration (TRMF) and the concentration mode of filtration (CMF) (Figure 5.1). In a TRMF test, both retentate and permeate are recycled into the feed tank and thus the feed quality is assumed to be constant since the feed volume is kept constant throughout the experiment. This is done as a first step in order to evaluate the performance of the membrane under stable conditions. However, this approach is not valid for the real applications since wastewater recovery is achieved by the reduction of feed volume accompanied by a continuous worsening of the feed quality. By performing the CMF tests, the membrane performance can be evaluated in a more realistic way.

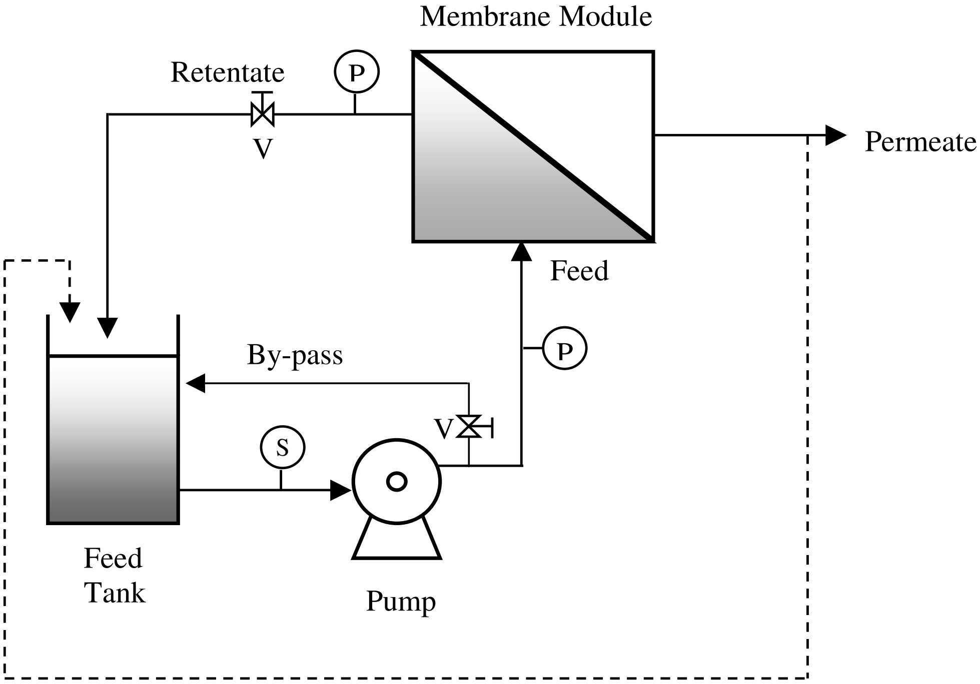


Figure 5.1. Schematic Diagram of the UF/NF Systems

(P: Pressure Gauge, S: Suction Gauge, V: Valve)

The TRMF tests were conducted with 4-6 L of feed wastewater whereas 25-40 L of wastewater was used in the CMF tests. In the TRMF tests, the filtration duration ranged from 3 to 10 h, depending on the achievement of the steady state permeate fluxes and the separation performance, which were periodically monitored by the permeate volume and UVA measurements. The permeate volumes were divided by the time of permeate collection and the effective membrane area to find the permeate fluxes. The filtration tests were ended when the steady state permeate fluxes and UVA readings were obtained. Before ending the tests, the permeates were sampled for further analysis for the parameters shown in Table 5.6. In case of CMF tests, there was continuous reduction in the feed volume, resulting in a continuous flux decline and increased or decreased separation performance. Therefore, the criterion to end the CMF tests was the volume reduction (VRF), which is calculated as follows:

$$VRF = \frac{V_f}{V_r}$$

where V_f and V_r are the initial volume of feed and the volume of the retentate, respectively. A VRF of 1 means that there is no water recovery.

The permeate flux and the UVA were also monitored throughout the CMF tests. In order to determine the flux declines, the fluxes were measured in four steps:

1) Initial clean water flux (I): This is the first flux determined with the virgin or clean membrane, which was subjected to an initial chemical cleaning procedure by the manufacturer's recommendation,
2) Wastewater flux (W): This is the wastewater flux stabilized with respect to time during filtration,

3) Clean water flux of the fouled membrane (F): Clean water flux was measured with the fouled membrane after the filtration of wastewater had been finished,
4) Clean water flux of the cleaned membrane (C): This is the last flux measured with clean water after the membrane had been subjected to chemical cleaning.

The flux declines were evaluated based on the calculations shown in Table 5.4. In this way, the extent of concentration polarization and fouling was determined.

Table 5.4. Flux Decline Calculations

Calculation	**Explanation**
I-W	Total flux decline
F-W	Flux decline due to concentration polarization
I-F	Flux decline due to fouling (irreversible + reversible)
C-F	Flux decline due to reversible fouling
I-C	Flux decline due to irreversible fouling

5.2.4. Membrane Cleaning

All the membranes used in membrane filtration tests were cleaned before the first use and after the experiments run with the wastewaters. The membranes were cleaned by clean-in-place (CIP) method, i.e., they were kept in the module while the cleaning solutions were circulated through the system for a given time, the permeate and retentate being continuously discarded. The cleaning procedure was applied according to the manufacturer’s recommendation (DSS LabStak M20 Operation Manual). A solution of HNO_3 at a pH of 3 followed by a solution of NaOH at a pH of 9-10 were circulated in the system under a low inlet pressure of 2 bars (gauge). The acidic solution was prepared by adding approximately 0.8 mL of HNO_3 (Merck) into 10 L of ultrapure water (0.002 M) to yield a pH of 3. The basic solution was prepared by adding 3-4 mL of 2.5 M stock solution of NaOH into 10 L of ultrapure water (0.001 M) to yield a pH of 9-10. Each solution was circulated for periods of time varying from 15 to 60 min in order to remove the organic and inorganic precipitates from the surface of the membranes. The cleaned membranes were always kept wet in a 0.25% sodium bisulfite solution in order to avoid bacterial growth on the membranes.

5.2.5. Membrane Pre-treatment

Most of the NF membranes used for the treatment of ADBW were observed to have no flux at all although the initial cleaning had been applied. These membranes seemed to be very dry and hence they were soaked into 10% isopropanol solution for 1 min to provide extra wetting. A few runs were performed with both pre-treated and not pre-treated membranes to make sure that extra wetting by isopropanol did not affect the performance of the NF membranes.

5.3. Membrane Specifications

The specifications of the MF, UF and NF membranes used throughout this study are given in Table 5.5. According to the manufacturer data, the NF membrane NFT-50 consists of three layers: an ultrathin polyamide barrier layer, a microporous polysulfone interlayer and a high strength polyester support. It is stated to be a hydrophilic membrane with a contact angle of 40° (Wilhemy Method) and has negative surface charge. The $MgSO_4$ rejection is reported as $\geq$99% by the manufactuer (measured on 2000 ppm $MgSO_4$ at 9 bar pressure and 25 °C temperature).

Table 5.5. Membrane Specifications

Process	Filter	Material	Pore Size/ MWCO	Effective membrane area (m^2)	WW
MF	Whatman 1	Cellulose	11 µm	0.0014	PDW
	Whatman 42	Ashless Cellulose	2.5 µm	0.0014	PDW
	Whatman GF/B	Glass microfiber	1.0 µm	0.0014	PDW ADBW
	Millipore	Cellulose mixed esters	0.45 µm	0.0014	ADBW
	Sartorius	Cellulose acetate	0.20 µm	0.0014	ADBW
UF	Osmonics HZ 15	Polyethersulfone	50000 Da	0.0155	PDW ADBW
	DSS GR 51 PP	Polyethersulfone	50000 Da	0.0360	PDW
	DSS GR 61 PP	Polyethersulfone	20000 Da	0.0360	PDW
	DSS GR 95 PP	Polyethersulfone	2000 Da	0.0360	PDW
	DSS ETNA 01PP	Composite fluoro polymer	1000 Da	0.0360	PDW
NF	DSS NFT-50	Thin film composite on polyester		0.0360	PDW ADBW

5.4. Analytical Methods

COD was measured following USEPA approved HACH Method 8000 using HACH DR-2000 Model spectrophotometer at waveleghts of 620 (high range) and 420 nm (low range), respectively. Color measurements were performed by the same instrument at 455 nm. UVA values were determined by Varian Cary 100 Model spectrophotometer via scanning the specrum from 190 to 700 nm. The non-purgeable fraction of the organic carbon (NPOC) was measured with a Shimadzu 5000A Model TOC analyzer. Turbidity was measured with a HACH Model 2100A turbidimeter and total solids content of the samples were determined by gravimetric analysis. All the analyses except COD were performed according to the Standard Methods (APHA, 1995) (Table 5.6).

Table 5.6. Analysis Methods

Parameter	Standard Method No.
NPOC	5310 B
UVA	5910 B
Color	2120 B
Turbidity	2130 B
Total Solids	2540 B
Total Hardness (as $CaCO_3$)	2340 C
Conductivity	2510 B
Chloride	4500-Cl^- B
pH	4500-H^+

5.5. Process Selection Strategy

In selecting the most suitable pre-treatment and treatment processes for PDWs and ADBWs, respectively, the alternatives depicted in Figures 5.2 to 5.6 were considered. The whole process trains were developed stage by stage based on a "branch-and-bound" approach.

For the pre-treatment stage of PBWs, the first option taken into consideration was MF in order to capture the biggest particles in the wastewater so that rapid fouling of the following membranes could be avoided. However, the applicability of the MF became impossible due to very rapid clogging of the filter media tested, bringing chemical precipitation (CP) into the scene. Four alternatives towards the most economical pre-treatment process was compared, i.e., CP with optimised alum dose, CP with low alum dose followed by MF, CP with high alum dose followed by UF, and CP with optimised alum dose and polyelectrolyte aid (Figure 5.2). The decision was made based on the highest removal efficiencies achieved by these processes.

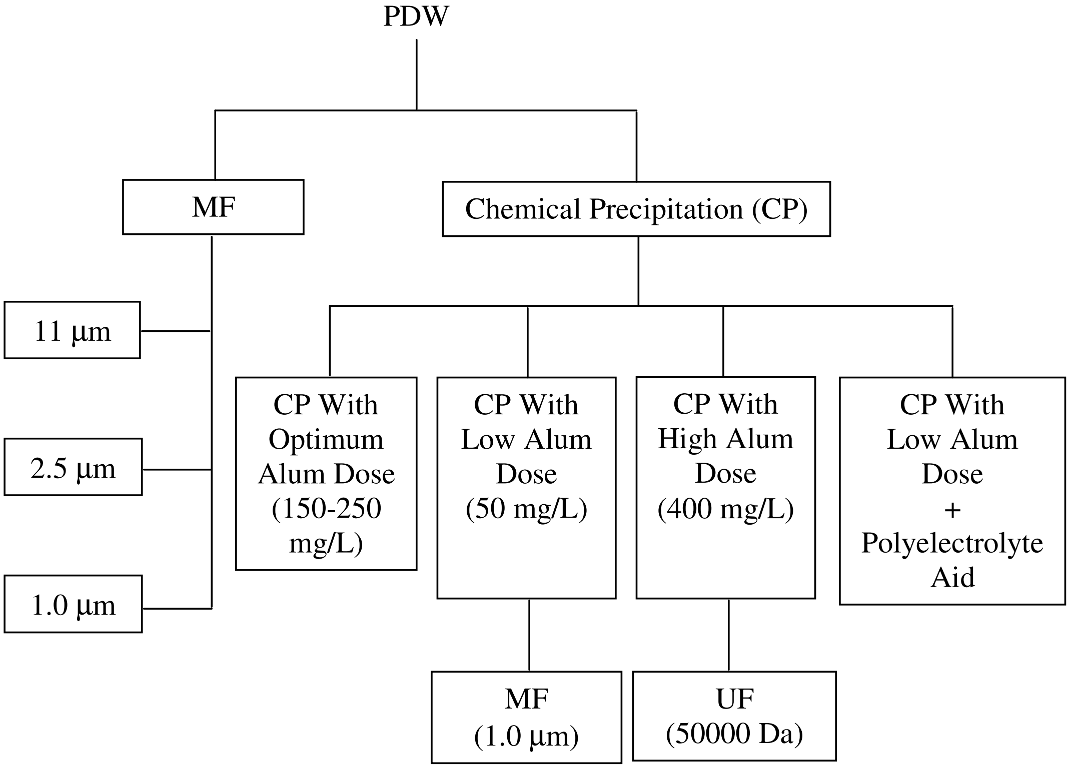


Figure 5.2. Pre-treatment Alternatives for PDWs

MF was again the first option for the pre-treatment stage of ADBWs. MF media with pore sizes shown in Figure 5.3 were tested in single and sequential modes of dead-end filtration to achieve the highest removal performances for color and turbidity, which were the parameters of interest for fouling control. Filtration rate was also considered as a factor in finally choosing the pre-treatment stage for ADBWs due to the difficulty of filtering very large volumes of wastewaters by a vacuum filtration apparatus in dead-end mode of filtration.

For the treatment of PDWs, single NF was tested against single UF where UF membranes with MWCO ranging from 1000 Da to 50000 Da were used. The performances were evaluated based on the comparison of the NF and UF permeate qualities to the reuse criteria and original process water quality, and also the flux decline levels observed in each process. Finally, for minimization of the NF flux decline levels, sequential application of UF and NF was tested where one loose UF (20000 Da) and alternatively one tight UF (1000 Da) membrane was followed by the same NF membrane (Figure 5.4). The final decision was made depending on the removal performances of each process and the accompanying flux decline levels.

Regarding the superior performance of NF for PDWs, the first treatment option considered for ADBWs was single NF. However, sequential NF had to be considered in order to meet the relevant reuse criteria, and therefore two and three stage NF was adopted. Despite the achievement of adequate permeate quality with sequential NF, a new alternative was sought to simplify the developed process train. To this end, pH neutralization was undertaken before single NF as the last treatment option (Figure 5.5).

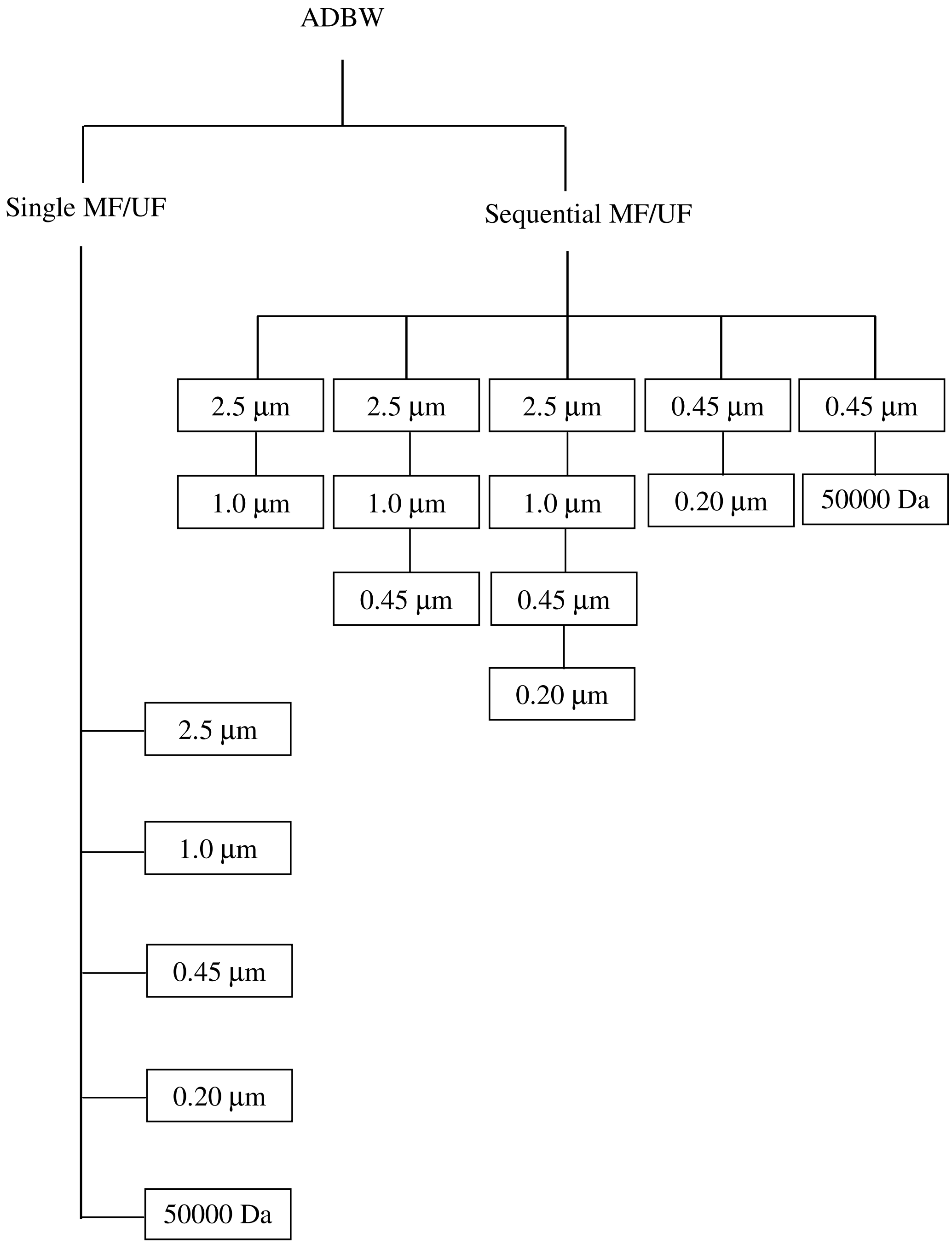


Figure 5.3. Pre-treatment Alternatives for ADBW

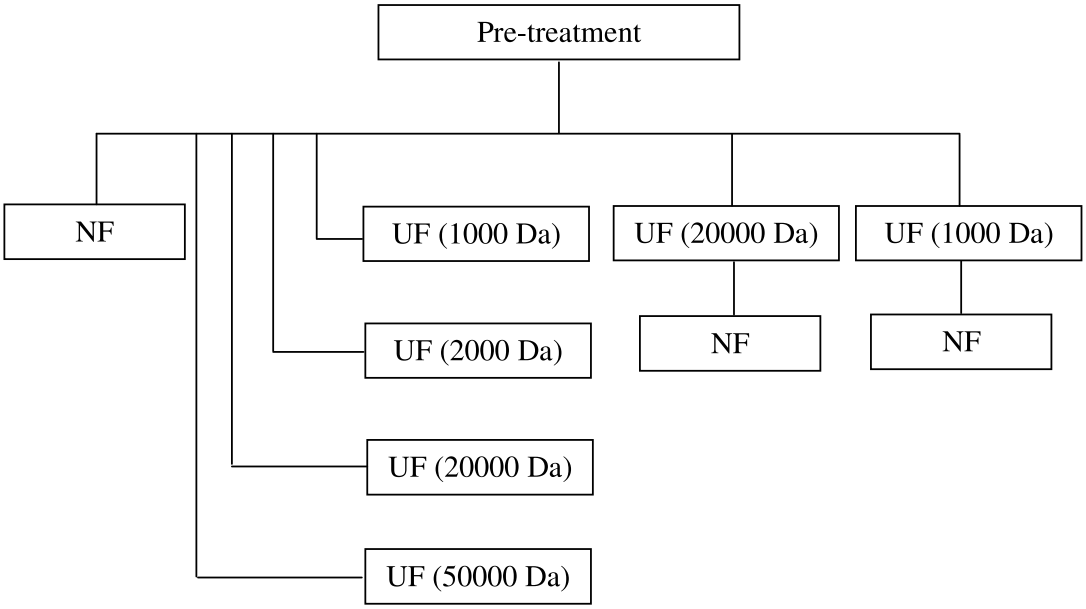


Figure 5.4. Treatment Alternatives for PDWs

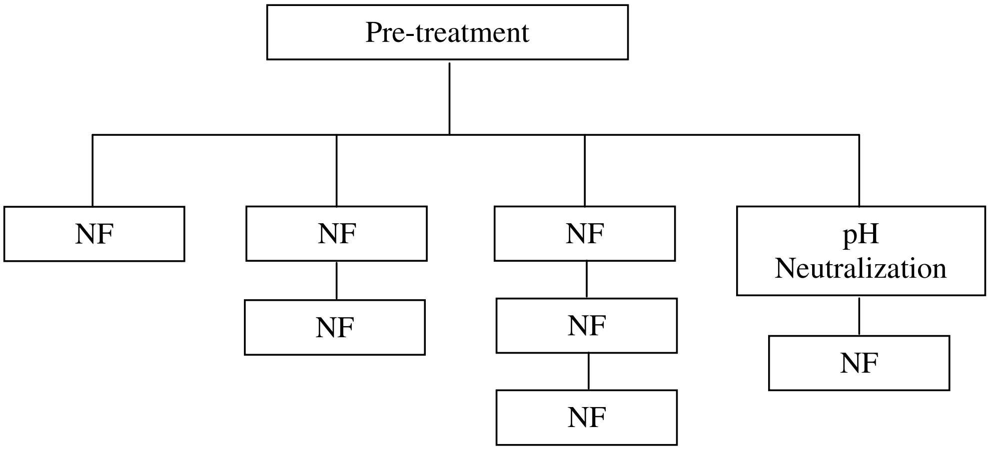


Figure 5.5. Treatment Alternatives for ADBWs

After the development of the process trains for PDWs and ADBWs separately, a very attractive alternative arose due to the necessity of pH neutralization for achieving the highest removal performance for ADBWs. The new alternative was to mix PDWs and ADBWs in order to increase the pH of ADBW from acidic to neutral values, which would bring the benefit of avoiding chemical consumption for this task. Therefore, PDWs and ADBWs were mixed at a volumetric ratio of 4:1 (original generation ratio of these wastewaters) and 1:1 (assuming generation at equal volumes, which would increase the effect of ADBW in the mixture). The final decision of the treatment scheme, as shown in Figure 5.6, was made based on the comparison of the performances of NF for individual wastewaters to those obtained for their mixtures. The flux decline levels and the efficiency of the cleaning procedure were also compared for the final evaluation.

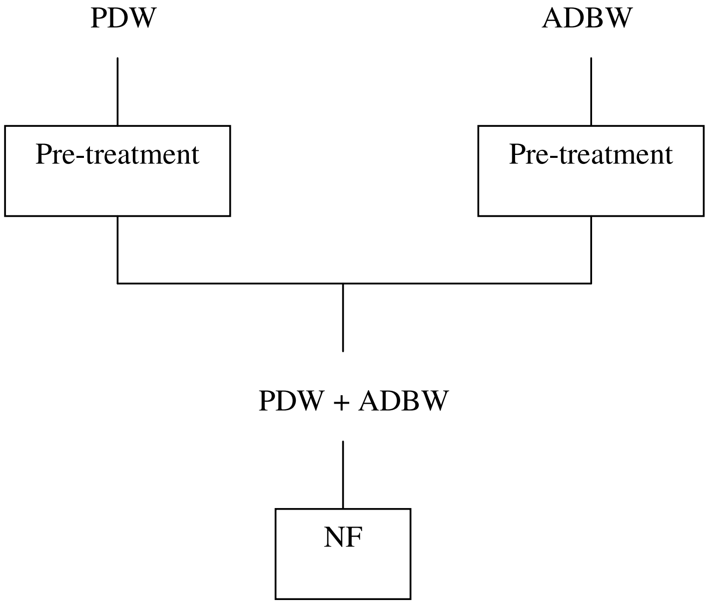


Figure 5.6. Treatment Scheme for PDW + ADBW Mixture

5.6. Justification of Using Mixtures Rather Than Individual Samples

When the characteristics of wastewaters collected from the SCF dye house were realized to be highly variable (Appendix B), it was thought that evaluating the membrane performance using an arbitrarily taken wastewater sample would not be very realistic as the next sample with different characteristics would result in a different performance of the membrane. Also regarding the batch nature of the dyeing process that would already necessitate the use of a collection and equalization basin in a real application, it was decided to run the membrane experiments with the composite mixtures of the wastewater samples rather than the individual samples. In order to test the validity of this strategy, membrane pre-treatment experiments were run with both the individual ADBW samples and also with their mixtures. The results shown in Table C.1 (Appendix C) revealed that the removal performances for the mixture were among the worst as compared to those for the individual samples, which justified that the decision of working with mixtures was a good strategy as it would not lead to the over-estimation of the membrane performance.

CHAPTER 6

RESULTS AND DISCUSSION

The development of the process trains for PDW and ADBW consisted of two steps for each; first the determination of the pre-treatment stages, and second the determination of the membrane-based treatment stages so that a complete process train would be developed for the recovery of these wastewaters. In Part 6.1, the results of all the experimental work carried out for PDW is described, and the overall treatment scheme is given. Then the same strategy was applied for ADBW and all the related experimental results are given in Part 6.2, including the overall treatment scheme for ADBW. The decisions for both the pre-treatment and the treatment process alternatives were made following a "branch-and-bound" method, where the results of the first alternative led to the formation of the next alternative. After testing almost all the possible and logical alternatives, the overall treatment schemes were determined. All the experimental conditions are presented in Appendix D referring to the figure numbers used in this chapter.

6.1. Process Train Development For Print Dyeing Wastewaters (PDWs)

6.1.1. Pre-treatment of PDWs

Implementation of the right pre-treatment process is very important to control the permeate flux decline and hence maintain an efficient membrane separation process. The most commonly adopted pre-treatment processes for textile effluents are MF, UF, chemical precipitation (CP), sand filtration, and ozonation (Coste et al., 1996; Bottino et al., 2000; Bes-Pia et al., 2003; Marcucci et al., 2003). These processes may be implemented individually or in combination according to the characteristics of the particular wastewater. For PDW mixtures, the best pre-treatment process was determined among the possible alternatives listed below:

1. Dead-end MF,
2. CP with optimum coagulant dose with and without polyelectrolyte aid,
3. CP with low dose coagulant followed by MF,
4. CP with high dose coagulant followed by UF.

The experiments for the determination of the best pre-treatment process were performed using the PDW Mixture 1 (Table 5.1). All the alternatives are described in Sections 6.1.1.1 to 6.1.1.4. In evaluating the pre-treatment alternatives, color and turbidity removal efficiencies were considered since these parameters represent the potential membrane foulants causing flux decline.

6.1.1.1. Microfiltration (MF)

The first pre-treatment process considered for PDWs was dead-end microfiltration (MF), which may simulate sand filtration. The MF media having pore sizes of 11, 2.5 and 1.0 μm, whose specifications are given in Table 5.5, were tested in dead-end mode of filtration and color removals presented in Table 6.1 were obtained. However all the filter media were clogged rapidly, resulting in a significant reduction of the filtration rate in 5-10 minutes. The highest filtrate volume was as low as 88 mL obtained by 1.0 μm MF media in a period of 30 min, which yielded a cumulative filtration rate of 0.18 L/h. The rapid clogging of all the filter media indicated the high polluting potential of the PDW, which had complex characteristics due to the presence of synthetic fibers and unfixed metal-complex acid and reactive dyes as well as the residual printing paste, which contained surfactants. This composition may imply a diverse particle size and molecular weight distribution. Moreover, the printing pastes are highly viscous fluids as they contain polymeric thickeners and hence they tend to gel, which may be the cause of rapid clogging of the MF media. The results obtained showed that sand filtration was not an appropriate pre-treatment process for PDWs. Successful results have been reported in literature for sand filtration as a pre-treatment option for textile dyeing effluents, where sand filtration coupled with MF or UF was applied to the biologically treated effluents rather than untreated process wastewaters (Ciardelli et al., 2001; Marcucci et al., 2002). Therefore, the results obtained for the carpet printing wash waters have shown that it was not possible to apply direct MF with pore sizes of 1.0-11 μm as a pre-treatment process for PDWs, and therefore, it must be replaced or combined with another process.

A very coarse filter was also tested to have an idea of the pore size required for direct filtration without rapid clogging. The coarse filter was not clogged, however did not perform well as the others, and therefore it was not considered further for the purpose of pre-treatment.

Table 6.1. Color Removal Performances of Coarse Filtration and MF For PDW Mixture 1

Process	**Filtrate Color (Pt-Co)**	**Color Removal (%)**
Coarse filtration	287	5
MF (11 μm)	166	45
MF (2.5 μm)	171	43
MF (1.0 μm)	63	79

Original color of wastewater=301 Pt-Co

6.1.1.2. Chemical Precipitation (CP)

Chemical precipitation, which is one of the most effective pre-treatment methods for textile effluents, was adopted as the second alternative for the pre-treatment of PDWs. Aluminum sulphate (Al_2SO_4) was chosen as the coagulant due to the fact that it is a cheap and commonly used chemical. First of all the optimum dose of alum had to be found and therefore a range of 50-800 mg/L was applied. As presented in Figure 6.1, CP was very effective, where a sharp decrease in the effluent color and turbidity values between the alum doses of 200 and 400 mg/L were observed. According to these results, a dose of about 400-450 mg/L was the optimum for turbidity and color removals.

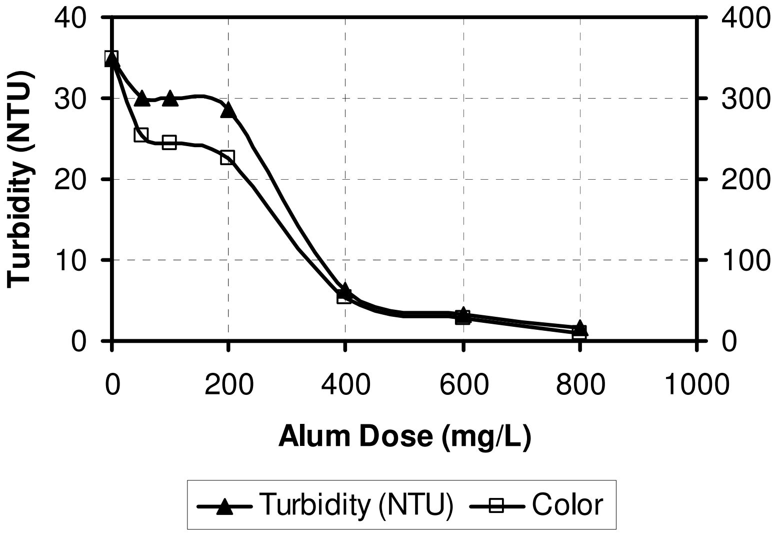


Figure 6.1. Effect of Alum Dose on Color and Turbidity Removal

When these results were evaluated, it was decided not to select an optimum dose, but carry out further experiments at different doses; the one giving the lowest removal and the one giving the highest removal. The target in this strategy was the need for optimizing the whole treatment sequence but not only the CP. Therefore the low dose (LD) and the high dose (HD) were selected to be 50 mg/L and 400 mg/L, respectively. The reason for selecting the HD as 400 mg/L instead of 800 mg/L was that, first 800 mg/L is a very high dose to be applied economically and second, 400 mg/L had already resulted in very high removal efficiencies. The objective here was to see how much the LD could reduce the burden of the next MF stage, which was planned to be applied after CP (LDCP + MF). The second alternative was decided to be the application of UF process following a high dose chemical precipitation stage (HDCP + UF) so that the MF stage might be omitted from the pre-treatment process train.

6.1.1.3. CP Followed by Membrane Separation

6.1.1.3.1. LDCP Followed by MF

The PDW Mixture 1 precipitated with the low dose (50 mg/L) of alum was subjected to dead-end MF where the filter media had a pore size of 1 μm (Whatman GF/B). The cumulative filtration rate was observed to increase from 0.18 L/h to 0.27 L/h by the application of LDCP before MF (1 μm) (Table 6.2). However, 56% of increase in the filtration rate was not sufficient as the filter media was clogged again rapidly. This result indicated that the pollutants were removed only partially and the sizes of the remaining molecules were bigger than the pore size of the filter media so that they still caused rapid clogging.

The performances of individual and sequential processes are given in Table 6.3. As seen, the performance of MF alone was much better than the LDCP, which had COD, color and turbidity removal efficiencies of 15%, 86% and 80%, respectively. LDCP alone had a poor performance, i.e., 28% and 14% removals of color and turbidity were achieved. These results indicated the removal of only a small fraction of the pollutants by 50 mg/L of alum. The performance of MF was slightly improved by the preceding LDCP, i.e., the removal efficiencies for COD, color and turbidity increased from 15% to 29%, from 86% to 91% and from 80% to 86%, respectively. Therefore, it was concluded that implementation of the LDCP stage before MF process was not beneficial in terms of increasing both the filtration rate and the removal performance. As the third alternative, a high dose of alum was used in the CP stage, which was followed by UF.

Table 6.2. Effect of Low Alum Dose on MF Rate for PDW

Process	**Filtration rate (L/h)***
MF (1 μm)	0.18
LDCP (50 mg/L) + MF (1 μm)	0.27

* total volume collected in 30 min divided by the filtration time

Table 6.3. Comparison of LDCP and MF Performances for PDW

Process	**Removal (%)**			
	COD	**UVA$_{194}$**	**Color**	**Turbidity**
MF (1 μm)	15	14	86	80
LDCP (50 mg/L)	-	1	28	14
LDCP + MF (overall)	29	15	91	86

Initial COD=423 mg/L, Initial UVA=3.1

6.1.1.3.2. HDCP Followed by UF

CP with 400 mg/L alum followed by UF was applied as another alternative pre-treatment process train. The UF experiment was conducted under an average TMP of 2.5 bar in total recycle mode of filtration with a UF membrane having a MWCO of 50 000 Da (Osmonics HZ 15). After being precipitated by 400 mg/L of alum, the PDW was fed to the UF module. The performances of these processes are compared in Table 6.4. As seen, HDCP achieved 15% COD, 16% UVA, 84% color and 82% turbidity removal efficiency. It was observed that the following UF process increased the removal efficiencies obtained by HDCP alone, however the extent of these increases was not significant. The overall removal efficiencies achieved by the combined process train was 39% and 18% for COD and UVA, respectively, and 99% for color and turbidity. Furthermore, the overall performances of LDCP + MF and HDCP + UF were observed to be very similar to each other, making the latter alternative useless in terms of removal performances.

Table 6.4. Comparison of HDCP and UF Performances for PDW

Process	**Removal (%)**			
	COD	**UVA_{194}**	**Color**	**Turbidity**
HDCP (400 mg/L)	15	16	84	82
UF (50000 Da)	28	3	97	93
HDCP + UF (Overall)	39	18	99	99

Initial COD=423 mg/L, Initial UVA=3.1

The HDCP + UF alternative was also evaluated for permeate flux. In the UF experiment, which lasted for 5 h, the PDW flux reached steady state in a period of 1 h (Figure 6.2). The wastewater flux decline with respect to the clean water flux

(J_{cw}) was 10% initially, and increased to 28% at the end of a filtration period of 1 h, after which it remained constant. However, a new steady state condition was reached after 2.5 h of filtration, and the flux decline decreased to 22%, which might have happened due to the swelling of the membrane. This level of flux decline did not indicate a very severe fouling, which might be due to the low rejection of organic matter (28%). Since the UF feed was precipitated with an alum dose as high as 400 mg/L, the small alum flocs that had not settled completely in 1 h sedimentation period were probably carried up to the membrane surface and thereby contributed to the flux decline of 22%.

HDCP+UF alternative was omitted since UF did not markedly contribute to the performance of HDCP, and also the overall removal performance of HDCP+UF was not significantly better than that of LDCP+MF. Therefore, LDCP+MF alternative with some modifications was reconsidered. As it had already been realized that the low dose of 50 mg/L was not sufficient to avoid the clogging of MF, a new alum dose higher than 50 mg/L but still lower than the optimum dose was needed. Changing the pore size of MF was thought to be another option. The modifications of the LDCP+MF are discussed in Section 6.1.1.3.3.

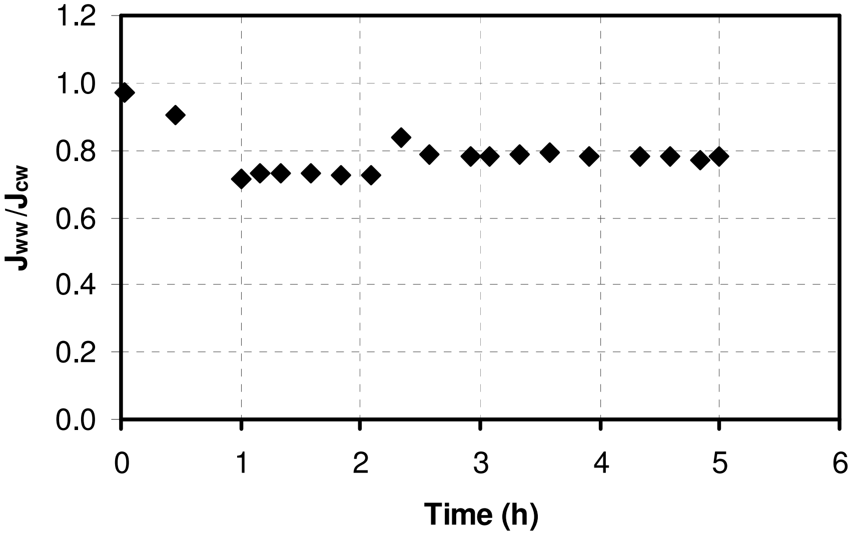


Figure 6.2. Change of Relative Flux in HDCP (400 mg/L) + UF

6.1.1.3.3. Optimization of Alum Dose and MF Pore Size

In order to increase the efficiency of the LDCP + MF process, the low alum dose and MF pore size were decided to be modified. First, the low alum dose of 50 mg/L, which was insufficient to significantly increase the filtration rate of MF media, was increased to 100-150 mg/L in the CP stage. Second, the MF pore size was changed from 1 μm to 2.5 μm for the same purpose. In this way, the combination of the sufficiently low alum dose and the best MF pore size were tried to be found to increase the filtration rate.

As seen from Tables 6.5 and 6.6, 2.5 μm MF performed worse than 1 μm MF in terms of filtration rate but better in terms of removal efficiencies, which is just the opposite of what was expected. This was thought to be due to the different structures of the filters used; Whatman GF/B (1 μm) filter was made of glass fiber and had higher thickness, which probably provided much higher pore volume and hence faster filtration. Whatman 42 (2.5 μm) filter was made of cellulose and provided slower filtration. The filtration rate was only one-third of that of the Whatman GF/B (1 μm) filter in the same filtration time period, which was 30 min.

Table 6.5. Effect of Alum Dose on MF Rates

Process	Filtration rate* (L/h)	Increase (%) wrt MF (1.0 μm)
MF (1 μm)	0.09	
CP (50 mg/L) + MF (1 μm)	0.17	89
CP (50 mg/L) + MF (2.5 μm)	0.06	none
CP (100 mg/L) + MF (1 μm)	0.20	122
CP (150 mg/L) + MF (1 μm)**	0.46	411
CP (150 mg/L) + MF (1 μm)**	28.7	31789

* Total volume collected in 30 min dead-end filtration divided by filtration time

** Results of duplicate run

Table 6.6. Performances of CP and MF Combinations

Process	**Removal (%) (wrt raw water quality)**		**Removal (%) (wrt preceding process)**	
	Color	**Turbidity**	**Color**	**Turbidity**
MF (1 μm)	89	84		
CP (50 mg/L)	28	15		
CP (50 mg/L) + MF (1 μm)	90	86	86	83
CP (50 mg/L) + MF (2.5 μm)	97	95	95	94
CP (100 mg/L)	32	17		
CP (100 mg/L) + MF (1 μm)	94	90	91	88
CP (150 mg/L)	35	9		
CP (150 mg/L) + MF (1 μm)	96	93	94	93
CP (150 mg/L)*	95	94		
CP (150 mg/L) + MF (1 μm)*	99	98	78	58

* The jar in which the time of alum addition is very close to the time of start of mixer

Increasing the alum dose from 50 mg/L to 100 mg/L did not affect the filtration rate markedly, i.e., it increased from 0.17 L/h to 0.20 L/h. In case of 150 mg/L alum dose, two very different results were obtained in two adjacent jars. Although all the conditions in these two jars were exactly the same; i.e., the alum dose, the wastewater volume, temperature, mixing speeds and durations, there was a very significant difference between the filtration rates of the wastewaters precipitated in these two jars, the second one being 62 times higher than the first one (Table 6.6). A series of jar-test experiments were conducted with alum doses of 50-150 mg/L to figure out the reason for this surprising outcome and the results given in Appendix E were obtained. It was realized that much higher alum doses were required for achieving a given removal efficiency unless initial mixing is provided in the jars before alum addition. The removal efficiencies increased from 35% to 95% for color, and from 9% to 94% for turbidity when initial mixing was provided before alum addition. After experiencing this very important fact about the working conditions of the jar-test apparatus for PDWs, further experiments were always carried out in a way that alum was added to all the jars at the same time while the wastewaters were already being mixed in the jars.

The optimum alum dose experiment was repeated since the experimental conditions were observed not to be the same for all the jars in the first experiment in which alum dose of 50-800 mg/L had been applied. Since 150 mg/L of alum resulted in very high removal efficiencies after correcting the operation conditions for the jar-test apparatus (95% for color and 94% for turbidity), the optimum dose was sought in a more narrow range of alum doses. The results are given in Table 6.7 and the corrected removal performances are depicted in Figure 6.3. These new results reveal that the optimum alum dose is 150 mg/L, but not 400 mg/L.

Table 6.7. Corrected Alum Performance for Optimum Dose (Under Initial Mixing Condition)

Alum dose (mg/L)	**Removal (%)**	
	Color	**Turbidity**
50	28	15
75	42	20
100	70	60
150	95	94
200	97	94

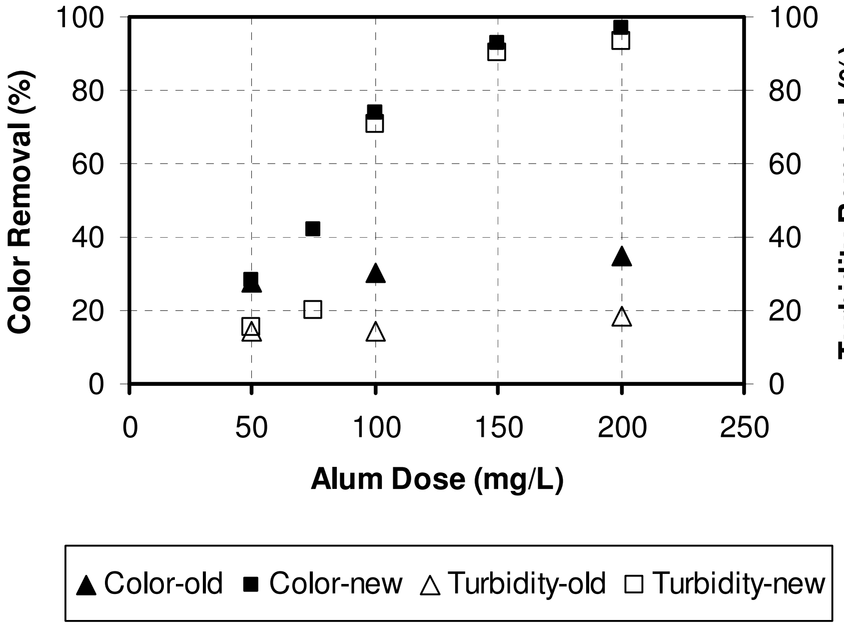


Figure 6.3. Optimum Alum Dose Efficiencies for Delayed and Initial Mixing

Since the presence of initial mixing was realized to be a very important factor influencing the determination of the optimum dose correctly, the intensity of mixing was also considered here to make sure that the mixing intensities applied in the jar test also provided the correct conditions for the precipitation of PDWs. The rapid mixing and slow mixing intensities were decreased from 100 rpm to 30 rpm, and from 30 rpm to 10 rpm, respectively. Table 6.8 shows the comparison of the results obtained for an alum dose of 100 mg/L. In the case of decreased mixing intensity, the flocs were much bigger in size and the removal efficiencies of color and turbidity were much lower. Moreover, the performances observed in two identical jars were significantly different when the mixing intensity was reduced. Therefore, the application of the conventional mixing intensities for rapid and slow mixing as “100 rpm for 1 min” and “30 rpm for 30 min” was found out to be appropriate.

Table 6.8. Effect of Mixing Intensity on CP Performance

Mixing Intensity (rpm)		Removal (%)	
Rapid	**Slow**	**Color**	**Turbidity**
100	30	75	74
		76	74
30	10	50	39
		25	12

Although very good removal efficiencies were achieved by the alum dose of 150 mg/L, the effect of a coagulant aid was also investigated as another operational parameter in order to see whether the settling characteristics could be improved and the optimum alum dose could be further reduced. The results of this part of the pre-treatment study are given in the following section.

6.1.1.4. CP With Polyelectrolyte Aid

The effect of a non-ionic polyelectrolyte (Stockhausen-Praestol 2500) on the CP performance was investigated in order to see whether the alum dose of 150 mg/L could be further reduced by the aid of the polyelectrolyte. Hence some additional sets of experiments were conducted with 50, 75 and 100 mg/L of alum (Table 6.9). The experiments with each dose of alum were conducted in duplicate runs in order to ensure reproducible results. As seen from Table 6.9, the polyelectrolyte had a slight improvement in the alum performance at a concentration of 0.2 mg/L. Increasing the polyelectrolyte concentration to 1 mg/L was observed to have an adverse effect on the removal efficiency of the alum, however the extent of it was not very significant. It was suggested that the reason for the polyelectrolyte not to be effective might be due to the complex nature of the PDW containing two different types of surfactants (anionic and non-ionic). Hence, the use of a coagulant aid was also omitted from the alternatives.

Table 6.9. Effect of Polyelectrolyte on CP Performance

Process	**Run no.**	**Removal (%)**		**pH**
		Color	**Turbidity**	
A 50	1	28	15	7.46
A 50 + P 0.2	1	16	12	7.16
	2	14	7	7.07
A 75	1	43	22	7.17
	2	40	17	7.19
A 75 + P 0.2	1	47	36	6.97
	2	42	29	7.02
A 75 + P 1	1	38	24	6.99
	2	33	24	7.15
A 100	1	72	61	6.95
	2	67	58	7.01
A 100 + P 0.2	1	70	61	7.02
	2	68	61	6.92
A 100 + P 1	1	69	59	6.88
	2	66	55	6.86

A: Alum, P 0.2: 0.2 mg/L polyelectrolyte, P 1: 1 mg/L polyelectrolyte

6.1.1.5. Summary of Pre-treatment Process Train Selection

After the evaluation of all the pre-treatment alternatives, CP with optimum alum dose was decided to be the most suitable process for PDWs since it allowed the removal of color and turbidity with the highest efficiencies in a single stage. Therefore, all the PDW mixtures were subjected to CP to make them ready for the membrane separation experiments. Since the characteristics of the three PDW mixtures were different from each other, optimum alum dose determination was performed for each mixture separately, and the whole wastewater sample to be used in membrane filtration tests was pre-treated by that dose of alum. Table 6.10 shows the optimum alum doses determined for the PDW Mixtures 2 and 3. As seen, the optimum alum dose, which had been determined as 150 mg/L for Mixture 1, was found out to be 250 mg/L for Mixtures 2 and 3. This was quite expected since the characteristics of PDW mixtures differed markedly. The performance of CP for PDW mixtures are given in Table 6.11, which show the overall removal efficiencies for high volumes of wastewaters (80-150 L) precipitated in the jar test apparatus in several stages.

Table 6.10. Optimum Alum Doses for PDW Mixtures 2 and 3

Alum dose (mg/L)	**Removal (%)**			
	Mixture 2		**Mixture 3**	
	Color	**Turbidity**	**Color**	**Turbidity**
50	10	5	0	0
100	12	3	5	0
150	24	12	26	8
250	90	93	93	95
400	96	96	97	98
600	96	95	97	97

Table 6.11. The Characteristics of Chemically Precipitated PDWs

Parameter	Precipitated Effluent Quality			Removal (%)		
	Mix 1	**Mix 2**	**Mix 3**	**Mix 1**	**Mix 2**	**Mix 3**
COD (mg/L)	301 ± 15	445 ± 12	423 ± 10	23	47	50
UVA $_{200}$	2.4 ± 0	2.8 ± 0	2.7 ± 0	22	27	27
Color (Pt-Co)	29 ± 1	44 ± 0	73 ± 2	91	92	90
Turbidity (NTU)	3.8 ± 0	3.4 ± 0.1	7.1 ± 0.1	91	94	90
T. Solids (mg/L)	575	683 ± 16	595 ± 7	5	4	8
T. Hardness (mg/L)	18 ± 0	10.5 ± 0	33 ± 0.1	9	19	0
Conductivity (µS/cm)	700 ± 0	864	793	0		
pH	6.80 ± 0	7.28 ± 0	6.80 ± 0			

Finally, the most efficient pre-treatment process for the carpet printing effuents came out to be chemical precipitation (CP). The complex characteristics of the print dyeing wastewaters did not allow direct application of dead-end MF, since the filter media were clogged rapidly. Therefore, it is suggested that dead-end MF cannot be the first step in the process train for the recovery of carpet printing wastewaters. The performance of MF was tried to be improved with CP at a low dose of alum, however the improvement was not significant due to the partial removal of pollutants with inadequate alum dose. As a consequence, the increase in the microfiltration rate was not sufficient. High dose of alum achieved high removal efficiencies, and the following UF stage did not contribute remarkably to the overall performance. Moreover, the removal performance of HDCP + UF was not significantly better than that of LDCP + MF. Since the combined processes were eliminated among the pre-treatment alternatives, the developed process train consisted of a single unit, i.e., chemical precipitation with alum. This is the most advantageous outcome since the least number of unit operations and processes would make the developed process train more attractive.

6.1.2. Treatment of PDWs

UF and NF were tested for the treatment of print dyeing wastewaters in order to produce permeates having qualities suitable for reuse in the carpet dyeing process. The experiments were conducted in total recycle mode of filtration (TRMF) first in order to evaluate the separation performances of the membranes. In TRMF tests, the volume reduction factor (VRF) was 1, which means that there is no water recovery, and the system reaches steady state in terms of flux decline and separation performance. Single NF was tested against single UF, where tight and loose UF membranes with MWCO ranging from 1000 Da to 50000 Da were used. In order to achieve water recovery, the VRF was increased in concentration mode of filtration (CMF) tests and the effect of water recovery on the separation performance and flux declines were monitored. The permeate qualities were compared to the reuse criteria given by the British Textile Technology Group (BTTG) and also the actual process water quality. The treatment alternatives are listed below:

1. Single NF,
2. Single UF (MWCO of 1000 Da, 2000 Da, 20000 Da, and 50000 Da),
3. Loose UF (20000 Da) followed by NF,
4. Tight UF (1000 Da) followed by NF.

6.1.2.1. TRMF Tests by Single NF and Single UF

The PDW Mixture 1, which had been chemically precipitated with 150 mg/L of alum was subjected to NF and UF in TRMF tests. For this, one NF membrane and four UF membranes with MWCO values of 1000, 2000, 20000, and 50000 Da, with specifications given in Table 5.5, were used. The performances of the membranes were monitored via; a) flux and b) UVA measurements of the samples taken from the permeate and the feed streams. Figure 6.4 depicts the normalized UVA values for all the membranes. As seen, the highest removals were observed for NF, being very close to 100%. On the other hand, UVA/UVA$_o$ varied between 0.8 to 1.0 for all the UF membranes, indicating very low or no removal. Being used as a surrogate for the organic matter content of the wastewater, this low level of UVA removal was also observed to be parallel to the COD removal efficiencies.

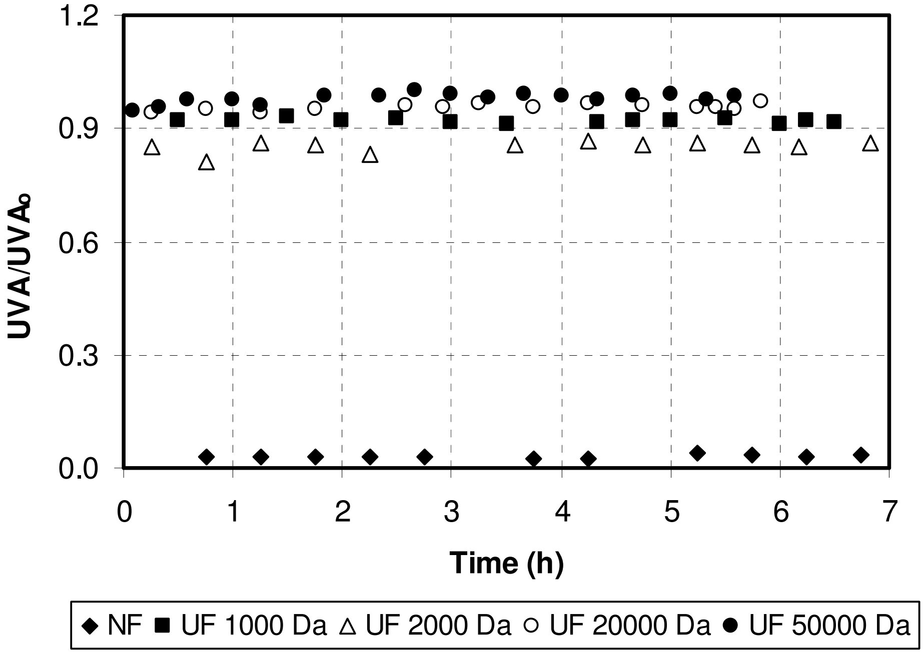


Figure 6.4. UVA Removal in Single NF and Single UF for PDW

The removal performances of the membranes are compared in Figures 6.5 and 6.6. As seen, the best performance was achieved by the NFT-50 membrane with almost complete retention of COD, complete removal of color and >90% removal of turbidity and total solids. All the UF permeates were similarly almost free of color and turbidity, however the retention of COD and total solids were quite low, i.e., the highest retentions were 25% and 37%, respectively (Figure 6.5). These low retentions were expected since the organic rejection of UF membranes is never complete, for which a wide range of 21-77% is reported (Erswell et al., 1988). The COD retention efficiency decreased from 25% to 8-11% with increasing MWCO of the UF membranes tested. All these results suggested that the organic matter present in the wastewater was mainly composed of small molecules such as the acid dyes, which permeated through the UF membranes.

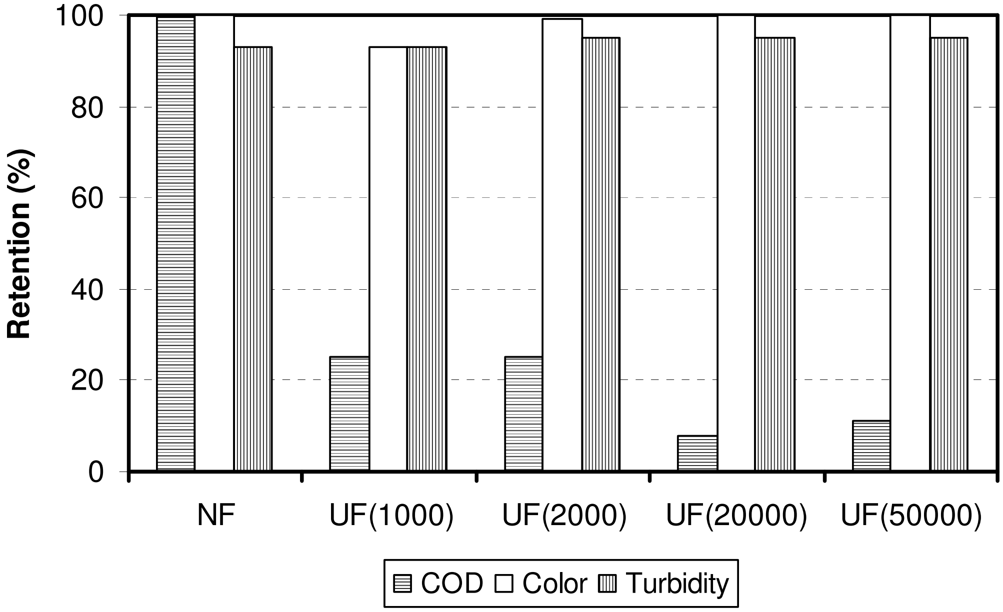


Figure 6.5. COD, Color and Turbidity Retentions in Single NF and Single UF

As total hardness causing cations have small atomic sizes, they were only partially retained by the NF membrane (Figure 6.6). The mechanism of retention of ions by the NF membranes is described by the electrostatic interactions between these ions and the surface charge of the membrane (Mulder, 1996; Scott, 1996). The surface of the NF membranes are generally negatively charged at neutral pH, and therefore they can attract cations (like Ca^{2+}), and avoid their passage to the permeate side (Chellam and Taylor, 2001). On the other hand, the UF membranes, having MWCO values much greater than the sizes of these ions, rejected hardness causing ions up to 10% only. Similarly, the highest conductivity retention was 37% by the UF (1000 Da) membrane (Figure 6.6).

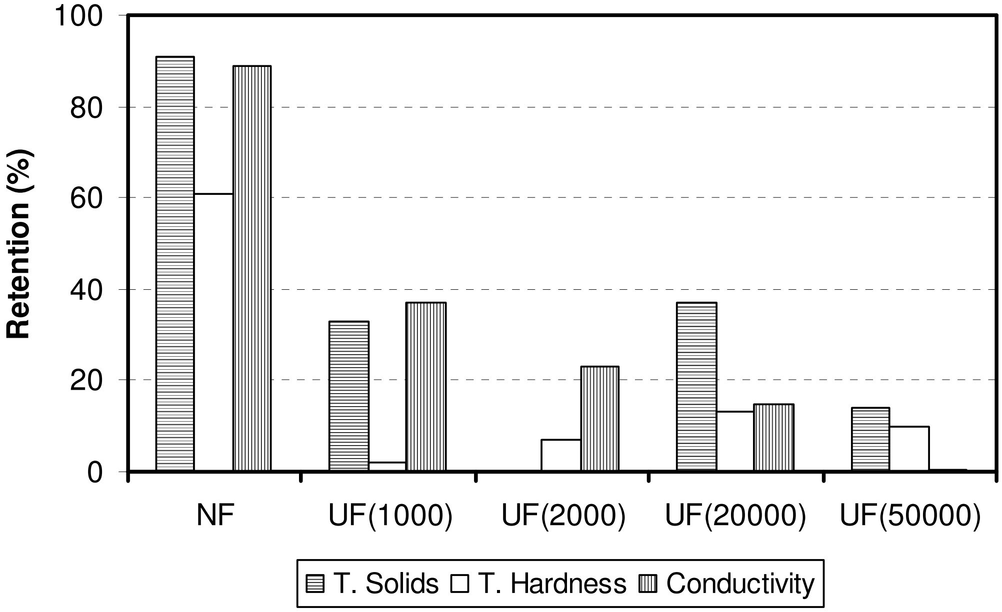


Figure 6.6. T. Solids, T. Hardness and Conductivity Retentions in Single NF and Single UF (The permeate total solids was not measured for UF (2000 Da), conductivity retention for UF (50000 Da) was 0.4%)

The flux declines monitored in NF and UF are shown in Figure 6.7. The flux decline levels were determined by dividing the steady state wastewater fluxes by the initial clean water fluxes of each membrane. As seen from Figure 6.7, the flux declines varied from 11 to 35% within a time period of 6 h. The NF membrane had a steady state flux decline of 19%, which did not indicate very severe fouling. For UF membranes, the lowest flux decline was 11%, which occured with the loosest UF (50000 Da) membrane. Having the lowest retentions, the pore size of this UF membrane seemed to be bigger than the sizes of the molecules in the wastewater. The highest flux decline was 35% with UF (2000 Da) and UF (20000

Da) membranes, which was higher than the flux decline of 19% observed for NF membrane. The reason for this was most likely pore blocking in UF membranes, in addition to the gel formation on the membrane surface, which resulted in the occurence of higher flux declines.

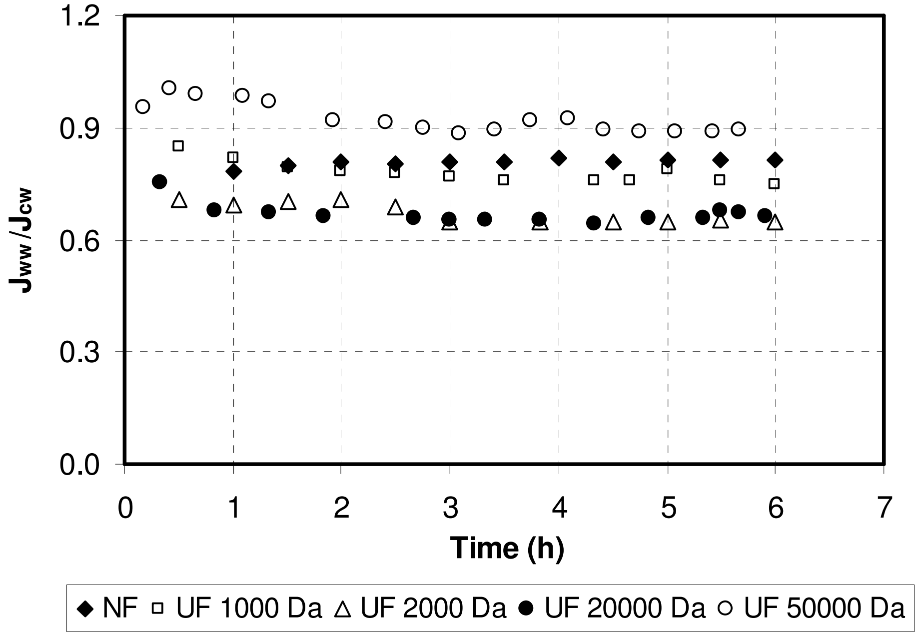


Figure 6.7. Relative Flux Declines in Single NF and Single UF

In a filtration period of 6 h, all the permeate fluxes reached steady state within 1-3 h. The time to reach steady state was 1.5 h for NFT-50 and UF (1000 Da), 1 h for UF (20000 Da), 2 h for UF (50000 Da) and 3h for UF (2000 Da). The occurence of the steady state permeate fluxes indicated that the build-up of the boundary layer close to the membrane surface leading to concentration polarization, reached steady state, after which the permeate flux remained constant.

In order to find the fraction of the total flux decline caused by concentration polarization, the clean water fluxes measured with the fouled membranes were divided by the steady state wastewater fluxes (Table 6.12). For ease of comparison, the fluxes were expressed in terms of permeances, which were obtained by dividing the flux values by TMP. The fractions of the flux decline for the loosest UF (50000 Da) membrane could not be calculated since the final clean water flux was observed to be higher than the initial one. The reason for this was probably irreversible swelling of the UF (50000 Da) membrane when it was exposed to the wastewater, which resulted in opening of the pores and hence increased final clean water flux. Another possible reason is that all the membranes except UF (50000 Da) were subjected to chemical cleaning when they were virgin before measuring their initial clean water fluxes. Since UF (50000 Da) was not cleaned initially, any possible effect of swelling became apparent during the filtration experiment for this membrane.

Table 6.12. Membranes Permeances and Flux Declines

Membrane	**Permeance (Flux/TMP) ($L/m^2.h.bar$)**			**Flux decline (%)**		
	Clean Water		**Wastewater**			
	Initial (I)	**Final (F)**	**(W)**	**Total (I-W)**	**Conc. Pol. (F-W)**	**Fouling (I-F)**
NF	1.80	1.74	1.45	19.4	16.7	2.9
UF (1000 Da)	17.59	16.40	13.15	25.2	19.8	6.7
UF (2000 Da)	2.36	2.04	1.53	35.2	25.0	13.6
UF (20000 Da)	54.43	47.06	35.14	35.4	25.3	13.5
UF (50000 Da)	52.44	57.93	46.48	11.4	*	*

* Could not be calculated since the final clean water flux was higher than the initial one.

As seen from Table 6.12, concentration polarization, which leads to a reversible flux decline is responsible for greater fraction of the total flux declines for all the membranes. Concentration polarization causes a reduction in water flux due to the increased osmotic pressure and/or increased solute concentration in the feed side. This effect is known to diminish by the release of the pressure applied across the membrane. If the concentration of soluble species in the boundary layer exceeds their solubility limits, precipitation or scaling will occur, which leads to fouling of the membrane (Madaeni and Mansourpanah, 2003). As seen from Table 6.12, the extent of fouling ranged from 3% to 14%, which was lowest for NF membrane and increased as the MWCO of UF membranes increased. This is expected since the foulants have a greater chance to accumulate within the pores in addition to the surface as the membrane gets looser, which would result in increased fouling.

In order to evaluate the suitability of the treated wastewater for the reuse purposes, the permeate qualities were compared to the reuse criteria set by the British Textile Technology Group (BTTG) and also the actual process water quality (Table 6.13). As seen, all the permeates met the BTTG reuse criteria. However, the turbidity content of all the permeates were slightly worse than that of the actual process water, and the UF permeates did not meet the actual process water quality in terms of total hardness. The total solids content of the UF permeates were also quite high as compared to the NF permeate, and the total solids content of the UF (50000 Da) permeate exceeded the actual process water quality.

The TRMF tests that were conducted under the conditions of constant volume and quality of the feed wastewater have revealed good results in terms of permeate qualities. In fact, to obtain more realistic results it is necessary to conduct the membrane tests under the conditions of decreasing volume and worsening quality of the feed wastewater, i.e., VRF must be higher than 1, which requires that the permeate is not returned to the feed tank but collected in a separate container, which is known to be “concentration mode of filtration”. The next section describes the results of the concentration mode of filtration (CMF) tests with PDW.

Table 6.13. Evaluation of Single NF and Single UF Permeate Qualities

Evaluation Reference /Applied Process	**Reuse Criteria/Permeate Quality**			
	Color (Pt-Co)*	**Turbidity (NTU)**	**Dissolved Solids (mg/L)**	**T. Hardness (mg/L)**
BTTG	5	15	500	60
Actual process water	1	0.15	446	11
Permeates				
NF	0 ± 0	0.28 ± 0.1	51 ± 13	9 ± 1
UF (1000 Da)	0 ± 0	0.20 ± 0	385 ± 1	20 ± 0
UF (2000 Da)	2 ± 1	0.27 ± 0		14 ± 0
UF (20000 Da)	0 ± 0	0.18 ± 0	365 ± 18	16 ± 0
UF (50000 Da)	0 ± 0	0.19 ± 0	494 ± 16	17 ± 1

*The unit of color is AU (absorbance units) for BTTG

6.1.2.2. CMF Tests by Single and Sequential UF and NF

The CMF tests were performed to achieve water recovery, and to understand whether the permeate quality would meet the reuse criteria under the condition of worsening feed quality due to increased VRF. Three alternative process trains were applied in this part of the study: 1) Single NF, 2) Loose UF (20000 Da) followed by NF, 3) Tight UF (1000 Da) followed by NF. The sequential uses of UF and NF (alternatives 2 and 3) were performed in order to minimize the flux decline of NF by rejecting larger molecules, which may plug the NF membrane, by the UF membranes applied in the first stage. The wastewater samples used for the first, second and third alternative trains were Mixture 2, 2 and 3, respectively. The VRF achieved by all the alternative processes are given in Table 6.14.

Table 6.14. Volume Reduction Factors (VRF) For Sequential NF and UF

Process	**Stage**	**Feed Volume (L) (V_f)**		**Retentate Volume (L) (V_r)**	**VRF** $\frac{(V_{fi}-V_{fs})}{V_r}$
		Initial (V_{fi})	**Sampled for Analysis (V_{fs})**		
Single NF	NF	40	3.5	3.1	11.8
Loose UF + NF	UF (20000)	40	3.0	1.3	28.5
	NF	27	2.5	1.8	13.6
Tight UF + NF	UF (1000)	40	3.0	4.0	9.3
	NF	24	2.0	3.8	5.8

6.1.2.2.1. Single NF

The first alternative was chosen to be single NF depending on the performances observed during the TRMF experiments. The performance of the membrane NFT-50 was monitored by UVA and flux measurements during the experiments. The feed and the permeate were periodically sampled after passing a few liters of wastewater through the membrane. At each sampling, 500 mL of permeate was collected for the analyses. As seen from Table 6.14, the VRF was 11.8 for single NF, which means that a feed volume of 36.5 L was reduced to 3.1 L. In calculating the VRF, the feed volumes sampled for analysis (V_{fs}) were deducted from the initial feed volumes (V_{fi}).

The change of UVA values and the reduction of feed volume are depicted in Figure 6.8. As seen from the figure, there was a steep increase in the permeate UVA values after 30 h of filtration period. On the other hand, the change of the feed UVA values was not significant throughout the experiment, implying that the

UVA causing compounds in the wastewater were deposited on the membrane rather than going back into the retentate stream and formed a cake on the membrane surface. This gel-like cake formation was also observed visually after the experiment had ended.

The performances of single NF for all the parameters are depicted in Figures 6.9 to 6.14. The change of feed and permeate COD values are depicted in Figure 6.9. Both feed and permeate COD levels increased five-fold from the start to the end of the experiment, where a VRF of 11.8 was achieved. Although the feed COD increased from around 500 mg/L up to 2500 mg/L, the corresponding initial and final permeate COD were only 11 mg/L and 54 mg/L, respectively. The performance of the NFT-50 membrane was perfect in terms of COD removal, with almost complete removal of the organic matter. The COD of the recovered textile effluents reported in literature vary between 10 to 40 mg/L, and this range is stated to be suitable for the dyeing of even the light colors (Table 2.9).

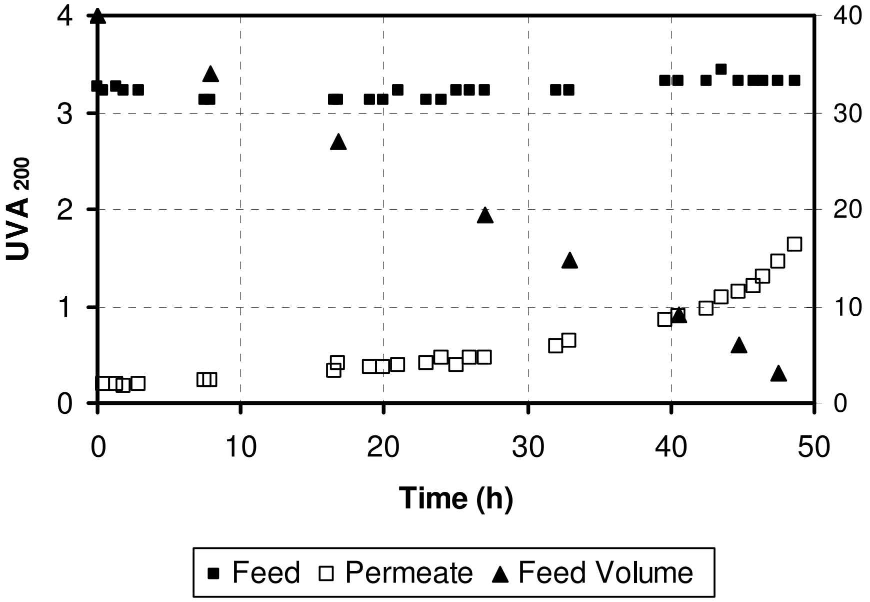


Figure 6.8. Change of UVA and Feed Volume in Single NF

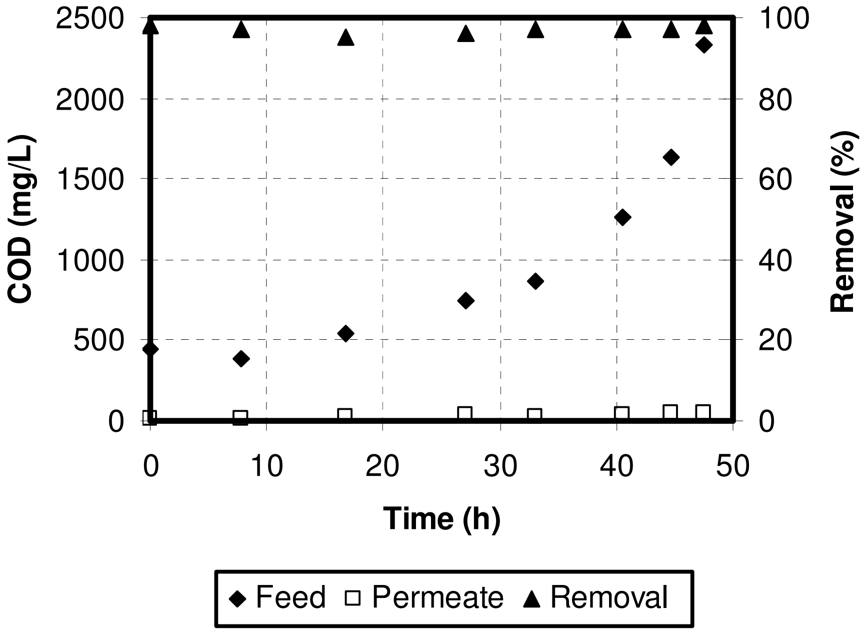


Figure 6.9. COD Removal Performance of Single NF

The color and turbidity changes were interesting in the NF feed as the values of color and turbidity decreased for the first 20-25 L of the wastewater filtered, and then started to increase, ending up with the initial values (Figure 6.10 and 6.11). This behavior was due to the accumulation of color and turbidity causing compounds on the membrane, which lead to the cake formation. However, color and turbidity values in the feed stream started to increase after 30 h of filtration, which seemed to be due to the thickness of the cake layer reaching a maximum level, after which no more increase was possible. On the other hand, the permeate quality was excellent till the end of the experiment, as a colorless permeate with a very low turbidity of 0.25 NTU was produced although the VRF increased up to 11.8, which means that increase in gel layer thickness or increase in feed concentration had no adverse effect on permeate quality. The permeate quality was much better than the BTTG reuse criteria for color and turbidity. The actual process water quality was also satisfied.

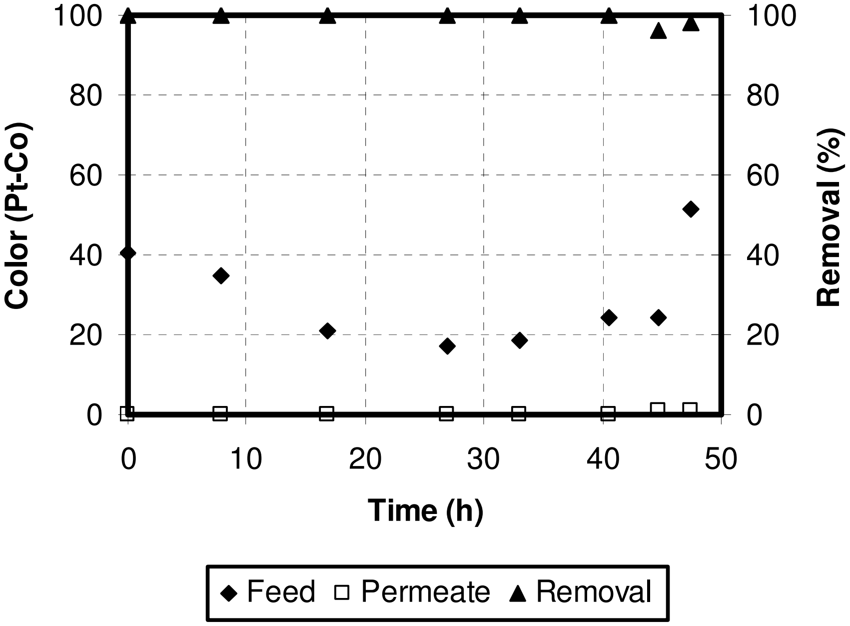


Figure 6.10. Color Removal Performance of Single NF

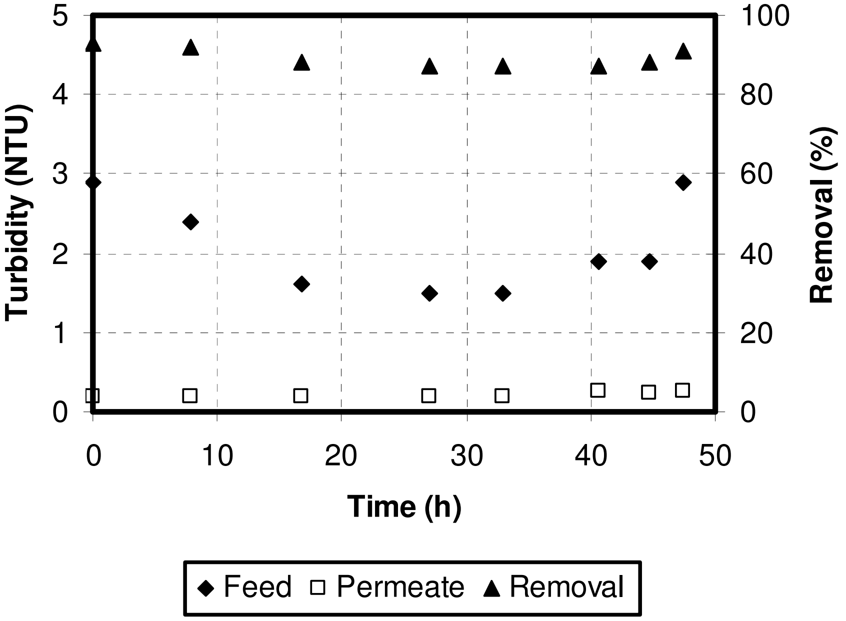


Figure 6.11. Turbidity Removal Performance of Single NF

The removal efficiency of single NF for total solids was also high, with a value of greater than 90% throughout the experiment (Figure 6.12). As in the case of other parameters, the permeate quality remained relatively constant despite the worsening feed quality. Although the solids content of the feed exceeded 3000 mg/L, the permeate solids content was only 256 mg/L at a VRF of 11.8, which is well below the BTTG reuse criteria of 500 mg/L.

Hardness causing ions are not desired in the process waters since they adversely affect the dyeing process and may cause non-uniform color and spots on the surface of the carpet. Although the total hardness content of the raw wastewater was already low due to the softening of the process water at the plant, the performance of NF was investigated under increasing total hardness content of the feed for determining whether the permeate content would exceed the limits or not. The total hardness of the feed was 10 mg/L (as $CaCO_3$) and increased to 55 mg/L at the end of the experiment. On the other hand, the permeate hardness was zero (Figure 6.13), which indicated perfect rejection of the hardness causing ions by the NFT-50 membrane. The criteria for reuse is highly variable for this parameter. The values reported in literature range from 1.4 mg/L to 300 mg/L (Table 2.9). The BTTG reuse criteria is 60 mg/L while the actual process water used in the plant had a hardness of 11 mg/L. The NF permeate, with zero hardness, is therefore very suitable for reuse.

Figure 6.14 depicts the removal efficiency for conductivity, which was as high as 90%, resulting in a conductivity value of 500 μS/cm in the permeate stream. No reuse criteria was set for conductivity by BTTG, however the permeate qualities are in good agreement with literature values of 35-2050 μS/cm (Table 2.9).

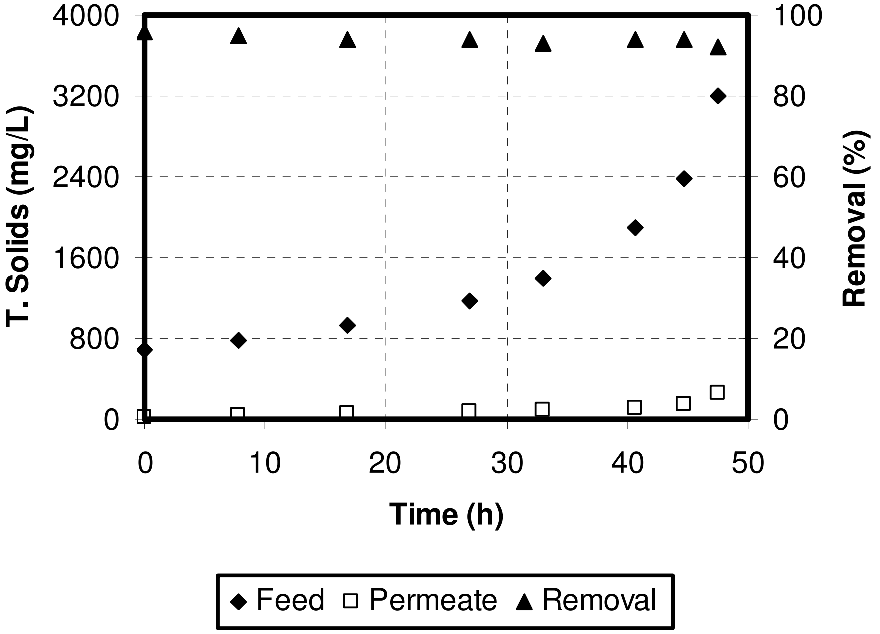


Figure 6.12. Total Solids Removal Performance of Single NF

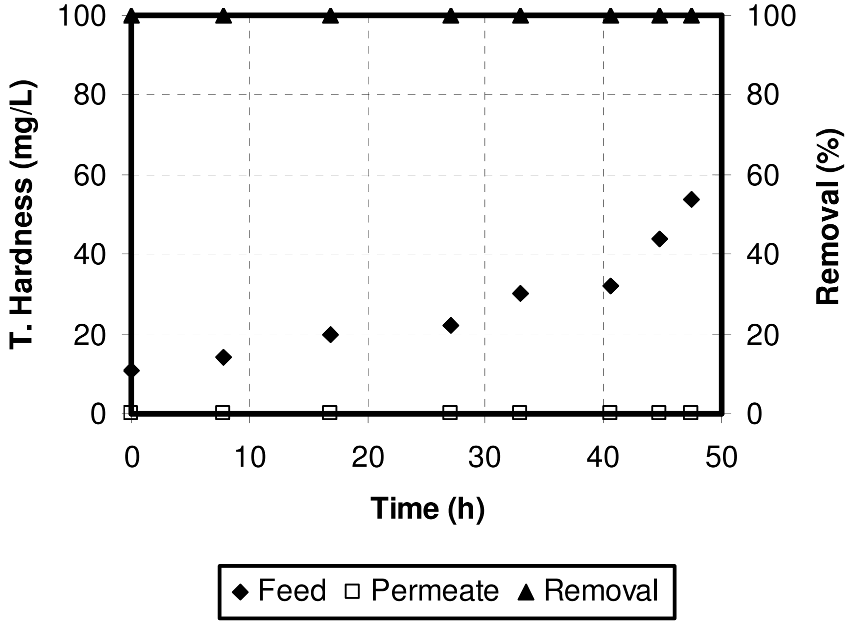


Figure 6.13. Total Hardness Removal Performance of Single NF

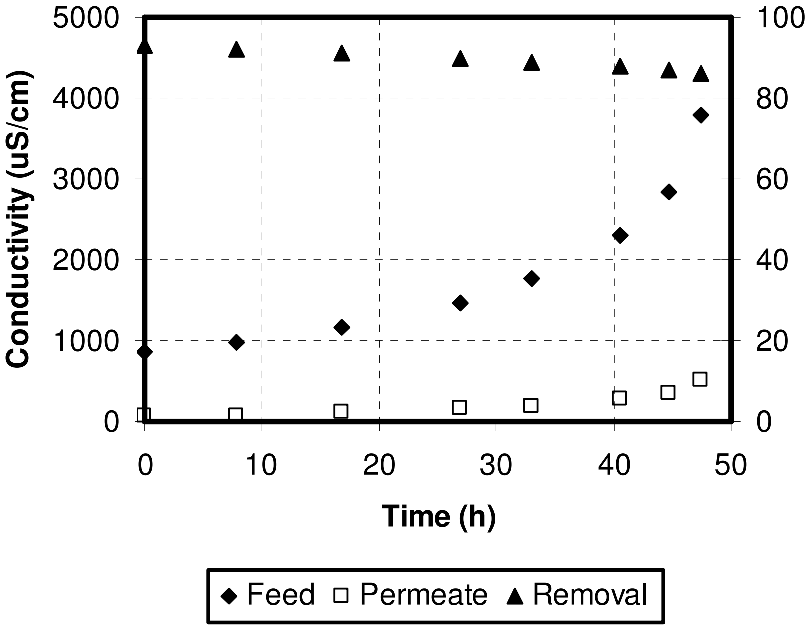


Figure 6.14. Conductivity Removal Performance of Single NF

The change of pH was also monitored during the CMF tests (Figure 6.15). The pH of the PDW, being originally neutral, gradually increased from 7.36 to 8.01 in the feed stream. The permeate pH was initially 6.92 and it increased up to 8.33 at the end of the experiment. Therefore, both feed and permeate pH had a trend to increase towards basic side. The change of pH during filtration is related to the increased or decreased concentrations of H^+ ions in the feed and the permeate streams. Since the NF membranes have generally charged surfaces, their interactions with the ions present in the fluids play an important role in their rejection performances. The reason for the change of pH observed with NFT-50 membrane can be speculatively explained. Since the surface of the NFT-50 membrane is probably negatively charged at neutral pH, they must attract the H^+ ions. The permeate pH was initially lower than the feed, which means that H^+ ions can pass easily to the permeate side, resulting in lower pH. This is logical since H^+ ions are very small as compared to the membrane pores. Meanwhile, the feed pH increased with time, which indicated a decrease of H^+ ions in the feed side. The feed and the permeate pH became equal after 30 h due to the continuous increase of permeate pH, indicating that the passage of H^+ ions to the permeate side had stopped. The H^+ ions might be trapped on the membrane surface due to cake formation. Since then, the H^+ ions might be accumulating on the membrane surface, leading to decreased H^+ ion concentrations in the feed and the permeate, which results in the increase of pH towards basic side in both streams.

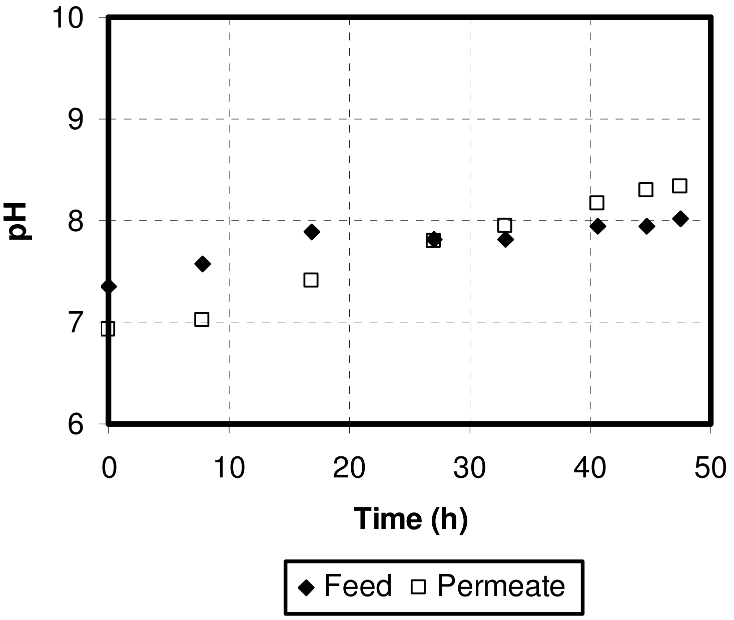


Figure 6.15. The Change of pH in Single NF

The wastewater fluxes (J_{ww}) were monitored during the CMF test and the relative flux decline was determined by dividing the J_{ww} values by the clean water fluxes (J_{cw}) as depicted in Figure 6.16. The permeate flux decline started with 16% and remained constant during the first 30 h. After this time, the flux started to decrease, and it reached to 31% at a VRF of 11.8. This result indicated that the filtration might be stopped here for the cleaning of the membrane so that severe fouling is avoided. The clean water flux of the NFT-50 membrane determined initially was 12.50 L/m^{2}h, which was recorded as 12.65 L/m^{2}h with the fouled membrane after the CMF experiment. And it was observed to increase to 14.63 L/m^{2}h after chemical cleaning. This increase might be expected, as the membrane may get more hydrophilic when exposed to chemicals, resulting in more water to be permeated. Another reason for increased flux may be swelling, which is the opening of the pores, due to the adverse effect of chemicals on the surface. The data comparing the effect of cleaning on flux recovery for all the process alternatives are given in Table 6.16, which is presented at the end of the Section 6.1.2.2.3. Accordingly, it was realized that the cleaning procedure was very effective in restoring the initial clean water flux in single NF, which is a very important indication of technical and economical applicability of the membrane processes for the recovery of carpet dyeing wastewaters.

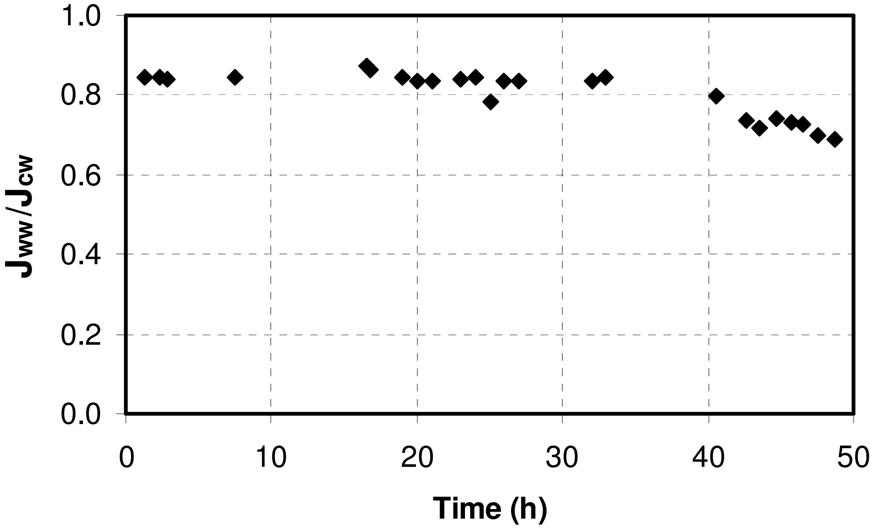


Figure 6.16. Relative Flux Change in Single NF

6.1.2.2.2. Loose UF Followed by NF

A loose UF membrane preceding NF was considered as the first stage in the sequential process train, aiming at minimizing the flux decline of single NF. For this purpose, the UF membrane named GR 61 PP having a high clean water flux and a MWCO of 20000 Da was chosen. A PDW volume of 40 L was filtered through the UF membrane first, and then the permeate was filtered through NFT-50 membrane, yielding a VRF of 28.5 and 13.6, respectively (Table 6.14).

The change of UVA values and the reduction of feed volume are depicted in Figure 6.17. In the UF stage, the feed UVA of 2.76 was rejected at 6% initially and the rejection increased up to 18% at the end. This is an expected result as it had been observed previously with the UF (20000 Da) membrane, showing that the pore size of this membrane is quite big to reject the UVA causing compounds. In the NF stage, the UVA removal was 88% in the beginning, and gradually decreased to 52% in the end. This decrease was due to relatively constant feed UVA, which changed from 2.60 to only 3.03. However, the permeate UVA value increased from 0.32 to 1.46 and the difference between the feed and the permeate UVA indicated an accumulation of UVA causing compounds on the NF surface.

The removal efficiencies achieved by the sequential application of UF and NF are depicted in Figures 6.18 to 6.23. The UF and NF performances were parallel to those observed in the TRMF tests. As seen from Figure 6.18, COD removal was quite low in the UF stage. The permeate COD was 289 mg/L in the beginning of the experiment and increased to 394 mg/L in the end, where 92% wastewater volume reduction was achieved. Since the rejection of COD was not high, the COD content of the feed did not increase significantly in the UF stage. However, the removal of COD was as high as 97% in the NF stage as observed in single NF process.

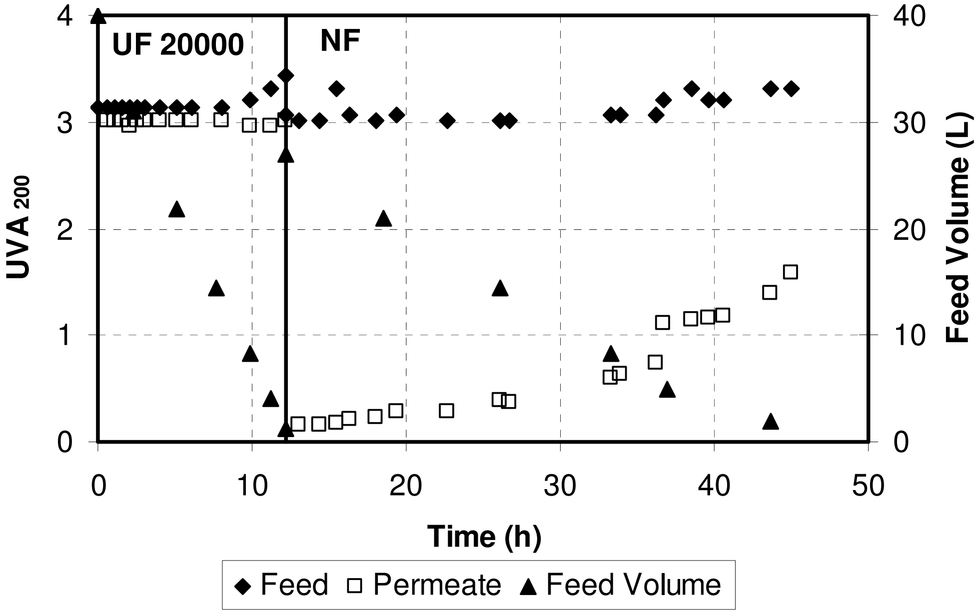


Figure 6.17. Change of UVA and Feed Volume in UF (20000 Da) + NF

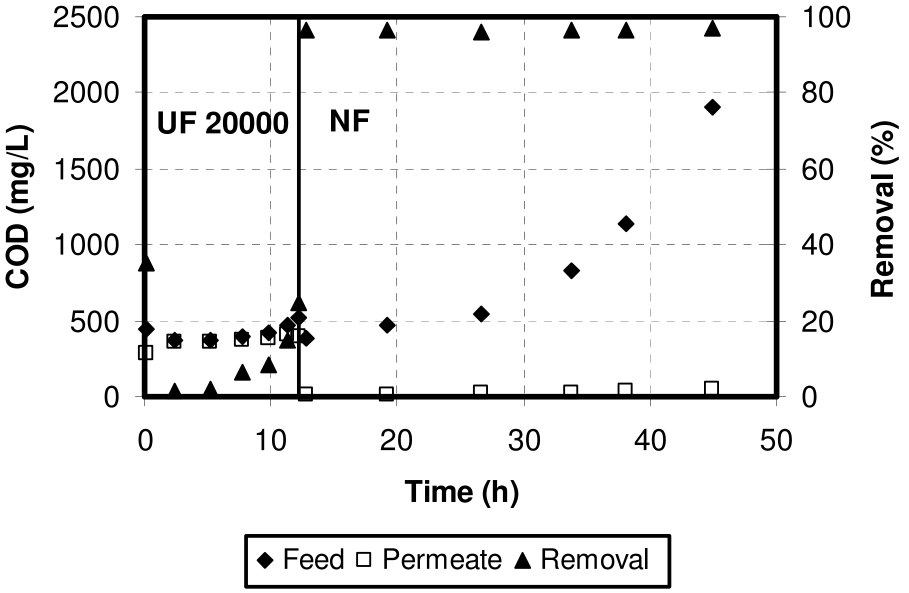


Figure 6.18. COD Removal Performance of UF (20000 Da) + NF

The color and turbidity rejections were perfect with UF membrane, where the permeate quality was identical to that of NF. The UF permeate had at most 4 Pt-Co of color (Figure 6.19) and 0.20 NTU of turbidity (Figure 6.20). Since color and turbidity were almost completely removed by UF, there was nothing left to be removed by the NF membrane connected in series to the UF stage.

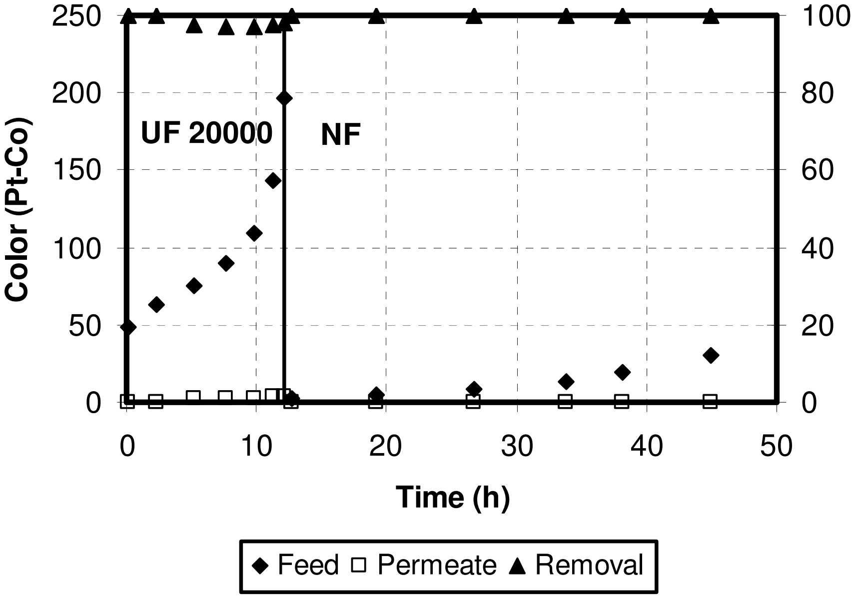


Figure 6.19. Color Removal Performance of UF (20000 Da) + NF

The total solids removal efficiency of the sequential process train was similar to those observed for COD. The highest removal was 41% in the beginning of the UF stage, and it was as high as 96% in the NF stage. (Figure 6.21). Similarly, the removal of total hardness was as low as 20-42% in the UF stage, and a complete removal was observed in the NF stage. Therefore, the final permeate contained no hardness causing ions (Figure 6.22). The removal of conductivity was again low in the UF stage, providing a feed value of 763 µS/cm for the NF stage, where it was further removed and a final permeate quality of 76-389 µS/cm was achieved (Figure 6.23).

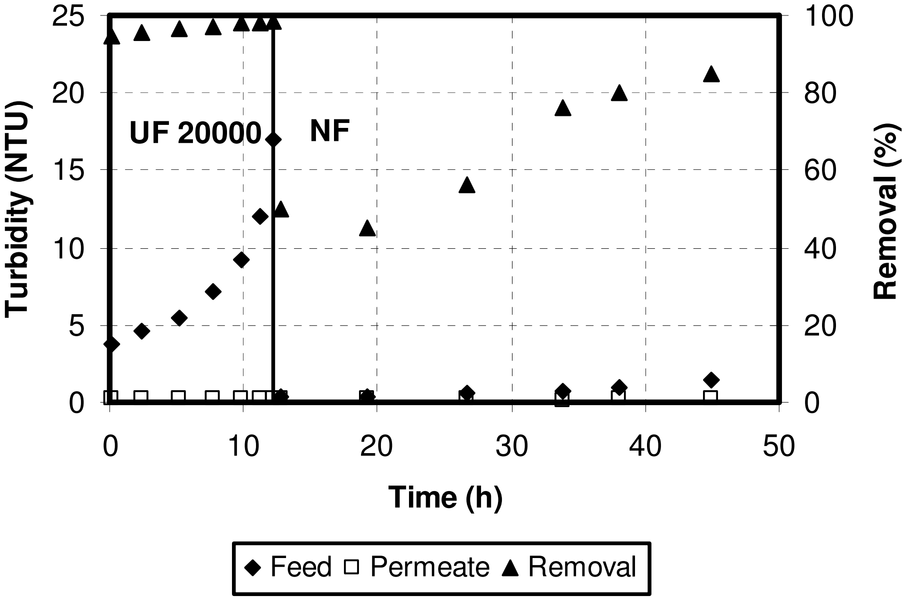


Figure 6.20. Turbidity Removal Performance of UF (20000 Da) + NF

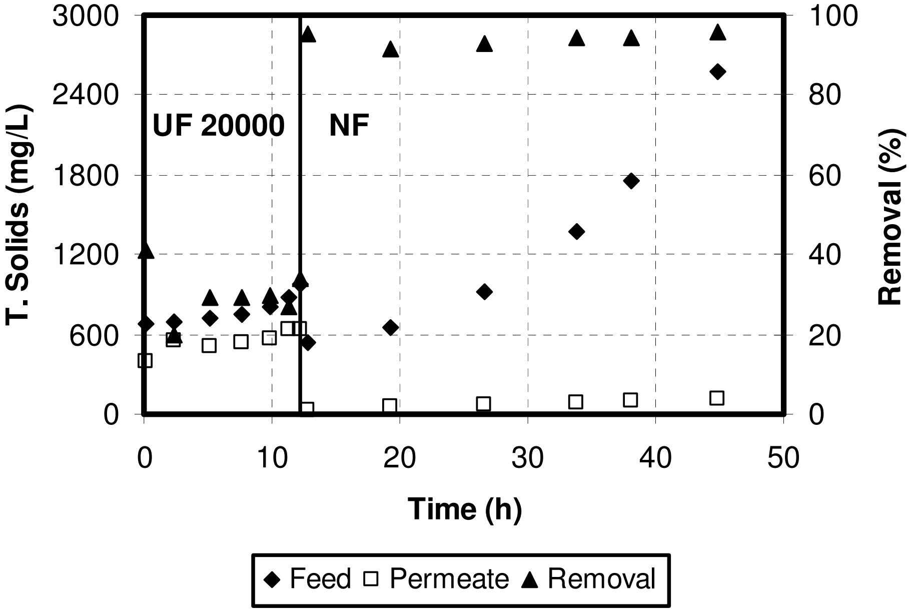


Figure 6.21. T. Solids Removal Performance of UF (20000 Da) + NF

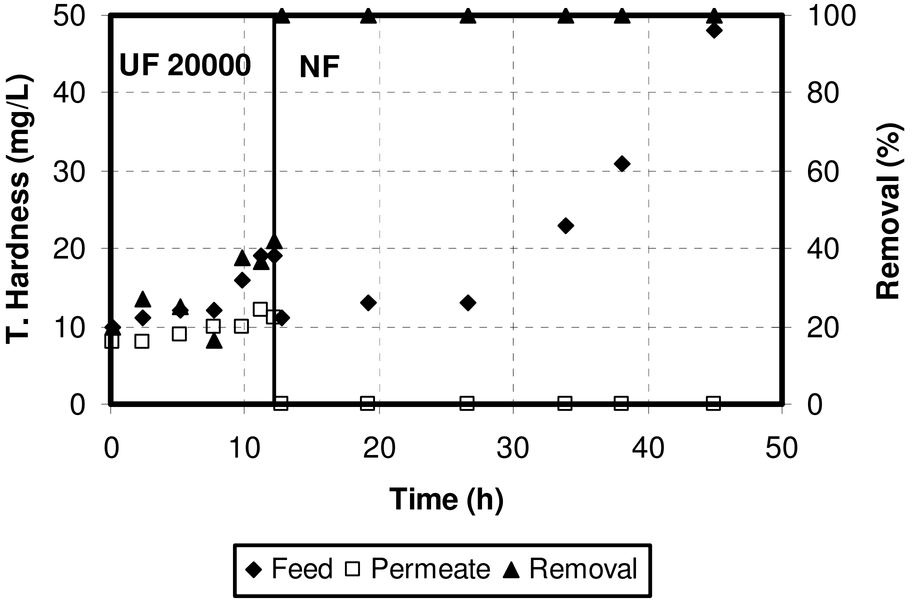


Figure 6.22. T. Hardness Removal Performance of UF (20000 Da) + NF

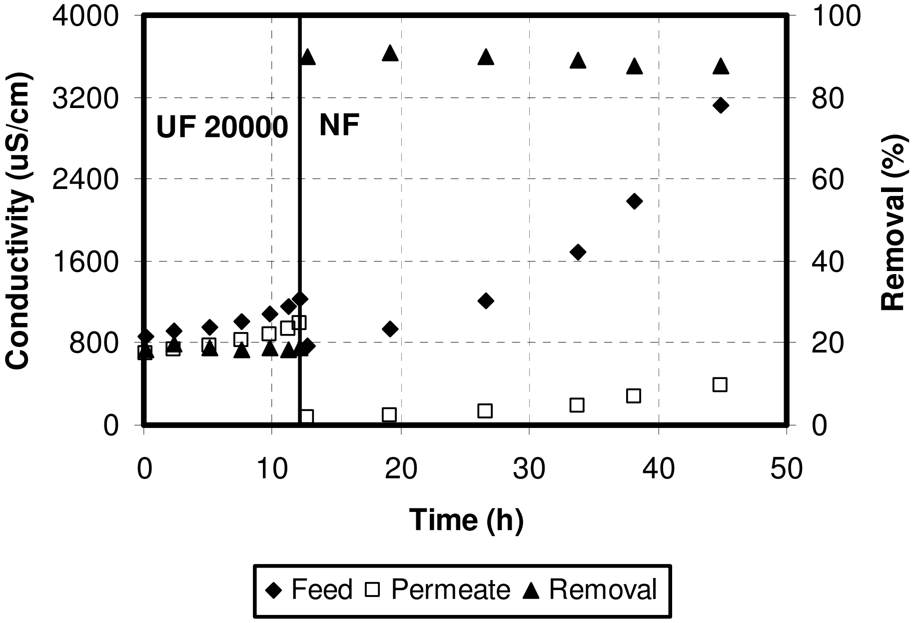


Figure 6.23. Conductivity Removal Performance of UF (20000 Da) + NF

The pH of the feed and the permeate streams were also monitored (Figure 6.24). It was observed to be constant at around 7.5 in the feed and the permeate of the UF membrane. However, it increased from 7.78 to 8.41 in the NF feed and from 6.99 to 8.67 in the NF permeate. Therefore, the pH of the feed and the permeate became almost equal at the end, which was also observed in single NF. The final pH of both streams exceeded 8.0 towards slightly more basic side in NF.

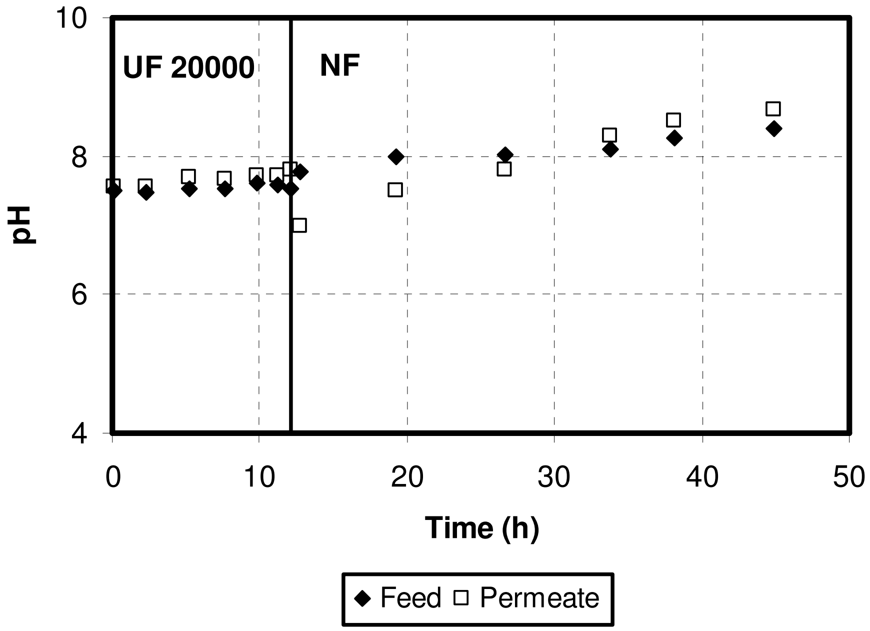


Figure 6.24. The Change of pH in UF (20000 Da) + NF

The flux decline levels were also monitored. Actually, the sequential application of a loose UF and NF arose from the idea of minimizing the flux decline in the NF stage. However, the flux declines in the UF stage were severe (Figure 6.25) and did not help reduce the flux decline that occured in the NF stage. The initial flux decline was 29% for the UF membrane, and it increased to 59% at the end of a time period of 13 h, where the VRF reached 28.5. These flux decline levels indicate severe fouling of the UF (20000 Da) membrane, which also showed poor performance in removing the pollutants except those causing color and turbidity. The flux decline observed in the NF stage was initially 19% and increased to 29% at the end of a time period of 33 h. Remembering that the flux decline was initially 16% and finally 31% in the single NF stage, the sequential application of a loose UF and NF was realized to be of no use for minimizing the flux decline levels.

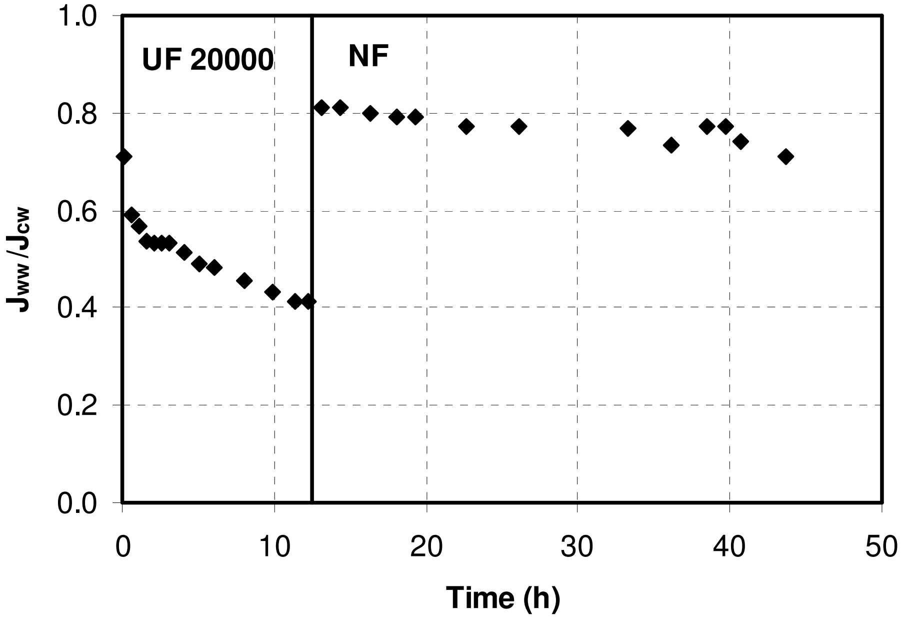


Figure 6.25. Relative Flux Change in UF (20000 Da) + NF

After the CMF tests, all the membranes were cleaned with HNO_3 and NaOH solutions and water fluxes were measured again. It was found out that the initial clean water flux of the NF membranes was recovered by the cleaning procedure, whereas the clean water fluxes of the UF membrane GR 61 PP (20000 Da) could not be recovered, indicating the occurence of irreversible fouling, possibly due to pore blocking (Table 6.16). This makes the use of a loose UF membrane economically unfeasible, as the product flux will be very low by severe fouling problem. Therefore, the sequential application of UF followed by NF was decided to be performed by a tight UF membrane. As the third and final alternative, the

MWCO of the UF membrane was changed to 1000 Da as it was the tighest UF membrane available from the manufacturer.

6.1.2.2.3. Tight UF Followed by NF

Considering the possibility of maintaining a reduced flux decline by a UF membrane with a MWCO of less than 20000 Da in the UF stage, which, in turn, may help minimize the flux decline in the NF stage, the PDW (Mixture 3) was treated in a process train consisting of a tight UF (1000 Da) followed by NF.

The performances of the loose and tight UF membranes are compared in Table 6.15, in which the permeate qualities and the removal efficiencies corresponding to a VRF of 1 (beginning of the test) and 9.3 (end of the test) are given for each parameter. As seen, the removal performances of UF (20000 Da) and UF (1000 Da) were very similar to each other despite their different MWCO values. In both cases, color and turbidity removal efficiencies were higher than 95%, whereas the removal efficiencies for COD, total solids and total hardness were all less than 40%. These similar performances can be interpreted such that the loose UF membrane may not be loose enough and similarly, the tight UF membrane may not be tight enough, making the MWCO values reported by the manufacturer doubtful. Indeed, this is very probable, since the manufacturers determine the MWCO of membranes by permeation tests performed with model compounds of known molecular weights, and the molecular weight of such a compound, which is rejected by 90% is reported as the MWCO of that membrane.

Table 6.15. Performances of Loose (20000 Da) and Tight (1000 Da) UF

Parameter	**VRF**	**UF Permeate Quality**		**Removal (%)**	
		20000 Da	**1000 Da**	**20000 Da**	**1000 Da**
COD (mg/L)	1	289	335	35	24
	9.3	405	362	15	43
Color (Pt-Co)	1	0	1	100	99
	9.3	4	1	98	99
Turbidity (NTU)	1	0.2	0.2	95	98
	9.3	0.2	0.2	99	98
T. Solids (mg/L)	1	403	405	41	36
	9.3	642	685	27	32
T. Hardness (mg/L as $CaCO_3$)	1	8	31	20	6
	9.3	12	44	37	45

Figure 6.26 depicts the change of UVA values and the wastewater volume during the CMF tests. Although the UF membrane (1000 Da) had much smaller pore size than the previous one (20000 Da), the UVA rejection was still as low as 16%. The performance of the third alternative train was similar to that of the second one.

Figures 6.27 to 6.32 present the removal performances of the UF (1000 Da) + NF process. Despite the poor rejection of COD by the UF (1000 Da) membrane, the NF membrane almost completely removed it, as in the case of single NF (Figure 6.27). The average permeate COD, which was 259 mg/L at a VRF of 9.3 in the UF stage was further decreased to 11 mg/L by the NF process at a VRF of 5.8. The COD removal efficiencies were observed to be higher than the UVA removal efficiencies at both processes, indicating the presence of some UV absorbing but not chemically oxidizable inorganic matter that permeate through the UF and NF membranes.

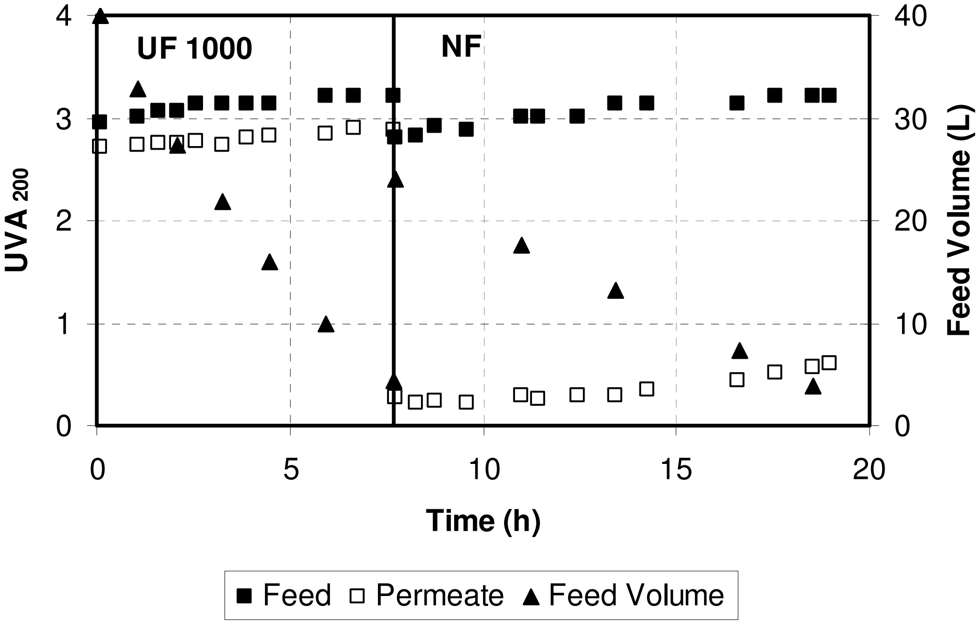


Figure 6. 26. Change of UVA and Feed Volume in UF (1000 Da) + NF

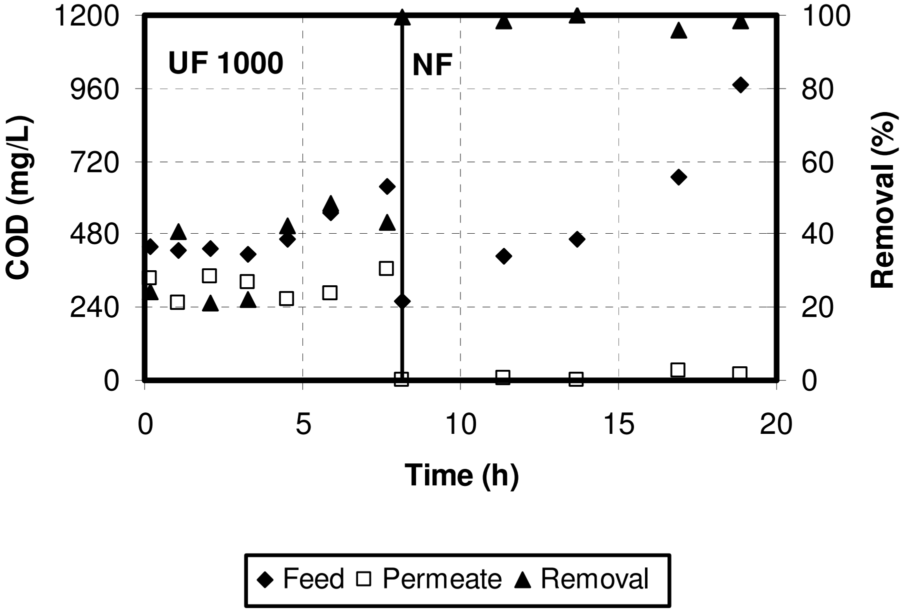


Figure 6.27. COD Removal Performance of UF (1000 Da) + NF

As presented in Figure 6.28, the UF (1000 Da) membrane removed color almost completely, and a permeate color of 4 Pt-Co was fed to the NF membrane, which produced a colorless permeate. Similarly, the NF feed contained a turbidity of 0.4 NTU due to the very high rejections in the UF stage. Turbidity removal efficiencies were comparably low (40-76%) in the NF stage since almost no turbidity was left to remove (Figure 6.29).

Figure 6.30 depicts the total solids removal performances of the UF (1000 Da) and following NF membranes, which are very close to the performances of UF (20000 Da) and following NF. The total solids content of the UF (1000 Da) feed increased from 637 mg/L to 1001 mg/L, corresponding to an increase from 405 mg/L to 685 mg/L in the permeate. The removal efficiency for total solids was around 30%. On the other side, the total solids of NF feed increased from 531 mg/L to 1590 mg/L, whereas it was only 53-132 mg/L at the permeate side, resulting in a removal efficiency higher than 90%. The total solids rejection performance of the removal performance was realized to be parallel to that of COD.

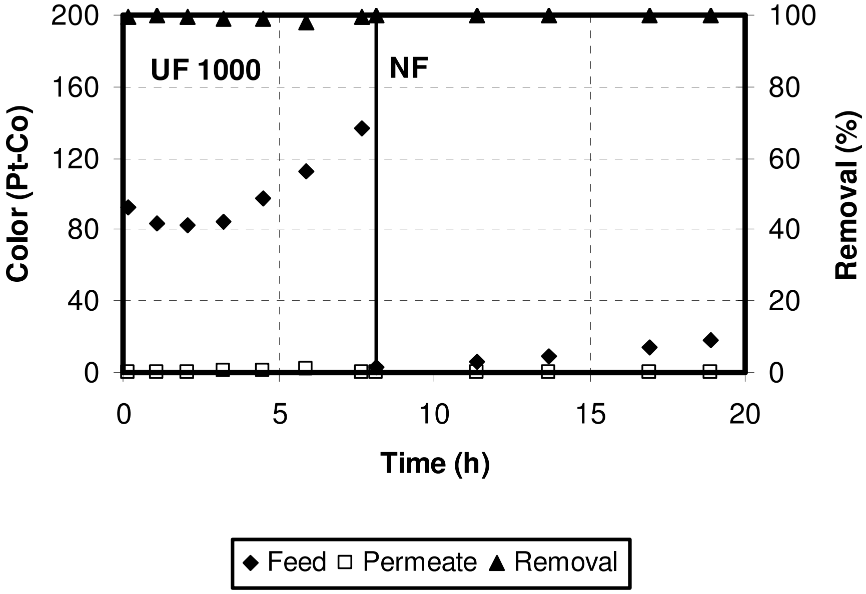


Figure 6.28. Color Removal Performance of UF (1000 Da) + NF

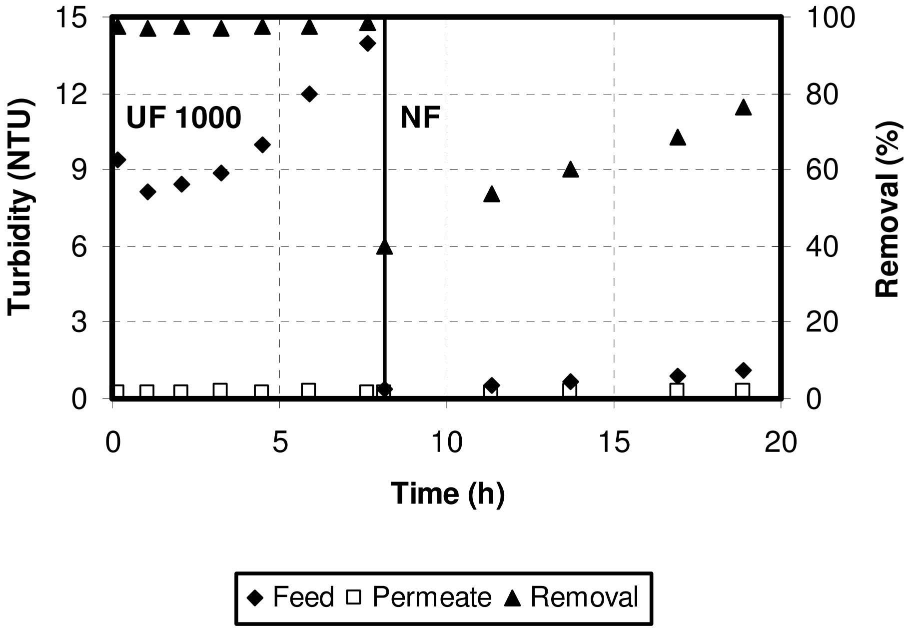


Figure 6.29. Turbidity Removal Performance of UF (1000 Da) + NF

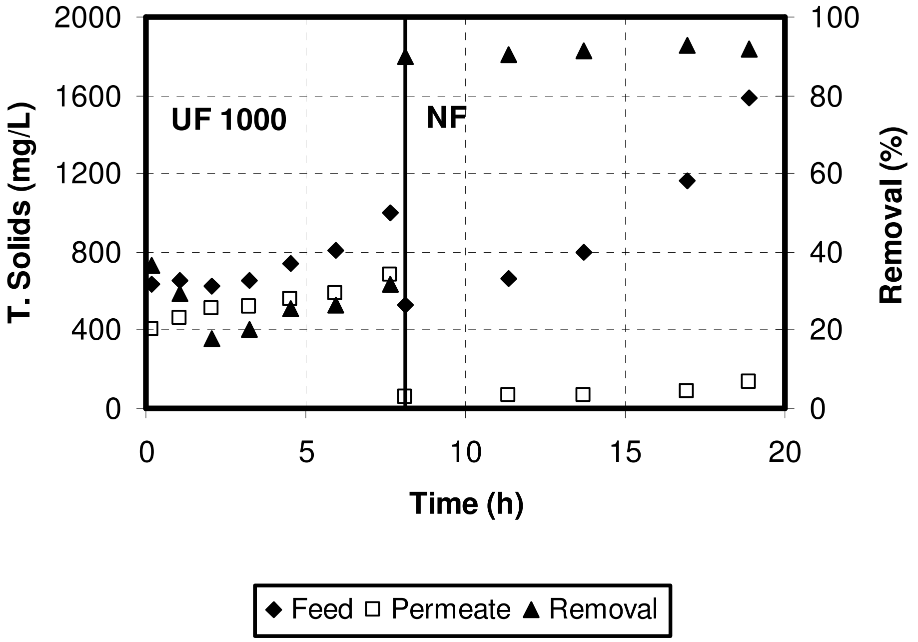


Figure 6.30. T. Solids Removal Performance of UF (1000 Da) + NF

A similar removal trend was observed for total hardness, which is one of the most important parameters for dyeing process water. The UF (1000 Da) membrane did not remove the hardness causing ions efficiently, as they are very small molecules with respect to the MWCO of the UF membrane (Figure 6.31). The NF membrane removed hardness completely, resulting in the production of a very soft permeate, which satisfies the desired quality for dyeing process. The conductivity removal performance was similarly low for the UF (1000 Da) membrane and the following NF membrane removed conductivity at 90% (Figure 6.32).

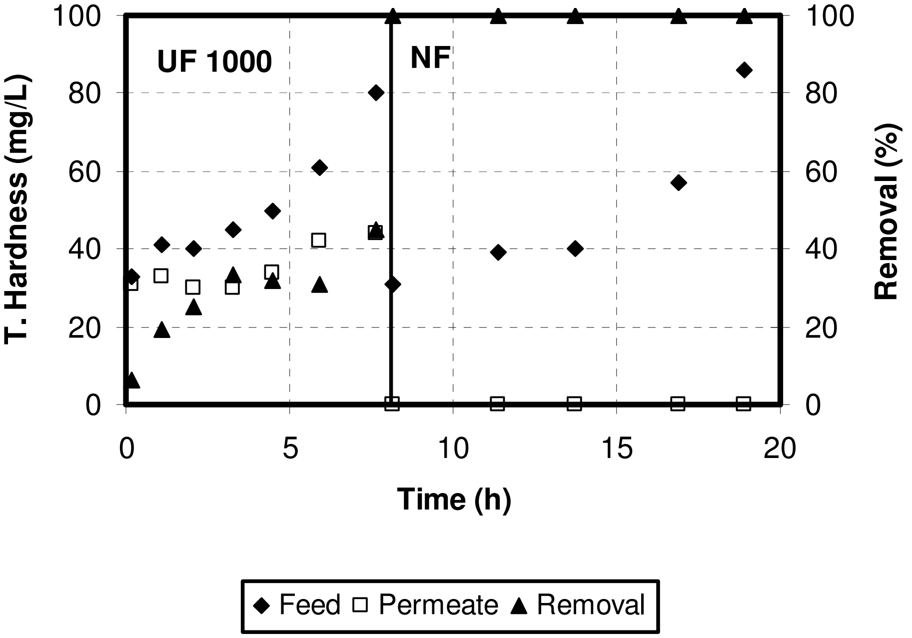


Figure 6.31. T. Hardness Removal Performance of UF (1000 Da) + NF

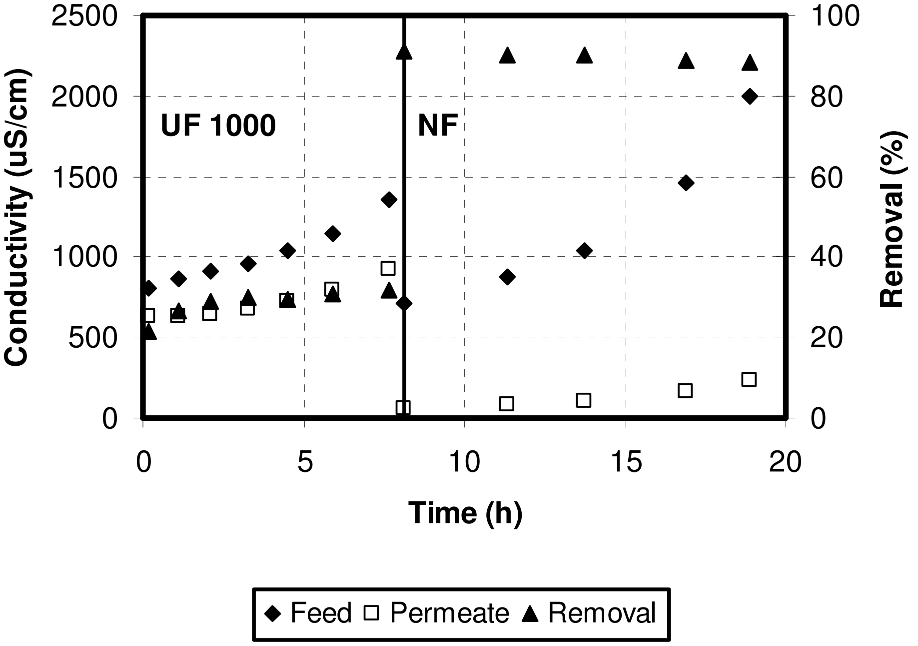


Figure 6.32. Conductivity Removal Performance of UF (1000 Da) + NF

The pH of the feed and the permeate were almost the same in UF (1000 Da) and NF stages (Figure 6.33). The pH, being neutral at the beginning of the UF experiment, increased from 7.30 to 8.00 in the permeate stream. The NF feed and permeate pH values increased from 7.90 to 8.39 and from 8.00 to 8.84, respectively. Therefore both the feed and the permeate finally became slightly more basic. As stated before, this effect might have occurred due to the accumuation of H^+ ions in the cake formed on the membrane surface, resulting in decreased H^+ concentration, and thus, increased pH in the feed and the permeate streams.

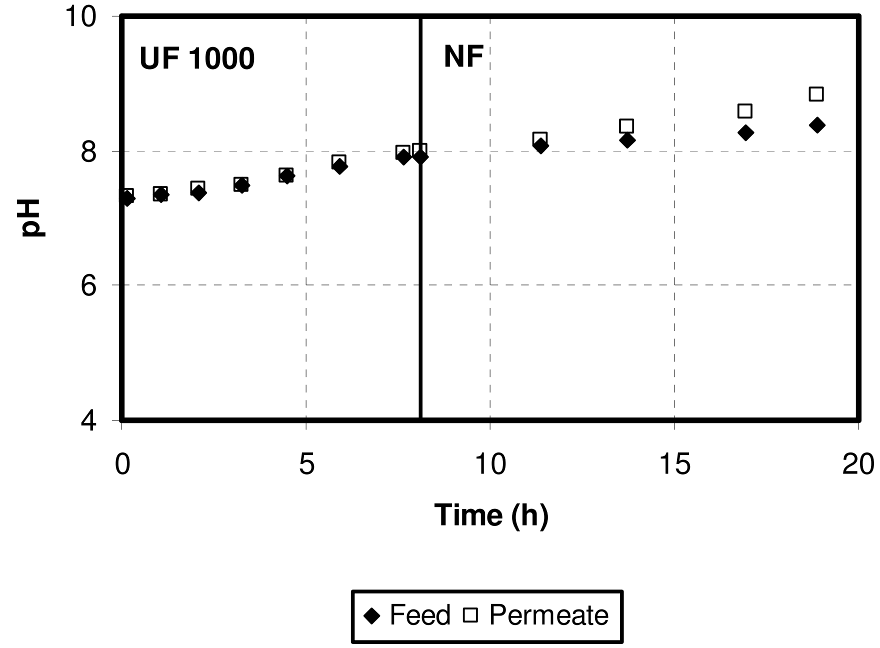


Figure 6.33. The Change of pH in UF (1000 Da) + NF

The monitoring of the wastewater flux throughout the CMF test resulted in the data presented in Figure 6.34. In the UF stage, the flux decline started at 11% and increased up to 60% at the end, indicating a very severe flux decline, while maintaining a VRF of 9.3. These levels of flux declines were almost the same as those observed in loose UF (20000 Da) stage. Hence, using a tight UF membrane instead of a loose one before NF did not help avoid the severe flux decline in the UF stage. Moreover, the flux declines in the NF stage was higher, which started with 20% and increased to 28% at the end of a VRF of 5.8, which may be due to the use of different mixtures in alternative processes.

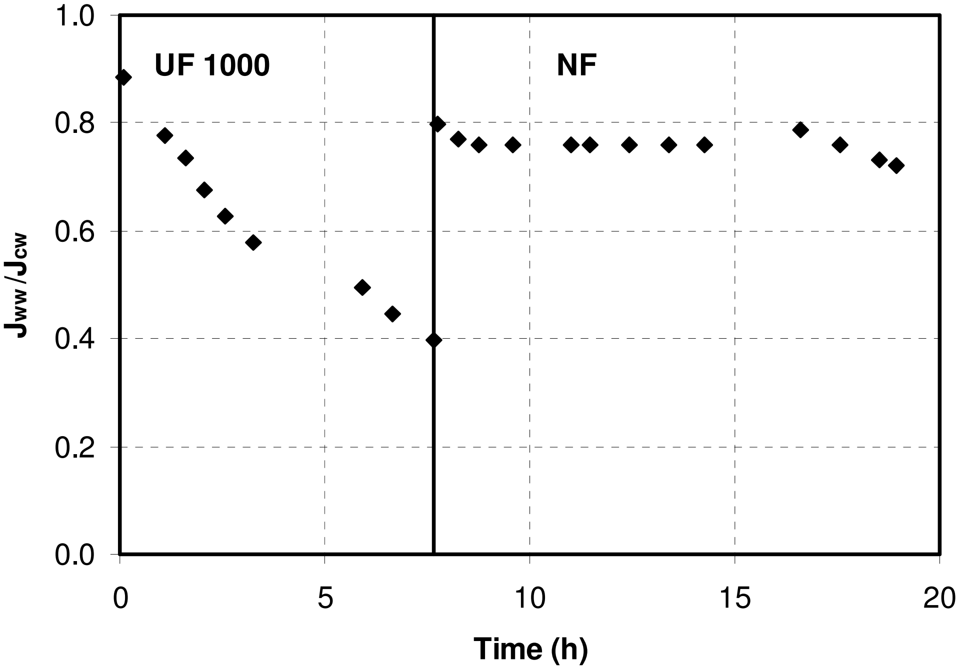


Figure 6.34. Relative Flux Change in UF (1000 Da) + NF

The permeances and flux declines of the UF and NF membranes were summarized in Table 6.16 for ease of comparison. The effect of cleaning on flux recovery was also presented. The initial clean water flux of the tight UF membrane was recovered whereas the cleaning procedure was not effective in restoring the initial clean water flux of the loose UF membrane. This indicates pore blocking in UF (20000 Da) membrane. The flux decline for NF was highest when it followed the tight UF stage and it was the same for other two alternatives (single NF versus loose UF+NF). This was thought to be due to the variable characteristics of the PDW mixtures.

Table 6.16. Comparison of NF and UF Permeances

Process	Permeance (L/m^2/h/bar)				Flux Decline (%) (Initial/Final)
	Clean Water			Wastewater (Initial/Final)	
	Initial (I)	Final (F)	Cleaned (C) *	(W)	(I-W)
NF	2.1	2.1	2.5	1.8/1.4	15/31
UF (20000) + NF	45.9	30.2	33.2	32.4/18.9	29/59
	2.4	2.5	2.5	2.0/1.7	16/31
UF (1000) + NF	17.2	16.0	18.2	15.1/6.8	11/60
	3.4	3.1	3.6	2.7/2.4	20/28

* Circulation of HNO_3 solution followed by NaOH solution for 30 min each.

The flux decline is a major problem in membrane processes since it directly affects the economy of the process. High flux declines require frequent cleaning cycles, which, in turn reduces the membrane life and increases the cost. Therefore it is always desirable to have low flux declines in such processes. For the treatment of PDW, the NF flux decline could not be minimized by both alternatives of loose and tight UF stages applied before NF. Therefore it was concluded that the best treatment sequence for PDW is chemical precipitation (CP) followed by single NF. This is a very good outcome since the developed process train would be more economical with the least number of unit operations and processes. The single NF permeate was evaulated in Section 6.1.2.2.1 for its suitability for reuse and a comparison with BTTG criteria had revealed that the NF permeate satisfies the desired quality and can be used in the dyeing process as the process water.

6.1.3. Testing The Process Train Performance at High Color Contents

Color is one of the most important parameters for the process water quality since the process water is required to be free of any color for an efficient dyeing process. Even very low levels of color are not allowed in dyeing of light colors. Therefore, the performance of the membrane separation systems for rejection of color must be perfect for producing process waters with acceptable qualities.

The color content of the carpet dyeing wastewaters were relatively low as compared to other textile subcategories due to two reasons: 1. The dyes used in the print dyeing process are 1:2 metal-complex dyes, which have high fixation rates on the synthetic fiber and therefore result in relatively low-colored wastewaters, 2. The print dyeing wastewaters originate from the washing tank where carpets are washed after dye fixation process, leaving a low-colored wash water in the tank. Moreover, about 90% of color was removed by CP at the pre-treatment stage. During the course of this study, the color of the sampled PDWs were 300-700 Pt-Co, and it reduced to 30-70 Pt-Co after the pre-treatment stage, which is quite low for a typical textile wastewater. However, the color content of the carpet dyeing wastewaters increases from time to time due to the variations in the product specifications, as in the case of specially ordered dark colored carpets. To this end, the performance of the developed process train for treating highly colored carpet dyeing wastewaters needed to be tested.

In order to test the performance of NF for high color case, the color of the PDW was increased up to a value of 1000 Pt-Co. This was done by spiking the wastewater with dye solutions prepared by LANASET dyes that had originally been used in the dyeing process. As seen in Figure 6.35, PDW (Mixture 3) was spiked with the dye solutions after the chemical precipitation stage in order to avoid the removal of color in this stage.

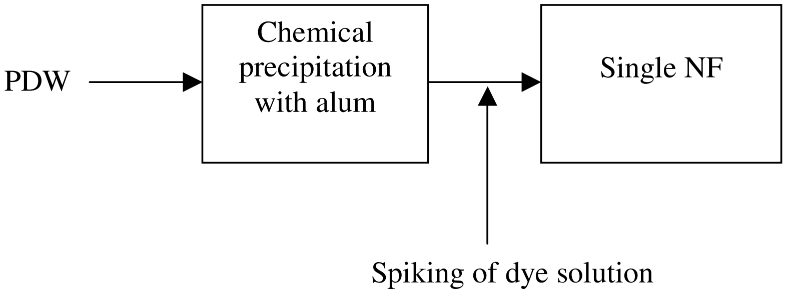


Figure 6.35. Spiking of PDW with LANASET Dyes

The effect of high color on the performance of NF was studied by TRMF tests using three dyes, which were originally present in Mixture 3 wastewater, namely Yellow 2R (Y2R), Red G (RG), and Grey G (GG). The dye concentrations are given in Table 6.17. These dye concentrations correspond to the aimed high color values in the wastewater, i.e. approximately 500 Pt-Co and 1000 Pt-Co (Table 6.18). The effects of single dye and three dye mixture were studied separately, and since these three dyes had no significant differences, Yellow 2R was chosen randomly for the effect of single dye. Spiking was done into the PDW and also into the distilled water (DW) to understand whether the flux decline is basically due to the dye itself or not.

Table 6.17. Spiked Dye Concentrations

Sample	**Number of Spiked Dyes**	**Names of Spiked Dyes**	**Dye concentration (mg/L)**
PDW (Mixture 3)	1	Y2R	10
	1	Y2R	30
	3	Y2R, RG, GG	10, 10, 10
DW	3	Y2R, RG, GG	10, 10, 10

The results obtained by the NF membrane (NFT-50) are given in Table 6.18. As seen, the performance of the NF membrane under high color conditions was as good as its performance at very low color conditions, such that the permeate color content was only 13 Pt-Co even at a feed color value of 908 Pt-Co. This was observed in the case of three dyes added into the wastewater. When the wastewater was spiked with single dye (Y2R) at a concentration of 30 mg/L, the permeate contained only 4 Pt-Co of color. In addition, all the other parameters were removed as efficiently as in the case of no dye spiking. The permeate quality satisfied the BTTG criteria and therefore it was ensured that NF can be used safely for the treatment of highly colored PDWs.

The color was monitored continuously in the spiking experiments and a decrease of 20-30% was observed immediately in the feed, indicating the accumulation of the dyes on the membrane surface (Figure 6.36). This was also visually observed when the membranes were taken out of the module and could not be removed completely by the cleaning procedure.

The flux decline occurred during the spiking experiments were also monitored and the relative flux decline is depicted in Figure 6.37. As seen from the figure, the flux decline occurred as 17% when the PDW was not spiked with dyes. The increase of Y2R concentration from 10 mg/L to 30 mg/L resulted in almost two-fold increase in the flux decline (from 14% to 23%). The highest flux decline of 26%, which was observed when three dyes were spiked at a total dye concentration of 30 mg/L, was very close to the flux decline of 23% observed with single dye at the same concentration. Therefore, it was concluded that dye concentration had a more significant adverse impact on the flux decline than the number of dyes present.

Table 6.18. Effect of Dye Concentrations on NF Performance

Parameter	**Spiked Dye Concentration (mg/L)**				
	0	**10**	**30**	**30**	**30**
		Y2R in PDW	**Y2R in PDW**	**Y2R + RG + GG in PDW**	**Y2R + RG + GG in DW**
COD					
Feed (mg/L)	418 ± 6	446 ± 15	465 ± 26	431 ± 16	25 ± 3
Permeate (mg/L)	16 ± 2.3	11 ± 3	17 ± 2	19 ± 2	0 ± 0
Removal (%)	96	98	97	96	100
Color					
Feed (Pt-Co)	66 ± 1.4	384 ± 4.2	1044 ± 17	908 ± 8.5	922 ± 0
Permeate (Pt-Co)	0 ± 0	0 ± 0	4 ± 1	13 ± 0.7	8 ± 1.4
Removal (%)	100	100	99	99	99
T. Solids					
Feed (mg/L)	496 ± 3	501 ± 16	580 ± 6	666 ± 8.5	-
Permeate (mg/L)	36 ± 7	29 ± 1	27 ± 7	86 ± 20	-
Removal (%)	93	94	95	87	-
T. Hardness					
Feed (mg/L)*	34 ± 0	-	-	-	-
Permeate (mg/L)	0	0	0	0	0
Removal (%)	100	100	100	100	100

* Could not be measured in colored samples due to color intereference

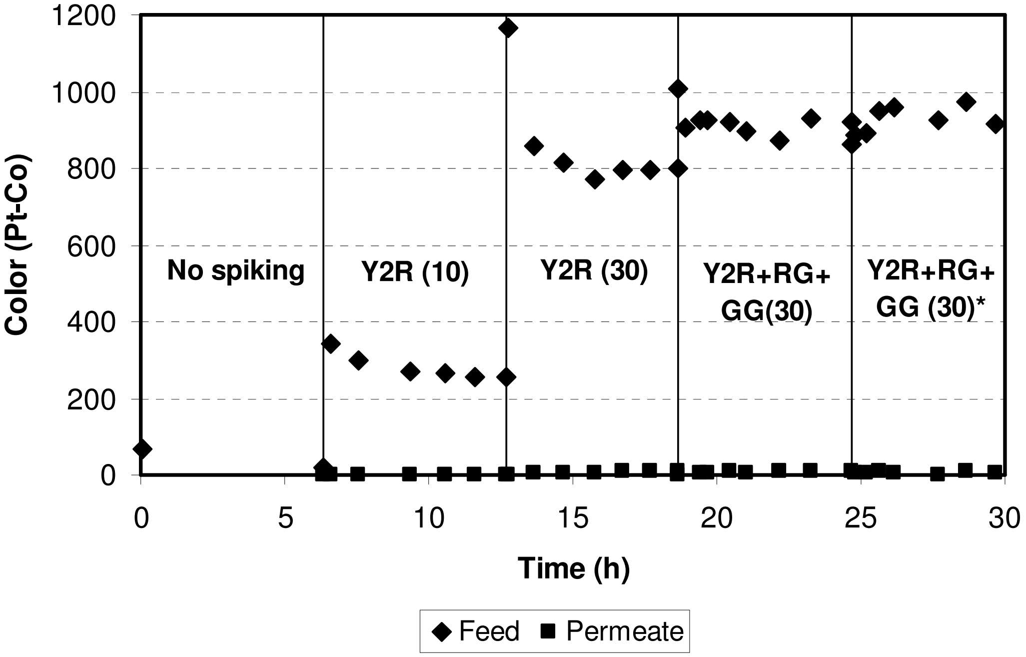


Figure 6.36. Change of Color for PDW Spiked with Dye (*spiked into DW)

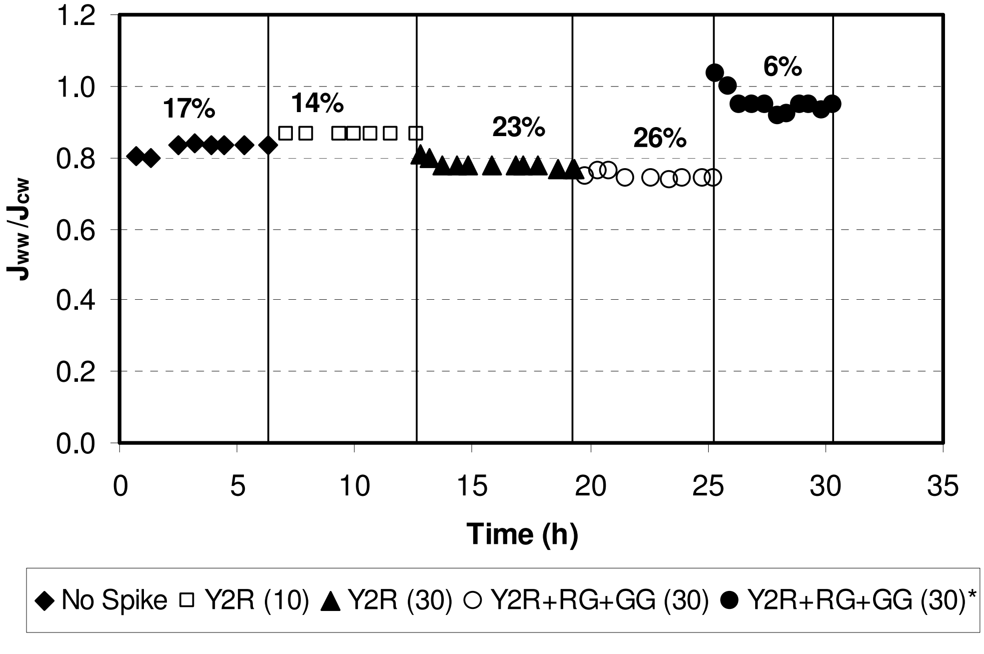


Figure 6.37. Change of Relative Flux for PDW Spiked with Dye (*spiked into DW)

The results observed for the spiking of distilled water revealed a flux decline of only 6%, which in turn, indicated that the flux decline observed with PDW was due to the auxiliary chemicals themselves or their interactions with the dyes to a greater extent rather than the dyes alone. Therefore, determination of the correct chemical doses in preparing the print paste comes out to be a very important issue for maintaining a longer membrane life and a more economical wastewater recovery operation.

In an attempt to distinguish between the fractions of flux declines caused by the auxiliary chemicals and the dyes, three sets of TRMF experiments were run. The concentration of the dye Red G (RG) was chosen based on the previous spiking tests and the concentrations of the two auxiliary chemicals were calculated based on their concentrations used in the actual dyeing processes. A solution with the third auxiliary chemical, Tanaprint ST 160, could not be prepared since it did not disperse in water. The specifications of the prepared solutions are shown in Table 6.19.

Table 6.19. Synthetic Water Compositions

Run	**Contents of Solution**	**Concentrations (mg/L)**	**Specifications**	
			COD (mg/L)	**Color (Pt-Co)**
1	RG	10	18	376
2	RG + Tanasperse CJ*	10 + 0.2	415	382
3	RG + NeFome 1125**	10 + 0.1	59	435

* non-ionic penetrant for increasing wetting and penetration
** antifoaming agent

The removal performances of the NF membrane (NFT-50) for the prepared solutions are presented in Table 6.20. As seen, the presence of non-ionic penetrant (Tanasperse CJ) in addition to the dye RG resulted in a decrease in the COD removal efficiency from 100% to 91% whereas the presence of antifoaming agent (NeFome) had no adverse effect on the COD removal efficiency. In all the cases the permeate was colorless or had negligible color.

Table 6.20. Effect of Auxiliary Chemicals on NF Performance

Run	Contents	Permeate Quality		Removal (%)	
		COD (mg/L)	**Color (Pt-Co)**	**COD (mg/L)**	**Color (Pt-Co)**
1	RG	0	0	100	100
2	RG + Tanasperse CJ	38	1.5	91	99.6
3	RG + NeFome 1125	0	0.8	100	99.8

The changes in flux declines were also monitored and they are shown in Figure 6.38. The flux decline was 4%, 10% and 7% for Run 1, 2, and 3, respectively. The flux decline of 4%, which was caused by 10 mg/L of single dye (RG) spiked into distilled water was very close to the flux decline of 6%, which was caused by 30 mg/L of three dyes (Y2R+RG+GG) (Figure 6.37). This result indicated that a three-fold increase in the dye concentration had no significant effect on the flux decline of synthetic water. On the other hand, increasing the dye concentration from 10 mg/L to 30 mg/L for the dye Y2R had resulted in the increase of flux decline from 14% to 23%, when the dye was spiked into actual wastewater. Therefore, the dye concentration seemed to be a factor influencing the flux declines in real wastewaters (Table 6.18).

In all the cases, the presence of an auxiliary chemical in addition to the dye resulted in increased flux declines, although it was not high. The presence of non-ionic penetrant caused higher flux decline (10%) as compared to the antifoaming agent (7%). This result is in agreement with the removal performance, as the COD removal efficiency was reduced only by the presence of the non-ionic penetrant.

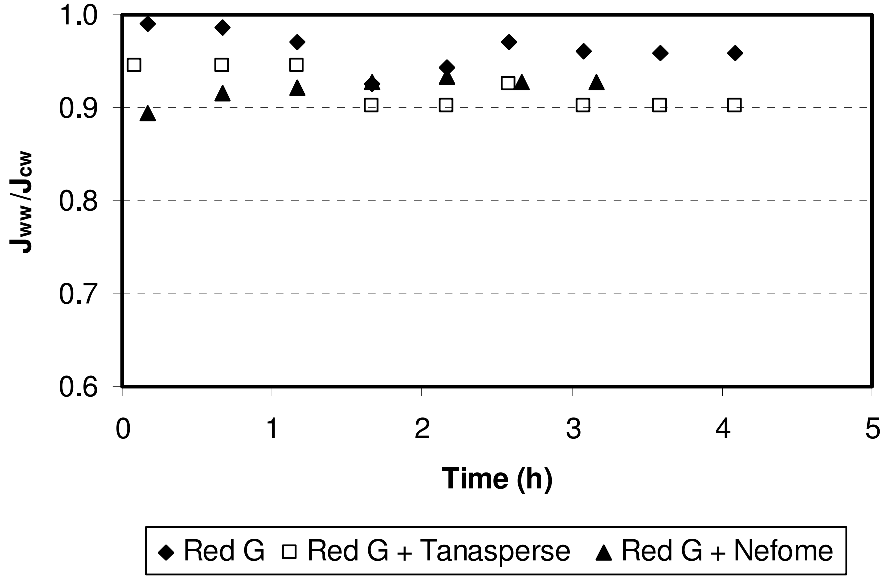


Figure 6.38. Effects of Dyes and Auxiliary Chemicals on Flux Decline

The flux decline levels observed here for the spiking of the DW are much lower than that observed for the actual PDW samples, which was 17% under very similar experimental conditions (Figure 6.37). This is quite expected since the effects of the auxiliary chemicals were studied separately whereas they have combined effects in the actual PDW sample. Moreover, the actual wastewater mixture also contains the third auxiliary chemical that is Tanaprint ST 160, which could not be added into the prepared solution, as it did not disperse in the DW. As a result, it was concluded that the combined effects of dyes and the auxiliary chemicals on the flux declines were much significant than the individual effects of the dyes themselves.

A general evaluation of the separation performances of UF and NF tested in this study revealed that water can be recovered from carpet printing wastewater streams by membrane technology, provided that a suitable pre-treatment stage is included in the process trains. NF and UF produced permeates with different qualities, where NF permeate, being very soft and free of color and turbidity, was suggested to be suitable for all the carpet dyeing processes, including the most demanding ones such as the dyeing of light colors. On the other hand, UF permeates had worse quality in terms of COD, total solids and total hardness as compared to NF permeates, therefore they were suggested to be suitable for washing of the printed carpets or dyeing of the dark colors. For more demanding dyeing processes, these UF permeates may be mixed with the actual process water in varying proportions. Besides, the UF permeate quality can be accepted as satisfactory if color and turbidity removal is the main target in water recovery.

The flux declines of NF and UF membranes ranged from low to moderate at steady state conditions (VRF=1). Furthermore, their reversible fractions were higher than the irreversible fractions since concentration polarization had a more pronounced effect on flux decline rather than fouling. However, UF flux declines became very severe as the VRF increased during water recovery. This indicated that UF is not feasible for water recovery from carpet printing wastewaters as the severe flux declines would require frequent cleaning, and hence increase the operational costs and reduce the membrane service life. On the other hand, NF flux decline remained stable at moderate levels with increasing VRF. In an attempt to minimize the NF flux declines, one loose and one tight UF membrane preceded the NF membrane in two alternative trains, however the NF flux declines did not improve. Therefore, the sequential UF and NF alternatives were eliminated from the process train, and hence the best process train for water recovery from carpet printing wastewater stream was decided to be chemical precipitation followed by single stage NF.

6.2. Process Train Development for Acid Dye Bath Wastewaters (ADBWs)

6.2.1. Pre-treatment of ADBWs

The wastewater characterization study showed that color and turbidity contents of ADBW samples were much lower as compared to PDW samples, whereas they had higher COD and total solids. The acid dye bath wastewaters were generated in the dye-beck system where carpets were dyed under acidic pH in a dye bath containing acid dyes, antifoaming agent, uniformity agent and acetic acid. As a result, the characteristics of ADBW were remarkably different than those of PDW. Therefore, it was foreseen that chemical precipitation, which was the best pre-treatment process for PDW, would not be required for ADBW. To this end, the pre-treatment alternatives considered for ADBW was MF and UF. Four MF and one UF media with the specifications given in Table 5.4 were tested in single and sequential stages of filtration with Mixture 1 and Mixture 2. MF was simulated by a conventional vacuum filtration apparatus in dead-end mode and UF was simulated by the lab-scale membrane separation unit, SEPA CF Module in cross-flow mode. The best pre-treatment process for ADBW was determined among the alternatives listed below:

1. Single MF (pore sizes of 2.5 μm, 1.0 μm, 0.45 μm and 0.2 μm),
2. Sequential MF (pore sizes of 2.5 μm, 1.0 μm, 0.45 μm and 0.2 μm),
3. Single UF (MWCO 50000 Da),
4. MF (0.45 μm) followed by UF (50000 Da).

6.2.1.1. Single and Sequential MF

The performance of dead-end MF was compared for MF media with pore sizes varying from 2.5 μm to 0.2 μm (Table 5.4), and the results shown in Tables 6.21-6.22 were obtained. The COD and total solids removal efficiencies were very low for all the media tested. This was quite expected since MF is able to remove particulates mostly and the COD causing organic matter is generally in dissolved form to a great extent. Therefore COD and total solids were expected to be removed in further membrane stages, i.e., UF or NF.

In single filtration, the best removal efficiency was achieved by the MF media having the smallest pore size of 0.2 μm for both mixtures. Color was removed completely whereas turbidity removal was 97% for Mixture 1 and 86% for Mixture 2. The removal performances of the MF media were significantly different for Mixture 1 and 2, being better for the latter. This result indicated that the particle size distribution of these wastewaters were quite different from each other. However, it was observed that removal trends were similar, such that the removal efficiencies improved with decreasing pore size for both mixtures.

In sequential filtration, the extent of improvement of the removal performances was from none to little, with respect to single filtration (Tables 6.21-6.22). For example, the color and turbidity removal efficiencies of MF (0.45 μm) were 100% and 97%, respectively for Mixture 1, and the sequential MF (2.5+1.0+0.45 μm) provided 100% and 98%, respectively. Therefore sequential filtration became an unnecessary option for the pre-treatment of ADBW and eliminated from the alternatives.

Table 6.21. MF Performance for ADBW Mixture 1

Parameter	Removal (%)					
	Pore Sizes in Single Filtration (μm)				Pore Sizes in Sequential Filtration (μm)	
	2.5	1.0	0.45	0.2	2.5 + 1.0 + 0.45	0.45 + 0.2
COD	3	5	5	0	10	5
Color	0	7	77	100	82	100
Turbidity	19	17	47	97	52	98
T. Solids	5	4	4	15	11	15

Table 6.22. MF Performance for ADBW Mixture 2

Parameter	Removal (%)						
	Pore Sizes in Single Filtration (μm)				Pore Sizes in Sequential Filtration (μm)		
	2.5	1.0	0.45	0.2	2.5 + 1.0	2.5 + 1.0 + 0.45	2.5 + 1.0 + 0.45 + 0.2
COD	4	5	5	5	5	3	5
Color	15	49	100	100	50	100	100
Turbidity	62	68	79	86	68	82	84
T. Solids	10	10	13	12	16	15	25

6.2.1.2. Single UF

Single UF was applied as an alternative to MF where a loose UF membrane (Osmonics HZ 15) with a MWCO of 50000 Da was tested in a TRMF experiment for the pre-treatment of ADBW. In this experiment, Mixture 2 was used only since Mixture 1 was discarded due to fungal growth. The UVA and wastewater fluxes were recorded during the experiment (Figures 6.39 and 6.40). As seen from Figure 6.39, UVA/UVA_o is around 1.0, indicating no reduction of UV absorbing matter at all. The analysis of the UF permeate also revealed that the removal efficiencies for COD and total solids were almost none, i.e., 2% and 5%, respectively (Table 6.23). On the other hand, color was removed completely. Since acid dyes are known to have much smaller molecular sizes as compared to the MWCO of the loose UF membrane (50000 Da), their complete rejection can be interpreted such that the dyes may interact with the surfactants to form a complex, which would have a much bigger size than the dye itself, and hence promote the rejection of the dye, i.e., color.

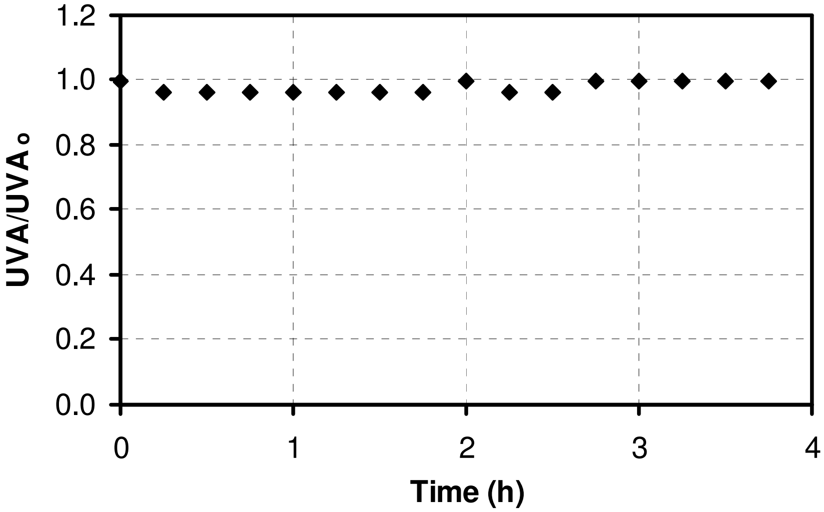


Figure 6.39. UVA Removal in Single UF (50000 Da)

The turbidity removal efficiency of the UF (50000 Da) membrane was 67% (Table 6.23), which was observed to be same with that of MF (1.0 μm), and lower than those of MF (0.45 μm) and MF (0.2 μm) (Table 6.22). Actually, the lower performance of UF membrane for turbidity removal was due to the fact that the turbidity content of the Mixture 2, which was originally 2.9 NTU while performing the MF tests, decreased to 1.9 NTU when performing the UF test, which might have occurred due to insufficient mixing of the raw wastewater before collecting the required volume of the wastewater to be used in the UF experiment. Therefore, this reduction in the UF feed turbidity content caused a reduction in the removal efficiency calculated for turbidity. Indeed, both the UF permeate and the MF (0.45 μm) filtrate had a turbidity of 0.62 NTU.

Table 6.23. Single UF (50000 Da) Performance for ADBW Mixture 2

Parameter	**Permeate Quality**	**Removal (%)**
COD (mg/L)	1403	2
Color (Pt-Co)	0	100
Turbidity (NTU)	0.62	67
T. Solids (mg/L)	765	5

The wastewater flux decreased continuously during the UF test, and stabilized within 2 h, leaving 28% of its initial value at the end of a filtration period of 4 h. Similarly, the wastewater flux with respect to clean water flux decreased by 35% in the first 15 min, and further decreased by 70% within 4 h of filtration (Figure 6.40). Single UF was eliminated from the alternatives as it did not provide better performance than single MF, and in addition the flux decline was severe. As the last alternative, sequential application of MF and UF was considered in order to minimize the flux declines observed with single UF.

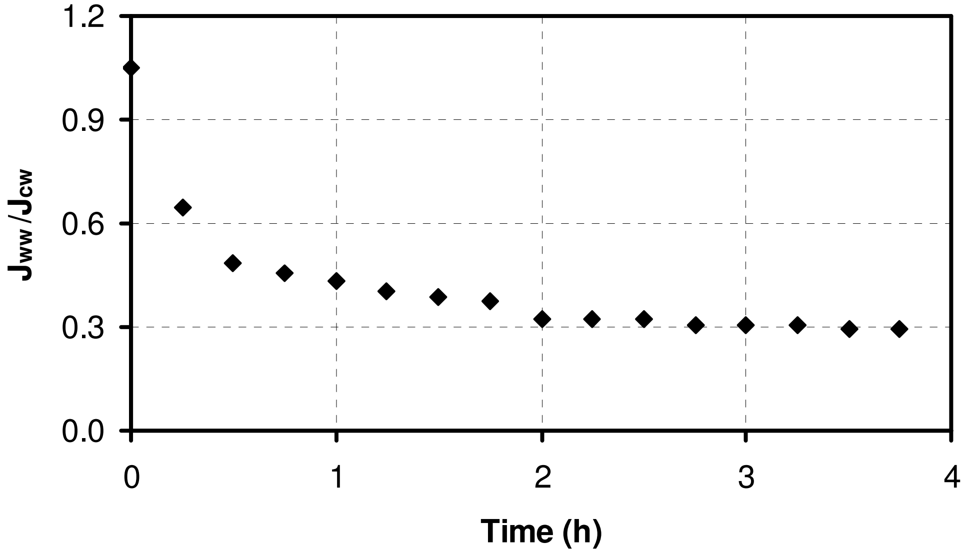


Figure 6.40. Change of Relative Flux in Single UF (50000 Da)

6.2.1.3. MF Followed by UF

The sequential filtration of ADBW Mixture 2 was performed with MF (0.45 μm) and UF (50000 Da) membranes. The first reason for choosing the 0.45 μm pore size in the MF stage was that the performance of MF (0.45 μm) media was almost equivalent to that of MF (0.20 μm) media for Mixture 2 (Table 6.22) and the second reason was that it provided faster filtration, as experienced during vacuum filtration experiments.

The changes in normalized UVA values in the UF stage of sequential filtration are depicted in Figure 6.41. As in the case of single UF (Section 6.2.1.2.), no UVA rejection was achieved, meaning that all the UVA causing compounds had passed through the MF and UF membranes, which indicated that the size of these compounds are smaller than 50000 Da.

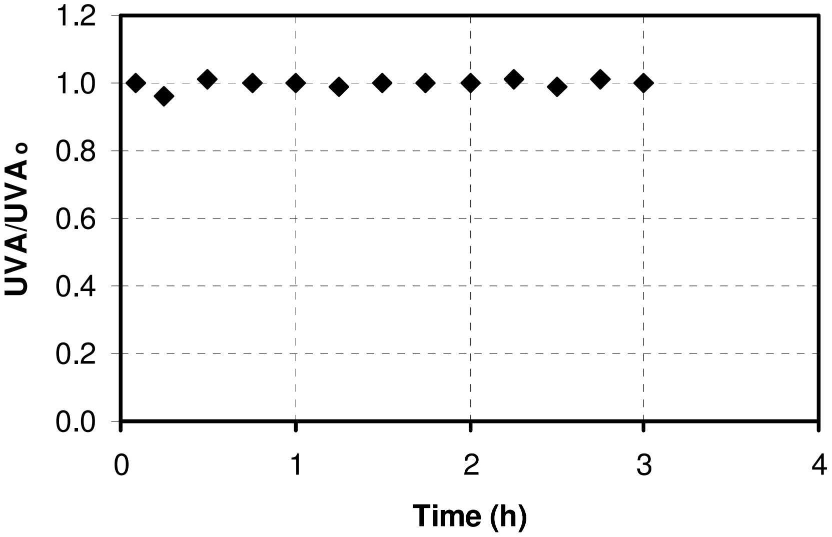


Figure 6.41. UVA Removal in MF (0.45 μm)+UF (50000 Da)

Table 6.24 compares the removal performance of MF and UF. As seen, MF did not improve the removal performance of the following UF membrane at all. The color and turbidity removal efficiencies, which were 96% and 60% in the MF stage increased to 100% and 78%, respectively, by the implementation of the UF stage. This improvement was negligible, and hence sequential filtration of MF and UF was found useless in terms of removal performances. Furthermore, the flux decline of the UF membrane was again 70% (Figure 6.42), which was the same as that of single UF (Figure 6.40). Therefore, there was no improvement in the UF flux decline by implementing the MF stage beforehand. Therefore, it was concluded that the sequential filtration of MF and UF had no benefit over single UF, and hence eliminated from the alternatives.

Table 6.24. MF (0.45 μm) and UF (50000 Da) Performances for Mixture 2

Parameter	**Removal (%)**		
	MF (0.45 μm) (1. stage)	**UF (50000 Da) (2. stage)**	**MF + UF (overall)**
COD	1	2	3
Color	96	100	100
Turbidity	60	45	78
T. Solids	8	0	8

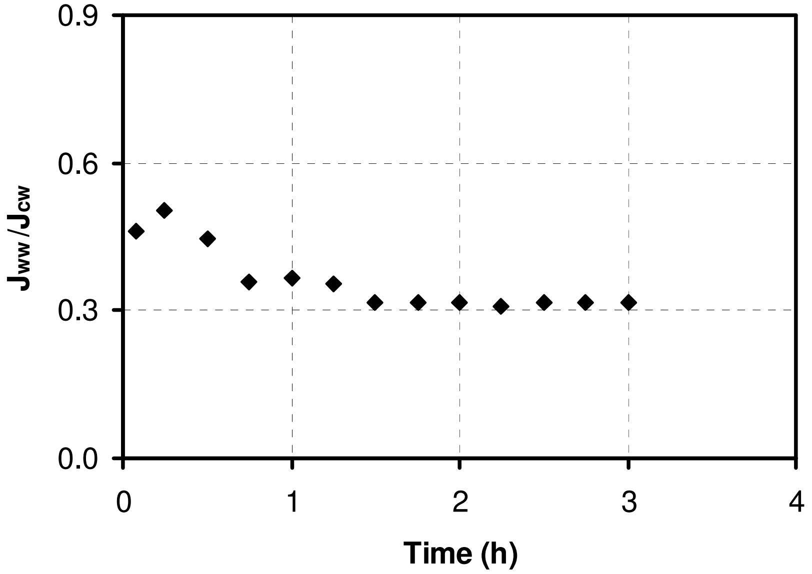


Figure 6.42. Relative Flux Decline in MF (0.45 μm) + UF (50000 Da)

Finally, a comparison of all the pre-treatment alternatives revealed that the removal performances of all the alternatives were close to each other. Therefore, among the alternative processes of MF and UF considered, selection of the simplest and the cheapest one was feasible; that is single MF (0.45 μm).

6.2.1.4. Optimisation of MF Pore Size for ADBW Samples

Since the characteristics of acid dye bath wastewater samples changed very quickly during the storage, sampling was repeated several times during the experimental studies. Among the ADBW mixtures, Mixture 2 and 3 were discarded due to fungal growth after a few experiments and Mixture 4 and Sample 42 were totally used in further NF separation experiments.

After discarding Mixture 2, Mixture 3 was subjected to pre-treatment where MF was applied. Although the pore size of the MF media was chosen as 0.45 μm for Mixture 2, filtration through MF (1 μm) was also considered for Mixture 3 due to the fact that the qualities of the filtrates obtained by both media were acceptable to be fed to the further NF membranes, which was experienced previously with pre-treated PDW mixtures. Moreover, filtration through 1 μm media, which was 60 L/h, was 12 times faster than that of 0.45 μm media, providing a much faster filtration operation (Table 6.25). These two MF media were compared for their color and turbidity removal efficiencies and the results are given in Table 6.25. As seen, the MF (1.0 μm) filtrate quality is very similar to the pre-treated PDW characteristics, which was previously used as the NF feed. Recalling that the flux decline levels were not severe with the PDW feed of quality similar to that of ADBW, which was pre-treated by MF (1.0 μm), it was decided to change the MF pore size from 0.45 μm to 1.0 μm in the pre-treatment stage of ADBWs. Therefore, all the ADBW mixtures and samples that were going to be used in the NF separation experiments were filtered through the MF (1.0 μm) media and the results are shown in Table 6.26.

Table 6.25. Comparison of MF (0.45 μm) and MF (1.0 μm) Performances

Process	Effluent Color (Pt-Co)	Color Removal (%)	Effluent Turbidity (NTU)	Turbidity Removal (%)	Filtration Rate (L/h)
MF (0.45 μm)	6	94	1	91	5
MF (1.0 μm)	33	69	2.7	76	60

Initial Color=102 Pt-Co, Initial Turbidity=11 NTU (ADBW Mixture 3)

Table 6.26. The Characteristics of ADBWs Pre-treated with MF (1.0 μm)

Parameter	MF (1.0 μm) Filtrate Quality			Removal (%)		
	Mix 3	Mix 4	Sample 42	Mix 3	Mix 4	Sample 42
COD (mg/L)	918 ± 9	1394 ± 14	1832 ± 7	10	1	5
UVA $_{200}$	3 ± 0	2.95 ± 0	3.15 ± 0	3	4	3
Color (Pt-Co)	20 ± 1	19 ± 1	33 ± 1	81	82	35
Turbidity (NTU)	1.1 ± 0	0.9 ± 0	3.2 ± 0	90	77	3
T. Solids (mg/L)	802 ± 1	909 ± 4	1204 ± 88	2	5	3
T. Hardness (mg/L as $CaCO_3$)	22 ± 0	44 ± 0	18 ± 0	8	0	9
Conductivity (μS/cm)	635	748	806	0	3	0
pH	4.76 ± 0	4.82 ± 0	5.30 ± 0			

6.2.2. Treatment of ADBWs

In order to achieve water recovery from the acid dye bath wastewater stream, NF was applied in TRMF and CMF tests. UF was not considered for ADBW recovery, since even the NF process had poor performance as compared to the results obtained for PDWs by the same NF membrane, especially for COD. In selecting the treatment alternatives, the results obtained in one alternative lead to the consideration of the next one. Accordingly, the following alternatives were considered:

1. Single NF,
2. Sequential NF with two NF stages,
3. Sequential NF with three NF stages,
4. Single NF with pH neutralization.

6.2.2.1. Single NF

The ADBW Mixture 3, which was pre-treated by MF (1.0 μm), was subjected to NF in a TRMF test first (VRF=1). The UVA and flux changes were recorded during the experiment and depicted in Figure 6.43 and 6.44, respectively. The UVA removal was around 60%, which was very close to the COD removal efficiency of 65% as shown in Table 6.27. Total solids removal efficiency was also low (57%) as compared to that achieved for PDW (around 90%) by the same NF membrane. Since color and turbidity were completely removed, some of the remaining materials in wastewater, which were measured as total solids, were thought to be the sodium salts, which are present in the structure of the acid dyes. Since the acid dyes ionise to a negatively charged anion in water, Na^+ may be released into the wastewater, which can easily permeate through the NF membrane due to its small size. Similarly, low removal of hardness causing cations (Ca^{2+}, Mg^{2+}) may have contributed to the total solids content of the NF permeate.

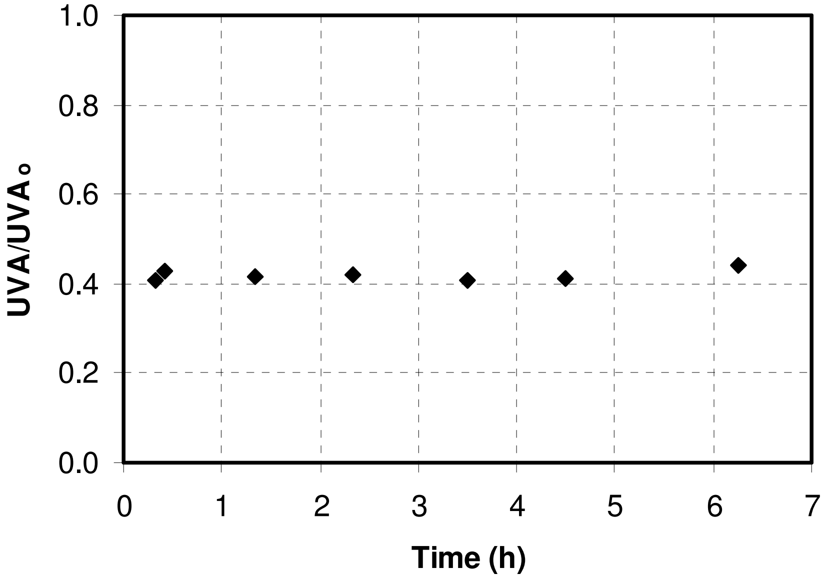


Figure 6.43. Change of UVA/UVA $_o$ in Single NF For ADBW Mixture 3

Table 6.27. Single NF Performance for ADBW Mixture 3

Parameter	NF Permeate Quality	Removal (%)
COD (mg/L)	310	65
Color (Pt-Co)	0	100
Turbidity (NTU)	0.24	92
T. Solids (mg/L)	332	57
T. Hardness (mg/L)	9	59
Conductivity (µS/cm)	316	48

The flux declines are shown in Figure 6.44. As seen, the initial wastewater flux was slightly higher than the clean water flux, which may indicate irreversible swelling of the membrane when exposed to the wastewater. The wastewater flux stabilized within 1 h. In addition, no flux decline was detected in a filtration period of almost 7 h.

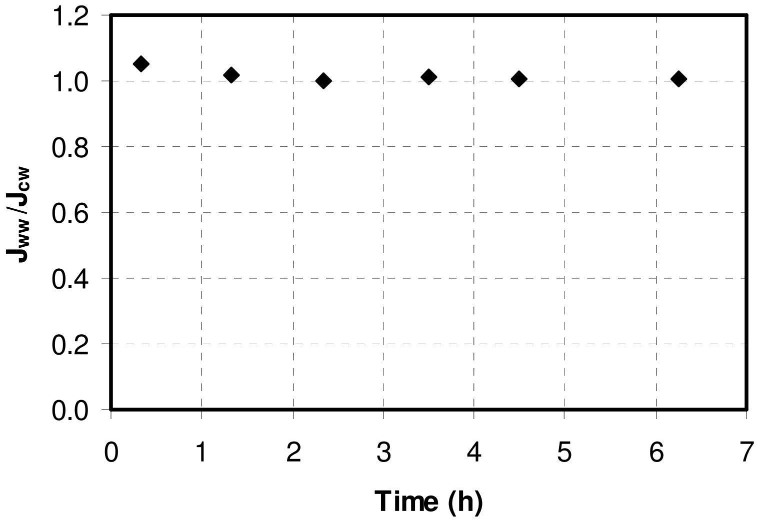


Figure 6.44. Change of Relative Flux Decline in Single NF for Mixture 3

The quality of the ADBW permeate was compared to the BTTG reuse criteria and the actual process water quality (Table 6.28). The permeate quality met the BTTG reuse criteria and the actual process water quality was also satisfied. The turbidity of the NF permeate, which was 0.24 NTU was slightly higher than that the actual process water, however it is already a very low value of turbidity, and hence can safely be accepted.

Table 6.28. Evaluation of the NF Permeate Qualities

Evaluation Reference/ Applied Process	**Reuse Criteria/Permeate Quality**			
	Color (Pt-Co) *	**Turbidity (NTU)**	**Dissolved Solids (mg/L)**	**Total Hardness (mg/L)**
BTTG	5	15	500	60
Actual process water	1	0.15	446	11
NF Permeate (Mixture 3)	0 ± 0	0.24 ± 0	328 ± 25	8 ± 0

*The unit of color is AU (absorbance units) for BTTG

Although NF was applied to ADBW under the same experimental conditions of PDW, the significant difference between their performances was interesting. The reason for the poorer performance of NF for the ADBW needed to be figured out in order to be able to develop the best process train for the recovery of this wastewater.

The first reason for the low removal efficiencies was suspected to be due to the wetting of the NF membranes with isopropanol for increasing flux before the experiments conducted with ADBW since these membranes originally had very low or no flux. The possibility of causing the pores to be opened by isopropanol was questioned. In order to understand whether this was the case or not, experiments were conducted with NF membranes that were wetted and not wetted by isopropanol. The comparison of the performances of these membranes for ADBWs and PDWs revealed that wetting by isopropanol was not responsible for the poor membrane performance but only helped increase the fluxes (Appendix F). Thus, there had to be some other reasons for the poor performance of the NF membrane for the treatment of ADBW, which can be listed as follows:

1. Higher load (ADBW is more polluted than PDW in terms of organic matter),
2. Different component size and distribution (ADBWs and PDWs contain different types of dyes and chemicals),
3. Different pH (ADBW is acidic whereas PDW is neutral)
4. Combined effects of some or all the above factors.

In order to understand whether the reason for poor performance was due to the higher load, it was decided to subject the ADBW to a series of NF processes, so that the feed COD would decrease at each additional NF stage, and the effect of feed COD on the membrane performance could be observed for varying feed COD levels. All the experimental results are presented in the following sections.

6.2.2.2. Sequential NF

The sequential NF process was applied in three stages, where the experiments simulating the first and the second stages were conducted in CMF tests so that the permeate of each stage could be used as the feed in the following stage. The third stage, being the last step, was performed in a TRMF test. The volume reduction factors were also calculated as shown in Table 6.29.

Table 6.29. Volume Reduction Factors (VRF) For Sequential NF of ADBW

NF Stage	**Feed Volume (L) (V_f)**		**Retentate Volume (L) (V_r)**	**VRF** $\frac{(V_{fi} - V_{fs})}{V_r}$
	Initial (V_{fi})	**Sampled for Analysis (V_{fs})**		
1. Stage	40	3.5	2.7	13.5
2. Stage	20	2.5	1.8	9.7

6.2.2.2.1. First Stage NF

In the CMF test simulating first stage NF, Mixture 4 was used where the feed and the permeate were sampled eight times; and at each sampling, 500 mL of wastewater was collected for the analyses. A VRF of 13.5 was achieved in the first stage NF (Table 6.29). The change of UVA values and the reduction of feed volume are depicted in Figure 6.45. As seen from the figure, the permeate UVA values were almost constant in the first 5 h of filtration period, and then they started to increase. On the other hand, the feed UVA values were almost constant in the first 15 h of the filtration period, and a steep increase was observed after this time. This behavior of the membrane for ADBW was different than in the case of PDW, where the PDW feed UVA values remained almost constant throughout the experiment lasting for 50 h. Therefore, the UVA causing compounds in ADBW, which were rejected by the NF membrane were supposed to return back the feed side instead of accumulating on the membrane.

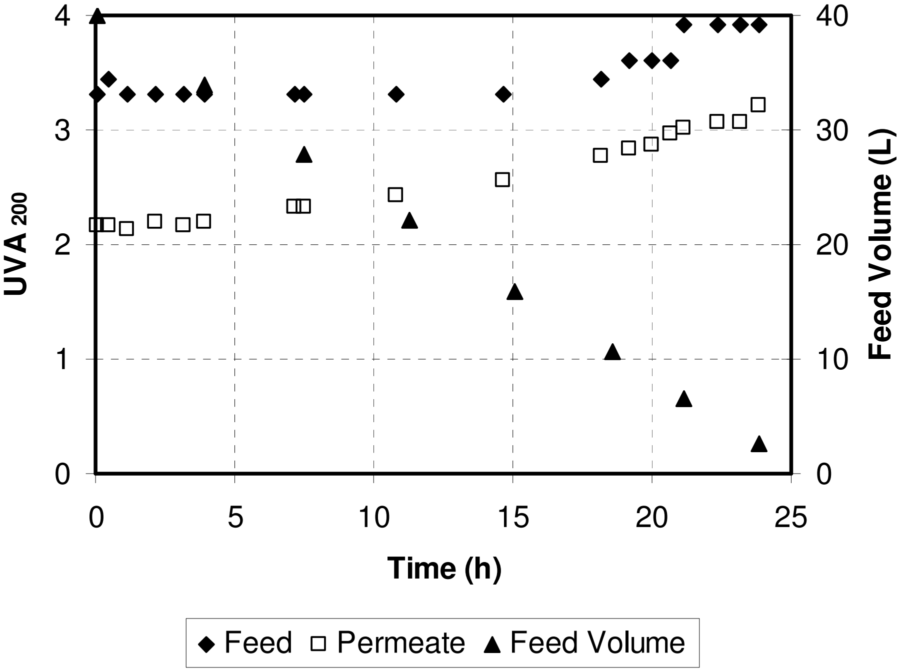


Figure 6.45. Change of UVA and Feed Volume in the First Stage NF

The performances of the first stage NF for all the parameters are depicted in Figures 6.46 to 6.51. As shown in Figure 6.46, the feed COD level increased from 1245 mg/L up to 5049 mg/L, whereas the permeate COD level increased from 460 mg/L to 691 mg/L only. The initial removal efficiency of 63% increased to 86% at the end of the experiment due to the four-fold increase in the feed COD content. Although the ADBW feed COD level was three times higher than that of the PDW, the ADBW permeate COD level was almost ten times higher than the PDW permeate COD level. On the other hand, the NF membrane performance for color and turbidity was very high for ADBW, producing a permeate without color and having a turbidity of 0.15 NTU (Figures 6.47 and 6.48).

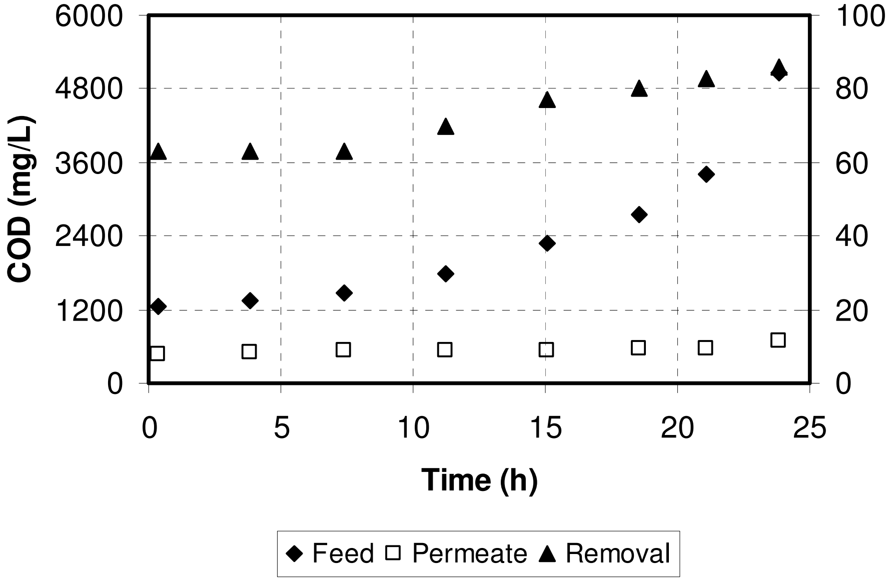


Figure 6.46. COD Removal Performance of the First Stage NF

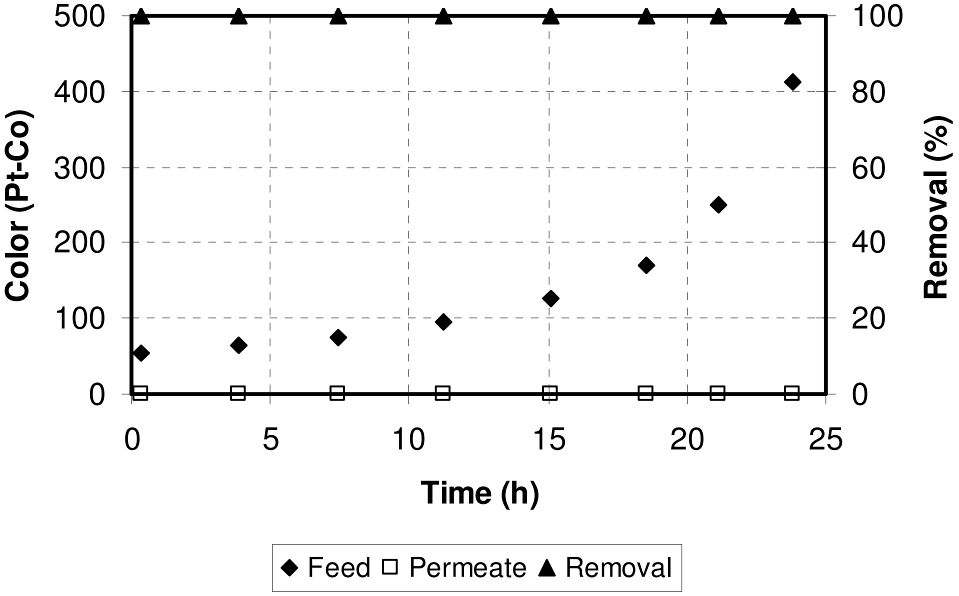


Figure 6.47. Color Removal Performance of First Stage NF

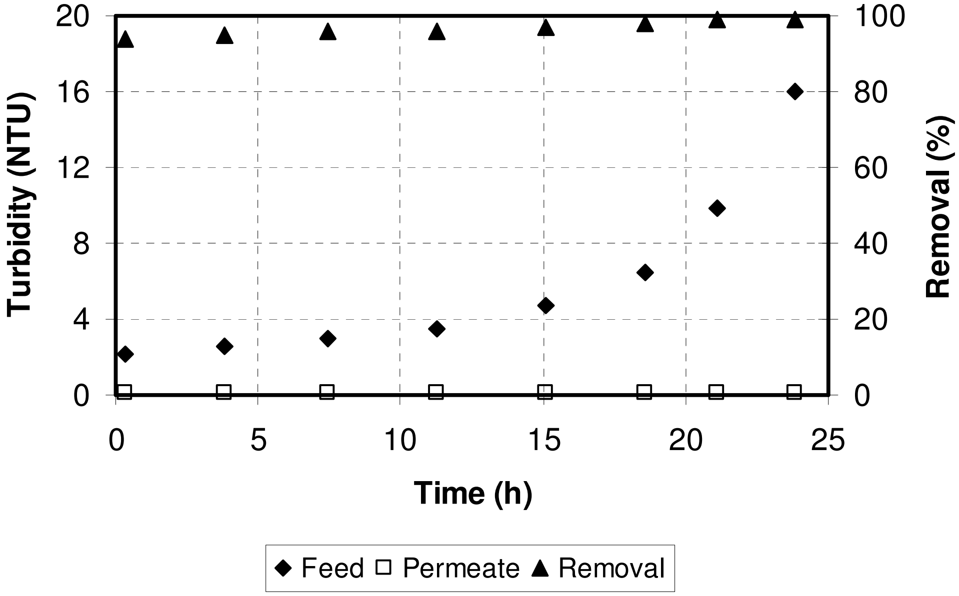


Figure 6.48. Turbidity Removal Performance of First Stage NF

The total solids removal performance of NF followed the same trend as its COD removal performance; it started with 52% and reached to 80% due to the four-fold increase of the feed content (Figure 6.49). The total solids content of the permeate reached the BTTG reuse criteria of 500 mg/L when a permeate volume of 16.4 L was collected, which corresponds to a VRF of 1.8. The total solids was 700 mg/L at the permeate at a VRF of 13.5.

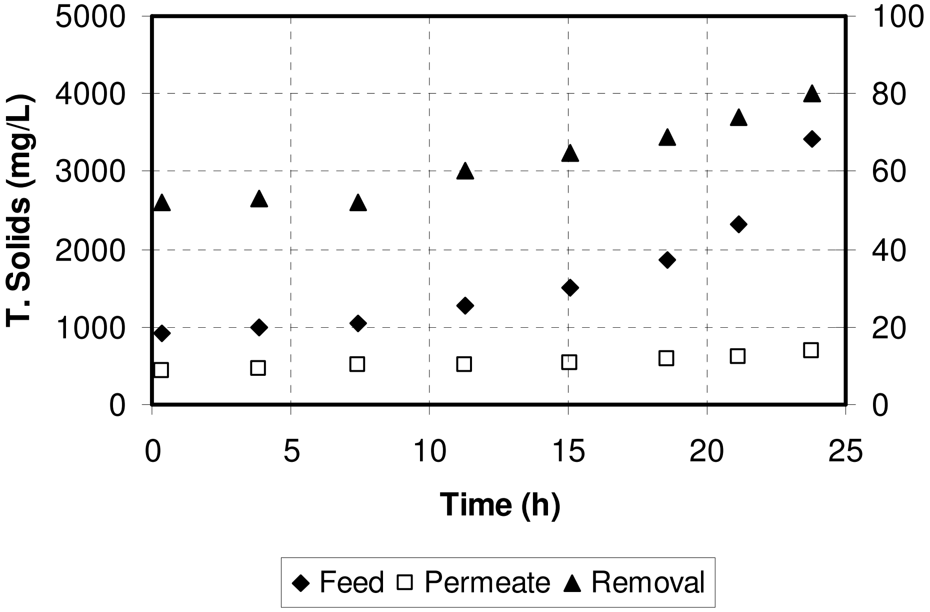


Figure 6.49. T. Solids Removal Performance of First Stage NF

Total hardness removal efficiency varied from 73% to 87%, resulting in an permeate total hardness content of 12-30 mg/L with increasing VRF from 1 to 13.5, which is well below the BTTG reuse criteria of 60 mg/L (Figure 6.50). However, the actual process water contained 11 mg/L of total hardness, and the permeate total hardness was already 12 mg/L at a VRF of 1. The performance of NF for the removal of hardness causing ions was realized to be worse for ADBW than for PDW. Complete removal of total hardness had been achieved by the same NF process for PDWs. Although ADBW feed had a total hardness of 44 mg/L, which was higher than the PDW feed hardness of 11 mg/L, the reason for the worse rejection for hardness causing cations in ADBW cannot be the higher feed concentration. Because the hardness rejection was still 100% when the PDW feed hardness content increased from 11 mg/L to 44 mg/L in concentration mode. However, the ADBW permeate had 12 mg/L of total hardness at the same feed hardness level of 44 mg/L.

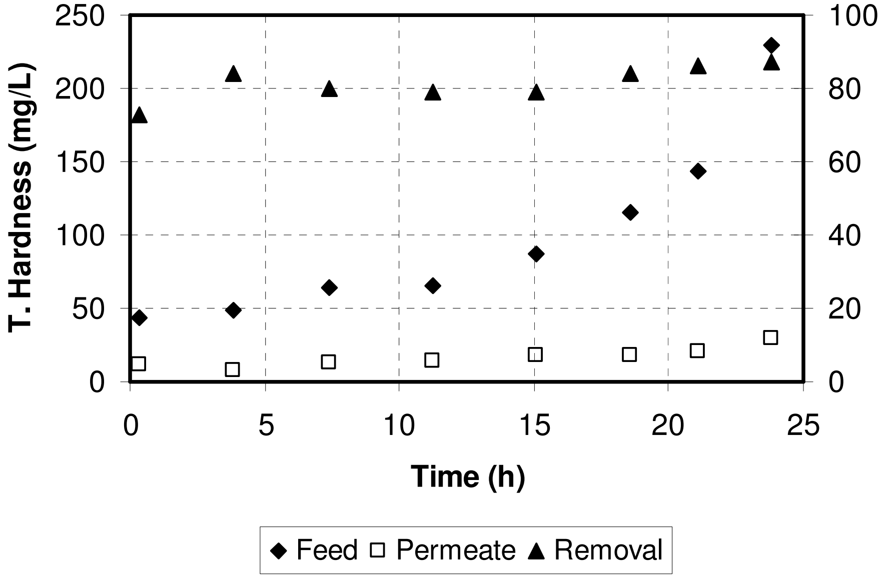


Figure 6.50. T. Hardness Removal Performance of First Stage NF

The conductivity rejection varied from 39% to 61%, with the feed content increasing from 770 µS/cm to 1900 µS/cm. Although the conductivity of ADBW feed was very close to that of PDW originally, the increase of the feed conductivity with respect to increasing VRF was less for ADBW. The PDW feed conductivity increased up to 3800 µS/cm at a VRF of 11.8, which was twice the ADBW feed content at a VRF of 13.5. This is because of the higher rejections achieved for PDW, resulting in a more concentrated feed stream. Since the ADBW was not treated as good as the PDW, the NF membrane allowed the conductivity causing ions to pass through, creating a more polluted permeate stream, and hence a less concentrated feed stream (Figure 6.51).

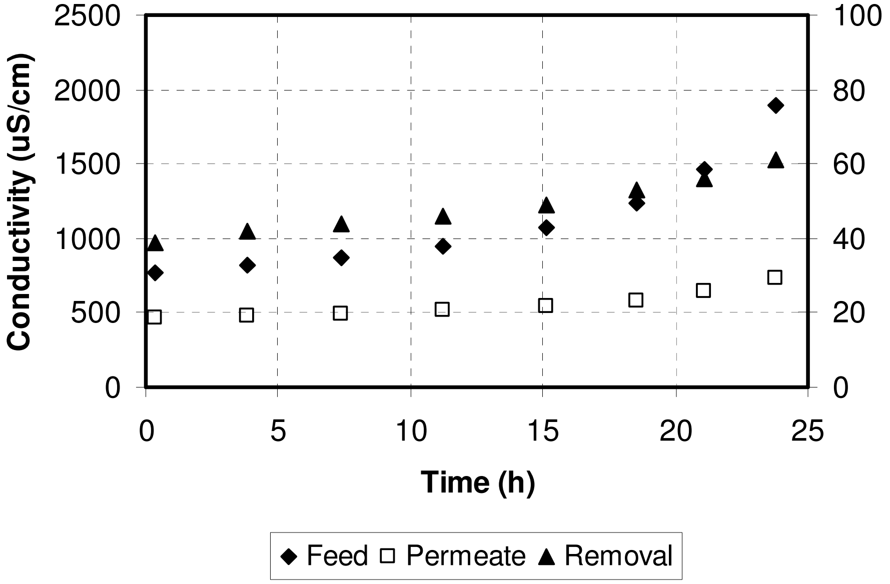


Figure 6.51. Conductivity Removal Performance of First Stage NF

The pH of ADBW was about 5 and increased to about 6 in the feed stream during filtration (Figure 6.52). The pH change for the permeate followed a similar trend and increased to about 5.5. Like in the PDW treatment, the permeate pH increased towards the feed pH, with the exception that it became slightly basic in PDW whereas it was slightly acidic in ADBW.

The wastewater flux decline is presented in Figure 6.53. As shown, the flux decline started at 6% and remained constant in the first 4 h. Then the wastewater flux increased to 22.5 L/m^2.h, which was greater than the clean water flux of 22.1 L/m^2.h. After a filtration period of 11 h, the flux decreased again, and the flux decline occurred as 21% at a VRF of 13.5 (Figure 6.53). These flux decline levels of 6-21% observed for ADBW were lower than those observed for PDWs, which had been recorded as 16-31%.

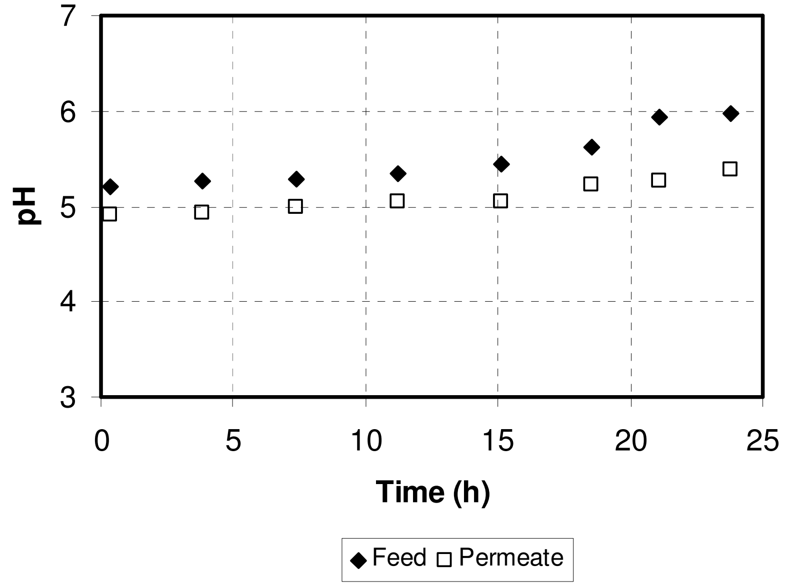


Figure 6.52. The Change of pH in First Stage NF

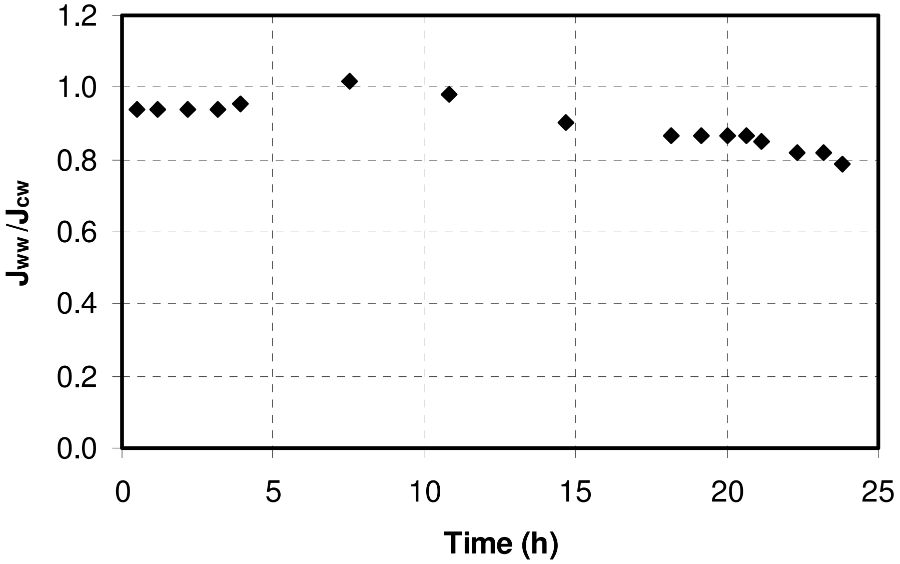


Figure 6.53. Change of Relative Flux in First Stage NF

The performances of the NFT-50 membrane obtained for ADBW in the TRMF and CMF tests were in general similar. In the CMF test, the initial rejection efficiencies of COD, total solids and total hardness, which were around 60%, were observed to increase up to 80-90% as the flux decline increased from 6% to 21%. The increase in the rejections can be explained by the change in the selectivity of the NF membrane. The higher molecular weight compounds that are rejected completely, i.e., color and turbidity causing compounds, form a kind of second or dynamic membrane on the membrane surface, which results in higher rejection for the lower molecular weight solutes, i.e., acetic acid, Ca^{2+}, Mg^{2+}, Na^{+}. Since the rejections of pollutants were all very high for PDW from the start to the end of the CMF test (Table 6.30), the change of the selectivity and hence the increase of rejections was not observed.

Table 6.30. Comparison of Single Stage NF Performance for ADBW and PDW

Parameter	**VRF**	**Permeate Quality**		**Removal (%)**	
		ADBW	**PDW**	**ADBW**	**PDW**
COD (mg/L)	1	460	11	63	98
	12-14	691	54	86	98
Color (Pt-Co)	1	0	0	100	100
	12-14	0	1	100	98
Turbidity (NTU)	1	0.13	0.20	94	93
	12-14	0.14	0.25	99	91
T. Solids (mg/L)	1	433	25	52	96
	12-14	700	256	80	92
T. Hardness (mg/L as $CaCO_3$)	1	12	0	73	100
	12-14	30	0	87	100

6.2.2.2.2. Second Stage NF

The second NF stage in sequential NF was applied under the same experimental conditions of the first one. The purpose of applying the second NF was to understand whether the low removal of organic matter was due to the high organic load of the ADBW or not. The change in UVA of the feed and the permeate streams and feed volume are depicted in Figure 6.54. As seen, the feed and permeate UVA values in the second stage are much lower than those in the first stage. Unlike the first NF stage, the UVA values in the feed and the permeate of the second NF started to increase immediately and the feed UVA reached its original value at the end of a filtration period of 10 h. The parallel trend in the increase of feed and permeate UVA values indicated that there was less accumulation of material on the membrane surface as compared to the first stage NF. This was an expected result since the first stage had already removed a significant fraction of the pollutants.

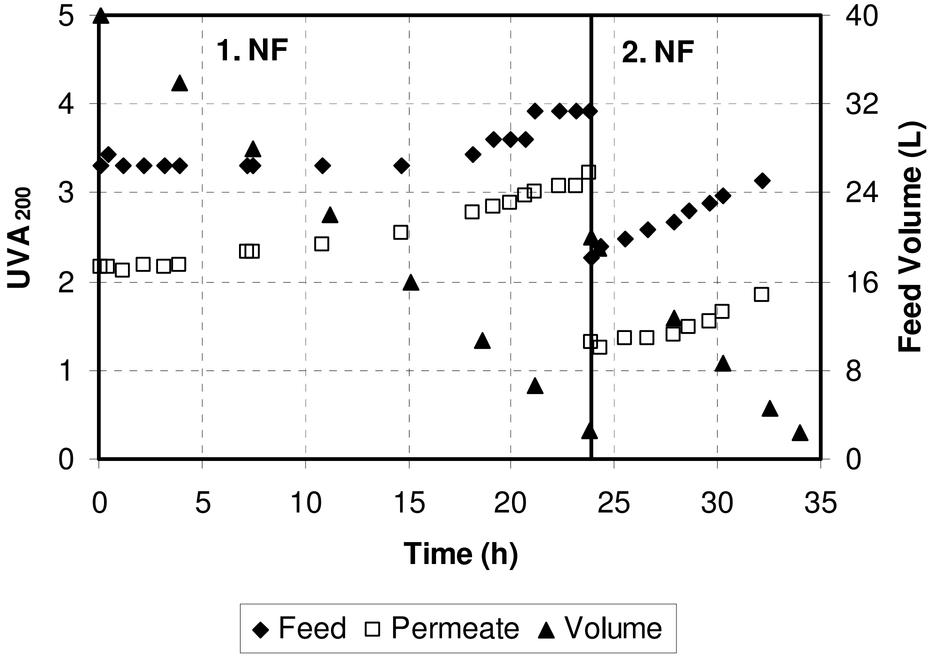


Figure 6.54. Change of UVA and Feed Volume in First and Second Stage NF

Figure 6.55 presents the change of COD at the feed and the permeate sides, where the removal performance was observed to be 63-86% in first stage NF. An additional COD removal of 31-42% was achieved in second stage NF, yielding a total COD removal of 71% and a permeate COD content of 356 mg/L. The additional COD removal observed in the second stage indicates that the higher organic load of the ADBW is a factor affecting the separation performance of the NF membrane. In order to understand whether this was the only factor or not, the separation performances of ADBW and PDW were compared (Table 6.31).

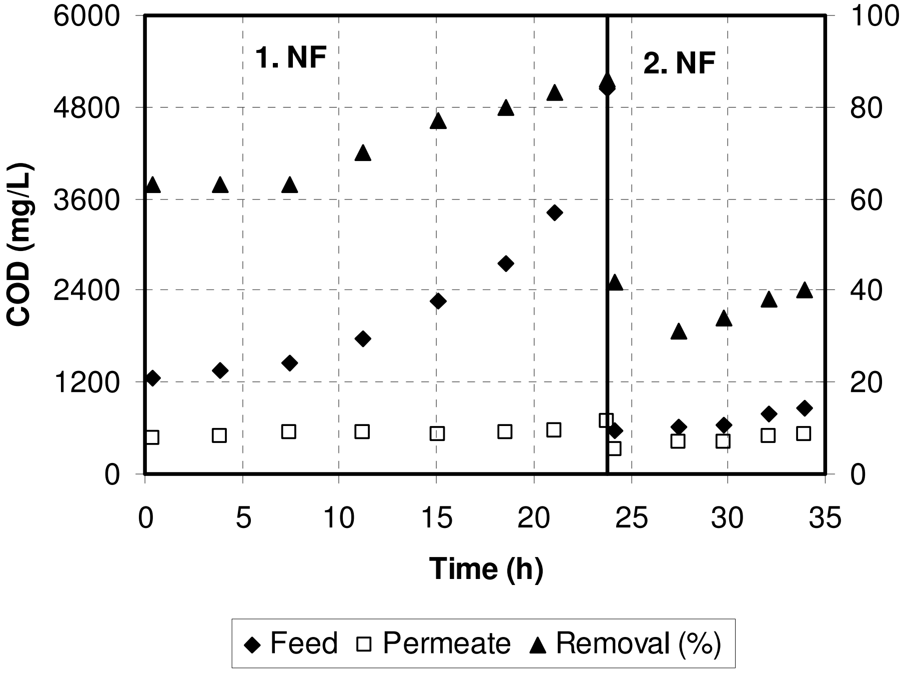


Figure 6.55. COD Removal Performance of First and Second Stage NF

As seen from Table 6.31, the permeate COD contents of the two wastewaters are not the same at the same feed COD contents. When the feed COD level increased to 1258 mg/L in the PDW, the permeate COD was 39 mg/L. However, the permeate COD of the ADBW was as high as 460 mg/L at a feed COD level of 1245 mg/L. The situation is similar at lower feed COD levels such that; the permeate COD was only 26 mg/L at a feed COD of 535 mg/L for PDW, whereas the permeate COD was 327 mg/L at a feed COD of 560 mg/L for ADBW in the second NF stage. At both low and high feed COD conditions, the ADBW permeate COD was more than ten times higher than the PDW permeate. Therefore it is obvious that the higher COD load of ADBW is not the only factor causing the poor separation performance of NF, and the component size and distribution of the ADBW also affects the NF performance.

Table 6.31. COD Removal Performances of Single NF for PDW and ADBW

Wastewater	**VRF**	**COD (mg/L)**		**Removal**
		Feed	**Permeate**	**(%)**
PDW (Mixture 3)	1.0	445	11	98
	1.2	380	13	97
	1.5	535	26	95
	2.0	742	33	96
	2.6	863	30	97
	4.1	**1258**	**39**	**97**
	6.1	1638	43	97
	11.8	2330	54	98
ADBW (Mixture 4)	1.0	**1245**	**460**	**63**
	1.2	1356	501	63
	1.4	1460	540	63
	1.7	1782	542	70
	2.4	2266	526	77
	3.5	2761	550	80
	5.6	3416	569	83
	13.5	5049	691	86

As shown in Figures 6.56 and 6.57, the removal performances for color and turbidity were perfect for ADBW. The permeate was colorless in the first NF stage and had almost no turbidity. Therefore, the feed to the second stage NF had initially no color and turbidity at all. However, color and turbidity of the feed slighly increased during the test. The low removal efficiencies obtained for these parameters in the second stage therefore did not mean poor performance.

Total solids removal, which was 52-80% in the first stage NF, further increased at the second stage by 31-42%. The total solids separation performance followed the same trend of COD removal performance in the sequential application (Figure 6.58). The permeate of second stage NF had a total solids content of 432 mg/L. This is much lower than the permeate of the first stage NF, which was measured as 635 mg/L. Therefore, the permeate quality met the BTTG reuse criteria of 500 mg/L of dissolved solids only after second stage NF.

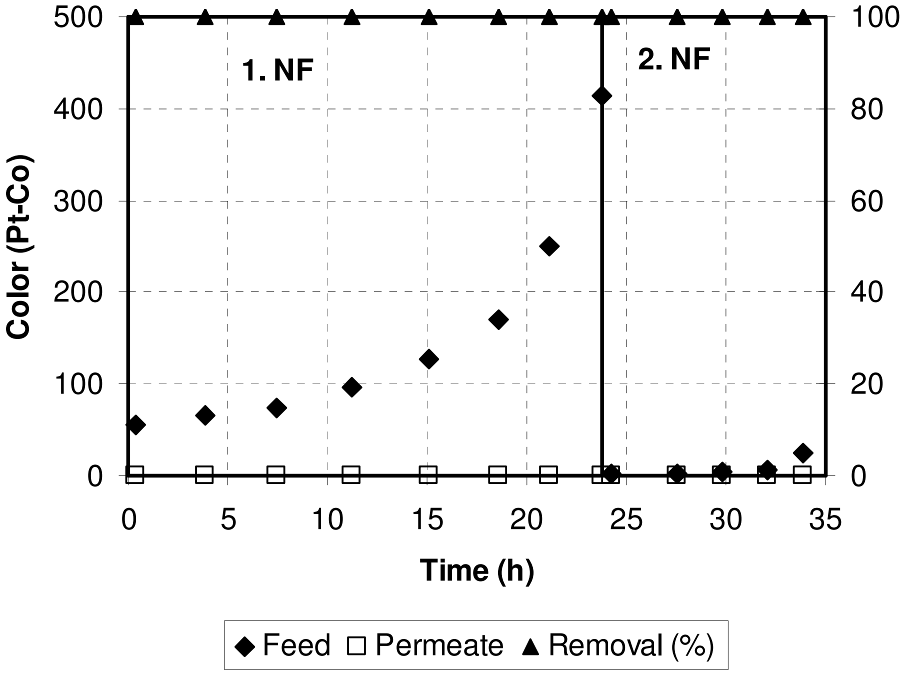


Figure 6.56. Color Removal Performance of First and Second Stage NF

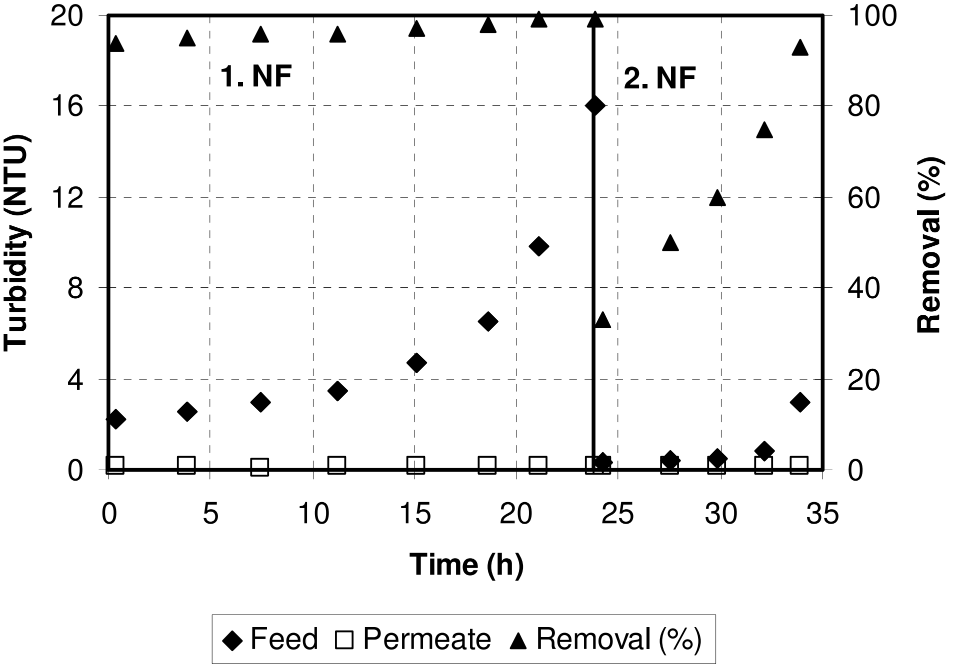


Figure 6.57. Turbidity Removal Performance of First and Second Stage NF

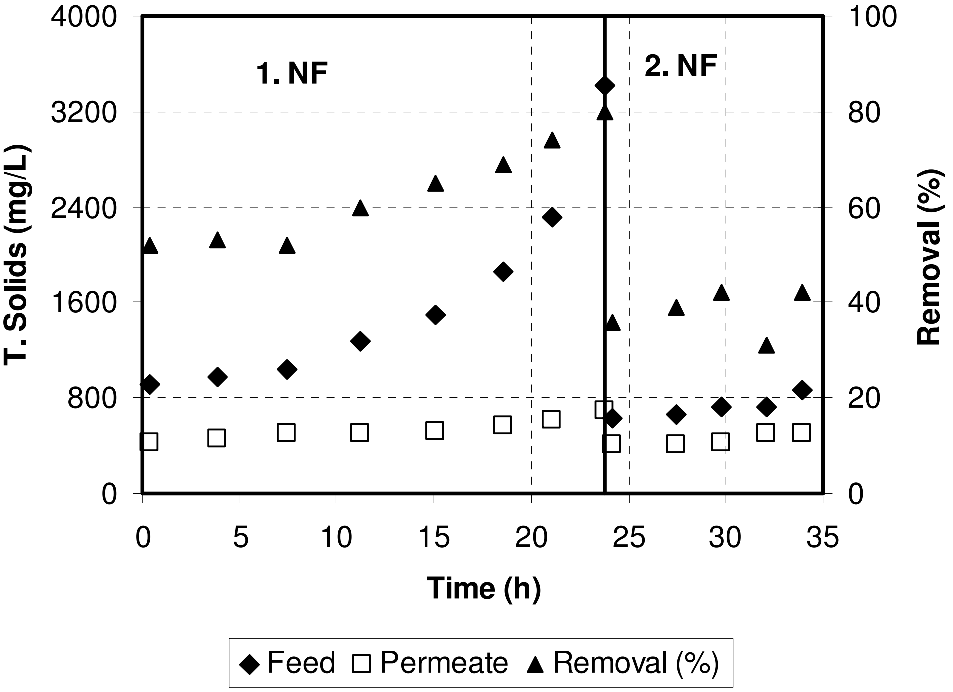


Figure 6.58. T. Solids Removal Performance of First and Second Stage NF

The total hardness removal efficiency was higher in the first NF than in the second one since the feed of the second NF had a low hardness content, resulting in a lower removal efficiency (Figure 6.59). The first stage permeate contained 12 mg/L of total hardness, which is below the BTTG reuse criteria of 60 mg/L. Therefore the second stage NF is not required to satisfy the reuse criterion for total hardness.

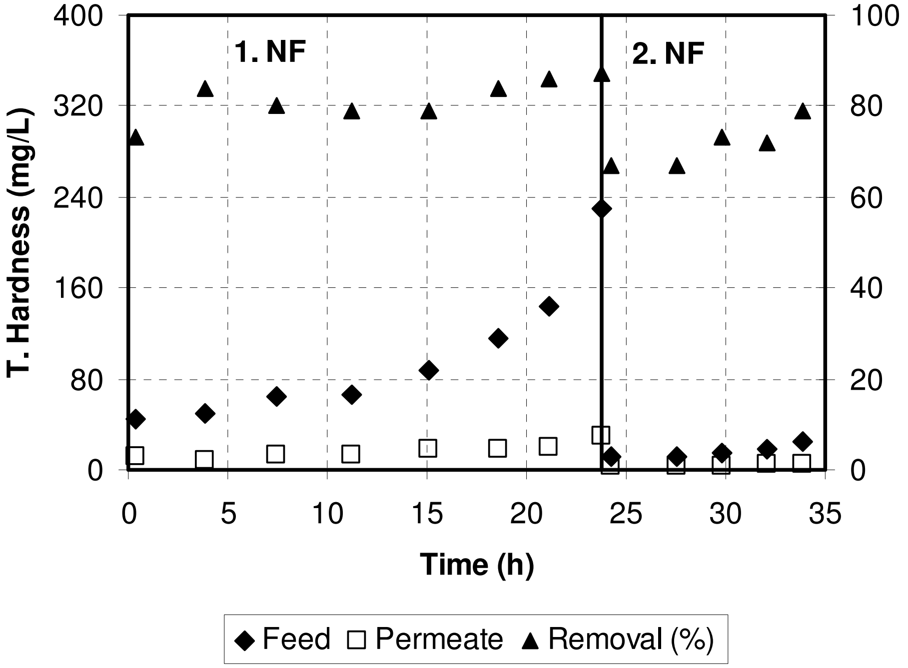


Figure 6.59. T. Hardness Removal Performance of First and Second Stage NF

The performance of single NF was better for PDW, with complete rejection of the hardness causing ions. The difference in the separation performances for these wastewaters is possibly originating from their different pH values; the PDW has almost neutral pH whereas ADBW has acidic pH due to its acetic acid content. The effect of feed pH on the separation performance of the NF membranes for ions is reported in literature (Hagmeyer and Gimbell, 1998; Childress and Elimelech, 2000; Ozaki et al., 2002; Szoke et al., 2002; Tanninen and Nystrom, 2002). In a study, acetic acid rejection was reported to increase from 32% in the non-charged form at pH 3 to 100% in the negatively charged form (acetate ion) at pH 9, which is most likely due to electrostatic repulsion at the membrane surface. The increase in the rejection of acetate ion at pH values above the pK_a was most likely caused by the increasing negative surface charge of the membrane repulsing the negatively charged acetate ion (Ozaki and Li, 2002). These results emphasize the importance of solution pH on the membrane performance.

Figure 6.60 depicts the conductivity removal performance of sequential NF. The feed conductivity of 770 μS/cm was reduced to 490 μS/cm in the first stage and further reduced to 394 μS/cm in second stage NF, providing a total removal efficiency of 49%. On the other hand, single NF achieved a conductivity removal as high as 90% for PDW, producing a permeate conductivity of approximately 220 μS/cm. As in the case of hardness removal, the reason for the very different separation performance for these wastewaters is possibly due to the same effect of the feed pH. It may be possible that the separation of cations is adversely affected by the acidic pH of the ADBW.

The pH of the feed and the permeate monitored during sequential NF are depicted in Figure 6.61. The feed and permeate pH values were observed to be very close to each other in both stages, and they slightly increased at the first stage. However, the pH of the both streams did not increase significantly as in the case of PDWs and the permeate pH values did not exceed the feed pH values. This difference is probably due to the acidic pH of the ADBW, which might have changed the surface charge of the NFT-50 membrane. Qin et al. (2004) reported that feed pH significantly affected the permeate pH and ion rejection due to the change of membrane surface charge. They determined critical feed pH values for different solutions below which NF permeate pH was higher than the feed pH. These critical pH values were realized to be very close to the isoelectric point of the NF membrane used.

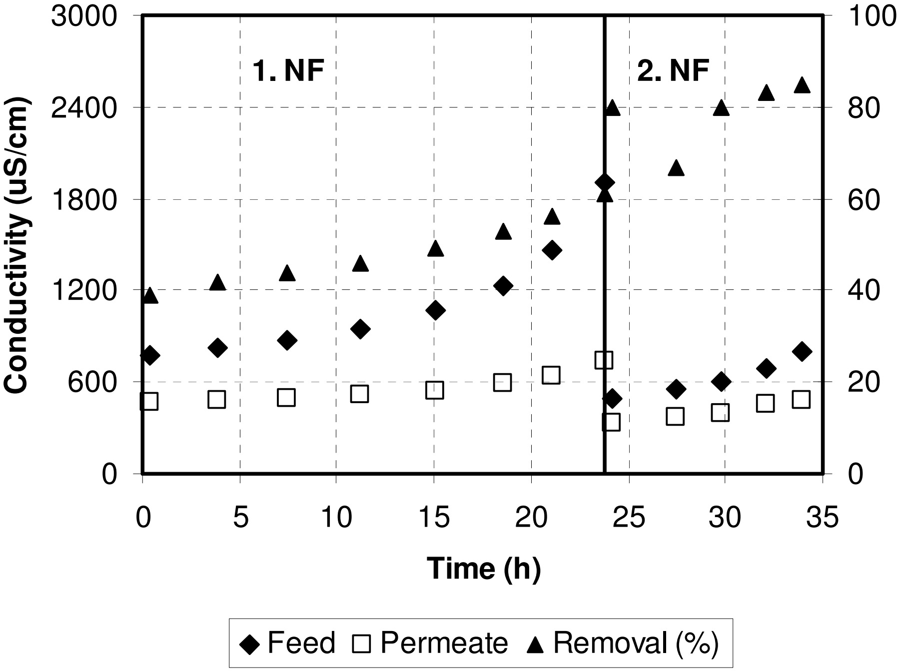


Figure 6.60. Conductivity Removal Performances of First and Second Stage NF

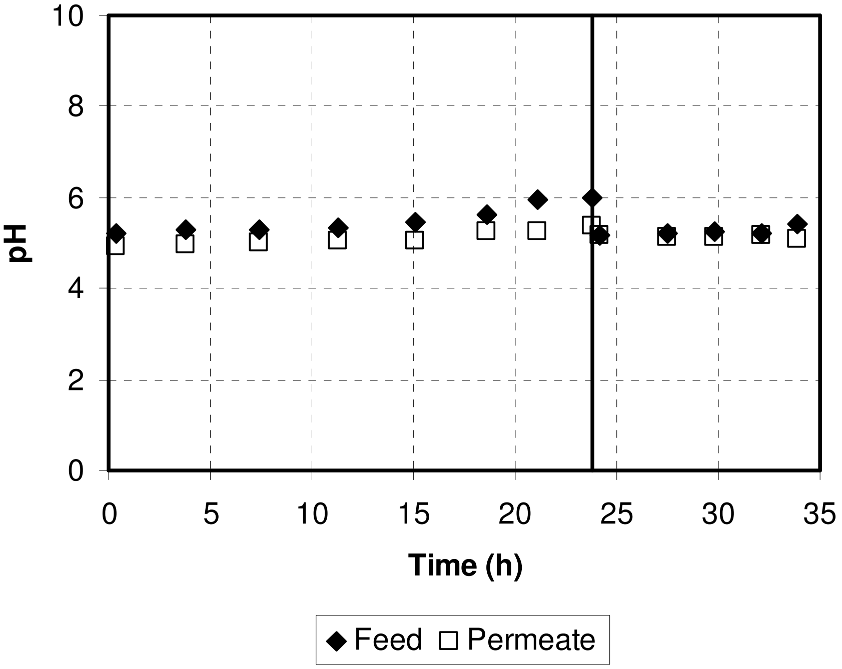


Figure 6.61. Change of pH in First and Second Stage NF

The relative flux decline levels observed during sequential NF are depicted in Figure 6.62. The flux decline occurred for a VRF of 13.5 was 21% at the end of the first stage NF, which is less than the flux decline of 31% observed during single NF for a smaller VRF of PDW, that is 11.8. The ADBW flux decline further reduced to 12% at the end of second stage NF, which is an expected outcome, since a less polluted feed is treated here. Therefore, it can be concluded that sequential application of NF is useful to extend the membrane cleaning cycles and hence provide a longer service life.

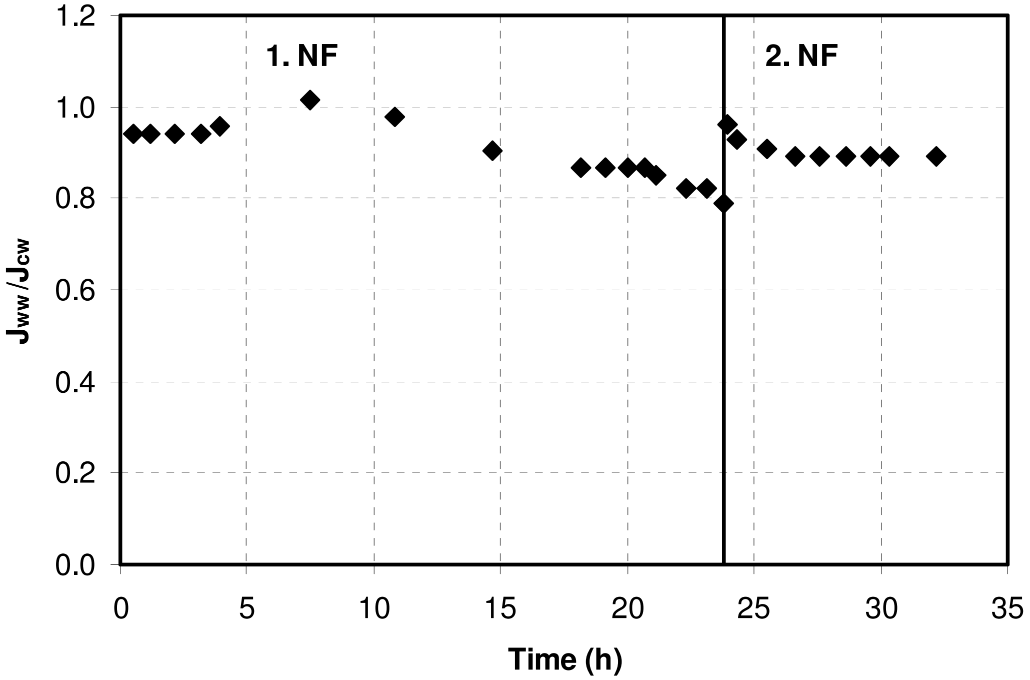


Figure 6.62. Change of Relative Flux in First and Second Stage NF

Although the permeate produced by sequential NF has acceptable quality in terms of reuse criteria, another NF stage was applied in order to figure out whether the organic compounds would be further removed by the NF membrane under the condition of reduced feed COD content. The results of the third stage NF are presented in the following section.

6.2.2.2.3. Third Stage NF

Third stage NF was applied in a TRMF test since it was the last stage in the sequential NF process. The UVA values monitored during the experiment are depicted in Figure 6.63. As seen from the figure, 50% removal of UVA was achieved in third stage NF. The removal performances observed for other parameters are shown in Table 6.32. All the parameters were further removed by third stage NF except color and turbidity, which were already completely removed in the second stage. COD removal was 79% with a permeate COD of 76 mg/L. This value is still higher than the permeate COD of 13 mg/L achieved by single NF for PDW having a similar feed COD of 380 mg/L (Table 6.31). This result again implied that the feed COD level is not the only factor resulting in the poor separation performance of NF but the detailed composition of the feed is also important. Another factor affecting the membrane separation performance was suspected to be the difference in the pH of these wastewaters.

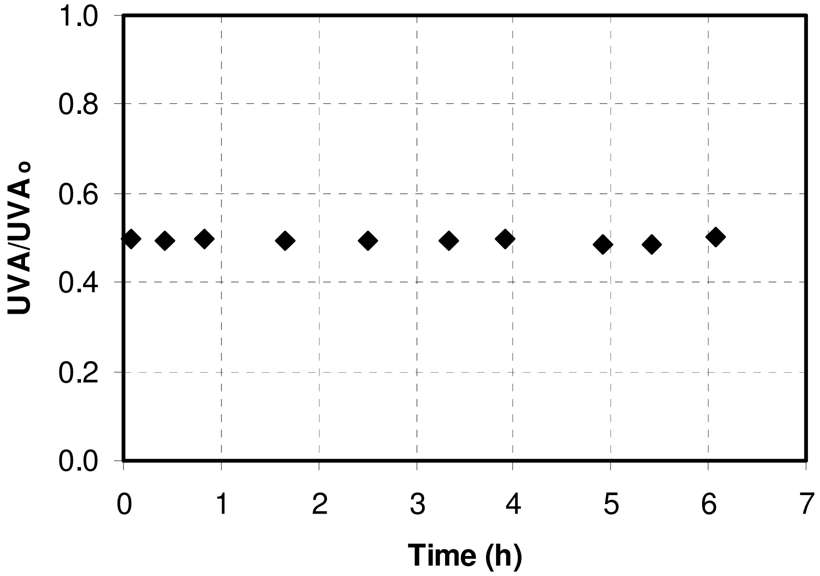


Figure 6.63. Change of UVA/UVA $_o$ in Third Stage NF

Table 6.32. Third Stage NF Performance for ADBW Mixture 4

Parameter	**ADBW Quality**		**Removal**
	Feed	**Permeate**	**(%)**
COD (mg/L)	356	76	79
Color (Pt-Co)	0	0	-
Turbidity (NTU)	0.18	0.14	22
T. Solids (mg/L)	432	277	36
T. Hardness (mg/L as $CaCO_3$)	0	0	-
Conductivity (µS/cm)	394	265	33

The flux decline was even reduced by the third stage NF from 12% to 9% (Figure 6.64). In order to investigate the effect of chemical cleaning on flux recovery, the cleaning procedure was applied before and after each stage in sequential NF and the data shown in Table 6.33 was obtained. As can be depicted, the cleaning procedure provided a complete recovery of the initial clean water fluxes of the NFT-50 membranes. Moreover, the initial clean water fluxes were exceeded after cleaning, which might have resulted from the increased hydrophilicity of the membranes or swelling due to exposure to chemicals. The low levels of flux declines and their complete restoration by the cleaning procedure implied that NF is a suitable process for the recovery of ADBW, provided that it is adopted in serial application.

The fractions of the total flux decline caused by concentration polarization and fouling were determined as 3% (F-W) and 6% (I-F), respectively. Since the clean water flux of the cleaned membrane (C) was greater than the initial clean water flux (I), reversible and irreversible fractions of fouling could not be calculated.

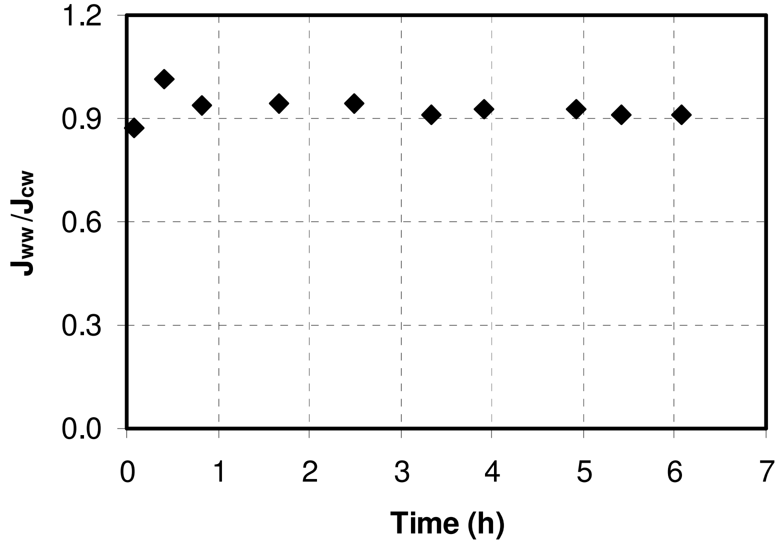


Figure 6.64. Change of Relative Flux in Third Stage NF

Table 6.33. Effect of Cleaning on the Flux Recovery in Sequential NF for ADBW

Process	**Permeance (L/m^2/h/bar)**				**Flux Decline (%) (Initial/Final)**
	Clean Water			**Wastewater (Initial/Final)**	
	Initial (I)	**Final (F)**	**Cleaned (C)**	**(W)**	**(I-W)**
1. Stage NF	3.8	3.9	4.1	3.5/3.0	6/21
2. Stage NF	4.1	4.0	4.0	4.0/3.7	4/12
3. Stage NF	3.7	3.5	4.5	3.4*	9

* Steady state permeance value

In summary, the ADBW was treated effectively by three stage NF and the permeate quality met the BTTG reuse criteria. However, PDW was treated with the same efficiency in single stage NF. Moreover, the COD content of the ADBW permeate was still higher than that of PDW. As mentioned before, the most remarkable difference between these wastewaters is pH, which is known to affect the membrane separation performance. Therefore, it was decided to test a new alternative for the treatment of ADBW, i.e., single stage NF after neutralizing the ADBW. If this new alternative would be successful, it would definitely lead to the development of a more practical and more attractive process train for the recovery of ADBW. The evaluation of this new alternative is presented in Section 6.2.3, which describes the effect of the pH on NF separation performance.

6.2.3. Effect of pH on NF Separation Performance

Since pH was thought to be an important operational parameter affecting the performance of the NFT-50 membranes based on the significantly different removal efficiencies for organic matter in ADBW and PDW, a few set of new TRMF tests were conducted using ADBW Mixture 4 and Sample 42 under neutral and acidic pH conditions, where pH adjustments were done by HNO_3 and NaOH. The UVA values were monitored for Mixture 4 (Figure 6.65). As seen from the figure, higher the pH, better was the UVA removal efficiency. The separation performances of single NF for other parameters are shown in Table 6.34. As seen, pH has a very significant effect on the removal performance of all the parameters except color and turbidity, which were almost completely removed anyway in all cases. Neutral pH condition was observed to provide very high removal efficiencies for COD, total solids, total hardness and conductivity. Therefore, neutralization of the ADBW improved the performance of single stage NF to the level achieved for PDW. A comparison of the permeate qualities indicated that PDW and ADBW can be treated to the same level at neutral pH (Table 6.35).

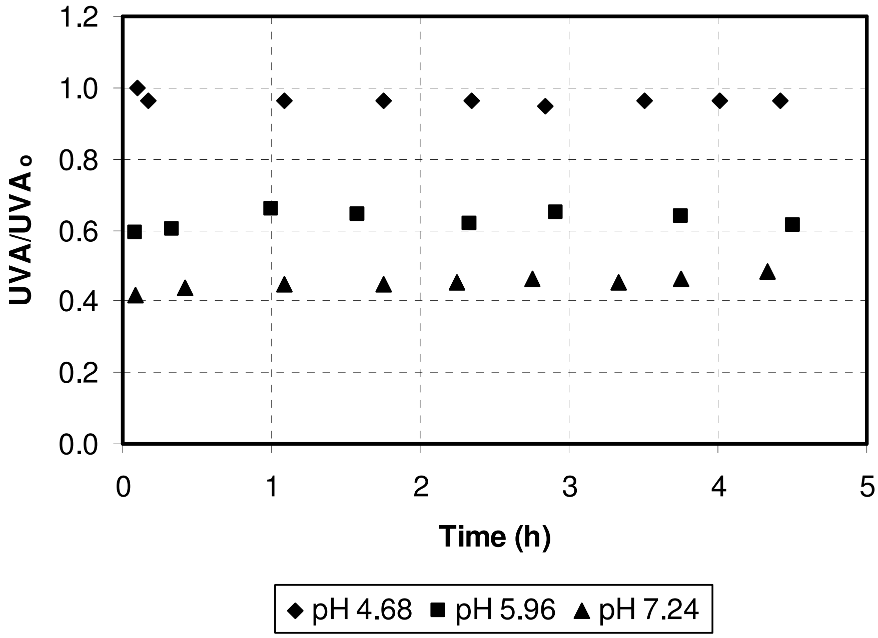


Figure 6.65. Effect of pH on UVA Removal Efficiency for ADBW Mixture 4

Table 6.34. Effect of pH on Single Stage NF Performance for ADBW Mixture 4

Parameter	**Removal (%)**		
	pH 4.68 *	**pH 5.96 ****	**pH 7.24 *****
COD	58	78	97
Color	100	100	100
Turbidity	98	98	92
T. Solids	47	74	94
T. Hardness	59	100	100
Conductivity	27	70	91

* HNO_3 ** original pH *** 1 mM NaOH

Table 6.35. ADBW and PDW Permeate Qualities in Single NF at Almost Neutral Feed pH

Parameter	Permeate Quality	
	ADBW	**PDW**
COD (mg/L)	36	19
Color (Pt-Co)	0	0
Turbidity (NTU)	0.16	0.24
T. Solids (mg/L)	60	75
T. Hardness (mg/L as $CaCO_3$)	0	0
Conductivity (µS/cm)	72	106
pH	6.85	8.65

The effect of pH on the wastewater flux decline was also considered, and the fluxes were monitored (Figure 6.66) under all pH conditions. Unlike separation performances becoming better at pH around neutral, the flux declines were observed to be lower at acidic pH. The flux decline was 8% for pH 4.68 whereas it was 23% and 20% for pH 5.96 and pH 7.24, respectively. These could be due to higher degree of removals causing stronger concentration polarization and/or thicker gel formation at pH of 6-7. Therefore adding nitric acid into the ADBW mixture seemed to influence the characteristics of the wastewater so that concentration polarization and/or fouling occurred to a lesser extent.

Depending on the results obtained under acidic and neutral pH for ADBW, it can be concluded that pH neutralization followed by single NF is a better treatment alternative as compared to sequential NF, which makes the process train much simpler and more attractive.

A detailed characterization of the NFT-50 membrane and the ADBW characteristics are required to exactly find out the reason for the positive effect of pH neutralization on the separation performance of NF. However, the low organic matter rejection at acidic pH may be due to the presence of acetic acid (CH_3CO_2H) in ADBW, which has a small molecular weight (60 Da) as compared to the MWCO of most NF membranes. Moreover, rejection of acetic acid is greatly influenced by the solution pH and the membrane surface charge (Ozaki and Li, 2002). Acetic acid is negatively charged at pH 4.8. The original pH of ADBW was around 4.8, indicating that acetic acid was in negatively charged form, i.e., the acetate ion ($CH_3CO_2^-$) in the wastewater, whose rejection is supposed to be due to the electrostatic interactions with the membrane surface charge. The surface charge of the NFT-50 membrane is accepted as negative at neutral pH based on the manufacturer information. Therefore, rejection of acetic acid at neutral pH is probably due to the repulsive forces between the membrane negative surface and the negatively charged acetic acid, which might have resulted in higher rejections of organic matter.

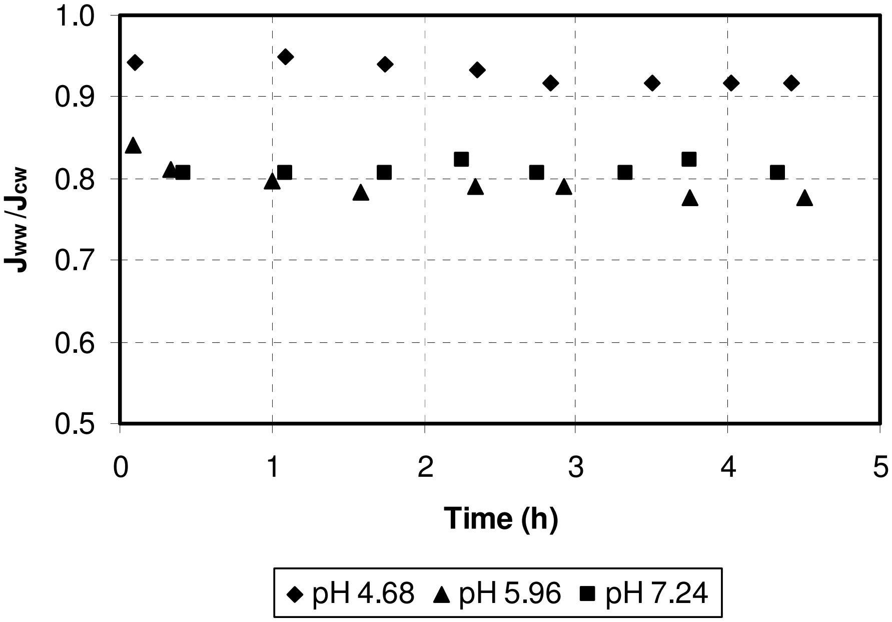


Figure 6.66. Effect of Feed pH on Relative Flux Change for ADBW Mixture 4

The dependence of COD removal on pH can be clearly seen in Figure 6.67, which plots the permeate COD as a function of pH with the data obtained in the all the experiments conducted with ADBW. A sharp decrease was observed in the permeate COD when the pH was increased from 5 to 7, which is a narrow range indeed. This graph clearly demonstrates the importance of pH as an operational parameter in the treatment of acid dye bath wastewaters of the carpet dyeing processes since the organic matter rejection efficiency is highly influenced by pH.

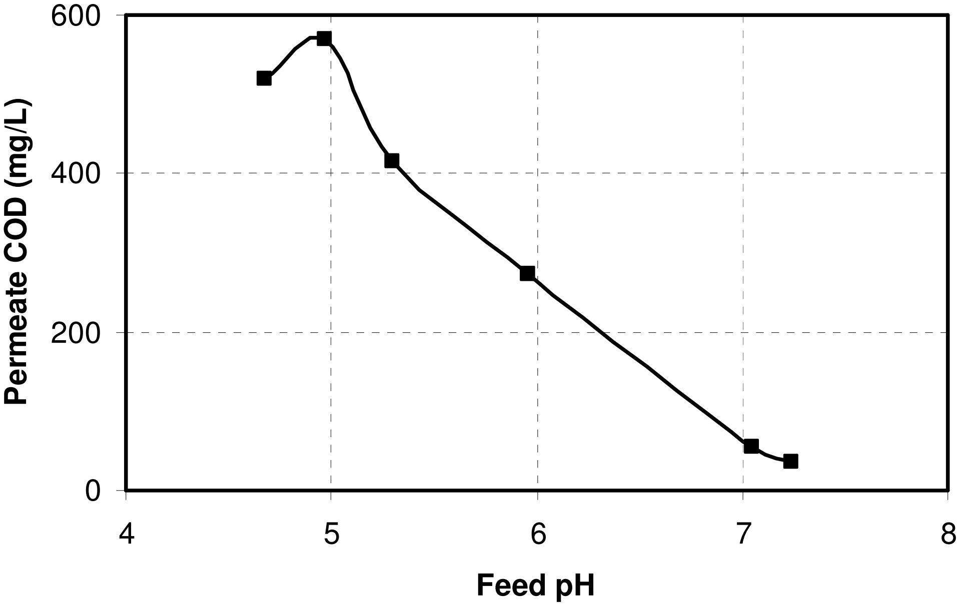


Figure 6.67. Effect of Feed pH on Permeate COD for ADBW

In order to understand whether the effect of pH would be the same on the filtration of individual samples of ADBW, the TRMF experiment was repeated for ADBW Sample 42 under acidic and neutral pH conditions. The change of normalized UVA values is depicted in Figure 6.68. As in the case of ADBW Mixture 4, the effect of pH was similar for the ADBW Sample 42. The UVA rejection increased from 35% to 55% by increasing the pH from 5.30 to 7.05. The removal performances of the NFT-50 membrane for other parameters are shown in Table 6.36. Similarly, better results were obtained for Sample 42 at neutral pH.

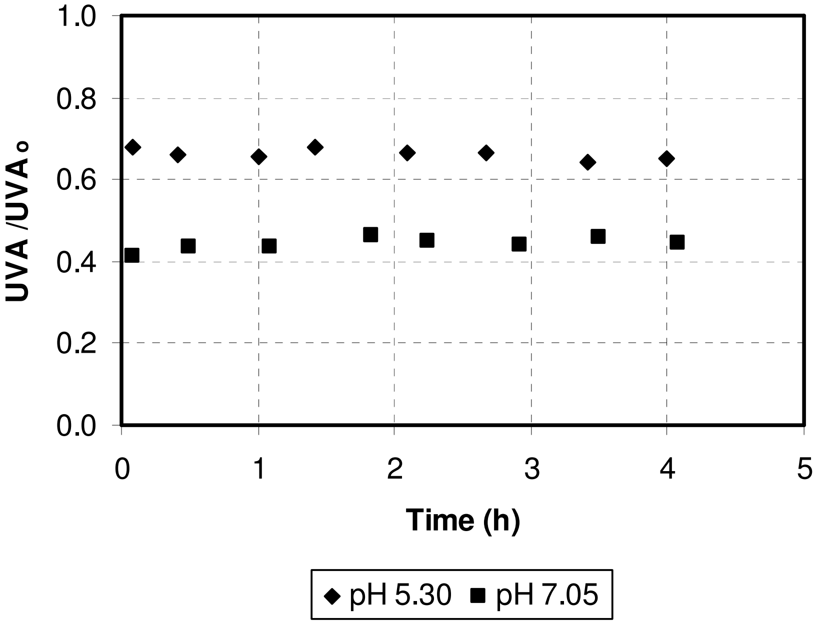


Figure 6.68. Effect of pH on UVA Removal Efficiency for ADBW Sample 42

Table 6.36. Effect of pH on Single NF Performance for ADBW Sample 42

Parameter	**Removal (%)**	
	@ pH 5.30 *	**@ pH 7.05 ****
COD	77	97
Color	100	100
Turbidity	94	96
T. Solids	56	93
T. Hardness	89	100
Conductivity	39	90

* original pH   ** 1.4 mM NaOH

Flux decline was also monitored during NF applied for Sample 42 (Figure 6.69). As shown, neutralization adversely affected the flux, and the flux decline increased from 14% to 25% when the pH was increased from 5.30 to 7.05. This result was also in agreement with the effect of feed pH on the flux declines observed for Mixture 4. Therefore, it was concluded that it is possible to treat the ADBW individual samples as efficiently as its mixtures by neutralizing the pH.

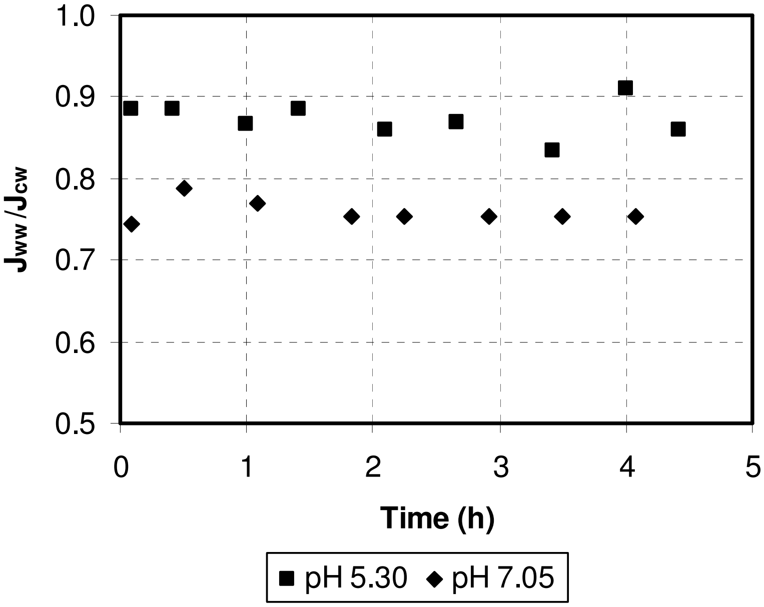


Figure 6.69. Effect of Feed pH on Relative Flux Change for ADBW Sample 42

The effect of cleaning on the recovery of clean water fluxes was also evaluated by performing cleaning procedure under all the pH conditions for Mixture 4 and Sample 42. As seen from Table 6.37(a), the fluxes (expressed as permeances) were restored by acidic and basic cleaning. Moreover, the permeances measured after cleaning generally exceeded the initial clean water fluxes, which indicates opening of the pores, resulting in more water passage through the membrane. Although pH neutralization seemed to be a disadvantage in terms of flux decline, effective cleaning helped restore the clean water fluxes. Therefore, the advantage gained by reducing three stage NF into single stage NF by pH neutralization outweighs the disadvantage of increased flux declines.

Table 6.37(a). Effect of pH on NF Permeances for ADBW

Sample	**pH**	**Permeance (L/m^2.h.bar)**			
		Clean Water			**Wastewater**
		Initial (I)	**Final (F)**	**Cleaned (C)**	**(W)**
Mixture 4	4.68	3.7	3.2	3.7	3.3
	5.96	3.9	3.2	3.9	3.1
	7.24	3.7	3.6	4.0	3.0
Sample 42	5.30	3.3	2.9	3.2	2.8
	7.05	3.2	3.0	3.4	2.4

Table 6.37(b) gives the levels of flux declines caused by concentration polarization and fouling. The reversible and irrevesible fractions of fouling could not be calculated since the clean water fluxes obtained after cleaning were higher than their initial values, which mean swelling of the membrane (Mutlu et al., 1999). As seen from the table, for both Mixture 4 and Sample 42, the contribution of concentration polarization became significantly larger as the pH was increased from around 5 to 7. In other words, the contribution of fouling to total flux decline, which was dominant at acidic pH reduced significantly at neutral pH. This is another benefit of pH neutralization since concentration polarization has reversible effect on flux decline.

Table 6.37(b). Effect of pH on Flux Decline for ADBW

Sample	pH	Flux Decline (%)				
		Total (I-W)	Conc. Pol. (F-W)	Fouling		
				Reversible (C-F)	Irreversible (I-C)	Total (I-F)
Mixture 4	4.68	8.2	*	*	*	*
	5.96	23.2	3.6	18.1	2.7	20.4
	7.24	20.1	16.3	*	*	4.5
Sample 42	5.30	14.1	1.3	10.3	3.0	13.0
	7.05	24.8	19.3	*	*	6.7

* these data could not be calculated since the clean water fluxes obtained after cleaning were greater than the initial values

In an attempt to better understand the possible reason of the positive effect of pH neutralization, the question of whether the ADBW or the NFT-50 membrane or both were affected by the pH change was tried to be answered by conducting a new set of TRMF tests under the conditions of same NF membrane, same pH, but different wastewater type, i.e., PDW. The filtration test conducted under acidic pH condition was repeated in two ways; first the initial feed pH was adjusted to 4.83 and second the feed pH was adjusted to 4.81 and kept constant throughout the experiment by the addition of HNO_3. This was done in order to compare the separation performances under increasing acidic pH and constant acidic pH. The change of UVA values monitored during these experiments are depicted in Figure 6.70. This plot is very similar to the plot given in Figure 6.66 for ADBW such that the UVA rejection achieved as 90% at neutral pH reduced to almost none at acidic pH. Actually, addition of HNO_3 into the wastewater was observed to result in the same UVA readings in the feed and the permeate, which in turn, resulted in no UVA removal. Therefore, the performance comparisons were decided to be done considering the parameters other than UVA for pH related experiments. The results obtained for all the other parameters are given in Table 6.38.

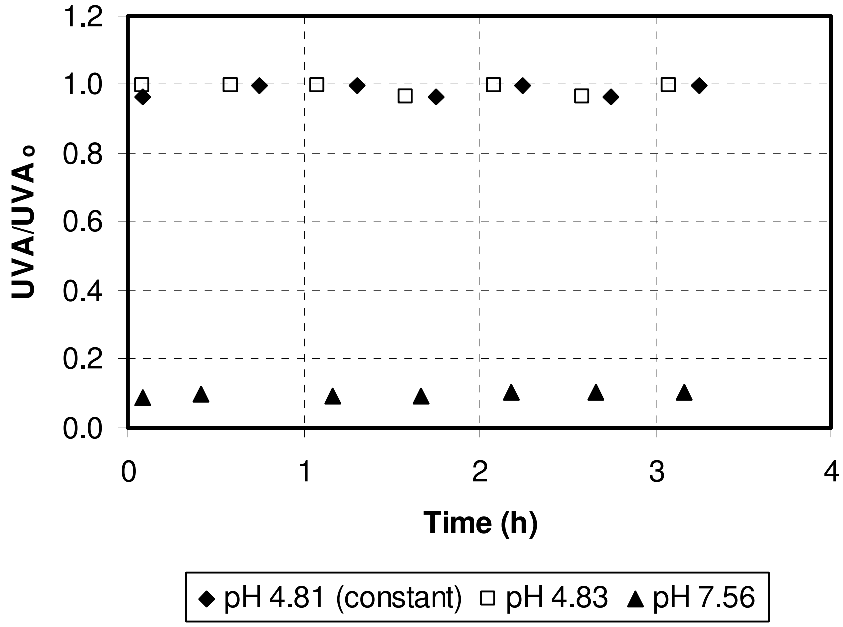


Figure 6.70. Effect of pH on UVA Removal Efficiency for PDW Mixture 3 (pH 4.81 was kept constant during filtration, and 4.83 and 7.56 are initial pH values)

Table 6.38. Effect of pH on Single NF Performance for PDW Mixture 3

Parameter	**Removal (%)**		
	pH 4.81 *	**pH 4.83 ****	**pH 7.56 *****
COD	92	95	96
Color	100	100	100
Turbidity	98	99	95
T. Solids	53	67	87
T. Hardness	81	100	100
Conductivity	44	60	87

* kept constant during filtration by HNO_3 ** initially adjusted by HNO_3 *** original pH

The separation performance of the NFT-50 membrane was not significantly affected by the acidic pH conditions and the removal efficiencies for COD, color and turbidity were almost the same under acidic and neutral conditions. However, the removal performances for total solids and conductivity were observed to decrease to some extent, but were still higher than those for ADBW at acidic pH. The reduced separation performances observed for ions in PDW was probably due to the permeation of HNO_3. As seen from Table 6.38, the removal efficiencies were even lower at pH 4.81 than at pH 4.83 due to the addition of more HNO_3 to keep the pH constant. The most significant difference between these wastewaters under acidic and neutral pH conditions was realized to be the COD removal efficiency. All these results indicated that pH neutralization affected the ADBW characteristics to a great extent. On the other hand, these results did not clearly indicate whether the membrane was affected by the pH changes or not.

The flux decline was also monitored during the experiments conducted with PDW (Figure 6.71). As in the case of ADBW, the flux decline was only 8% at pH 4.81 but it increased to 15% and 17% at pH 4.83 and 7.56, respectively. Therefore, the flux decline was observed to be minimum at acidic pH for both wastewaters.

The effect of cleaning on the recovery of clean water fluxes is shown in Table 6.39(a) for all the pH conditions. The fluxes (expressed as permeances) were efficiently recovered by the cleaning procedure. Table 6.39(b) gives the levels of flux declines caused by concentration polarization and fouling. Unlike ADBW, the extent of flux decline caused by fouling was not affected by pH change, and fouling effect was higher than concentration polarization at all pH values. Therefore, it can be concluded that the flux decline caused by PDW occurs due to the fouling of the membrane but not the concentration polarization, which can be removed by cleaning only. On the other hand, the flux decline caused by ADBW is reversible to a greater extent, i.e., concentration polarization is dominant. Another conclusion can be inferred such that lowering the pH of PDW did not significantly influence its characteristics since the dominant fraction of flux decline was the same for all pH values.

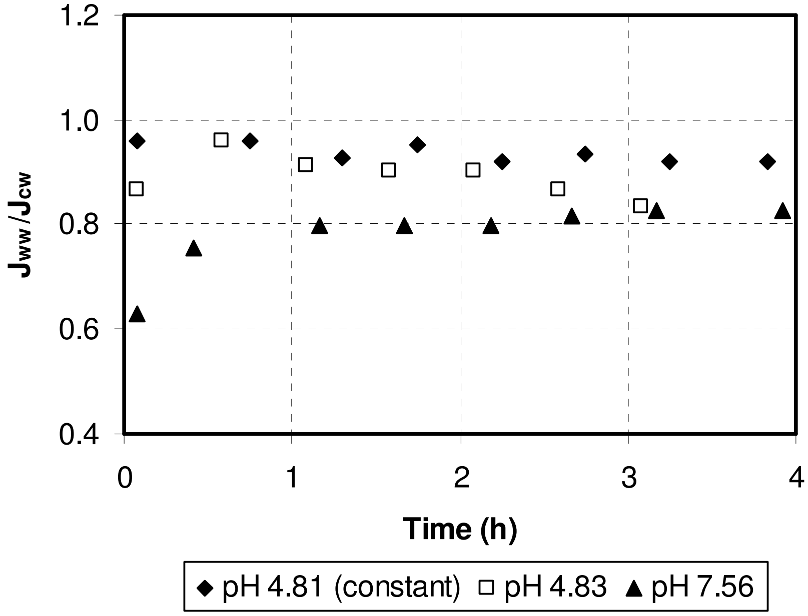


Figure 6.71. Effect of Feed pH on Relative Flux Change for PDW Mixture 3

Table 6.39(a). Effect of pH on NF Permeances for PDW

pH	Permeance (L/m^2.h.bar)			
	Clean Water			Wastewater
	Initial (I)	Final (F)	Cleaned (C)	(W)
4.81 [a]	3.41	3.23	3.70	3.14
4.83 [b]	3.59	3.12	3.47	3.05
7.56 [c]	3.15	2.80	3.22	2.60

[a] kept constant during filtration, [b] initially adjusted by HNO_3, [c] original pH

Table 6.39(b). Effect of pH on Flux Decline for PDW

pH	Flux Decline (%)				
	Total (I-W)	Conc. Pol. (F-W)	Fouling		
			Reversible (C-F)	Irreversible (I-C)	Total (I-F)
4.81[a]	8.1	2.8	*	*	5.3
4.83 [b]	15.1	2.2	3.4	10.1	13.2
7.56 [c]	17.4	7.1	*	*	11.1

[a] kept constant during filtration, [b] initially adjusted by HNO_3, [c] original pH

* could not be calculated since the clean water fluxes obtained after cleaning were greater than the initial values

As a summary, it can be concluded that the NF separation process must be applied under neutral pH conditions for the recovery of ADBW in order to maximize the separation performance. Neutralization of the pH is also required due to another reason, that is, the process water currently used in the factory already has neutral pH for maintaining the correct dyeing procedures. Therefore, pH neutralization is a necessity for an efficient recovery of ADBWs by the proposed single stage NF, which is definitely a more practical and more attractive process train to be implemented when compared to two or three stage sequential NF.

All these results suggest that pH is a very important process parameter to be controlled due to two reasons:

1. It affects the characteristics of the feed wastewater,
2. It affects the characteristics of the membrane.

The findings of this study suggest that a detailed investigation of the effects of pH on the characteristics of the wastewater and the membrane is needed, on which little information exists in the current literature.

The pH of ADBW can be raised from acidic to neutral conditions by addition of chemicals in industrial scale treatment. Although single stage NF by pH neutralization has been advised here as a better treatment scheme for ADBW, addition of one more chemical into such a complex wastewater sounds unpleasant and it is against the objectives of this study, which aims the minimization of chemical usage. Therefore, a more attractive option arises for increasing the pH of ADBW; mixing the acidic ADBW with the neutral PDW to obtain a wastewater mixture having neutral pH. This new alternative seems very attractive since the pH would be increased without using additional chemicals. However, the performance of this alternative treatment scheme must be verified, which is presented in the following section.

6.3. Process Train Development for the Mixture of ADBWs and PDWs

The treatment of ADBWs and PDWs in the same process train is considered to be a very practical solution, as it would provide the recovery of these wastewaters in the simplest process train possible due to the following factors:

1. PDW already has neutral pH,
2. Excellent removal performance is achieved by single stage NF for PDW at neutral pH,
3. The generation rate of PDW is four times higher than that of ADBW,
4. The pH of ADBW would naturally rise to neutral when mixed with PDW at a ratio of 4:1.

In order to evaluate the performance of this alternative, PDW (Mixture 3) and ADBW (Mixture 4 and Sample 42) were mixed at a volumetric ratio of 4:1 and 1:1, which are expressed as “PDW(4) + ADBW(1)” and “PDW(1) + ADBW(1)”. Increasing the mixing ratio to 1:1 was due to the fact that the generation rates of these wastewaters are subject to significant fluctuations, which would lead to the changing mixing ratios. At present, the capacity of the dye house of Samur Carpet Factory provides a mixing ratio of PDW and ADBW changing from 8:1 to 1:1, therefore the highest ratio was considered to be 1:1. These new wastewater mixtures were then fed to single stage NF in TRMF tests. The effect of pH was also studied by keeping the pH of the mixture at its original value in the first test and then by making it acidic in the second test.

The feed and the permeate values obtained by single stage NF for PDW, ADBW, and their mixtures are given in Table 6.40 and the removal performances are compared in Figures 6.72 and 6.73. Slight decreases in the removal performance of the NF were observed for COD and total solids when the pH was reduced from 6.94 to 5.73 for 4:1 mixture. The highest decrease realized for conductivity was from 78% to 55%.

Table 6.40 (a). Single NF Performances for PDW and ADBW

Parameter	**PDW Mixture 3 (pH 7.56*)**		**ADBW Mixture 4 (pH 5.96*)**		**ADBW Sample 42 (pH 5.30*)**	
	Feed	**Permeate**	**Feed**	**Permeate**	**Feed**	**Permeate**
COD (mg/L)	476	19	1250	272	1832	415
Color (Pt-Co)	57	0	59	0	36	0
Turbidity (NTU)	5.10	0.24	4.90	0.12	3.60	0.20
T. Solids (mg/L)	577	75	943	247	1204	535
T. Hardness (mg/L as $CaCO_3$)	38	0	46	0	18	2
Conductivity (µS/cm)	812	106	742	226	863	530
pH	7.56	8.65	5.96	6.15	5.30	5.41

* original pH

Table 6.40 (b). Single NF Performances for PDW(4) + ADBW(1)

Parameter	**PDW(4) + ADBW(1) (pH 6.94*)**		**PDW(4) + ADBW(1) (pH 5.73**)**	
	Feed	**Permeate**	**Feed**	**Permeate**
COD (mg/L)	691	25	789	68
Color (Pt-Co)	97	3	74	0
Turbidity (NTU)	9.50	0.26	6.40	0.21
T. Solids (mg/L)	751	136	773	197
T. Hardness (mg/L)	34	0	35	0
Conductivity (μS/cm)	844	188	904	405
pH	6.94	6.56	5.73	5.77

* original pH kept constant by HNO_3 ** initially adjusted to 5.73 and kept constant by HNO_3

Table 6.40 (c). Single NF Performances for PDW(1) + ADBW(1)

Parameter	**PDW(1) + ADBW(1) (pH 6.66*)**		**PDW(1) + ADBW(1) (pH 5.73**)**	
	Feed	**Permeate**	**Feed**	**Permeate**
COD (mg/L)	816	17	877	235
Color (Pt-Co)	35	0	34	0
Turbidity (NTU)	1.8	0.10	1.8	0.10
T. Solids (mg/L)	765	36	797	146
T. Hardness (mg/L)	40	0	40	0
Conductivity (μS/cm)	755	71	777	205
pH	6.66	6.39	5.73	6.01

* original pH ** initially adjusted to 5.73 by HNO_3

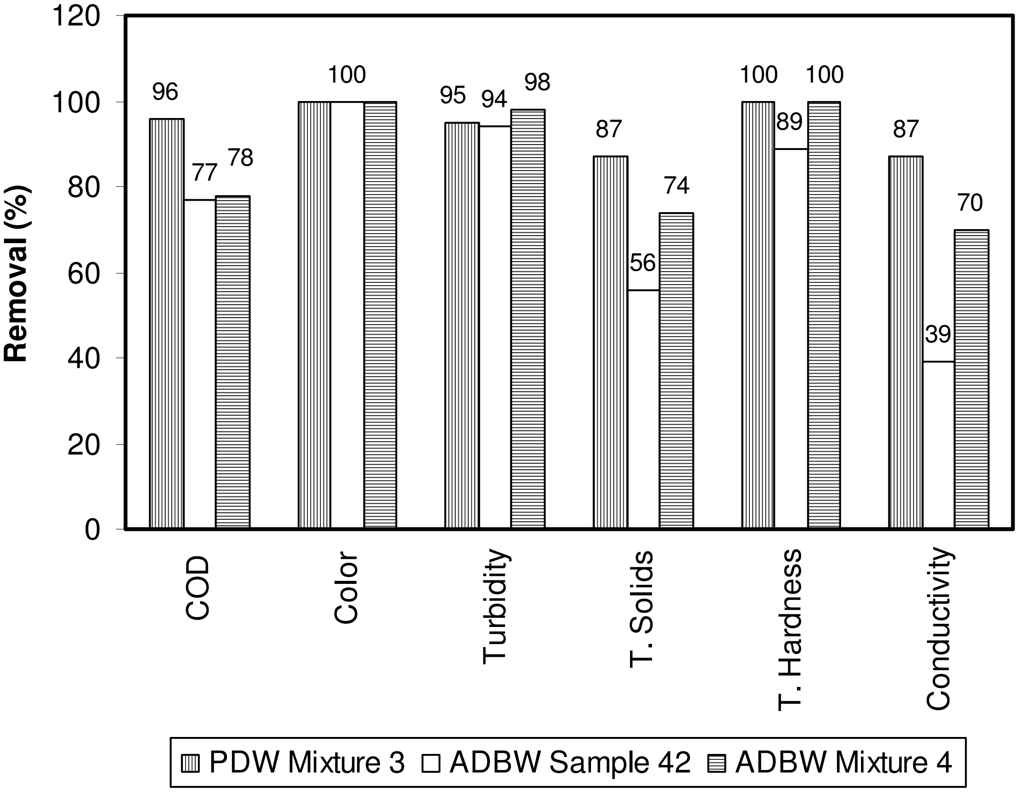


Figure 6.72. Single NF Performances for PDW and ADBW at their original pH

Increasing the mixing ratio to 1:1 at almost neutral pH did not adversely affect the separation performance of NF. Indeed, the removal efficiencies were generally slightly higher at 1:1 ratio, for which the reason might be the difference in the characteristics of ADBW samples used for two different mixing ratios (ADBW Sample 42 was used for the mixing ratio of 4:1 whereas ADBW Mixture 4 was used for the mixing ratio of 1:1). When the pH was lowered to 5.73 at the mixing ratio of 1:1, the removal efficiencies for COD, total solids and conductivity were reduced. The most significant reduction was observed for COD, as from 98% to 73%. This result revealed that as the fraction of the ADBW in the mixture was increased from 4:1 to 1:1, the effect of pH becomes more significant, necessitating the neutral pH condition to be fulfilled.

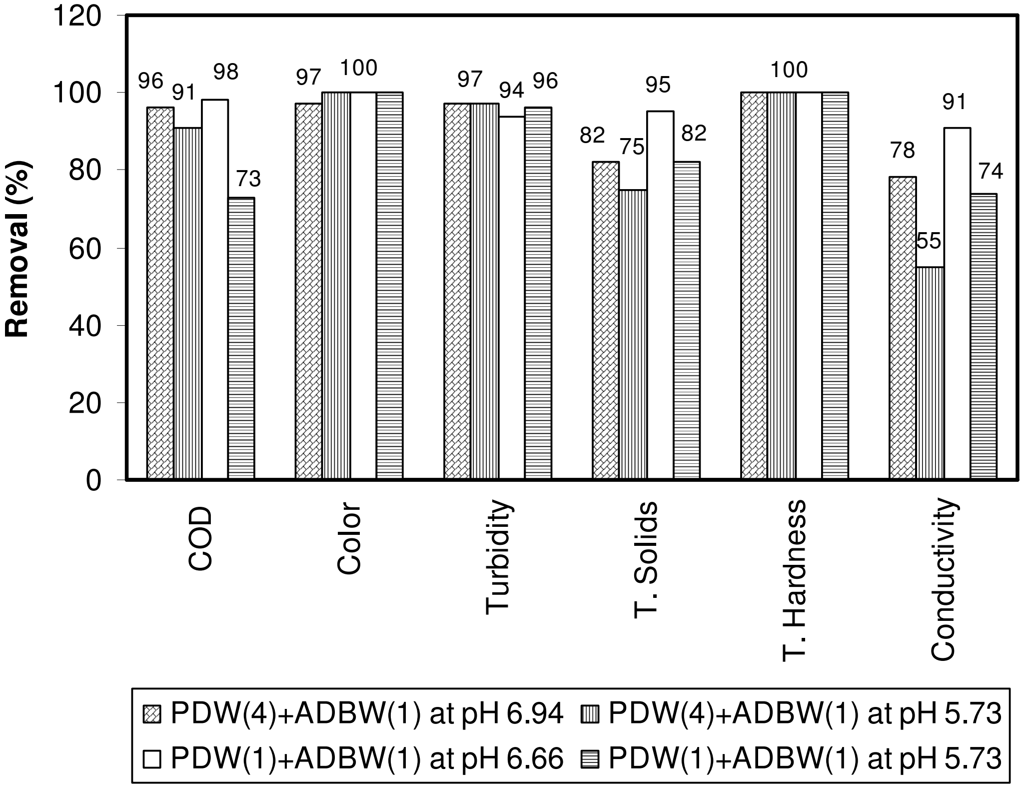


Figure 6.73. Effect of pH on NF Performance for Mixtures of PDW and ADBW

The relative fluxes as a function of time were plotted in Figures 6.74 and 6.75. The flux decline was 17% for PDW Mixture 3, 14% for ADBW Sample 42 and 23% for ADBW Mixture 4. For the mixing ratio of 4:1, the flux decline was 24% and 18% at pH 6.94 and 5.73, respectively. Similarly, the flux decline for the mixing ratio of 1:1 was 25% and 23% at pH 6.66 and 5.73, respectively. As seen, increasing the mixing ratio did not increase the flux decline level at neutral pH, whereas an increase from 18% to 23% occurred at acidic pH due to the increase of the mixing ratio from 4:1 to 1:1. Therefore, it can be concluded that as long as the neutral pH condition is fulfilled, these wastewaters can be mixed up to equal volumes with no increase in flux declines. However, mixing these wastewaters resulted in higher flux declines as compared to PDW treatment alone.

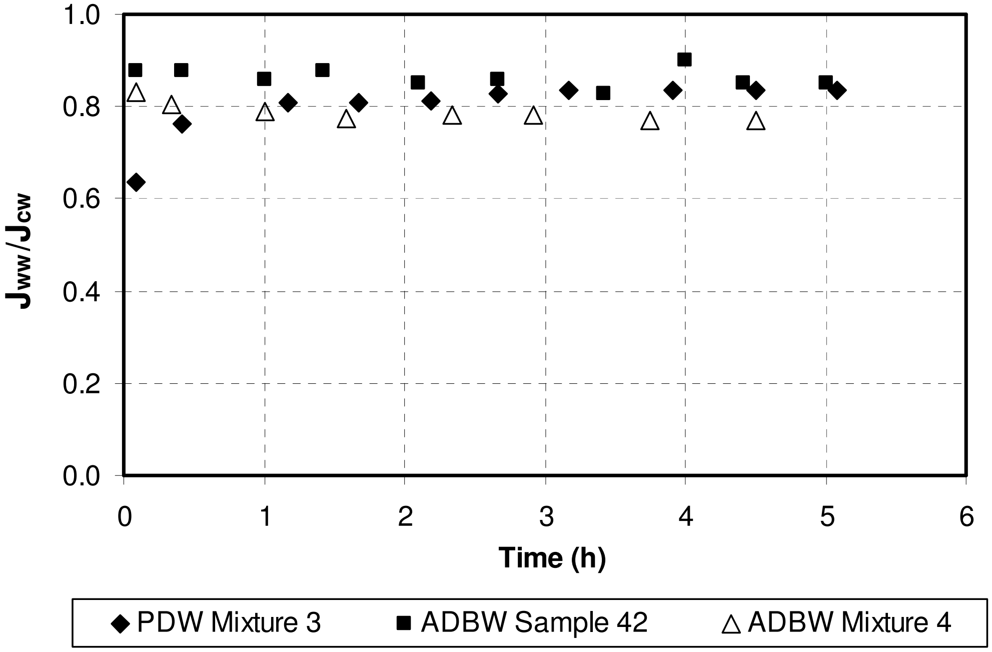


Figure 6.74. Relative Flux Decline for PDW and ADBW

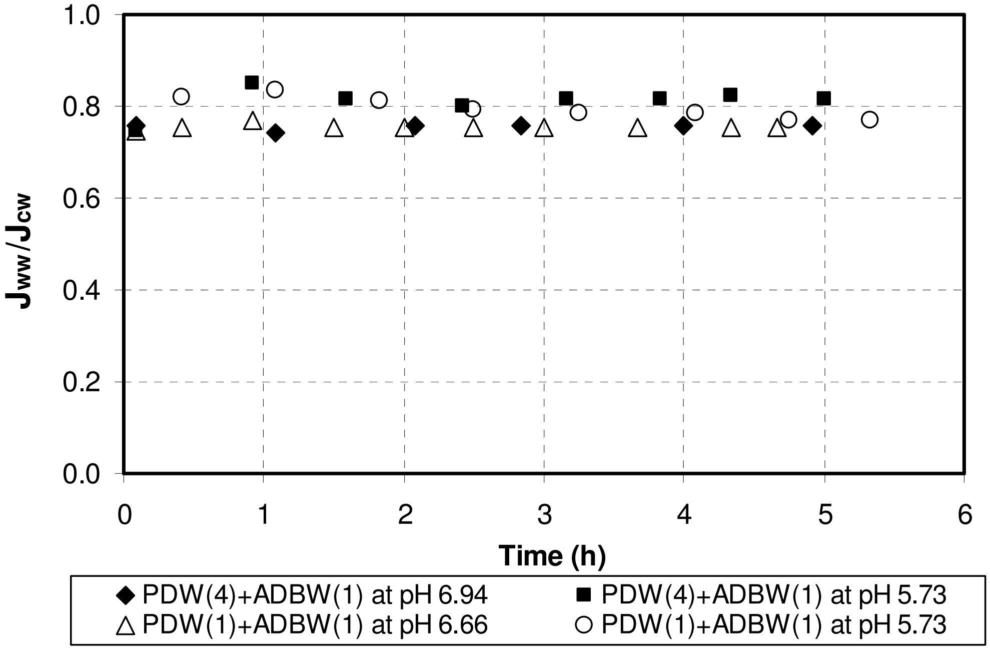


Figure 6.75. Effect of pH on Flux Decline For Mixtures of PDW and ADBW

The effect of cleaning on the recovery of clean water fluxes is shown in Table 6.41(a). The cleaning procedure was proven to be quite effective in restoring the fluxes for the wastewater mixtures; however some of the initial permeances of the membranes could not be recovered totally. This may be achieved by increasing the duration of cleaning.

Table 6.41(a). Effect of Cleaning on Flux Recovery for PDW and ADBW

Sample	**pH**	**Permeance ($L/m^2.h.bar$)**			
		Clean Water			**Wastewater**
		Initial (I)	**Final (F)**	**Cleaned (C)**	**(W)**
PDW Mixture 3	7.56	3.2	2.8	3.2	2.6
ADBW Sample 42	5.30	3.3	2.9	3.2	2.8
ADBW Mixture 4	5.96	3.9	3.2	3.9	3.1
PDW(4) + ADBW (1)	6.94	3.7	3.1	3.5	2.8
	5.73	3.2	2.7	3.2	2.6
PDW(1) + ADBW (1)	6.66	3.7	3.3	4.0	2.8
	5.73	4.0	3.4	3.6	3.1

The flux declines caused by concentration polarization and fouling were also compared in Table 6.41(b) for the cases of mixing PDW and ADBW. The flux declines were also compared to those obtained for PDW and ADBW alone. As seen from the table, the PDW flux decline was due to fouling to a greater extent at both acidic and neutral pH. On the other hand, the flux decline was highly due to fouling at acidic pH, which became reversible due to concentration polarization at neutral pH.

Table 6.41(b). Effect of Mixing Ratio on Flux Decline

Sample	pH	Flux Decline (%)				
		Total	**Conc. Pol.**	**Fouling**		
		(I-W)	**(F-W)**	**Reversible (C-F)**	**Irreversible (I-C)**	**Total (I-F)**
PDW Mixture 3	4.83	15.1	2.2	3.4	10.1	13.2
	7.56	17.4	7.1	*	*	11.1
ADBW Sample 42	5.30	14.1	1.3	10.3	3.0	13.0
	7.05	24.8	19.3	*	*	6.7
ADBW Mixture 4	5.96	23.2	3.6	18.1	2.7	20.4
	7.24	20.1	16.3	*	*	4.5
PDW(4)+ADBW(1)	5.73	18.4	2.1	14.7	2.3	16.7
	6.94	24.4	9.8	10.8	6.1	16.2
PDW(1)+ADBW(1)	5.73	23.3	9.3	6.4	9.6	15.5
	6.66	24.5	15.1	*	*	11.1

* these data could not be calculated since the clean water fluxes obtained after cleaning were greater than the initial values

In case of mixing these two wastewaters, the situation at 4:1 mixing ratio was similar to that of PDW alone, i.e., the effect of fouling was dominant at both pH values and the fraction of concentration polarization was higher at neutral pH than at acidic pH. This result is expected since the volumetric ratio of PDW is four times higher than that of ADBW, creating similar results with the case of PDW alone. Although fouling was dominant, the reversible fouling was higher than the irreversible fouling, which was also confirmed with the effectiveness of cleaning. On the other hand, the results obtained for 1:1 mixing of PDW and ADBW resembled those obtained for ADBW alone, i.e., the effect of concentration polarization, whose contribution was lower than that of fouling in general, became much higher at neutral pH than at acidic pH. In addition, the level of reversible fouling increased at the mixing ratio of 1:1 at acidic pH, which was higher than irreversible fouling at the mixing ratio of 4:1.

The total flux decline levels observed for mixing cases were in the range of 18-25%, which were close to those obtained for individual wastewaters. The flux decline was lowest for PDW alone (15-17%) at both pH and for ADBW (14%) at acidic pH. On the other hand, the flux declines for ADBW at neutral pH (20-25%) were almost equal to the flux declines observed for mixing conditions (18-25%). Increasing the mixing ratio from 4:1 to 1:1 did not adversely affect the total flux decline at neutral pH, which remained constant at around 25%. Furthermore, the clean water fluxes were effectively restored by cleaning for mixing cases (Table 6.41(a)). Therefore it was concluded that treating PDW and ADBW together was not a disadvantageous alternative in terms of flux declines since the necessity of neutralization of ADBW had already been confirmed with previous removal performance data.

The qualities of the permeates obtained from the wastewater mixtures were compared to the BTTG reuse criteria in Table 6.42. As seen, the BTTG reuse criteria were satisfied for all the parameters for both mixing ratios. The actual process water quality was also met except for turbidity, which in fact, is so low that it can be easily accepted for reuse purposes.

Considering all the results obtained in this study, the final conclusion to be made is that PDW and ADBW, after being subjected to different pre-treatment processes, can be combined and treated by single stage NF at neutral pH to achieve water recovery at desired qualities. The final version of the developed process train is depicted in Figure 6.76. This is a very important conclusion in terms of the management of these two wastewaters, as the cost of the developed process train will be reduced by decreasing the number of membrane units.

Table 6.42. Evaluation of NF Permeate Qualities for Mixtures of PDW + ADBW

Evaluation Reference/ Applied Process	**Reuse Criteria/Permeate Quality**			
	Color (Pt-Co)*	**Turbidity (NTU)**	**Dissolved Solids (mg/L)**	**Total Hardness (mg/L)**
BTTG	5	15	500	60
Actual process water	1	0.15	446	11
NF Permeates				
PDW(4) + ADBW(1)	0-3	0.21-0.26	136-197	0
PDW(1) + ADBW(1)	0	0.10	36-146	0

*The unit of color is AU (absorbance units) for BTTG

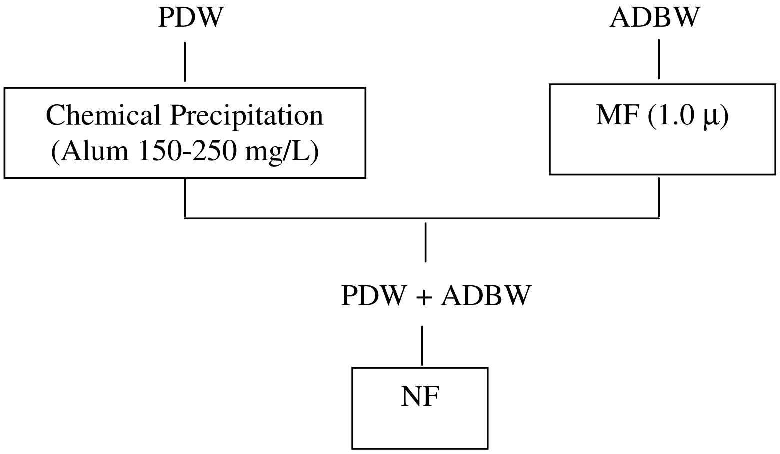


Figure 6.76. Developed Process Train for the Mixture of PDW and ADBW

CHAPTER 7

CONCLUSIONS

The discussions of the results obtained in this study are summarized as follows:

1. The most efficient pre-treatment process for PDW was found out to be chemical precipitation (CP) among the alternatives of MF, CP, combined processes of CP followed by MF, and CP followed by UF. The optimum alum dose in the CP process varied from 150 mg/L to 250 mg/L due to the changing characteristics of the PDW samples.

2. NF versus UF (1000, 2000, 20000 and 50000 Da) was tested for treatment of PDWs. A very soft permeate free of color, turbidity, having very low organic matter was produced by NF. However, only up to 25% COD removal efficiency was obtained by all the UF membranes tested. At no water recovery, i.e., the volume reduction factor (VRF) was 1, the steady state flux decline of 20% was observed for NF membrane whereas it ranged from 11% to 35% for UF membranes. The effect of concentration polarization on the flux decline was more pronounced than fouling.

3. Three alternative process trains were tested for water recovery from the pre-treated PDW, namely, single NF, loose UF (20000 Da) followed by NF and tight UF (1000 Da) followed by NF. The removal performances obtained in concentration mode of filtration (CMF) tests at VRF > 1, were similar to those obtained in total recycle mode of filtration (TRMF) tests at VRF=1. The NF separation performance remained stable at high removal efficiencies, and the UF separation performances remained low as the VRF

increased. As the VRF increased from 1 to 11.8 (the feed volume was concentrated 11.8 times), the flux decline of the NF membrane increased from 16% to 31%, which is close to the flux decline of 20% observed in TRMF test. The flux declines of NF were almost completely reversible as the initial water fluxes were restored by chemical cleaning. However in the sequential UF and NF processes, the flux declines were severe in both loose and tight UF membranes, reaching to 40-60% at a VRF of 9.3. The initial clean water flux of the loose UF membrane could not be recovered by chemical cleaning, indicating irreversible fouling, which may be due to pore blocking. The flux declines observed in single NF following the UF stages in two alternatives were almost the same with the flux declines obtained for single NF. Therefore, the flux decline of NF applied in the second stage did not improve by the implementation of the UF stages in the first stage. Since the separation performance of single NF was already very high, the sequential application of UF and NF did not provide any benefits in terms of separation performances. Therefore, the best process train for the recovery of PDWs was decided to be CP followed by single stage NF.

4. The process train developed for PDWs was tested against high color contents of the PDW, where PDW was spiked with varying concentrations of metal complex dyes. The permeate had no color even at a feed color value of 1000 Pt-Co. Hence, the developed process train can safely be used for PDWs having color as high as 1000 Pt-Co.

5. The spiking of metal-complex dyes into distilled water caused a flux decline of only 6%, which is much less than the PDW flux decline of 20%. Moreover, addition of an antifoaming agent or a non-ionic penetrant into the dye solution only slightly increased the flux decline. Therefore, it was concluded that it is not the single component causing the flux decline in

PDW, but the combined effects of all the wastewater components are responsible for the flux decline.

6. The most efficient pre-treatment process for ADBW was found to be MF (1 μm) among the alternatives of single and sequential MF with varying pore sizes, single UF (50000 Da), and MF (0.45 μm) followed by UF (50000 Da).

7. The separation performance of single stage NF for ADBW was lower than that achieved for PDW, especially for COD, total solids and total hardness. Hence sequential NF was adopted; i.e., two stage and three stage NF. The COD removal efficiency increased from 65% to 94% by the implementation of third stage NF. However, the PDW permeate quality obtained by single stage NF was still better than ADBW permeate quality achieved by three stage NF, which was observed to be due to the pH differences of these wastewaters, i.e., PDW has neutral and ADBW has acidic pH.

8. pH neutralization in single stage NF was adopted as a practical alternative to three stage NF that had been tested at the original acidic pH of ADBW. The separation performance of single stage NF at neutral pH provided very high removal efficiencies, and the permeate COD was realized to be directly related to feed pH, decreasing sharply as the pH was increased in a narrow range of 5-7. Therefore, it was decided that pH is a very important operational parameter for the treatment of ADBWs by NF, necessitating pH neutralization for achieving the best removal efficiencies.

9. The effect of pH was studied for both PDW and ADBWs in order to figure out whether pH neutralization was affecting the wastewater or the membrane. The separation performance of single stage NF did not differ significantly for PDW at acidic and neutral pH, whereas a very significant improvement was observed for ADBW at neutral pH. This was thought to

be due to improved rejection of acetic acid at neutral pH by the electrostatic interactions between the membrane surface charge and the acetic acid. Therefore it was concluded that pH neutralization affected the ADBW characteristics rather than the membrane itself. This conclusion was strengthened by the flux decline analysis, i.e., the major fraction of the flux decline was fouling for PDW at both acidic and neutral pH, whereas concentration polarization became dominant for ADBW when pH was increased from around 5 to 7, which in turn, may imply a possible change in the structure of the wastewater components.

10. PDW and ADBW were mixed and treated together in single NF after being subjected to different pre-treatment stages, since the best process train for both wastewaters came out to be single stage NF at neutral pH. The separation performance of single stage NF achieved at the volumetric mixing ratios of 4:1 and 1:1 was as high as that observed for individual wastewaters. However, the pH needed to be kept at neutral for increased volume fractions of the ADBW due to the deterioration of the permeate quality, especially in terms of COD. Although the flux decline observed for the mixture of PDW and ADBW was higher than those observed for PDWs, they were almost the same as those observed for ADBWs. Increasing the volume fraction of ADBW increased the reversible fraction of the flux decline, resulting in increased total flux decline at acidic pH. The permeate qualities of the mixtures of PDW and ADBW satisfied the reuse criteria at both acidic and neutral pH.

11. Cleaning of the membranes, performed by circulation of acidic and basic solutions after each run was proven to be quite effective in restoring the original clean water fluxes.

Based on the discussions summarized above, it was concluded that membrane technology is technically feasible for water recovery from the PDW and ADBW streams, provided that a suitable pre-treatment stage is included in the process trains. Once these two wastewaters of significantly different characteristics are separately subjected to the most suitable pre-treatment processes, they can be mixed and treated together. Although separate routes have also been determined for the recovery of the PDWs and ADBWs, the most efficient route was found out to be mixing these wastewaters in the treatment stage, since it will provide the simplest and the most energy efficient process train to be implemented.

Several approaches have been adopted in this study for the development of the best process trains including MF, UF, CP, and NF. Among these processes, UF was eliminated from all the alternative process trains in the pre-treatment stages of both wastewaters due to the lack of a significant benefit over other methods. In the treatment stage, the UF permeate quality, being much worse than the NF permeate quality, was suggested to be improved by mixing with the fresh process water at desired proportions.

To achieve water recovery, the best pre-treatment stages for PDWs and ADBWs were determined as CP and MF, respectively. The treatment stage was determined as single stage NF, provided that the pH is neutral. Neutral pH conditions were found out to remarkably improve the separation performance of NF for ADBW, i.e., single stage NF at neutral pH performed better than three stage NF at acidic pH. Therefore, pH significantly affected the treatment scheme. To this end, it was concluded that pH is a very important operational parameter to ensure maximized removal efficiencies in minimized number of unit processes.

CHAPTER 8

FUTURE WORK

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

12. The performance of the process train developed for water recovery from the dyeing effluents of carpet manufacturing industry should be tested for other textile wastewaters with similar characteristics in an attempt to generalize the conclusions obtained in this study.
13. A detailed study regarding the effect of pH on the separation performance of the membranes for the recovery of carpet dyeing effluents should be performed. In this way, it should be determined whether the pH is effective on the wastewater or the membrane characteristics, or both.
14. Membrane characteristics is very important in evaluation of its performance, therefore a detailed study is recommended for membrane characterization, for which measurement of zeta potential for the determination of membrane surface charge, measurement of contact angle for determining whether the membrane is hydrophilic or hydrophobic, or even the preparation of the membrane itself may be required. A more detailed characterization of the wastewater is also required for understanding the mechanisms of rejections better.

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

16. Economical feasibility of the developed process train should be determined.

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APPENDIX A

DESCRIPTION OF THE SAMUR CARPET DYEING PROCESS

Samur Carpet Factory (SCF), located on Çankırı Road on the way to Esenboğa Airport, is an important establishment for İç Anadolu Region, where wall-to-wall tufted carpet and carpet yarn are produced. The average carpet production is 45000 m^2 per day with 650 employees. The fresh water consumption is stated to be 0.018 tons per m^2 of carpet manufactured (Düzgün, 2001). The water used in the process is supplied from the wells and SCF does not pay for it. However, the groundwater is treated by sand filtration followed by ion exchange to obtain soft and particle free process water. The carpets are woven by synthetic yarns produced from polyamide (PA) and polyester and then they are dyed into the desired color. The effluents of SCF involve the wastewaters generated by carpet dyeing and covering processes and also the domestic wastewater. Figure A.1 depicts the carpet manufacturing process lines, where the dashed lines show the wastewater streams.

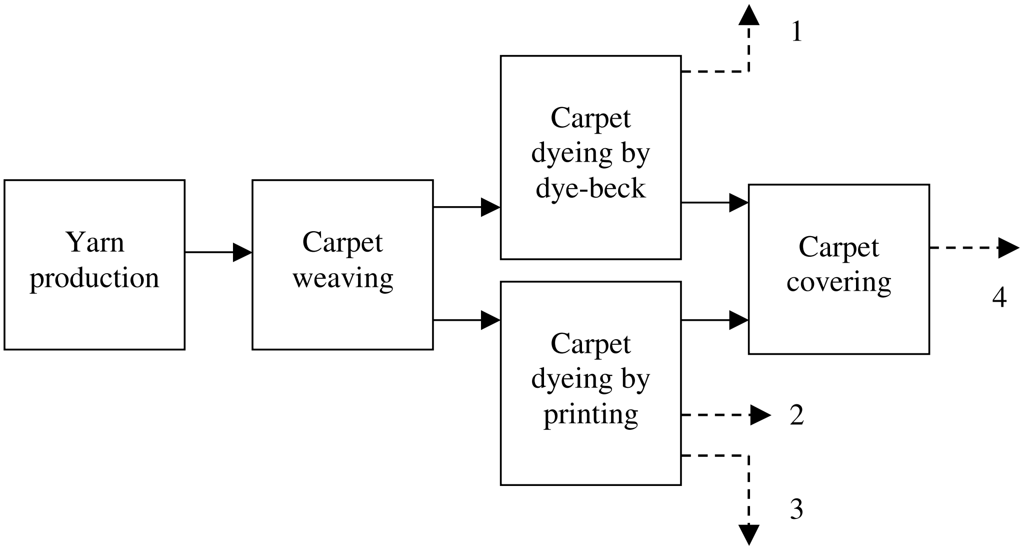


Figure A.1. Samur Carpet Manufacturing Process

A. 1. Wastewaters Generated From Dye Beck Process

There are four boilers in the SCF dye house, in which carpets made of PA 60 and PA 66 (nylon) are dyed with acid dyes and polyester carpets are dyed with disperse dyes. The carpets can be dyed into single colors by this system. Dyeing is performed by contacting the carpet with the dyeing solution at elevated temperature (approximately 100 °C) and acidic pH (4.5-5). For carpets made of PA, the dye bath is prepared by introducing the selected acid dyes and the chemicals listed in Table A.1 into the process water. The continuous movement of the carpet, which is rolled on a rotating bar, into and out of the dye bath, provides mixing and good contact between the carpet and the dyeing solution. The dyeing process usually takes 3-4 hours until all the dye is fixed on the carpet. When the dyeing process is finished, the spent dye bath solution is sent to the treatment plant (Line 1 in Figure A.1). The wastewater quantity produced in one boiler is approximately 25 m^3/day, and typically 2 or 3 boilers are used each day. Dye beck system is used for six days a week; therefore, the weekly wastewater generation rate is approximately 300-450 m^3, which is subject to high fluctuations during special periods of the year such as the holidays or the summer.

Table A.1. Contents of the Acid Dye Bath Solution for PA Carpets

Acid Dyes* (CI Name)	Chemicals
• Yellow 2R • Yellow 2G (Acid Yellow 169) • Red 2B (Acid Red 361) • Red 599 • Orange 4G • Blue 4R (Acid blue 277) • Blue 608	• Acetic acid (for pH adjustment) • Lyogen PAM (aromatic polyethersulfonate and polyglycolether, for uniformity) • Antimussol HT-2S (stable, non-ionic, silicon-free antifoaming agent, based on hydrocarbons)

*CIBA Tectilon Series

A. 2. Wastewaters Generated From Print Dyeing Process

In printing process the standard carpets made of PA 60 and specially ordered carpets made of PA 66 are dyed by a computer-controlled printer system. The carpet passes through a vacuum first to be cleaned before dyeing. Then it passes through a pre-steam room to provide that all the hair of the carpet is of equal length. Then the carpet is dyed using a print paste (PP). The PP is prepared by mixing the metal-complex dye solution with the mixture of chemicals given in Table A.2 at acidic pH and a certain viscosity. After printing, the carpet is sent to the main steam room to fix the dye on the carpet. Then comes the vacuum system to separate the excess PP left on the carpet, which is later precipitated by Al_2SO_4 in the sedimentation tanks provided. Second vacuum is applied to the carpet in case any PP is left on it, and the carpet is washed in a water tank by slowly moving through the tank, where fresh water is continuously added to keep the water level constant in the tank. After washing, the carpet is dried in an oven. Later it is trimmed to make the surface uniform. Finally the surface is covered with teflon to provide dirt protection.

The wastewaters generated in print dyeing system are PP at a rate of 18 m^3/day, and the print after wash water at a rate of 204 m^3/day. The system works continuously for six days of the week, producing a total weekly wastewater quantity of 1350 m^3 on the average. The wastewaters produced in this stream are shown by Lines 2 and 3 in Figure A.1.

Table A.2. Contents of the Print After Wash Water

Metal-Complex Dyes* (CI Name)	Chemicals
• Yellow 2R • Yellow 4GN • Blue 2RA (Acid Blue 781) • Blue 5G (Acid Blue 526) • Black B (Acid Black 1051) • Red G (Acid Red 78) • Gray G • Navy R (Acid Blue 176)	• Citric acid (for pH adjustment) • Tanaprint ST 160 Conc (high electrolyte-resistant synthetic thickener, an anionic ammonium salt for adjusting the viscosity) • Nefome 1125 (antifoaming agent) • Tanasperse CJ (non-ionic penetrant, for increasing wetting and penetration and producing homogeneous paste)

* CIBA Lanaset Series (1:2 pre-metallized acid and reactive dyes)

A.3. Carpet Covering

The back of the carpets is covered to provide durability, noise and heat insulation. For this purpose, a mixture containing latex and other chemicals given in Table A.

3 are used. The generated wastewater, shown by Line 4 in Figure A.1, is sent to a coagulation tank in the treatment plant where $CaCO_3$ is precipitated. The carpet covering process produces only 3 m^3/wk of wastewater.

The overall weekly wastewater quantity produced for carpet manufacture is 1650-1800 m^3 on the average. A small volume of domestic wastewater is also mixed with the dye house effluents at the treatment plant, after passing through a rotary drum screen. All wastewaters generated are sent to the wastewater treatment plant, except the PP and latex wastewaters. These wastes are first precipitated with Al_2SO_4 and then sent to the treatment plant where the sludge is disposed. The schematic representation of the treatment plant is given in Figure A.2. Treatment plant mainly consists of an equalization basin where pH is adjusted, and then comes an activated sludge system with aeration and sedimentation tanks. The dye house wastewaters first enter a precipitation tank where $FeCl_3$ is added for settling the waste, and then mixed with the domestic waste in the equalization basin. The sludge formed in the treatment plant is sent to the sludge thickener in which centrifugation is applied. The treatment plant performance is monitored by the analyses of BOD, COD, TSS, color, pH, metals, oil and grease.

Table A. 3. Chemicals Used in Carpet Covering

Chemicals
• Latex
• Sulfapon 101 S (Latex foaming agent)
• TF 045 (Latex foaming agent)
• Chalk powder (Filling agent)
• Orgal M 420 (Thickener)
• Aluminium Hydroxide (Additive for non-burning property)
• Zonyl TCA (Teflon for avoiding dirt)
• Genaminox CS (Teflon foaming agent)

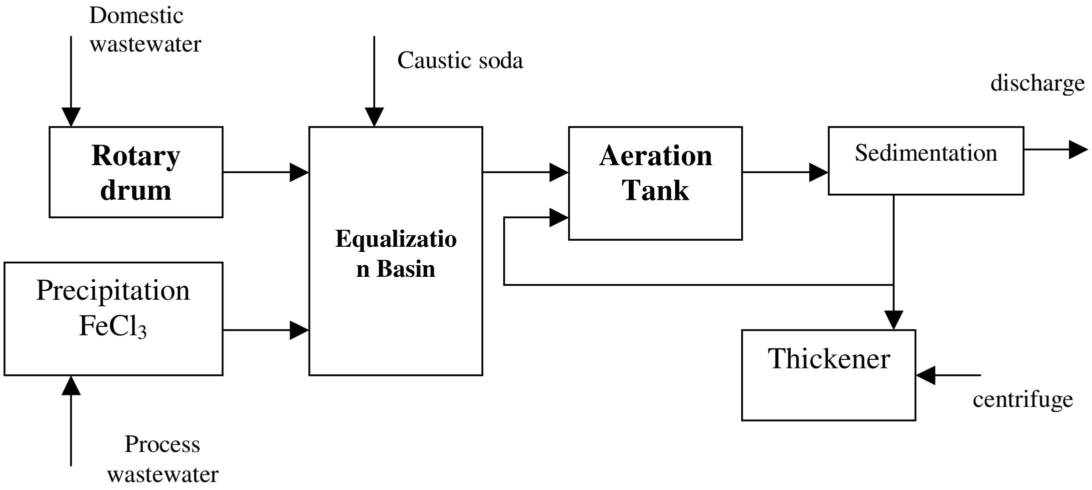


Figure A.2. Schematic Representation of Samur Wastewater Treatment Plant

APPENDIX B

PDW AND ADBW CHARACTERIZATION

Table B.1. PDW Characteristics in Sampling 1 Program

	Carpet Name (Sampling Date)					
Parameter	1. Special Order (05.09.01)	2. Mırnav (25.09.01)	3.Anıttepe (10.10.01)	4. Misket (24.10.01)	5. Çiftetelli (14.11.01)	6. Mavi Karnaval (21.11.01)
COD (mg/L)	438	1034	415	612	458	682
NPOC (mg/L)	293.3	441.7	154.3	136.7	155.0	110.3
UVA $_{195\text{-}200}$	3.05	4.01	3.72	3.42	3.37	3.81
Color (Pt-Co)	292	413	65	450	396	433
Turbidity (NTU)	17	58	38	24	110	33
T. Solids (mg/L)	508	774	507	644	640	746
Conductivity (μS/cm)	800	800	700	700	800	680
Chloride (mg/L)	12	15	9	21	9	10
pH	6.99	6.50	7.20	7.33	6.34	7.18

Table B.2. PDW Characteristics in Sampling 2 Program (Mixture 1 Obtained)

Parameter	Carpet Name (Sampling Date)					
	7. Special Order (11.11.02)	8. Special Order (11.11.02)	9.Special Order (11.11.02)	10. Çaydaçıra (11.11.02)	11. Beştepe (11.11.02)	12. Golden Light (11.11.02)
COD (mg/L)	532 ± 6	345 ± 42	135 ± 30	560 ± 52	450 ± 10	200 ± 11
UVA $_{195\text{-}201}$	3.61 ± 0	3.13 ± 0	2.58 ± 0	3.74 ± 0	3.56 ± 0	3.35 ± 0
Color (Pt-Co)	377 ± 1.4	256 ± 5	124 ± 4.2	402 ± 9.2	368 ± 0.7	310 ± 11
Turbidity (NTU)	40.0 ± 0	36.0 ± 1.4	14.5 ± 0.7	62.0 ± 0	60.0 ± 0	55.5 ± 0.7
T. Solids (mg/L)	625 ± 5	575 ± 10	534 ± 8	636 ± 28	612 ± 18	594 ± 18
Conductivity (μS/cm)	795 ± 7	695 ± 7	690 ± 0	705 ± 7	705 ± 7	720 ± 14
Chloride (mg/L)	32 ± 1.4	12 ± 1.4	11.5 ± 2.1	13.5 ± 0.7	14 ± 1.4	13 ± 0
pH	7.52 ± 0	7.60 ± 0	7.67 ± 0	7.48 ± 0	7.37 ± 0	7.71 ± 0

Table B.3. PDW Characteristics in Sampling 3 Program (Mixture 2 Obtained)

Parameter	Carpet Name (Sampling Date)			
	13. Special Order (11.04.03)	14. Kahve Karnaval (11.04.03)	15. Special Order (12.04.03)	16. Şölen Misket (12.04.03)
COD (mg/L)	641 ± 16	1022 ± 16	878 ± 21	906 ± 2
UVA $_{199-203}$	3.69 ± 0	4.00 ± 0.1	3.47 ± 0	3.79 ± 0
Color (Pt-Co)	595 ± 1.4	666 ± 2.8	466 ± 2.8	570 ± 2.8
Turbidity (NTU)	50.0 ± 0	79.0 ± 1.4	43.0 ± 0	59.5 ± 0.7
T. Solids (mg/L)	712 ± 6	829 ± 16	722 ± 26	651 ± 24
T. Hardness (mg/L)	10 ± 0	12 ± 0	20 ± 0	20 ± 0
Conductivity (µS/cm)	845	838	736	730
Chloride (mg/L)	25.5 ± 0.7	35.5 ± 0.7	14.5 ± 0.7	10 ± 0
pH	7.33 ± 0.01	7.23 ± 0.01	7.28 ± 0.01	7.24 ± 0.01

Table B.4. PDW Characteristics in Sampling 4 Program (Mixture 3 Obtained)

Parameter	Carpet Name (Sampling Date)			
	17. Samur Rug SR 41 (11.07.03)	18. Samur Rug SR 40 (11.07.03)	19. Şölen Misket 1 (11.07.03)	20. Şölen Misket 2 (11.07.03)
COD (mg/L)	638 ± 25	600 ± 19	806 ± 6	1206 ± 2
UVA $_{193\text{-}200}$	3.24 ± 0	2.64 ± 0	3.57 ± 0	3.96 ± 0
Color (Pt-Co)	416 ± 3.5	307 ± 0.7	561 ± 1.4	792 ± 2.8
Turbidity (NTU)	46 ± 0	30 ± 0	61 ± 0	100 ± 0
T. Solids (mg/L)	596 ± 14	635 ± 13	640	781 ± 7
T. Hardness (mg/L)	41 ± 1.4	34 ± 0	31 ± 1.4	39 ± 1.4
Conductivity (µS/cm)	710	714	734	753
Chloride (mg/L)	13 ± 0	16 ± 1.4	13.5 ± 0.7	15.5 ± 0.7
pH	7.23 ± 0.01	7.29 ± 0.02	7.14 ± 0.01	7.08 ± 0.01

Table B.5. ADBW Characteristics in Sampling 1 Program (Mixture 1 Obtained)

Parameter	Carpet Name (Sampling Date)			
	1. Special Order (Green) (05.09.01)	2. Special Order (Beige) (05.09.01)	3. Rubens (25.09.01)	4. İkizler (10.10.01)
COD (mg/L)	2103 ± 47	788 ± 23	1184 ± 121	1167 ± 25
NPOC (mg/L)	882.5 ± 13	601.7 ± 5.2	565.8 ± 7.6	294.7 ± 5.7
UVA $_{197\text{-}203}$	4.40	3.18	3.20	3.25
Color (Pt-Co)	1013 ± 13	101 ± 0	55 ± 0	58 ± 0
Turbidity (NTU)	100.0	1.5	68.0	9.2
T. Solids (mg/L)	1097	641	682	650
Conductivity (µS/cm)	700	700	750	690
Chloride (mg/L)	5	11	12	8
pH	4.60	4.68	4.48	4.91

Table B.5. ADBW Characteristics in Sampling 1 Program (Continued)

Parameter	Carpet Name (Sampling Date)				
	5.El Greco (24.10.01)	6. İkizler (14.11.01)	7. Boğa (21.11.01)	8.El Greco (03.12.01)	9. Yay (03.12.01)
COD (mg/L)	1076 ± 11	1434 ± 40	1442 ± 102	1357 ± 52	1530 ± 9
NPOC (mg/L)	352.7 ± 4.9	541.3 ± 8.0	377.0 ± 6.1	394.7 ± 4.7	450.7 ± 5.1
UVA $_{197\text{-}203}$	3.32	3.18	3.54	3.14	3.18
Color (Pt-Co)	274 ± 1.5	163 ± 0	120 ± 0	70 ± 0	95 ± 0.6
Turbidity (NTU)	24.0	17.0	36.0	1.0	2.0
T. Solids (mg/L)	686	565	640	784	792
Conductivity (µS/cm)	650	630	550	550	550
Chloride (mg/L)	12	20	9	12	13
pH	4.79	4.64	4.77	4.91	4.78

Table B.6. ADBW Characteristics in Sampling 2 Program (Mixture 2 Obtained)

Parameter	Carpet Name (Sampling Date)					
	10. Arslan (15.05.02)	11. İkizler (15.05.02)	12. Akrep (16.05.02)	13. Balık (16.05.02)	14. El Greco (16.05.02)	15. Oğlak (16.05.02)
COD (mg/L)	1540 ± 21	1472 ± 13	1402 ± 48	1471 ± 7	1510 ± 44	1579 ± 59
UVA $_{198\text{-}201}$	3.13 ± 0	3.18 ± 0	3.18 ± 0	3.16 ± 0	3.10 ± 0	3.13 ± 0
Color (Pt-Co)	17 ± 0.7	48 ± 2.1	47 ± 0.7	23 ± 0	9 ± 0.7	11 ± 0
Turbidity (NTU)	1.2 ± 0.07	4.0 ± 0.01	3.6 ± 0	2.6 ± 0.1	1.4 ± 0	1.6 ± 0
T. Solids (mg/L)	840 ± 31	852 ± 11	888 ± 14	999 ± 115	908 ± 40	863 ± 1
T. Hardness (mg/L)	22 ± 2.8	24 ± 5.7	80 ± 0	22 ± 2.8	4 ± 0	22 ± 2.8
Conductivity (μS/cm)	500 ± 0	505 ± 7	505 ± 7	525 ± 21	515 ± 7	520 ± 28
Chloride (mg/L)	11 ± 0	11 ± 0	15 ± 0	10.5 ± 0.7	10 ± 0	10 ± 0
pH	4.67 ± 0	4.72 ± 0	4.93 ± 0	4.70 ± 0	4.65 ± 0	4.68 ± 0

Table B.7. ADBW Characteristics in Sampling 3 Program

Parameter	Carpet Name (Sampling Date)					
	16. El Greco (13.06.02)	17. Cezanne (13.06.02)	18. Rembrant (13.06.02)	19. Botticelli (13.06.02)	20. Manet (13.06.02)	21. Goya (13.06.02)
Color (Pt-Co)	9 ± 0.7	8 ± 0.7	24 ± 0.7	8 ± 0.7	32 ± 0	11 ± 1.4
Turbidity (NTU)	1.4 ± 0.1	0.8 ± 0	2.0 ± 0	0.8 ± 0.2	3.0 ± 0	1.0 ± 0

Table B.8. ADBW Characteristics in Sampling 4 Program

Parameter	Carpet Name (Sampling Date)					
	22.Velazquez (10.10.02)	23. İkizler (10.10.02)	24. Dali (10.10.02)	25. Başak (11.10.02)	26. El Greco (11.10.02)	27. Oğlak (11.10.02)
COD (mg/L)	984 ± 111	1111 ± 28	1278 ± 108	1072 ± 26	2590 ± 56	1092 ± 47
UVA $_{195-199}$	2.75 ± 0.01	3.01 ± 0	3.00 ± 0	3.01 ± 0.01	3.07 ± 0	3.00 ± 0
Color (Pt-Co)	10 ± 0	8 ± 0.7	4 ± 0.7	14 ± 1.4	5 ± 0.7	12 ± 0
Turbidity (NTU)	1.3 ± 0.1	1.0 ± 0	0.9 ± 0.03	1.2 ± 0	1.0 ± 0.01	1.0 ± 0
T. Solids (mg/L)	316 ± 7	339 ± 6	410 ± 20	318 ± 10	524 ± 1	333 ± 3
Conductivity (µS/cm)	580 ± 14	550 ± 0	550 ± 14	545 ± 7	545 ± 7	545 ± 7
Chloride (mg/L)	12 ± 0	9 ± 0	7 ± 0	7 ± 0	8.5 ± 0.7	8 ± 0
pH	4.66 ± 0.03	4.59 ± 0	4.60 ± 0	4.59 ± 0.01	4.59 ± 0.01	4.55 ± 0.01

Table B.9. ADBW Characteristics in Sampling 5 Program

Parameter	Carpet Name (Sampling Date)					
	28. Degas (11.11.02)	29. El Greco (11.11.02)	30.Velazquez (11.11.02)	31. Blake (11.11.02)	32. Dali (11.11.02)	33. Rubens (12.11.02)
COD (mg/L)	1311 ± 35	1447 ± 24	1326 ± 16	1502 ± 47	1384 ± 32	1015 ± 44
UVA $_{198\text{-}201}$	3.06 ± 0.01	3.05 ± 0	3.01 ± 0.01	3.16 ± 0.01	3.02 ± 0	3.09 ± 0
Color (Pt-Co)	15 ± 1.4	12 ± 1.4	11 ± 0	25 ± 0	7 ± 0.7	68 ± 1.4
Turbidity (NTU)	0.9 ± 0	0.8 ± 0	0.9 ± 0	1.8 ± 0	1.0 ± 0	4.2 ± 0
T. Solids (mg/L)	752 ± 4	791 ± 8	779 ± 9	768 ± 40	754 ± 47	813 ± 14
Conductivity (µS/cm)	595 ± 7	585 ± 7	585 ± 7	600 ± 0	590 ± 0	590 ± 14
Chloride (mg/L)	13.5 ± 0.7	14.5 ± 2.1	11.5 ± 0.7	13 ± 0	13 ± 0	12 ± 1.4
pH	4.75 ± 0.01	4.78 ± 0	4.72 ± 0.01	4.59 ± 0.01	4.55 ± 0	5.12 ± 0.01

Table B.10. ADBW Characteristics in Sampling 6 Program (Mixture 3 Obtained)

Parameter	Carpet Name (Sampling Date)					
	34. Degas (11.04.03)	35. Yay (11.04.03)	36. Arslan (12.04.03)	37. El Greco (12.04.03)	38. Velazquez (14.04.03)	39. Van Dike (14.04.03)
COD (mg/L)	793 ± 16	1022 ± 14	661 ± 26	801 ± 7	1631 ± 20	1648 ± 4
UVA $_{196-201}$	3.08 ± 0.02	3.05 ± 0.01	2.89 ± 0	2.93 ± 0	3.21 ± 0	3.07 ± 0
Color (Pt-Co)	115 ± 2	84 ± 0.7	77 ± 0.7	66 ± 0.7	153 ± 1.4	130 ± 0.7
Turbidity (NTU)	14.0 ± 0	11.5 ± 0.7	4.0 ± 0	6.7 ± 0.1	18.0 ± 0	10.0 ± 0
T. Solids (mg/L)	747 ± 16	827 ± 13	726	715 ± 10	928	914 ± 6
T. Hardness (mg/L)	37 ± 4.2	16 ± 0	17 ± 1.4	30 ± 0	21 ± 1.4	20 ± 0
Conductivity (µS/cm)	646	625	638	652	615	638
Chloride (mg/L)	8 ± 0	8.5 ± 0.7	10.5 ± 0.7	10 ± 0	5.5 ± 0.7	13 ± 0
pH	5.26 ± 0.03	5.31 ± 0.01	6.37 ± 0.01	5.03 ± 0.01	4.74 ± 0.01	4.75 ± 0.01

Table B.11. ADBW Characteristics in Sampling 7 Program (Mixture 4 Obtained)

Parameter	Carpet Name (Sampling Date)	
	40. Boğa (11.07.03)	41. Balık (11.07.03)
COD (mg/L)	1424 ± 8	1552 ± 35
UVA $_{200\text{-}204}$	2.98 ± 0	3.00 ± 0.02
Color (Pt-Co)	12 ± 2.1	4 ± 0
Turbidity (NTU)	1.4 ± 0.1	0.5 ± 0
T. Solids (mg/L)	884 ± 11	983 ± 35
T. Hardness (mg/L)	42 ± 2.8	44 ± 2.8
Conductivity (μS/cm)	736	776
Chloride (mg/L)	12.5 ± 0.7	15 ± 0
pH	4.64 ± 0.01	4.81 ± 0.01

Table B.12. ADBW Characteristics in Sampling 8 Program (Sample 42 Obtained)

Parameter	Carpet Name (Sampling Date)
	42. Devis (18.11.03)
COD (mg/L)	1925 ± 30
UVA $_{200\text{-}208}$	3.25 ± 0.03
Color (Pt-Co)	50 ± 0
Turbidity (NTU)	3.3 ± 0
T. Solids (mg/L)	1326 ± 23
T. Hardness (mg/L)	18 ± 0
Conductivity (μS/cm)	837
Chloride (mg/L)	15 ± 0
pH	5.3 ± 0

APPENDIX C

COMPARISON OF REMOVAL PERFORMANCES FOR INDIVIDUAL SAMPLES AND THEIR MIXTURES

Table C.1. Pre-treatment Performance Comparison for ADBW Individual Samples and Their Mixtures

Parameter	Removal (%)						
	Rubens	İkizler-1	El Greco-1	İkizler-2	Boğa	El Greco-2	Mixture
COD (mg/L)	5.3	4.7	6.3	4.9	13.5	6.4	4.5
UVA $_{200}$	3.0	2.3	4.9	3.1	11.4	4.4	3.6
Color (Pt-Co)	82.7	79.7	75.6	75.3	97.0	100.0	77.4
Turbidity (NTU)	57.8	86.3	44.1	61.0	95.7	91.7	46.7
T. Solids (mg/L)	9.5	8.3	2.6	1.3	2.0	4.2	4.0

APPENDIX D

EXPERIMENTAL CONDITIONS IN MEMBRANE PROCESSES

Table D.1. Experimental Conditions for PDW Treatment

Figure	**Membrane**	**TMP (Bar)**	**T (°C)**	**Clean Water Flux ($L/m^2/h$)**	**Mode of Filtration**
6.2	UF 50000 Da	2.5	20	203.4	TRMF
6.4-6.7	NF	5.9	16-17	10.4	TRMF
	UF 1000 Da	5.8	16-17	13.7	
	UF 2000 Da	5.8	16	101.2	
	UF 20000 Da	1.8	16-17	98.0	
	UF 50000 Da	1.8	16	94.4	
6.8-6.16	NF	5.9	17-18	12.5	CMF
6.17-6.25	UF 20000 Da	1.8	17-19	85.0	CMF
	NF	5.9	18-19	14.1	
6.26-6.34	UF 1000 Da	5.9	18	100.4	CMF
	NF	5.8	18	19.8	
6.36-6.38	NF	5.9	18-22	29.7-38.8	TRMF

Table D.2. Experimental Conditions for ADBW Treatment

Figure	**Membrane**	**TMP (Bar)**	**T (°C)**	**Clean Water Flux ($L/m^2/h$)**	**Mode of Filtration**
6.39-6.40	UF 50000 Da	2.0	22	144	TRMF
6.41-6.42	MF 0.45 μm	-	-	-	Dead-end
	UF 50000 Da	2.0	22	455	TRMF
6.43-6.44	NF	5.9	18	23.2	TRMF
6.45-6.53	NF	5.9	18	22.1	CMF
6.54-6.62	NF	5.9	18-20	24.3	CMF
6.63-6.64	NF	5.9	18-20	21.7	TRMF
6.65-6.66	NF	6.0	18	21.8-23.4	TRMF
6.68-6.69	NF	5.9	18	18.8-19.4	TRMF
6.70-6.71	NF	5.9	18-19	18.6-21.2	TRMF

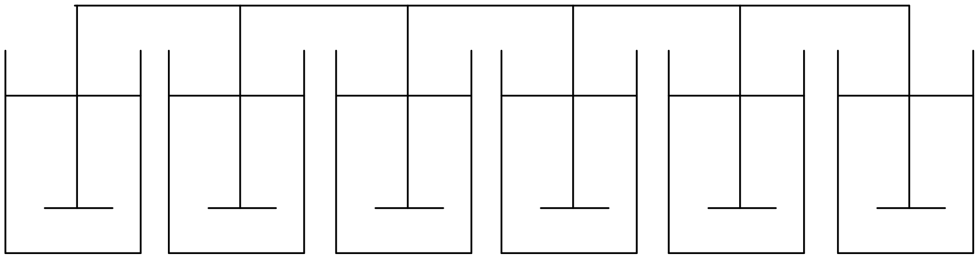
Table D.3. Experimental Conditions for PDW+ADBW Treatment

Figure	**Membrane**	**TMP (Bar)**	**T (°C)**	**Clean Water Flux ($L/m^2/h$)**	**Mode of Filtration**
6.72-6.75	NF	5.9	18-19	19-23.5	TRMF

APPENDIX E

EFFECT OF ALUM DOSING SEQUENCE AND THE PRESENCE OF INITIAL MIXING ON PRECIPITATION

While performing the chemical precipitation experiments using the jar-test apparatus for the determination of optimum alum dose, the experiments with each dose was done in duplicate. The position of the jars and the alum doses are depicted in Figure E.1. In Run 1, alum was dosed into all the jars first, starting from Jar 1 and ending with Jar 6, and then the mixers were started. Since it was not possible to make the mixers move independently, this procedure was followed deliberately to ensure that all the jars were mixed for the same period of time.



	Jar 1	Jar 2	Jar 3	Jar 4	Jar 5	Jar 6
Run 1:	50 mg/L	100 mg/L	200 mg/L	400 mg/L	600 mg/L	800 mg/L
Run 2:	50 mg/L	50 mg/L	100 mg/L	100 mg/L	150 mg/L	150 mg/L

Figure E.1. Position of the Jars and the Corresponding Alum Doses

In Run 1, the optimum alum dose was determined as 400 mg/L. However, it was later realized in Run 2 (by chance) that in the last jar (Jar 6) the removal was much higher than the previous jar (Jar 5) although the alum doses were the same (150 mg/L), and moreover, the removal efficiency obtained in Jar 6 with 150 mg/L was as high as that had been obtained by 400 mg/L of alum in Run 1. At first glance, the possible reason for this difference was thought to be the different mixing intensities in Jars 5 and 6. However, the mixers were monitored for the number of revolutions they made in a given period of time, and it was found to be the same. The only possible reason was then the difference of time period passed from the addition of alum to the start of mixers, which was always shortest for the last jar, because the mixer was started immediately after the addition of alum into the last jar. In other words, mixers were always started after the completion of alum addition into all the jars. In order to verify this possible reason, a number of experiments were conducted. For this purpose, only two jars (Jars 5 and 6) were used and the same amount of alum was dosed into them. The sequence of dosing and the start of mixers were changed (before dosing or after dosing) to provide the conditions of \`presence\` and \`absence\` of initial mixing. Any differences in the floc sizes in these identical jars were also observed visually.

The color and turbidity removal values determined for each jar are given in Table E.1. As seen from the table, higher removal efficiencies were always achieved under the condition of mixers being started before the addition of alum into the jars, which is the presence of initial mixing condition. The removal rates were observed to be lower in the jars, which were dosed first, i.e., absence of initial mixing condition. It was found out that the lack of mixing while the chemical was being added had a very significant effect on the performance of CP. The reason for this was not clearly understood, however, it might be due to a kind of interaction between the Al^+ ions and the surfactants when mixing was not provided, which reduced the efficiency of alum precipitation. A detailed experimental study should be carried out to figure out the reason.

Table E.1. Color and Turbidity Removal Efficiencies wrt Changing Sequence of Chemical Dosing and Starting of the Mixers

Alum Dose (mg/L)	Jar no.	Removal (%)		Sequence of Dosing and Mixing (Remarks)
		Color	Turbidity	
50	5	28	16	5-6-mixer*
	6	28	15	(Same floc size in both jars, low removal)
100	5	79	77	6-5-mixer
	6	31	14	(Smaller flocs and higher removal in Jar 5)
	5	34	15	5-6-mixer
	6	75	73	(Smaller flocs and higher removal in Jar 6)
	5	73	74	5 and 6-mixer
	6	76	77	(Same floc size and high removal in both)
	5	75	74	Mixer-5 and 6
	6	76	74	(Same floc size and high removal in both)
150	5	33	9	5-6-mixer
	6	93	92	(Smaller flocs and higher removal in Jar 6)
	5	94	90	Mixer-5 and 6
	6	89	85	(Same floc size and high removal in both)
200	5	98	94	Mixer-5 and 6
	6	96	93	(Same floc size and high removal in both)

* Alum was dosed into Jar 5 first, then into Jar 6, and then the mixer was started

APPENDIX F

EFFECT OF WETTING THE NF MEMBRANE BY ISOPROPANOL ON ITS PERFORMANCE

During the membrane separation experiments of the ADBW, the NF membrane NFT-50 was subjected to extra wetting by isopropanol in order to obtain clean water flux from the virgin membranes, which initially had very low or no clean water flux. These membranes were probably very dry and the initial cleaning procedure was not sufficient to obtain water flux. The extra wetting was performed by soaking the membrane into isopropanol solution for 1 min. The solution was prepared in varying concentrations of isopropanol; 1%, 10% and 60% by volume. This was done in order to find the optimum concentration of isopropanol solution. The corresponding clean water fluxes of different pairs of NFT-50 membranes are shown in Table F.1. As seen, at least 10% solution was required to increase the flux.

Table F.1. Effect of Wetting on Clean Water Flux of NFT-50 Membranes

Membrane	**Solution (%)**	**Clean Water Flux (L/m^2/h)**	
		Before Wetting	**After Wetting**
A	1	1.1	1.1
A	5	1.1	3.7
A	10	3.7	23.2
B	10	2.8	24.3
C	60	0.3	26.7

F.1. Effect on Membrane Performance for ADBWs

The effect of extra wetting on the membrane performance was also considered. In order to see whether soaking the membrane into isopropanol would open its pores and then worsen its performance or not, TRMF experiments were conducted with ADBW Mixture 3. The NF membranes B and C were used and the results were compared to the performance of another NF membrane, D, which had not been wetted with isopropanol. However membrane D had previously been used for the treatment of PDW and cleaned. As seen from Figure F.1, the normalized UVA values are very close to each other for all the membranes tested. However, the removal efficiencies given in Table F.2 do not indicate a very clear adverse effect of isopropanol. Total solids, conductivity and chloride removal efficiencies were 10-27% lower for wetted membrane B, whereas COD and total hardness removal efficiencies were 7-14% higher for the same membrane. On the other hand color and turbidity removal efficiencies did not change by the wetting procedure. These results do not directly indicate an adverse effect of wetting on the NF performance. The relative flux changes are depicted in Figure F.2. Flux decline did not occur in the membranes B and C, whereas a flux decline of 4% was observed with membrane D.

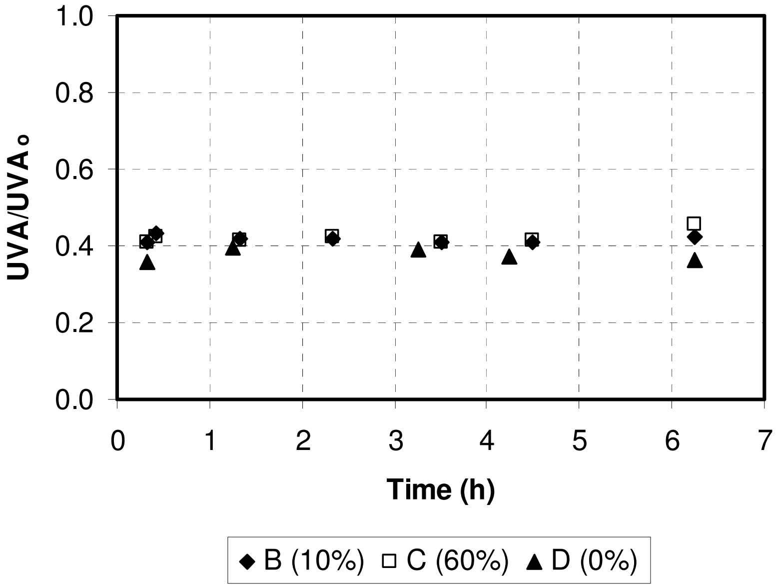


Figure F.1. Effect of Wetting on UVA/UVA$_o$ for ADBW Mixture 3

Table F.2. Effect of Wetting on NF Process Performance for ADBW Mixture 3

Parameter	**Removal (%)**		
	D (0%)*	**B (10%)***	**C (60%)***
COD	63	68	63
Color	100	100	100
Turbidity	94	93	93
T. Solids	66	56	55
T. Hardness	55	64	55
Conductivity	54	49	49

* Membrane D, B and C were wetted in 0%, 10% and 60% isopropanol, respectively

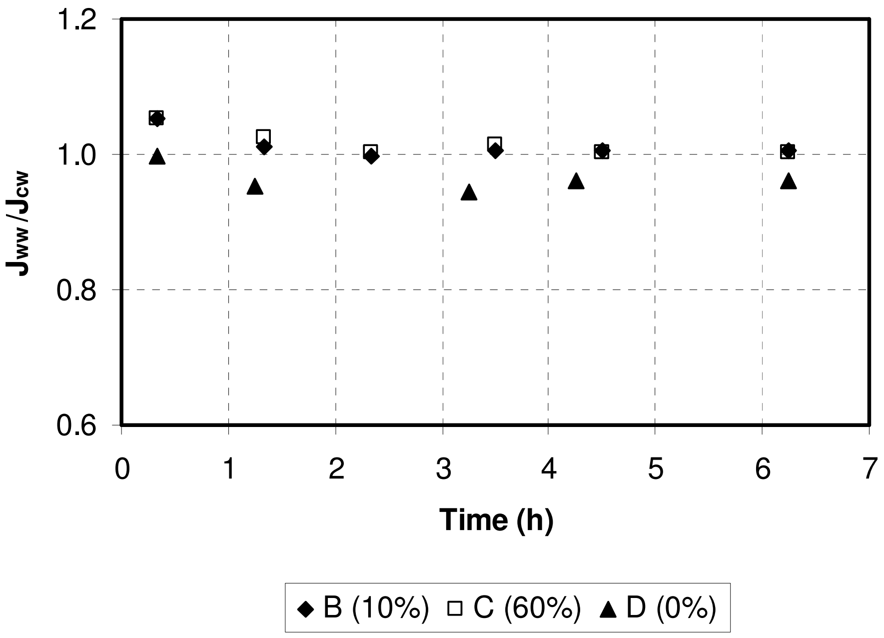


Figure F.2. Relative Flux Change for ADBW Mixture 3 (TMP=5.8 bar, T=19°C)

In order to make sure that wetting procedure did not cause the poor performance of the NF process, a new ADBW mixture (Mixture 4) and a new NFT-50 membrane (membrane E) with a low clean water flux was used in a new TRMF experiment. Membrane E was not wetted by isopropanol but only subjected to initial cleaning. The changes of UVA values monitored during this experiment are depicted in Figure F.3. As seen, the UVA rejection was even lower for Mixture 4, which was around 10%. For flux decline, membrane E had a very similar trend as membrane D, with a flux decline level of 5% (Figure F.4). The performance of the NF process for Mixture 4 is shown in Table F.3. As seen, the performance of membrane E was even worse with COD removal efficiency as low as 55%. Therefore, it can be concluded that the poor performance of the NF process for ADBW is not due to the wetting of the membrane by isopropanol.

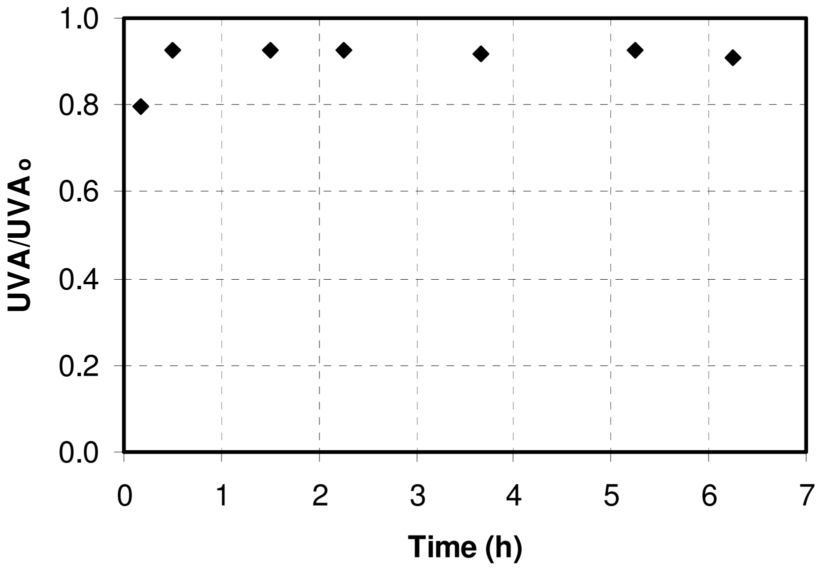


Figure F.3. Change of UVA/UVA$_o$ as a Function of Time for ADBW Mixture 4

Table F.3. NF Process Performance for ADBW Mixture 4

Parameter	**NF Permeate Quality**	**Removal (%)**
COD (mg/L)	568	55
Color (Pt-Co)	0	100
Turbidity (NTU)	0.21	85
T. Solids (mg/L)	514	47
T. Hardness (mg/L)	13.5	66
Conductivity (μS/cm)	519	32

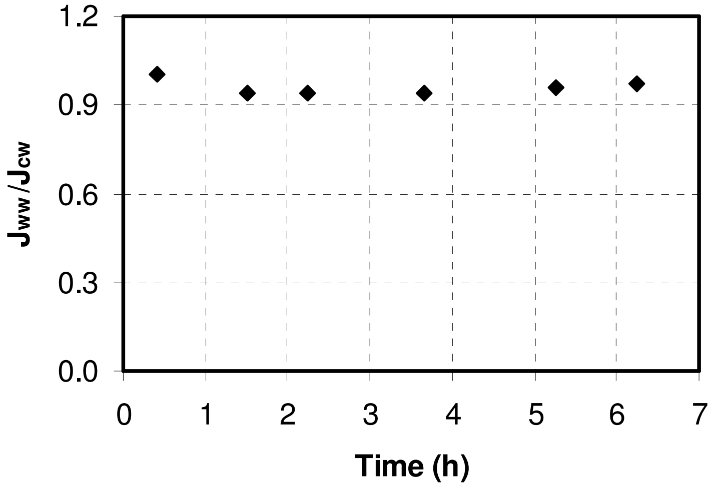


Figure F.4. Relative Flux Change for ADBW Mixture 4 (TMP=5.8 bar, T=18 °C, J_{cw} = 5.0 L/m^2.h)

F.2. Effect on Membrane Performance for PDWs

Although the comparison of the NF process performances for two different mixtures of ADBWs had showed that the performances for wetted and not wetted membranes were parallel to eachother, it was decided to see the behavior of the NF membranes for PDWs under the same conditions. In this way, a complete comparison could be made for the conditions of wetting and not wetting. To do this, the removal performances of the NF membranes used for ADBWs were compared to the performance of the same NF membranes used for PDW (Figure F.5). Here, the effect of wetting the NF membrane by isopropanol can easily be seen. Only color and turbidity were removed at similarly high efficiencies for both wastewaters, and wetting procedure had no effect on the removal efficiencies of these parameters. The rejections of the NF membrane for all the other parameters were significantly lower for ADBW. The performance of the wetted and nonwetted membranes for ADBWs were similar to eachother, and they were all lower than the removal performances achieved for PDWs. The performance of the NF process was not affected by the wetting procedure as seen from the removal values. Therefore, it can be concluded that the low performance of the NF process for ADBWs is basically due to the characteristics of the wastewater but not the wetting of the membrane by isopropanol. As a result, it was decided to apply the wetting procedure in order to obtain flux from the NF membranes purchased.

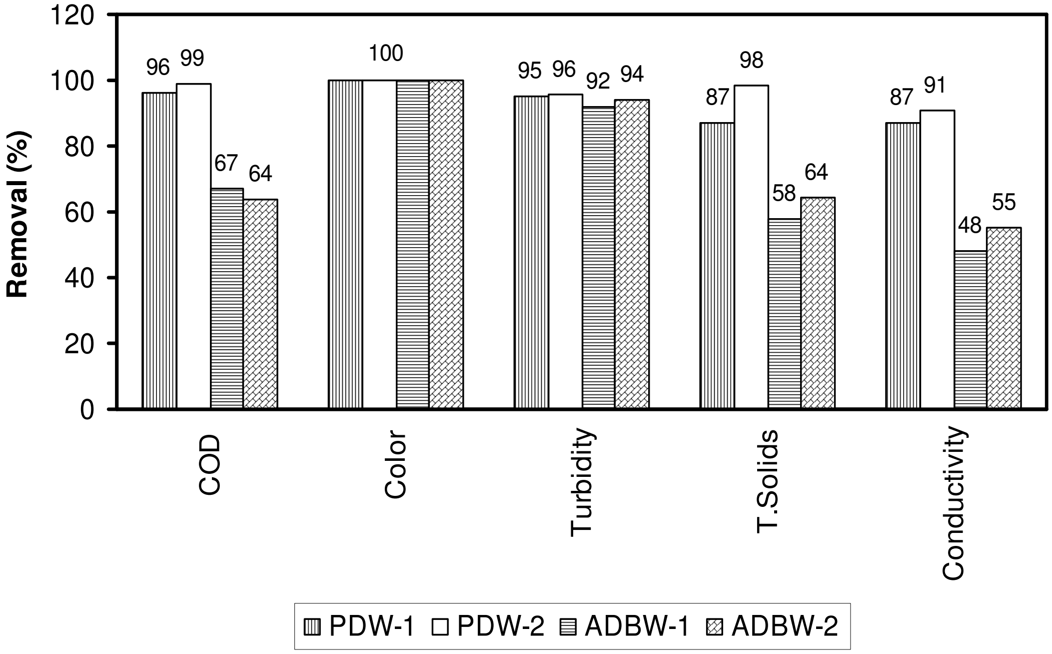


Figure F.5. Comparison of NF Performance for PDW and ADBW (1: NF membrane wetted by isopropanol, 2: NF membrane not wetted by isopropanol)

CURRICULUM VITAE

PERSONAL INFORMATION

Surname, Name: Çapar, Gökşen
Nationality: Turkish (TC)
Date and Place of Birth: 16 March 1972, Ankara
Marital Status: Married
Phone: +90 312 286 36 72
e-mail: gcapar@metu.edu.tr

EDUCATION

Degree	**Institution**	**Year of Graduation**
MS	METU Environmental Engineering	1998
BS	METU Environmental Engineering	1994
High School	TED Ankara College	1990

WORK EXPERIENCE

Year	**Place**	**Enrollment**
1997-2004	METU Department of Environmental Eng.	Teaching Assistant
1995-1996	TİTAŞ A.Ş.	Sales Engineer

SELECTED PUBLICATIONS

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