PROCESS OPTIMIZATION ON CLEAN WATER RECOVERY FROM REAL REACTIVE DYEING EFFLUENTS BY NANOFILTRATION

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ABSTRACT

PROCESS OPTIMIZATION ON CLEAN WATER RECOVERY FROM REAL REACTIVE DYEING EFFLUENTS BY NANOFILTRATION

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Clean water recovery from the reactive dyeing effluent of a cotton textile mill with membrane filtration was investigated. Lab-scale experiments were performed with wastewater samples taken from the last three steps of the dyeing line, comprising four sequential baths of dyeing, warm rinsing, washing with soap, and lukewarm rinsing. Waste dyeing bath was deliberately excluded considering its extremely high salt and color contents. Two sets of experiments were performed; direct nanofiltration (NF) and NF with pretreatment. In the direct application, NF90 membrane was tested at total recycle mode (TRM), under different trans-membrane pressures (TMPs) and cross-flow velocities (CFs). The best permeate quality was achieved at 14 bar TMP and 58.9 mL/s CF, with 99% TOC and 96% conductivity retentions where the permeate flux was 21.12 L/m^{2}h. Increase in CF did not cause any significant improvements in permeate quality and flux; while TMP increase reduced osmotic pressure influence. When the designated optimal conditions were tested at concentrated mode, till 2.06 volume reduction factor, permeate quality remained satisfactory.

In the second part, firstly, 0.45 µm MF and 150 kDa UF membranes were tested. UF was found more promising, so, NF after pretreatment studies were completed with UF. Minor improvements in NF permeate color were achieved. Besides, NF flux increased to 35.08 L/m^{2}h at 14 bar, due to serious reductions in concentration polarization and fouling.

Also, the possible effects of the inclusion of dyeing bath to the feed were examined. UF performance was not influenced; however, NF permeate quality and flux deteriorated dramatically.

Keywords: Membrane Separation, Nanofiltration, Reactive Dyeing Effluent

ÖZ

REAKTİF BOYAMA ATIKSULARINDAN NANOFİLTRASYON İLE TEMİZ SU KAZANIMINA YÖNELİK SÜREÇ OPTİMİZASYONU

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Pamuklu tekstil fabrikasındaki reaktif boyama prosesi atıksularından membran filtrasyon yöntemi ile temiz su geri kazanımı araştırılmıştır. Laboratuar ölçekli deneyler, boyama, sıcak durulama, sabunla yıkama ve ılık durulama banyolarını içeren boyama hattının son üç aşamasından alınan atıksu numuneleri ile gerçekleştirilmiştir. Boyama banyosu atıksuyu, aşırı yüksek tuz ve renk içeriği göz önüne alınarak, bilinçli olarak çalışmada kullanılacak besleme suyu karışımına dahil edilmemiştir.Deneyler doğrudan nanofiltrasyon ve ön arıtım sonrası nanofiltrasyon olmak üzere iki set olarak gerçekleştirilmiştir. Doğrudan uygulamada, NF90 membran farklı trans membran basınç ve çapraz akış hızları altında tüm geri çevirim modunda test edilmiştir. En iyi süzüntü suyu kalitesi 14 bar basınç ve 58.9 mL/s çapraz akışda %99 toplam organik karbon ve %96 iletkenlik giderimi ile elde edilirken, süzüntü akısı 21.12 L/m^{2}h olarak gözlenmiştir. Çapraz akışdaki artış hem süzüntü kalitesinde hem de akısında önemli bir iyileşmeye neden olmamışken trans membran basıncın arttırılması ozmotik basınç etkisini azaltmıştır. Belirtilen optimal koşullar konsantre modda test edildiğinde, süzüntü suyu kalitesi hacim azaltma faktörü 2.06 olana kadar tatmin edici kalmıştır.

İkinci bölümde, öncelikle, 0.45 µm MF ve 150 kDa UF membranları test edilmiştir. UF daha umut vaadedici bulunmuştur, bu nedenle ön arıtım sonrası NF çalışmaları UF ile tamamlanmıştır. NF permeans renginde küçük gelişmeler sağlanmıştır. Bununla birlikte, konsantrasyon polarizasyon ve kirlenmedeki ciddi azalmalara bağlı olarak, NF akısı 14 barda 35.08 L/m^2h seviyesine yükselmiştir.

Ayrıca, boyama banyosunun besleme suyuna ilavesinin olası etkileri incelenmiştir. UF performansı etkilenmemiştir; ancak, NF süzüntü suyu kalitesi ve akı dramatik bir şekilde bozulmuştur.

Anahtar Kelimeler: Membran Ayrıştırma, Nanofiltrasyon, Reaktif Boyama Atıksuyu

To my family…

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LIST OF ABBREVIATIONS

AFM	Atomic Force Microscopy
BAT	Best Available Techniques
BOD	Biochemical Oxygen Demand
CF	Cross Flow
CFV	Cross Flow Velocity
CIP	Clean in Place
CM	Concentrate Mode
COD	Chemical Oxygen Demand
EPA	Environmental Protection Agency
J	Flux
MBR	Membrane Bioreactor
MF	Microfiltration
MWCO	Molecular Weight Cut Off
NF	Nanofiltration
R	Resistance
RO	Reverse Osmosis
SAC	Spectral Absorption Coefficient
SEM	Scanning Electron Microscopy
TDS	Total Dissolved Solids
TMP	Trans Membrane Pressure
TOC	Total Organic Carbon
TRM	Total Recycle Mode
TSS	Total Suspended Solids
UF	Ultrafiltration
UPW	Ultra Pure Water
VRF	Volume Reduction Factor
WW	Wastewater

CHAPTER 1

INTRODUCTION

Industrial textile manufacturing comprises many processes such as pretreatment, dyeing, printing, and finishing. Among these production processes, dyeing process is considered as the most problematic because it generates the largest fraction of textile industry effluents (U.S. EPA, 1997). Huge amount of energy and water is consumed, besides, critical levels of chemical pollution is produced.

Reactive dyeing process is a widely used dyeing method in the textile industry especially for cotton manufacturing. More than 50 percent of cotton fibres are dyed with reactive dyes but, actually, reactive dyes are not the most favorable option in accordance with the ecological point of view (Allègre et al., 2006) To achieve reactive dyeing of one kilogram cotton, 70-150 L of water, 600-800 g of NaCl and 30-60 g of dyestuffs were required (Allègre et al., 2004). As 30 percent of reactive dyes remain unfixed (Chollom et al., 2015), reactive dyeing results in quite colored wastewater generation comprising high levels of COD and suspended solids with a very high salt content. Due to salinity problem associated with high salt concentration of effluents, the color problem and the huge amount of wastewater resulting from the excess use of water , wastewater coming from reactive dyeing process is needed to be well managed.

There are many conventional alternatives used for the reclamation of reactive dyeing effluents to meet the reuse standards. Because of the high toxicity of dyeing auxiliaries, low biodegradability of reactive dyes, variable pollutant concentrations and fluctuating flow rates, it is not possible to reach a satisfying water quality level with conventional methods.

As an advanced treatment technology, membrane filtration processes are quite promising options for the recovery and reuse of textile dyeing wastewaters. With the increase in water scarcity and continuous water demand, interest in the potential applications and improvements of membrane technology has raised. Compared to other pressure driven membrane filtration processes, NF is quite favorable option that eliminates the major problems by achieving complete decolorization and rejection of monovalent/divalent ions (Judd et al., 2003, Tang and Chen, 2002, Allègre et al., 2006).

1.1 Objective and Scope

The overall objective of this study is to designate optimal configuration and operating conditions for clean water recovery from reactive dyeing effluents with membrane-based treatment methods, basically nanofiltration.

The core of study was testing NF90 membrane for this purpose at different TMPs, CFs and configurations (with or without pretreatment). Mixture of effluents collected from rinsing with hot water, soaping and rinsing with warm water processes which were names as Bath#2, 3, and 4 following the reactive dyeing bath (Bath#1) were used as feed solution. Effluents coming from Bath#1 was excluded due to its extremely high salt and color contents and the mixture of the last three baths were used as feed solution during all experiments except the ones conducted to examine the possible effects of inclusion of dye bath to feed mixture.

In the first part of study, single stage NF experiments were conducted at two different CFs and three different TMPs, and their effects on treatment efficiency and fouling behavior of NF membrane were questioned to designate the optimal operating conditions. This part of the research also covers the evaluation of the effects of VRF and wastewater composition on the performance of NF90 membrane to perform more factual simulation of real systems.

Following the selection of pretreatment option by testing 0.45 µm MF and 150 kDa UF membranes with dead-end filtration, cross-flow pretreatment experiments was carried on in order to collect permeate. Secondary effluent was treated with NF and obtained results were compared with the direct application of NF to observe whether any enhancement in NF performance and the final product quality was achieved or not. The possibility of conducting NF at lower TMPs than optimal one after pretreatment while maintaining the enhancements achieved by pretreatment was also investigated. In addition, it was questioned whether assembling pretreatment prior to NF recompenses the possible inclusion of dye bath to feed solution mixture without any disturbance in both UF and NF performance.

During the research, evaluations were based on the treatment efficiency in terms of TOC, conductivity, and color in addition to filtration flux and the membrane fouling behaviors. Influence of osmotic pressure on NF performance was examined in detail.

CHAPTER 2

BACKGROUND

2.1 Textile Manufacturing Processes

Textile industry is a very long and complex manufacturing chain composed of a wide number of sub-sectors. The production chain starting with very first process of raw material harvesting ends with finishing treatments which are shaped with the type of raw material and the final product requirements. A general diagram of the processes followed during textile production chain is as shown in Figure 2.1. (European Commission, 2003).

There are two types of textile fibres differing from each other by their origins such as natural and man-made fibres. Natural fibres are basically cellulosic, protein or mineral fibres (Ibrahim, N. A., 2011), whereas man-made fibres include both transformed naturel polymers like viscose, synthetic fibres (e.g. acrylic, polyester and nylon) and fibres from inorganic substances (ceramic, glass, metals, etc.) (European Commission, 2011).

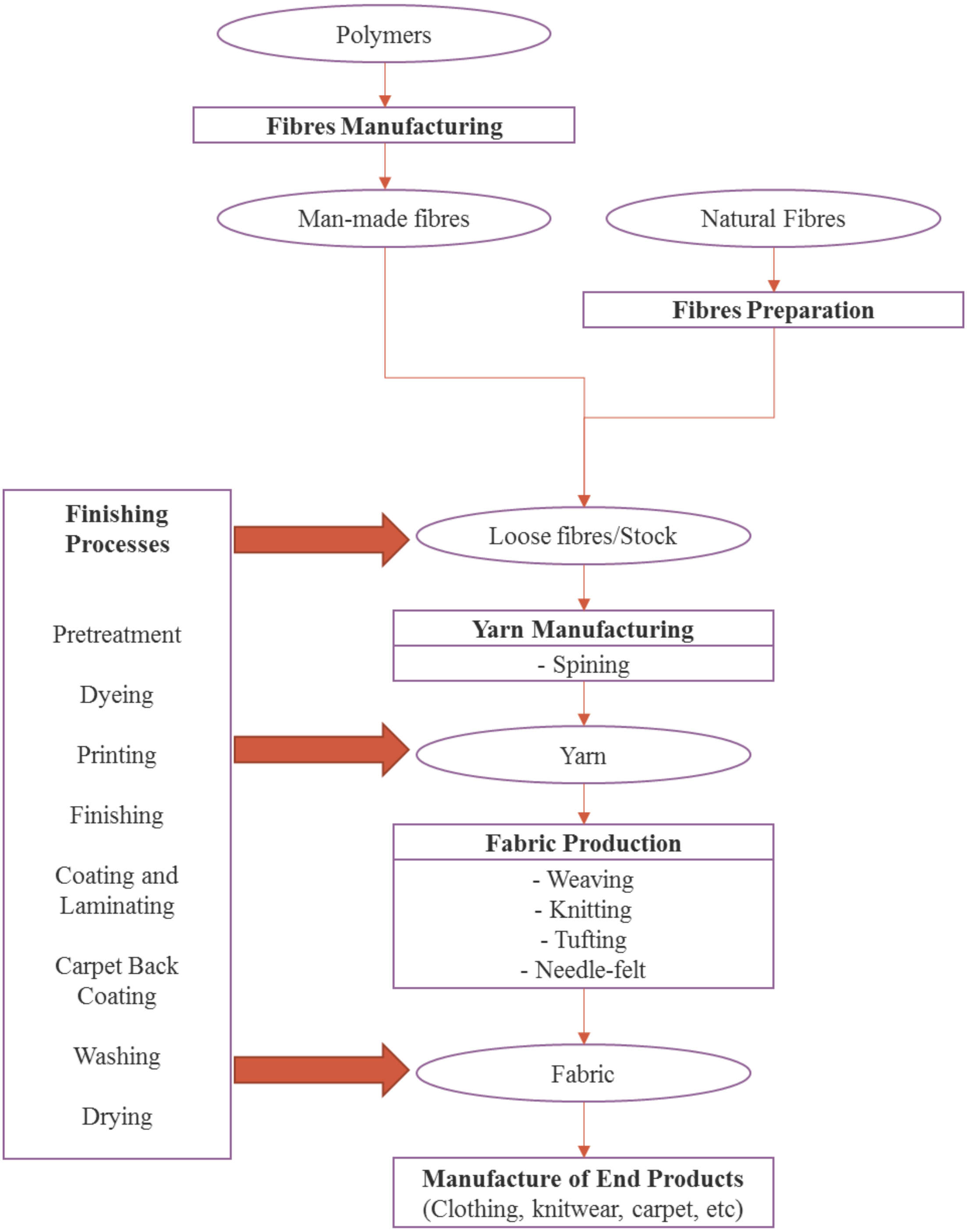

Figure 2.1: General Diagram of Textile Chain (European Commission, 2003)

During textile manufacturing chain, fabric passes through both dry processes such as yarn formulation (e.g. texturing, fiber preparation, spinning), fabric formulation (e.g. knitting, warping, slashing, weaving), and fabrication (cutting and sewing) and wet processes such as preparation, dyeing and/or printing and finishing. Detailed scheme showing wet processes is given at Figure 2.2 (U.S. EPA, 1997).

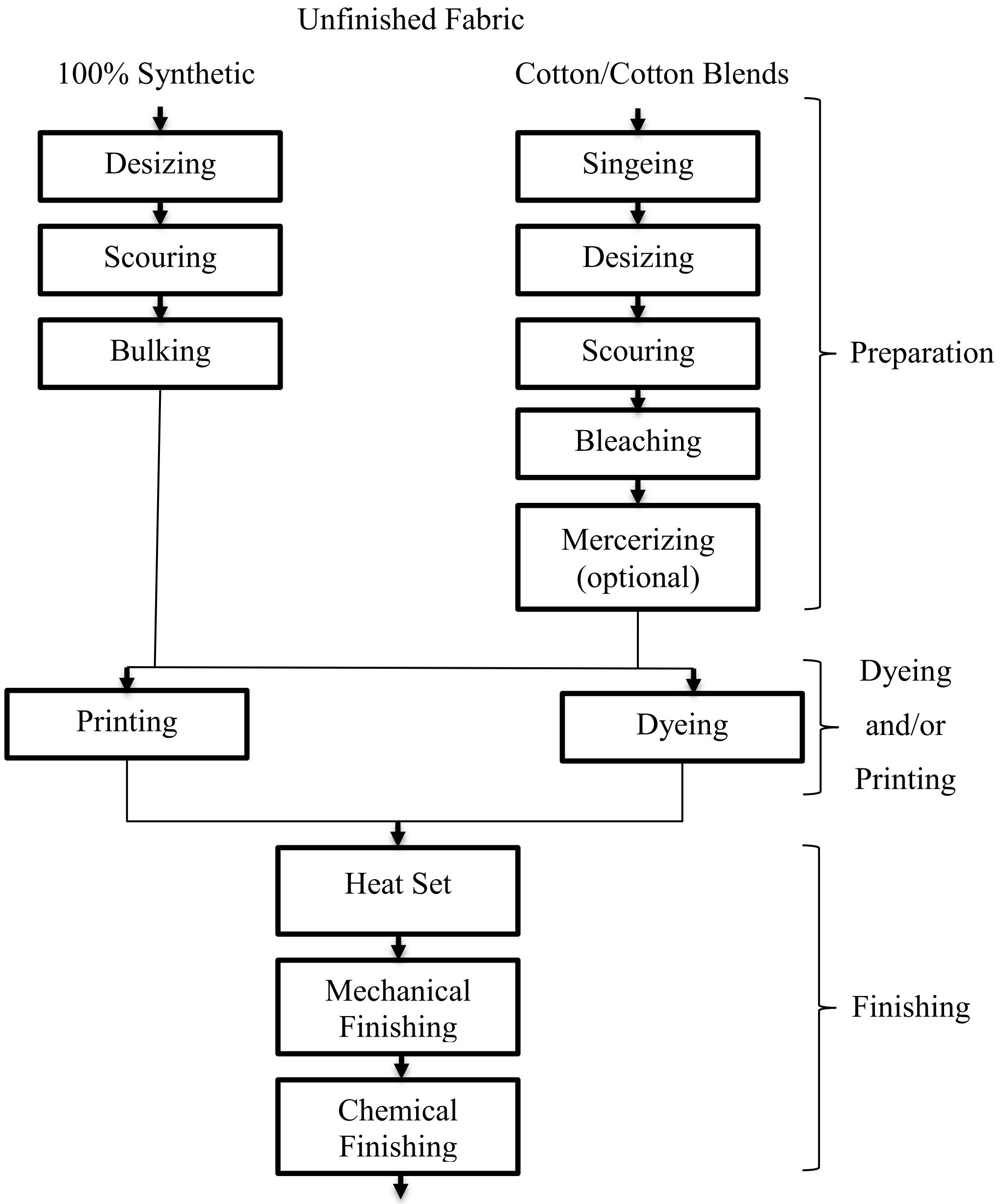

Figure 2.2: Wet Processes of Textile Production Chain (U.S. EPA, 1997)

These wet processes result in wastewater discharge causing adverse effects on the environment. Among them, dyeing is considered as the most problematic one. Dyeing effluent covers the largest fraction of total wastewater generation by textile manufacturing industry (U.S. EPA, 1997). Large amount of colored wastewater coming from dye bath and rinsing/washing baths, causes aesthetic problems while corrupting the state of receiving body.

2.1.1 Textile Dyeing Process

Dyeing of textiles are achieved by following three main steps starting with dye sorption by the substrate, followed by diffusion of dye into the substrate and ended with its fixation on the substrate (Aspland, 1998). It is possible to perform dyeing with different methods such as batch, continuous or semi-continuous (Clark, 2011) and machines are used for textile dyeing process during mass production (Chakraborty, 2010). There are many available types of dyeing machines such as package dyeing machines, beck dyeing machines, jet dyeing machines for batch dyeing method and continuous dyeing machinery consisting padder, dryer, thermosol oven, steamer, and wash boxes (Aspland, 1998) whereas dyeing machine type directly affects the water and energy consumption (Khatri et al., 2015).

During colorization of a fabric with intended color, final product quality, in terms of uniform and solid shade all over the fabric without any alteration, is affected by many factors such as texture, chemical and physical construction of the fabric, treatments which the fabric is exposed before and after the dyeing step. The type and extent of treatment that the textile undergoes before dyeing process enhance the absorbency and whiteness of substrate resulting in a successful dyeing application only if other factors are also appropriate. Factors like type and form of textile, formulation, and preparation of dyeing recipe, dyeing method and machinery, and temperature and pH of dyeing bath solution need to be well-matched with each other. Any adjustments done to promote this matching reduce the needed effort and dyeing cost. (Chakraborty, 2010), on the other hand, fiber type and dye class are the factors designating amount and type of chemical consumption and wastewater generation (Khatri et al., 2015).

There are many widely used classes of dyes such as direct, vat, sulphur, azoic, reactive, acid, disperse and basic dyes which are classified according to their chemical structure, fastness, synthesis reactions, color, way of application, invention date, etc. (Clark, 2011). It is not possible to color all fabrics with all types of dyes. The correct match between the type of dye and fabric is crucial to achieve levelness and bright colored textile. Table 2.1 shows the dye types and their area of application (Sharan, 2004) and their fixation ratios (U.S. EPA, 1997).

Table 2.1: Dye Types and Their Area of Application (Sharan, 2004) and Fixation Ratios (U.S. EPA, 1995)

Dye Type	Application	Fixation Ratio (%)
Direct	Cellulosic, rayon, silk and wool fibres.	70-95
Vat	High quality cotton like towel, denim fabric, etc.	80-95
Sulphur	Heavy cellulosic fibres.	60-70
Reactive	Cellulosic, rayon, silk and wool fibres.	60-90
Acid	Silk, wool and nylon.	80-93
Basic	Acrylic.	97-98
Disperse	Polyester, acetate, nylon and acrylic.	80-92

Among dye classes used for cotton dyeing, reactive dyes are favored due to their accessibility, fastness, and ability to produce bright shades of a variety of color (Hussain et al., 2009) while binding covalently to the textile.

2.1.2 Reactive Dyeing

Reactive dyeing is a very widespread and favored application in textile industry especially for cotton dyeing since its first introduction to the market at the year of 1956 (Chattopadhyay, 2011) due to its fastness, ability to give brilliant color on fibres and high resistance to sunlight degradation. In textile industry, reactive dyes; the largest dye class (U.S. EPA, 1997), cover 38% of cellulose textile market (Lewis, 2011).

Reactive dyes have a wide range of color and shade. Reactive dyes simply form covalent dye-fibre bonds (Lewis, 2011) and consist of four parts; the chromogen, the reactive system, bridging unit, and the solubilizing parts as shown in Figure 2.3 (Chattopadhyay, 2011). The structure of C.I. Reactive Black 5 is given in Figure 2.4 as an example of reactive dyes (Aspland, 1998). There are many groups of reactive dyes which are specified according to the type of the reactive group and also the number of functional group in the structure of dye (Khatri et al., 2015). Lewis (2011) listed these classes as halo-triazines, halo-pyrimidines, halo-quinoxalines, vinylsulphone dyes, acrylamide and substitude acrylamides, polyfunctional reactive dyes, neutral-fixable reactive dyes, and acid fixing reactive dyes. Among these reactive dye classes, mono-functional ones were available at earlier times. Then, with the advances, reactive dyes with multi-functional groups were created (Khatri et al., 2015).

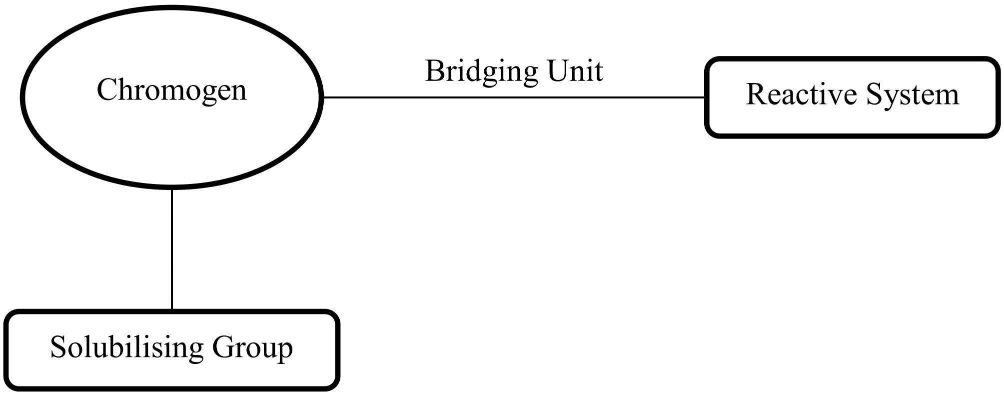

Figure 2.3: Main Structure of a Reactive Dye (Chattopadhyay, 2011)

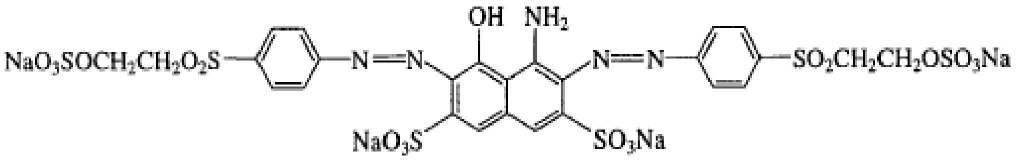

Figure 2.4: C.I. Reactive Black 5 (Aspland, 1998)

It is possible to conduct reactive dyeing only at a specific pH and temperature (Aspland, 1998). When applied to cotton cellulose, dye bath solution is needed to be alkaline. As shown in Figure 2.5, dye-fiber reaction results in attachment of dye to substrate with covalent bond (Chakraborty, 2014). At this point, high concentrations of salt may be needed to be added to dyebath solution to overcome any possible affinity deficiency (Chakraborty, 2014).

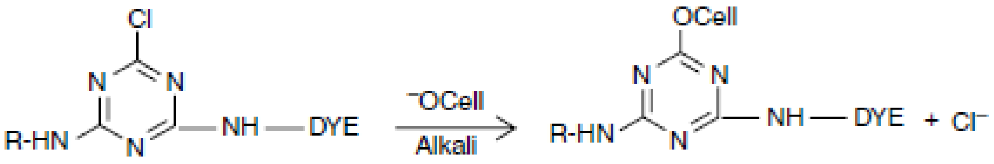

Figure 2.5: Dye-Fiber Reaction of Cotton Cellulose with Reactive Dye (Chattopadhyay, 2011.)

To reach targeted shade and color, fabric is generally dyed with mixture of three dyes resembling each other in terms of their reactive groups and exhaustion characteristics (Sultana et al., 2007).

2.1.3 Characteristics of Reactive Dyeing Effluents

During reactive dyeing method, huge amount of water is consumed at each step of the dyeing process. To achieve dyeing of 1 kg of fabric, 71-142 liters of water is needed and biggest portion of this usage is employed by rinsing which the fabric undergoes at several times during its dyeing (Chavan, N. D., European Commission, 2003).

For dyeing cotton, a pH of 9.5 to11.5 is needed where it is provided with $NaCO_3$ and/or NaOH. Also, salt (NaCl) is added to enhance dye bath exhaustion where surfactants play important role to draw away unfixed dye attached on dyed fabric after dyeing step is completed. Because of low fixation ratio of reactive dyes (60-90% which can be seen from Table 2.1), effluents from both dye and rinsing/washing baths includes very high concentrations of unfixed dye (Khatri et al., 2015). The needed temperature varies between 40 to 80ºC during different steps of reactive dyeing (European Commission, 2003). When basic conditions, high temperature and extreme salt content are banded together, the effluent becomes hard to be managed. The wastewater basically contains high concentrations of color, salt, alkali, unfixed dye, surfactants, defoamer and diluents (U.S. EPA, 1997). Examples on typical characteristics of textile dyeing wastewater given in literature are presented in Table 2.2 and Table 2.3.

Table 2.2: Composition of Reactive Dyeing Wastewater in Terms of COD, BOD, pH, Conductivity, TDS, Salinity, Turbidity, and Alkalinity (Aouni et al., 2012, Khatri et al., 2015, Mondal et al., 2016)

Parameter	Unit	Aouni, 2012	Khatri, 2015	Mondal, 2016
COD	mg/L	708	1400-1700	1400
BOD	mg/L	-	760-900	-
pH		7.11	9.8-11.8	11.2
Conductivity	µS/cm	3840	-	14000
TDS	mg/L	3137	6000-7000	10000
Salinity	g/L	-	-	8.1
Turbidity	NTU	4.02	-	-
Alkalinity	mg/L	-	17-22	-

Table 2.3: Color Contents of Different Bath Effluents from Exhaust Dyeing with Reactive Dyes in terms of Spectral Absorption Coefficients (SAC) (European Commision, 2003)

# of Bath	Bath Name	SAC 436 nm (1/m)	SAC 500 nm (1/m)	SAC 620 nm (1/m)
Light Shade				
1	Exhaust dyeing	43	18	6
2	Rinsing-I	9	4	2
3	Rinsing-II	4	2	1
4	Rinsing-III	2	1	1
5	Rinsing-IV	1	0.5	0.2
Dark Shade				
1	Exhaust dyeing	328	315	320
2	Rinsing	325	298	308
3	Neutralization	309	220	246
4	Rinsing-I	316	185	196
5	Rinsing-II	316	164	154
6	Soaping	321	177	132
7	Rinsing-III	205	94	61
8	Rinsing-IV	63	27	17
9	Rinsing-V	29	13	7

2.2 Literature Review on Reactive Dyeing Effluent Treatment

The high pollutant load of reactive dyeing effluents in terms of many water quality parameters, mentioned in Table 2.2 and Table 2.3 at the previous section, clearly demonstrates that discharge of reactive dyeing wastewater is highly problematic for the environment. Discharge of reactive dyeing effluent consisting of high concentrations of salt, COD, color, and turbidity causes color problem and salt deposition at receiving body while leading high consumption of limited water sources.

To decrease the amount and the pollutant load of dyeing effluents, it is possible to implement best available techniques (BAT) during the application of dyeing (Ozturk et al., 2016). On the other hand, effluent treatment after dyeing approach (Khatri et al., 2015) is crucial to meet legislative requirements or to reach needed water quality criteria (for reuse and/or discharge purposes) which are also given above (Table 2.4). This approach is needed to be taken under consideration carefully, because of the requirements of higher fixed and variable costs related with initial investments, and operational and maintenance expenses. Khatri et al. (2015) stated that there are three main treatment methods, which are physical, biological, and chemical treatments. Although in some cases only one of those treatment methods is enough to meet legislative requirements, the complexity of the reactive dyeing wastewater may create a need of using a combination of these methods. Method determination is mainly dependent to treatment purpose (Aouni et al., 2012) and the characteristic of wastewater. They all have their own advantages and disadvantages. Following sections cover descriptions and examples showing strengths and weaknesses of current treatment methods.

Table 2.4: Water Quality Criteria for Reuse in Textile Industry (Vajnhandl et al., 2014, Chollom et al., 2015) and Direct/Indirect Discharge (Arslan et al., 2016)

Parameter	**Water Reuse Criteria**	**Direct Discharge Criteria**	**Indirect Discharge Criteria**
COD (mg/L)	0-160	100	200
BOD_5 (mg/L)	0-20	25	50
Alkalinity (mg/L)	50-200	-	-
Hardness (mg/L)	0-100	-	-
TDS (mg/L)	100-1000	-	-
TSS (mg/L)	0-50	60	100
Turbidity (NTU)	15[1]	-	-
Conductivity (μS/cm)	800-2200	-	-
pH	6.5-8.0	6-9	6-9
Color (Lovibond Unit) (Pt-Co)	0-2 0-20[1]	70[2]	80[2]

1: Taken from the study of Chollom et al. (2015).
2: Given as dilution ratio.

2.2.1 Chemical Treatment Methods

2.2.1.1 Electrochemical Treatment

Decolorization of dyeing effluents can be achieved with electrochemical methods by the means of direct or indirect oxidation (Riera-Torres et al., 2011). Besides that, organic substances are degregaded by the electric current as a result of reactions on the surface of electrodes (Sanromán et al., 2004). Electrochemical treatment is a clean and cost-effective technology because no chemical addition is required and the waste generation is quite limited (López-Grimau et al., 2016, Sanromán et al., 2004).

Removal efficiency of electrochemical treatment enhances with the increase in the chloride concentration and current density (Rajkumar et al., 2007). Because of this and as stated by López-Grimau et al. (2016), electrochemical treatment is preferable for color removal of reactive dyeing wastewater including high salt content by its nature. 95-100 percent of color content reduction is possible with less electricity need and operational cost. On the other hand, removal of many different dyes was achieved by Sanromán et al. (2004).

Short electrolysis courses conclude in near to complete color removal. However, only 56 and 16 % of COD and TOC removal was reached, respectively (Riera-Torres et al., 2011, Rajkumar et al., 2007). Increase in the expenses related to the lifetime of the electrodes and electricity may restrict the application of electrochemical methods (Mook et al., Article in Press). Moreover, if initial pH is high and temperature increase during redox reaction is not controlled, color removal efficiency is lowered (Rajkumar et al., 2007).

2.2.1.2 Advanced Oxidation

Oxidation is an effective process achieving color removal and elimination of organic compounds by introducing active oxidants such as fenton reagent, ultraviolet photolysis, ozone, and some other reagents. Among them, ozonation has potential of eliminating toxicity while improving the biodegradability of wastewater. Ozonation pretreatment prior to biological treatment strengthens the treatment performance whereas Hu et al. (2016) mentioned the possibility of achieving decolorization level which satisfies the reuse criteria. Besides, oxidation capacity, lack of by-product generation, ease of operation and no requirements of energy input make ozonation preferable. Ozone dose and the temperature enhances the oxidation but ozonation is sensitive to wastewater characteristics including pH, salt content, and type, nature, and concentration of dye. Also, generation of by-products is the major weakness of advanced oxidation processes. The low cost-effectiveness and half-life are the other drawbacks (Dasgupta et al, 2015, Hu et al., 2016, Somensi et al. 2010, Wu et al., 2008).

2.2.1.3 Enzymatic Catalysis

When compared to other conventional physico-chemical treatment methods, enzymatic treatment is easier to apply and results in higher treatment efficiency. Ligninolitic enzymes are concentrated on where they seemed as a promising option to be used in enzyme processes for textile effluent treatment. Among the enzymes within this enzyme class, laccases are used in high amounts for many purposes in textile manufacturing like textile dye synthesis, effluent treatment, etc. Laccases have the ability to react with chromophoric part of dyestuff without any side reactions which enables its usage for decolorization. Its ease of dosage preparation, application, and removal from effluent after treatment reduces energy usage and costs (Khouni et al., 2011).

At a study conducted by López-Grimau et al. (2016), 93% of color was successfully removed. However, they also stated that this removal efficiency was found very sensitive and dependent to many factors which is confirmed by the statements of Khouni et al. (2011). As the reaction rate is regulated by the available enzyme concentration at the presence of limitless amount of substrate, concentrations of both enzyme and substrate are important parameters affecting the efficiency. Control of pH and temperature during treatment is very crucial which are directly influence the enzymatic activity. So, enzymatic catalysis with laccase was considered as applicable option only for the decolorization of reactive dyeing effluents (López-Grimau et al., 2016). On the other hand, it is known that no significant removal of COD and salinity can be achieved with this treatment method (Khouni et al., 2011).

2.2.2 Biological Treatment Methods

Wastewater is treated biologically by the means of microbial consumption of biodegradable organic portion of pollutants concluding in microbial growth at the presence of oxygen acting as electron acceptor (aerobic systems) or at the absence of oxygen (anaerobic systems). When compared with other treatment methods, biological treatment is a cleaner method because of no need of chemical addition and the sludge emerging as an end-product consisting insignificant chemical loads.

The sludge generated by suspended or attached microbial growth should be drained from the biological reactor when it reaches to the amount exceeding the reactor stability limit. This can be performed by either sedimentation tanks conventionally following biological treatment or membrane processes named as membrane bioreactor (MBRs). MBR results in better treatment efficiency because it enhances biodegradation. By increasing sludge age, it generates less waste sludge. Also, replacement of sedimentation tanks with membrane separation systems decreases the use of area (Arslan et al., 2016).

Despite the mentioned advantages together with high COD removal rates which can be easily achieved by biological treatment systems, these systems particularly aerobic ones do not seem applicable for reactive dyeing effluent treatment because of low biodegradability and toxicity of the dyestuff. Proper elimination of color cannot be completed, so effluent quality does not meet legislative requirements (López-Grimau et al., 2016, Lu et al, 2010) as most textile dyes show resistance to aerobic biological treatment (Allègre et al, 2004). Allègre et al. (2006) stated that biological elimination of toxic and non-biodegradable organic substances used in textile manufacturing processes, especially dyeing process, is possible with the addition of adsorbents or powdered activated carbon to biological treatment.

2.2.3 Physical Treatment Methods

2.2.3.1 Adsorption

Adsorption is a common, effective, and simple method used for the removal of both dissolved and undissolved pollutants. Adsorption of a substance on the surface of absorbents (e.g. activated carbon) is achieved by the attraction forces between the surface and substance (Arslan et al., 2016). Activated carbon is a preferred method for the decolorization of textile effluents. As a dye absorbent and a catalyst, activated carbon can be used for the enhancement of the other treatment methods such as coagulation, membrane filtration, electrochemical treatment, advanced oxidation, and biological treatment beside its separate application (Mezohegyi et al., 2012). A study, conducted by Órfão et al. (2006), investigated the amount of reactive dye which can be absorbed by a specific amount of activated carbon. Influence of the pH of the wastewater and the surface chemistry was significant whereas the adsorbed amount of the reactive red 241 was reported as 150-223 mg/g_{AC} (Órfão et al., 2006). Its very large specific surface area and high adsorption area are both advantages and disadvantages of activated carbon because they also increase regeneration need and difficulty (Mezohegyi et al., 2012).

2.2.3.2 Coagulation, Flocculation, and Sedimentation

Coagulation-flocculation processes employing different chemicals are efficient and easy to apply methods (Ellouze et al., 2012). Single coagulation-flocculation application can be preferred as treatment option for the removal of suspended colloidal particles (Ellouze et al., 2011) and dissolved organic substances (Khouni et al., 2011). It is possible to reduce dye content by inorganic coagulants and flocculant aids (Zahrim et al., 2011). Khouni et al. (2011) specified that 94 and 42 percent of color and COD content of reconstituted reactive dyeing effluent was removed, respectively, by polymeric aluminium sulphate coagulant and CHT flocculant. In another study conducted by Sanghi et al. (2005), removal of reactive dye by same coagulant was found between 50 and 65%.

This method is also used as pretreatment option prior to many other methods such as biological treatment and membrane filtration (UF, NF or RO). Aeration problem faced during biological treatment and fouling of membranes can be reduced by employing coagulation-flocculation pretreatment. Even the advantages of this method like decrease in sedimentation tank size, being applicable for all pHs and increase in treatment efficiency at the presence of auxiliaries (Zahrim, 2011), Ellouze et al. (2012) states that MF is a better option than coagulation-flocculation as pretreatment before NF in terms of removal of salinity and COD by NF. It can be explained with that no significant removal of dissolved substances like dyes and salts can be observed with coagulation/flocculation (Ellouze et al., 2011, Khatri et al., 2015).

Efficiency of coagulation is directly affected by salinity and pH of wastewater, and specific anions and cations included in dyeing wastewater (Ellouze et al., 2011), construction, mass, and charge of dye, and the auxiliaries (Zahrim et al., 2011). Beside these factors, the most important drawback of coagulation-flocculation is the great amount of sludge generation coming with sludge treatment and disposal costs (Khatri et al., 2015).

2.2.3.3 Membrane Filtration

From the previous sections briefly mentioning the literature on treatment technologies, it is concluded that all methods have their own strengths and weaknesses when they are considered for the treatment of reactive dyeing effluents. Also, conventional methods do not offer effective and sufficient treatment of textile dyeing wastewaters. Effluent of these methods still consists dyestuffs, salts, and toxicity. Further treatment is required to reach water quality level allowing any possible scenario of discharge to receiving body or reuse of both water and auxiliary chemicals.

As an advanced treatment technology, membrane separation is a promising option to be used as single stage or further treatment. In the past thirty years, interest in potential applications and improvements of membrane separation systems has grown with the increase in water scarcity and high water demand of industries (Judd et al., 2003).

Studies existing in literature have been approving the applicability of membrane filtration systems such as MF, UF, NF and RO for the recovery and reuse of textile dyeing wastewaters containing reactive dyestuffs. MF is efficient to remove colloidal dyes included in effluents of exhaust dyeing bath and following rinsing baths (Fersi et al., 2008). UF is an adequate process for the removal of specific dyes such as indigo, direct, disperse and reactive dyes and the reclamation of secondary textile wastewater. Where UF is effective for the separation of particles with dimensions greater than 1 nm (Ciardelli et al., 2001), NF and RO provide the filtration of low molecular weight substances (Xing et al., 2015) and dissolved solids like salts (Aouni et al., 2012, Khouni et al., 2011). NF systems offer better removal rates than UF and higher permeate flux declined less than RO (Gozálvez-Zafrilla et al., 2008). These systems are cost-effective, environmental friendly and more efficient for the removal of reactive dyes (Xing et al., 2015).

Aouni et al. (2012) investigated the applicability of UF and NF membranes for the treatment of both real textile dyeing wastewater taken from rinsing baths and model solution including 3 reactive dyes; Everzol Black, Everzol Blue, and Everzol Red, with different molecular weights of 991, 626, 788 g/mol, respectively. Experiments were conducted with 10 and 1 kDa UF membranes in addition to NF 200 and NF 270 membranes. As a tighter membrane with lower molecular weight cut-off, 1 kDa UF membrane achieved complete removal of blue and red colors where it also performed better conductivity removal. Even they stated that UF was sufficient for COD removal, 1 kDa UF membrane was offered as pretreatment placed prior to NF or RO for the reclamation of highly charged effluents. With both NF membranes, COD and color content of model solution was lowered at a rate higher than 90% beside conductivity removal of 85 percent. NF of real wastewater revealed the complexity of wastewater content contributing “rapid pore plugging”. NF was pointed as promising technology for the reclamation and reuse of textile finishing processes including reactive dyeing (Aouni et al., 2012). In another study, reactive dyeing effluent including five different reactive dyes with different molecular weights (reactive blue 15, reactive red 194, reactive yellow 145, reactive black 5, and reactive orange 16) was treated by “nano-membrane”. Dye molecule portion fixed to membrane lowered the filtration flux. Because of hybridization between reactive groups of dyes, obtained permeate had the COD concentrations of 3 to 9 mg/L. Also, conductivity was reduced sharply (Rashidi et al., 2015).

NF is preferable treatment for the decolorization of textile dyeing effluents whereas the mechanisms under its major problem, fouling, could not be completely understood, yet. However, studies, conducted recently, have been relating fouling behavior to transport mechanism (Van der Bruggen et al., 2001). Fouling results in lowered filtration flux and treated water quality (Tahri et al., 2012) which is caused by fouling agents like dyes interacting both with membrane and themselves. Dye adsorption both on the membrane surface and inside its pores was stated as major cause of flux decline due to physicochemical interactions. This also led to the change in pure water permeability of membrane due to lessened pore size. Dye adsorption mostly depended on the nature of membrane material, solute type, and concentration, CFV and the pH of solution. In a similar study conducted with wastewater including reactive dye, Aouni et al. (2011) were mentioned concentration polarization due to solutes on membrane surface and pore blocking which caused rapid decrease in initial permeate flux (Aouni et al., 2011, Aouni et al., 2012). Pore blocking together with adsorption was considered as fouling which caused decline in permeate flux at rate of 26-46% (Van der Bruggen et al., 2005).

Membrane fouling, faced during the treatment of reactive dyeing effluents, might be reversible or irreversible, as, reversible portion of fouling could be avoided easily by physical cleaning with clean water. However, irreversible portion was hardly removable and remained even the membrane was cleaned chemically (Tahri et al., 2012). Aouni et al. (2012) stated that extent of fouling and its elimination by chemical cleaning was highly affected by the correlation between the forces of electrostatic repulsion and hydrophobic adhesion. Van der Bruggen et al. (2001) pointed membrane fouling as a factor self-limiting the direct application of NF for the treatment of dyeing wastewater.

Adverse effects of dye and surfactant content of textile effluents on permeate flux and dye removal was reported as limited. On the other hand, permeate flux was found to sharply decrease by high ionic concentrations due to excess amount of salt presence during reactive dyeing and concentration difference between both sides of membrane which causing osmotic pressure. Theoretical calculation of osmotic pressure was possible to be made by The Van't Hoff model or Pitzer model. Osmotic pressure reduced the effectiveness of driving force, so, obtained permeate flux was lower beside its linear decline with the increase in salt content was found as 18 percent. The lowered flux resulting from osmotic pressure had been reversed by diminishing the concentration difference during water rinsing. However, removal rate of salt was reduced because of the decrease in the Donnan potential. These findings pointed out that the salinity of feed has adverse effects on performance of filtration in terms of both permeate flux and treatment efficiency, so the feed salt content was needed to be kept at a level having no significant influence on effective driving force (Van der Bruggen et al., 2001, Van der Bruggen et al., 2005).

As stated by Khouni et al. (2011), hybrid systems employing different type of treatment methods as pretreatment to NF achieve higher effluent quality. Recent studies on reclamation of effluents coming from dyeing processes focused hybrid systems because the textile effluents contain various types of pollutants which brings the need to use the advantages of more than one treatment process (Arslan et al., 2016). In the following paragraphs, examples related to studies on hybrid systems employing different pretreatment methods prior to NF process were given.

Comparison between NF of raw and biologically treated effluent showed that it is possible to reach good quality water in case of both situation (Chen et al., 2015). By applying NF following biological treatment with activated sludge, reached water quality was satisfying to be recirculated (Van der Bruggen et al., 2001).

Coagulation/flocculation was also evaluated as pretreatment prior to NF with many studies. Among these studies, Liang et al. (2014) stated that hybrid system consisting coagulation/flocculation and NF was examined for the treatment of dyeing effluent with dyes from different classes which was stated as a rarely encountered approach in literature. Results showed that combining these two methods helped to overcome drawbacks and weaknesses of each while enriching their effectiveness. NF step eliminated color still present in effluent from coagulation/flocculation whereas coagulation/flocculation performance was enhanced by treating concentrated steam of NF, and so, better removal efficiencies with less sludge formation were achieved. Additionally, pretreatment affected NF flux in a good manner. Filtration flux was increased and less flux decline was observed.

As an alternative to conventional treatment methods, membrane technologies such as MF and UF are considered as appropriate further treatment options prior to NF. It is possible to remove particles, however decolorization cannot be completed with these separation methods (Fersi et al., 2008).

As the most cost-effective pretreatment option (Tahri et al., 2012), MF reduces the colloidal dye content of effluents coming from exhaust dyeing and following baths (Marcucci et al., 2001) which eliminates flux decline by taking membrane fouling under control. A study conducted by Tahri et al. (2012) investigated the effect of pretreatment with 0.1 μm MF prior to NF membrane with MWCO of 150-300 Da. The effluent quality was reported as higher in terms of color and organic content but no significant enhancement in removal of salt was experienced. On the other hand, MF pretreatment raised the performance of NF regarding longer membrane life, higher filtration flux and minimized flux decline (Tahri et al., 2012).

A study comparing NF90 with SR90 NF membranes after UF pretreatment was conducted by Chollom et al. (2015) for recovery of water and salt from reactive dyeing effluent. Performance of membranes were evaluated in terms of treatment efficiency and permeate flux. Filtration flux was lowered during filtration at a rate of 25% and 61% for SR90 and NF90, respectively. As the contact angle of SR90 membrane was lower than NF90, their fouling tendencies so, the flux decline profiles during filtration showed differences. The flux decline was recovered 80% by chemical cleaning. With the UF pretreatment, 15% increase in filtration flux was provided. In addition to analysis on filtration flux and fouling behaviors, it is reported that NF90 showed better treatment performance with 76 μS/cm of permeate conductivity and 20 mg/L of permeate TOC than SR90. Yet, higher recovery of salt is achieved by SR90 whereas salt rejection declines with the increase in salt concentration because of concentration difference causing salt transportation through the membrane. Also, Chollom et al. (2015) stated that charge of membrane highly affects salt rejection. Conducted reuse experiments showed the NF90 permeate better met the reuse criteria even good results could only be obtained when reusing treated wastewater from light shade dyeing effluents for light shades and dark shade dyeing effluent for darks shades. Also, additional NaCl and fresh water were required to set NaCl concentration of permeate (Chollom et al., 2015).

UF pretreatment prior to NF was also tested for the effluent from biological treatment of textile effluent. This was adopted to improve performance of NF in terms of membrane fouling in addition to advance in water quality. By applying UF to secondary textile effluent, NF performance was enhanced in terms of turbidity, color, TDS, and conductivity rejections (Fersi et al., 2008). Flux decline and membrane fouling caused by cake formation and pore blocking were reduced by UF pretreatment. So, the membrane fouling limitation of NF membranes was overcome by reducing high solid content of biologically treated wastewater. Also, filtration run-time was increased where permeate flux was kept at steady state till higher VRFs.

As seen from the studies mentioned above, a well-optimized pretreatment enhances membrane filtration in many aspects. Another approach was examined with a study criticizing the applicability of two stage NF for the treatment of real textile wastewater involving four different reactive dyes. Removal rates of the first stage in terms of color, salt and COD was found as 95, 53, and 68 percent where as these values was raised to 99, 70, and 90 at the second stage, respectively. Fouling of membranes at the first and second stages also differed from each other. Flux recovery rate at the first stage was found 88%. At the second stage, lower flux decline was observed even its complete recovery was achieved. Conducted SEM and AFM analysis supported these results about membrane fouling behavior and flux recovery (Panda et al., 2015).

NF performance is directly related to operating conditions such as TMP and CF (Panda et al., 2015), the chemistry of waste solution, solute and membrane characteristic. One of the membrane characteristics is the contact angle referring the hydrophilicity or hydrophobicity of membrane surface. Hydrophilicity of surface is higher when the contact angle is lower which results in lower membrane fouling. A study of Aouni et al. (2012) comparing two NF membrane with different contact angles of 30.3° and 51.4° certified that hydrophobicity of membrane with higher contact angle was greater. As well, surface hydrophobicity caused lower fouling resistance and higher decline in filtration flux. The surface roughness is another physical characteristic of membrane. Roughness is used to describe surface morphology which was stated as related with fouling behavior of membrane (Aouni et al., 2012). Surface charge of membrane is another membrane feature according to which membranes are separated into three; neutral, positively charged and negatively charged membranes. Long-established neutral membranes were found insufficient for the treatment of wastewaters containing dyes and salts while having higher fouling tendency when compared with positively/negatively charged membranes. Moreover, negatively charged NF membranes were reported as promising for treatment of reactive dyeing effluents which mostly consisting negative charged dyes and NaCl or Na_2SO_4 salts because permeation was lowered by repulsive force between membrane and ions (Xing et al., 2015). Other features of membrane were listed by Marcucci et al. (2001) as membrane pore size designates passed and rejected substances, material of membrane affecting the fouling sensitivity and resistance to different factors like pH, temperature, etc. which limits application area, and, finally, the membrane shape designating the extent of clogging and cleaning procedure.

2.3 Membrane Processes

Water sustainability is a widespread issue within many countries. This forced the emergence of various water reclamation and reuse solutions with the ultimate goal of reducing water consumption and increasing wastewater reclamation. As Mulder (1996) and Fane (2007) stated, the main reason for investing in this technology is that decent product quality is obtained by using no supplementary chemicals.

Major disadvantages of using membrane processes (Strathman, et al., 2006) can be listed as:

- high costs, which is decreased by using membrane processes together with conventional processes
- mechanical brittleness, which may lead to membrane defects while running the processes
- and fouling by cause of chemical interaction with substances in feed, which induces the use of pre-treatment techniques.

Membrane filtration processes are classified using the size of particulate or molecule separated by the membrane. Figure 2.6 shows how membrane processes change based on the relevant size ranges.

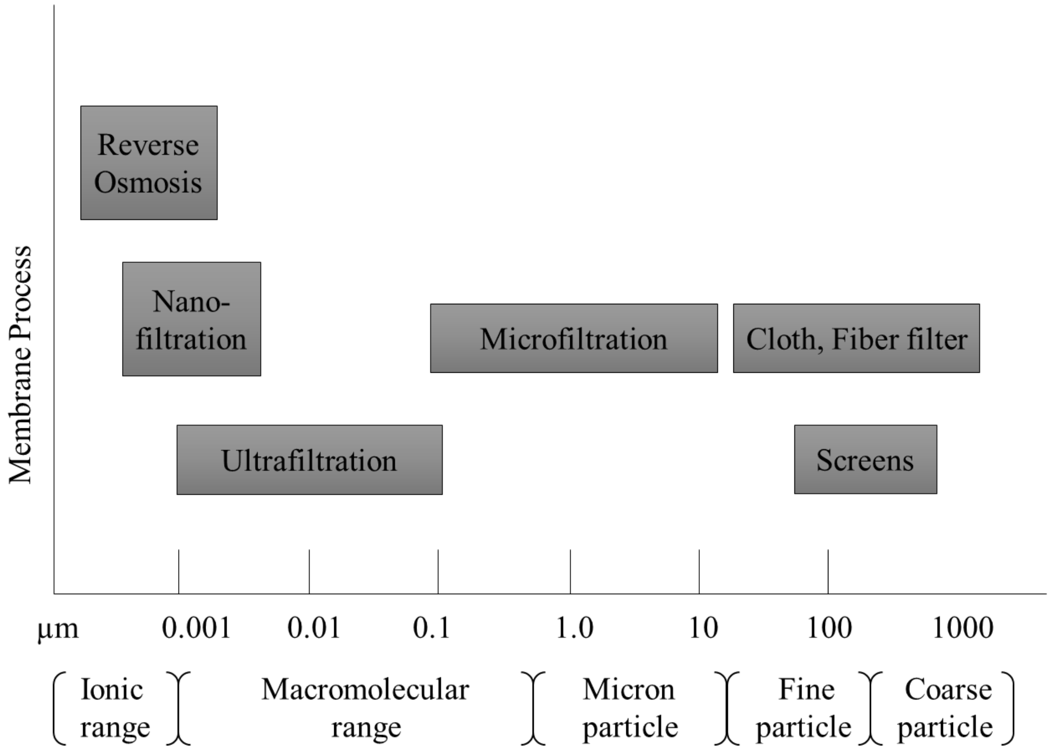

Figure 2.6: The Applicability Ranges of Different Separation Processes Based on Sizes (Cui et al., 2010)

In the following subsections, the important properties of these 4 membrane processes are explained.

2.3.1 Reverse Osmosis

RO is the most extensively used membrane process. In this process, while water passes through the membrane, dissolved substances in the retentate are rejected. The osmotic potential between saline retentate and clearer permeate is beaten by using enough pressure on the feed water. The design of the RO membranes is usually in spiral wound module. In each stage, 96% to 98% of the salt is rejected by the membrane. Feed water characteristics, product needs, and fouling requirements also affect the water treatment results. In order to improve the performance, pretreatment processes can also be used. "Filtration, softening of the water by cation exchange, activated carbon adsorption of chlorine and organics, and addition of chemicals" are examples of pretreatment processes prior to RO (Najafpour, 2007).

Pore size of RO is at the smallest level. As a result of this, RO membranes are also known as almost impervious membranes. In case of an appropriate RO membrane is used, more than 95% retention of monovalent salt (NaCl) occurs. Because of small pore size, the transmembrane pressure need is at 25-40 and sometimes higher atm. The separated resultant solute is transported via permeation. Permeation has three steps: solute molecules in the feed dissolve into the polymeric membrane matrix, solute molecules diffuse through the membrane matrix, solute molecules release to the permeate (De et al., 2013).

2.3.2 Nanofiltration

Pore size of NF membranes is in between the pore sizes of RO and UF membranes. So, NF membranes is also known as 'loose' RO membranes. Comparing the RO process, less transmembrane pressure (7-30 atm) is needed (Shon et al., 2013). By NF, 65% to 80% retention of monovalent salt (NaCl) can be achieved. NF is efficient for the removal of compounds with molecular weights in between 200 and 1000 Da. "Filtration of dyes and separation of smaller molecular weight organics like polyphenols" are examples of NF applied processes (De et al., 2013).

NF membrane has the capability of removing salts and metals efficiently from aqueous feed (Al-Rashdi, 2013, Pages et al., 2013). Also, it is convenient to use NF in removing comparably small organics in the examples of "organic micropollutants and color from surface water or groundwater, and degradation products from the effluent of biologically-treated wastewater" (Van Der Bruggen et al., 2003).

NF is quite successful process for TOC reduction, color removal, desalting, removal of disinfection by-products and lignin elimination. In addition, there are so many possible areas of NF application in which NF method preferred rather than other methods such as RO. For softening, even the RO provides an effective hardness removal, requirement of higher pressures reduces its preference against NF. Also, NF achieves high rejection sulfate at lower pressures than required for normal sea water RO which was needed to avoid precipitation threat during the oil extractions from undersea reserves. NF is even more favored for the concentration of sugar solutions because RO generates a salinity increase which is not faced during NF applications. In addition to RO, NF is a possible choice instead of granular activated carbon to remove pesticides (Cardew et al., 1999).

2.3.3 Ultrafiltration

Pore size of UF membranes is in between the pore sizes of NF and MF membranes. UF pore size is bigger than the pore size of NF membranes, so the need for transmembrane pressure is way lower (1-10 atm) (Shon et al., 2013). UF membranes are used to filter substances with molecular weights in between 1000 and 100,000 Da. "Filtration of protein, polymer and polysaccharides such as pectin" are examples of UF applied processes (De et al., 2013).

An important example of UF usage in industrial scale is in paint concentration operation. UF is also used in food processes as conventional methods like evaporation and freezing changes the protein structure and alter the taste of the foods. On the contrary to the conventional methods, membranes are found capable to be used in various temperatures in many cases. UF is also used in treatment of polluted and valuable effluents, as a result of environmental requirements. Last but not the least, UF can also be used as pretreatment prior to many treatment processes such as NF so that performance of further treatment would be enhanced (Cardew and Le, 1999).

2.3.4 Microfiltration

The average pore size of MF membranes is more than the pore size of UF membranes. So, the least transmembrane pressure is required (0.5-5 atm) in this type of processes (Shon et al., 2013). Particles with molecular weights more than 105 Da are removed by MF (De et al., 2013).

MF membranes can be used efficiently for removing substances that may lead to problems in additional treatment operations. As viruses and germs are not cleared away via MF membranes, it is only possible to use MF membranes as disinfection impediments if bacterial regrowth is blocked (Van Der Bruggen et al., 2003).

2.3.5 Treatment of Reactive Dyeing Effluents with Membrane Processes

These pressure-driven filtration methods have their own implementation areas regarding their different features such as pore size, material, and shape of the membrane (Marcucci et al., 2001), the wastewater characterization and “the desired quality of the permeation results” (Allègre et al. 2006). In literature, membrane technology was considered as a promising method for the recovery and reuse of textile dyeing effluents as the high color and salt content, and BOD/COD ratio of the reactive dyeing wastewater are needed to be dealed with advanced treatment processes. Reactive dyeing effluents consist of unfixed dye, dyeing auxilaries, organic substances, salts (sodium chloride and/or sodium carbonate) and also textile fibres (Allègre et al., 2006).

The application of MF membranes, with pore size range 0.1-5 μm (Cui et al., 2010), was stated as restricted for the recovery and reuse of effluents coming from textile manufacturing processes (Dasgupta et al., 2015) because filtration by MF is frequently influenced at low pressure differential (Dutta, 2007). Beside that, many studies confirmed that MF is applicable for the removal of turbidity and colloidal dyes from the effluents of dye baths and following rinsing baths whereas auxiliary chemicals present in the permeate (Allègre et al., 2006, Fersi et al., 2008, Koltuniewicz, and

Drioli, 2008, Juang et al., 2013). So, the MF is not a method to be used alone for the recovery of textile effluents but a sufficient pretreatment option to be employed in hybrid systems (Dasgupta et al., 2015). Tahri et al. (2012) pointed that it possible to enhance both the treatment performance, operation time and filtration flux of NF with MF pretreatment. In another study, NF permeate quality in terms of salt and COD concentrations were improved with MF pretreatment more than coagulation-flocculation (Ellouze et al., 2012).

Like MF, UF is considered as a suitable pretreatment option to be employed prior to NF or RO processes during the reclamation of textile effluents (Barredo-Damas et al., 2006). It is possible to remove macromolecules and particles with UF membranes but reuse standards cannot be met with single stage UF process because of incomplete decolorization (Allègre et al., 2004) as the UF membranes are not effective for the removal of dyes having low molecular weights (Petrinić et al., 2015). On the other side, Fersi et al. (2008) stated that the secondary textile effluents can be treated successfully by single stage UF treatment.

Compared to other pressure driven membrane filtration processes, NF is the most suitable treatment for effluents of textile industry as the NF membranes achieve decolorization at a level meeting reuse standards (Tang and Chen, 2002) by complete removal of unfixed reactive dyes (Allègre et al., 2006). In addition to organic compounds with low molecular weights, rejection of large monovalent and divalent ions is possible with NF (Allègre et al., 2004, Allègre et al., 2006). It was reported that NF is capable to remove 95% of sodium chloride, the most preferred salt during reactive dyeing (Allègre et al., 2004). Besides, Ellouze et al. (2012) emphasized on the possible requirement of a suitable pretreatment prior toNF process.

Removal of reactive dyes, chemical auxiliaries, monovalent/divalent salts can also be achieved by direct application of RO (Allègre et al., 2004). However, high salt content of reactive dyeing effluents causes osmotic pressure which reduces the effectiveness of RO. To reach a reasonable permeate flux, it is required to raise transmembrane pressure to excessive values that leads greater energy consumption and expenses

(Allègre et al., 2006, Petrinić et al., 2015). As NF process achieves same desalination rates with RO with lower cost, Petrinić et al. (2015) pointed NF as a possible alternative to RO during the recovery and reuse of reactive dyeing wastewaters.

CHAPTER 3

MATERIAL AND METHODS

3.1 Wastewater

The wastewater was supplied by a textile dyeing mill in Denizli, Turkey. In this mill, mostly cotton is processed both by continuous and exhaust dyeing. The samples used in this study was taken from exhaust dyeing achieved by circulating dyebath. Figure 3.1 shows main sections of circulating dyebath where numbers refer to venturi, inspection port, mixing tank, heat exchanger, pump, dyebath, fabric, and valves, respectively (Aspland, 1998).

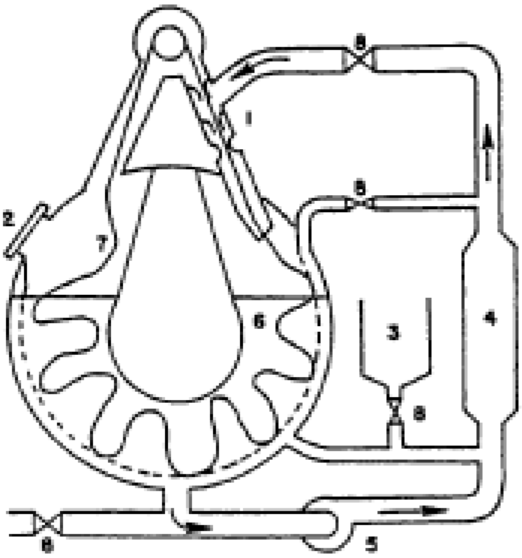

Figure 3.1: Circulating Dyebath and its Sections (Aspland, 1998)

Wastewater samples were taken from four different baths of dyeing; dyeing (Bath#1), rinsing with hot water (Bath#2), soaping (Bath#3), and rinsing with warm water (Bath#4). This sampling repeated at 3 different dates to provide samples from different dyeing recipes (Table 3.1). The effluents of each bath were separately stored at 4°C in laboratory and mixed right before filtration tests.

Table 3.1: Dyeing Recipes of Wastewater Samples

WW Sample #	Recipe
1	Reactive Orange S3R, Reactive Deep Red SB6, Remazol Ultra Navy Blue.
2	Everzol Gold Yellow BDF, Everzol Red ED 3B, Everzol Blue ED.
3	Everzol Yellow BDF, Everzol Red ED, Everzol Blue ED.

Wastewater characteristics of different bath effluents of different recipes are given in Table 3.2. Waste dyeing bath solution was deliberately excluded due to its extremely high salt and color contents and the mixture of the last three baths were used as feed solution during all experiments (Figure 3.2) except the experiment conducted to investigate the effects of inclusion of dyebath on filtration performance.

Table 3.2: Characteristics of WW Samples

WW Sample #	**Bath #**	**TOC (mg/L)**	**Turb. (NTU)**	**Cond. (mS/cm)**	**SAC (m^{-1})**		
					436 nm	**525 nm**	**620 Nm**
1	**1**	666.2	172.3	69.8	490	420	90
	2	818.7	47.7	24.4	160	160	40
	3	351.8	39.4	9.3	120	120	30
	4	310.6	43.7	7.5	110	100	30
	2,3,4[1,2]	259.4/568.0	38.1/49.3	14.3/16.2	131/234	133/315	29/53
2	**1**	415.2	15.8	73.3	233	452	30
	2	292	24.6	12.2	65	145	13
	3	28.4	25.0	1.7	35	50	8
	4	21.2	6.5	0.8	3	2	1
	2,3,4[1,3]	89.9/131.6	23.0/35.5	5.0/5.1	36/48	66/72	13/22
3	**1**	542.6	113.0	64.9	292	429	68
	2	322.9	65.0	39.0	196	334	43
	3	79.9	14.8	6.6	29	21	9
	4	43.8	19.3	1.6	43	77	7
	2,3,4[1,4]	134.1/156.9	24.4/32.0	14.9/16.4	83/97	140/151	14/23

[1] For all parameters, values of feed solution mixtures used during the conducted experiments showed variations. So, the feed load ranges were given as lowest value/highest value obtained during experiments conducted with the related mixture.

[2] The mixture was named as WW#1.

[3] The mixture was named as WW#2.

[4] The mixture was named as WW#3.

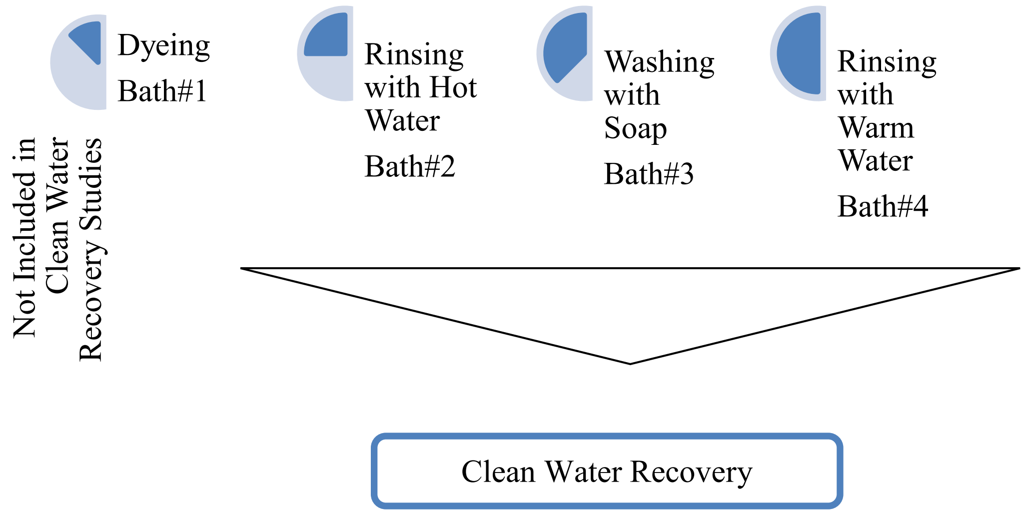

Figure 3.2: Bath Effluents Included in Clean Water Recovery Studies

3.2 Study Approach

At the very beginning of the study, a draft experimental layout was designed under two main section (Figure 3.3) to extract needed information and observations from experiments for the determination of optimal process configuration of clean water recovery from reactive dyeing wastewater.

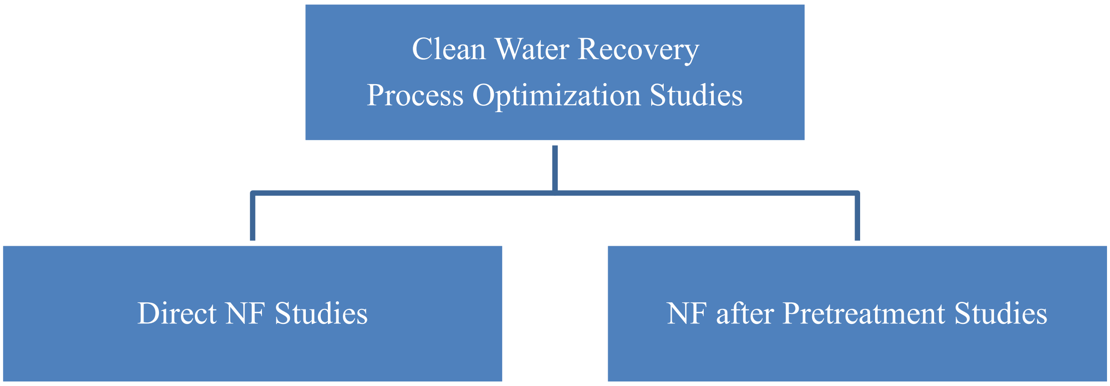

Figure 3.3: Basic Layout of Experiments

Direct NF studies were conducted under two different CFs and three TMPs and their effects on treatment efficiency and fouling behavior of NF membrane were examined. While CF and TMP values were determined, both literature and the operational limits of membrane and filtration system were considered. After determination of CF and TMP at which the highest removal rates and lower fouling of membrane were reached, experiments were conducted with different recipes and compared to see the effects of change in feed composition. Concentrate mode NF experiments were also completed at the optimal conditions for this purpose. Figure 3.4 shows the direct NF experiments that were conducted along with their purpose.

Under ‘NF after pretreatment studies’ section, testing alternative pretreatment membranes (MF and UF) with dead-end filtration was given priority. After determining the optimal alternative in terms of treatment efficiency and membrane fouling behavior, NF after pretreatment experiments conducted at optimal condition and compared with direct NF to observe whether any enhancement in NF was achieved or not. The possibility of conducting NF at lower TMPs than optimal one after pretreatment while maintaining the enhancements achieved by pretreatment was also investigated. In addition, it was questioned whether assembling pretreatment prior to NF recompenses the possible inclusion of dye bath to feed. (Figure 3.5).

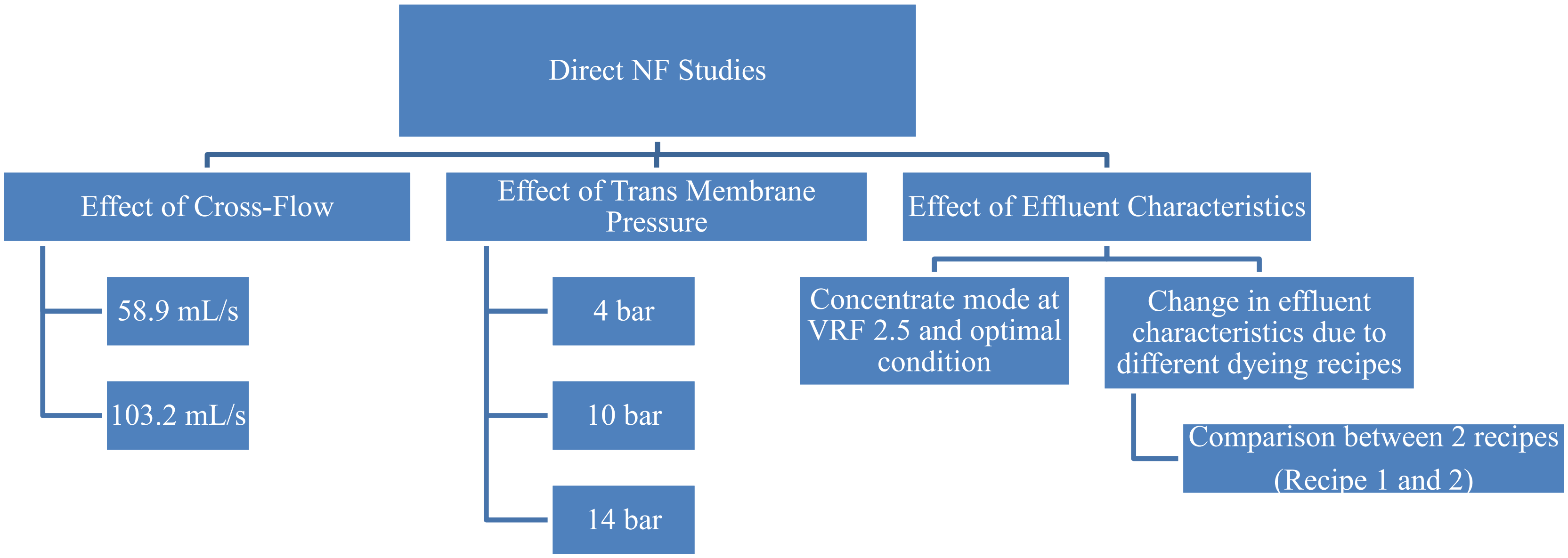

Figure 3.4: Direct NF Studies

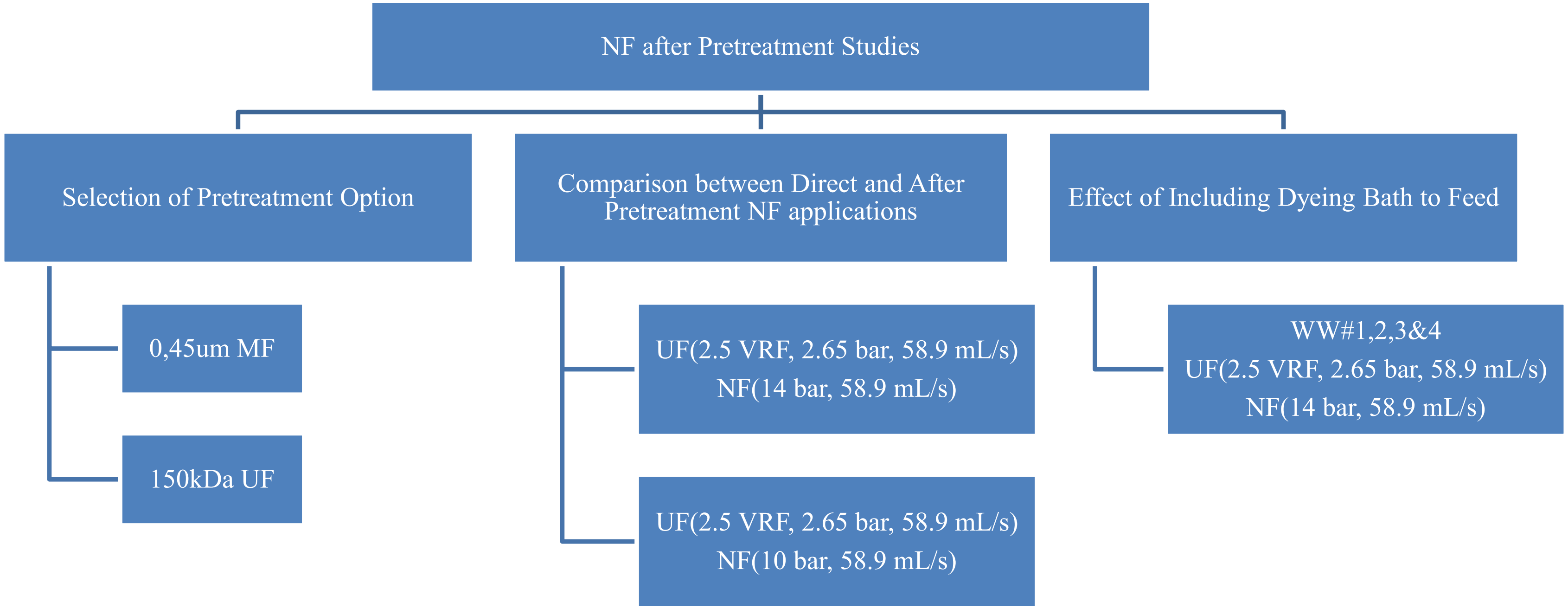

Figure 3.5: Pretreatment and NF after Pretreatment Studies

3.3 Membrane Specifications

A NF membrane namely NF90, a 150 kDa PES UF and a 0.45 μm PES MF membrane were tested during the clean water recovery studies. The specifications of the NF membrane used in the study are given in Table 3.3.

Table 3.3: NF Membrane Specifications

	Membrane	**Material**	**MWCO ($gmol^{-1}$)**	**Permeance (lmh/psi)**	**Rejection (%)**	**pH Range**
DOW	NF90	Polyamide	200-400	78.2-102 at 130 psi	97 NaCl	2-11

3.4 Experimental Setup

3.4.1 Dead-End Experiments

Studies on selection of pretreatment option were conducted by dead-end filtration with 400 mL 8400 model Amicon Stirred Cell (Figure 3.6). The unit was connected to nitrogen gas cylinder for needed pressure exposure. Initial temperature of feed was fixed as 24.0±0.5°C by placing feed bottle in Julabo F12 model cooling water bath till obtaining this temperature. Then, the feed solution was taken into the stirred cell from the feed bottle. No significant change in temperature was observed during dead-end filtration tests.

Figure 3.6: Amicon Stirred Cell (Merck Millipore Corporation, 2016)

Figure 3.7: Amicon Stirred Cell Filtration System and its Units

Table 3.4: Specifications of 8400 Model Amicon Stirred Cell

Parameter	Value
Max. Process Volume (mL)	400
Min. Process Volume (mL)	10
Membrane Diameter (mm)	76
Effective Membrane Area (cm^2)	41.8

3.4.2 Cross-Flow Experiments

NF and pretreatment stage prior to NF were tested by using lab scale cross-flow membrane filtration unit (Figure 3.8). Unit was connected to Hydracell high pressure pump with a capacity of 1.1 kW. With a control panel connected to pump, CF was set or changed. A rectangular flat membrane in dimensions of 19 to 14 cm was inserted between two components of filtration unit which occupies 140 cm^2 effective area. The cross-sectional area of unit was taken as 0.82 cm^2 as stated by Hoek et al. (2002). To keep feed temperature constant at 24±0.5°C during all stages of experiments, a 2-liter feed bottle is located in Julabo F12 model cooling water bath. Temperature of UPW circulated in water bath is frequently adjusted according to needed feed temperature.

Figure 3.8: GE OSMONICS SEPA CF Membrane Filtration System

Filtration system was often cleaned by circulating 1000 mL UPW, 500 mL acid (HNO_3 (pH 2.5)) 1000 mL UPW, 500 mL base (NaOH (pH 9.5)) and 1000 mL UPW for 1 hours, respectively, to avoid any interference caused by residues remaining after previous experiment.

A feed spacer was placed below membrane to make feed flow equally through effective area whereas another spacer was put onto membrane as permeate carrier. Figure 3.9 shows the schematic representation of SEPA CF membrane filtration unit elements.

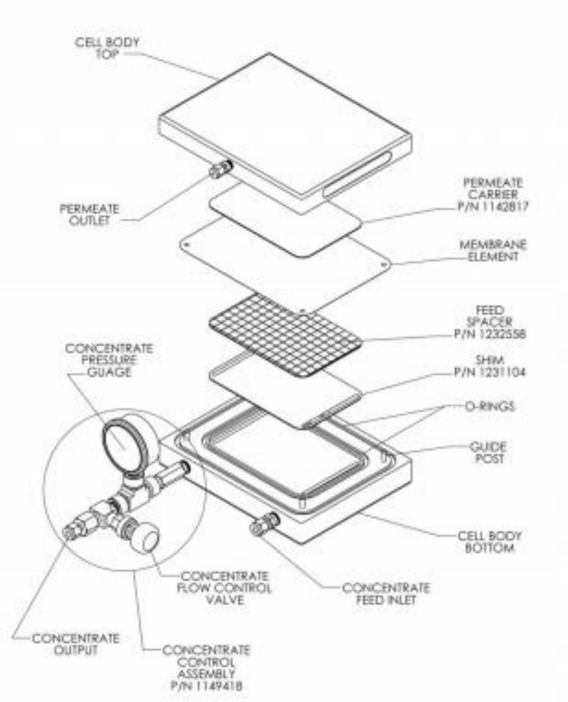

Figure 3.9: Cell Body Assembly (GE Osmonics, 2016)

3.5 Experimental Methods

During all experiments, basically, compaction, chemical cleaning of membrane, pure water flux measurements, filtration, pure water flux measurements after filtration and treatment efficiency analysis steps were followed as shown at Figure 3.10.

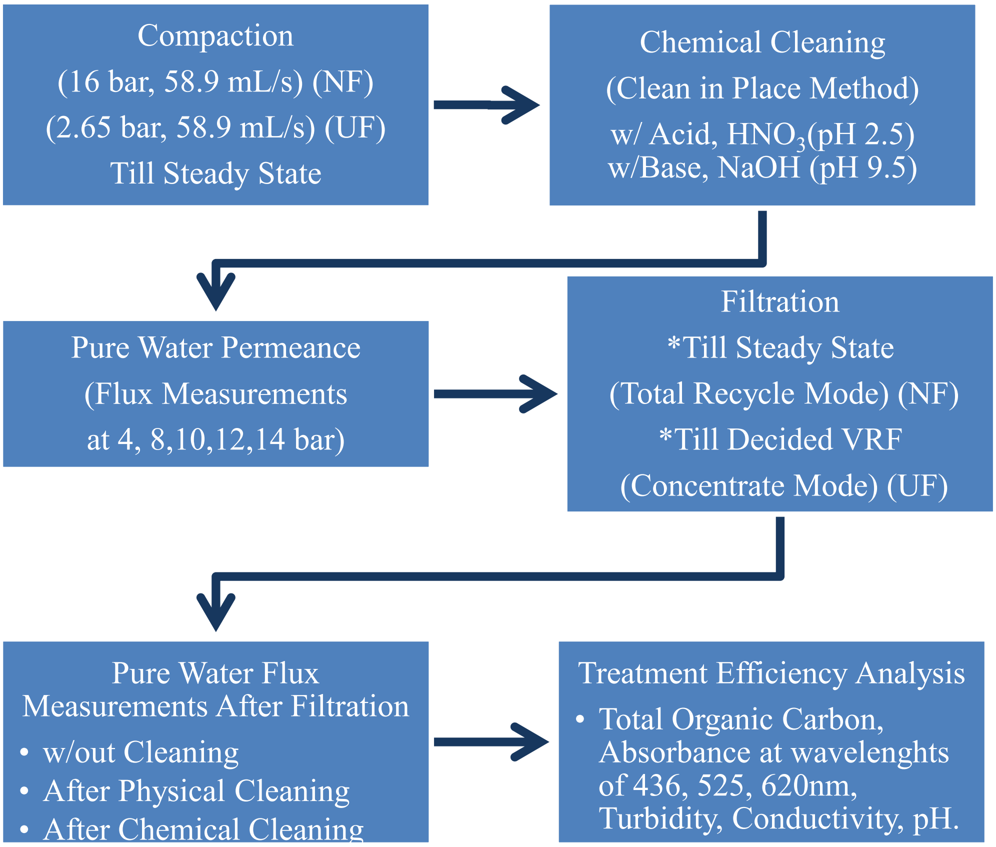

Figure 3.10: Basic Steps followed during CF Experiments

Detailed information about these steps are given under three main topics, membrane preparation, filtration, and membrane cleaning and storage.

3.5.1 Membrane Preparation

Membrane preparation steps followed before the first usage of a membrane were basically same but showed minor differences for MF, UF and NF membranes due to their different natures.

Membranes were firstly kept in a 0.25% sodium bisulfite solution for 24 hours to be wetted before compaction. After a day, membrane was taken from solution and its surfaces were washed up with UPW before being put into filtration cell for compaction.

By applying UPW under high pressure, steady state flux was aimed to be reached to get rid of any membrane compaction during filtration. For NF experiments, compaction with UPW was applied under TMP of 16 bar till steady state flux. Compaction of UF membranes were completed at 1 and 2.65 bar for dead-end and CF experiments, respectively. MF membranes were not needed to be compacted due to their very high flux. During compaction, 1500 mL of UPW was circulated in CF system whereas stirred cell was filled up with UPW 4-5 times at dead-end experiments. Conditions are listed at Table 3.5. The flux profiles of NF and UF membranes used for clean water recovery studies were given in Appendix A.

Table 3.5: Compaction Pressures

	Membranes	**Compaction Pressure(bar)**
Dead-End	MF	-
	UF	1
Cross-Flow	UF	2.65
	NF	16

After compaction, membranes were cleaned chemically. Chemical cleaning procedure was different for different membranes and systems. Table 3.6 shows the details of the cleaning processes applies.

Table 3.6: Chemical Cleaning Processes of Different Membranes

	Membrane	**Feed**	**Volume(mL)**	**Time(min) Pressure(bar)**	**Method**
Dead-End	MF	HNO_3 (pH 2.5)	300	Till the solution completely drawn from cell at 0.1 bar 100 rpm	CIP
		UPW	300		
		NaOH (pH 9.5)	300		
		UPW	300		
	UF	HNO_3 (pH 2.5)	300	Till the solution completely drawn from cell at 0.3 bar 100 rpm	
		UPW	300		
		NaOH (pH 9.5)	300		
		UPW	300		
Cross-Flow	UF	HNO_3 (pH 2.5)	500	30 min w/out Pressure	
		UPW	1000	30 min w/out Pressure	
		NaOH (pH 9.5)	500	30 min w/out Pressure	
		UPW	1000	30 min w/out Pressure	
	NF	HNO_3 (pH 2.5)	500	15 min w/out Pressure 15 min at 3bar	
		UPW	1000	15 min at 3bar	
		NaOH (pH 9.5)	500	15 min w/out Pressure 15 min at 3bar	
		UPW	1000	15 min at 3bar	

Chemical cleaning of membrane was followed by pure water permeance measurements. Permeance was found as the slope of UPW fluxes of membrane at different TMPs. During dead-end experiments, permeance of MF was calculated by monitoring flux at 0.5, 0.4 0.3, 0.2 and 0.1 bar whereas flux measurements were conducted at 1.0, 0.7, 0.5 and 0.3 bar of TMPs for pure water permeance of UF membranes. Because of the limits of operation conditions of CF membrane filtration system, UF permeance could only be calculated with the pure water flux at 2.65 bar of TMP which was the lowest value allowed by the system. Higher pressures were not suitable for UF membrane, so this value was also set as filtration pressure. Flux measurements were conducted at TMPs of 16, 14, 12, 10, 8 and 4 bar for permeance of NF membranes.

Table 3.7: Pressures at Which UPW Flux Measurements Were Conducted for Permeance Calculation of Different Experiment Set-up and Membranes

	Membranes	**Pressures at Which UPW Flux Measurements Conducted (bar)**
Dead-End	MF	0.1, 0.2, 0.3, 0.4, 0.5
	UF	0.3, 0.5, 0.7, 1.0
Cross-Flow	UF	2.65
	NF	4, 8, 10, 12, 14, 16

The UPW flux measured for permeance calculations at filtration pressure was set as J_{cwi} to be used during membrane fouling analysis.

3.5.2 Filtration

Filtration step of experiments was carried out by dead-end and CF membrane filtration systems. CF filtration was tested at two different operational modes, namely total recycle and concentrate modes (Figure 3.11 and Figure 3.12).

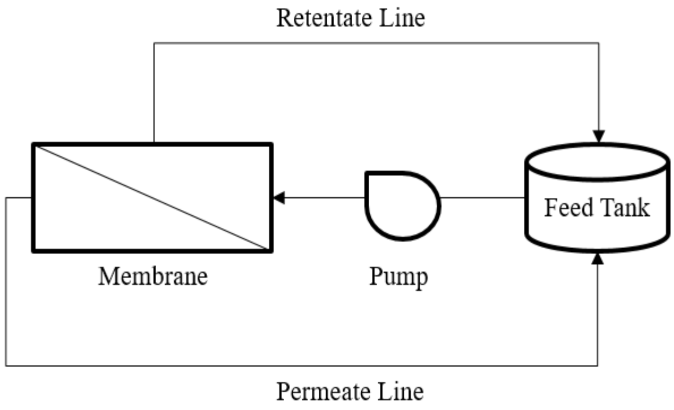

Figure 3.11: Total Recycle Mode

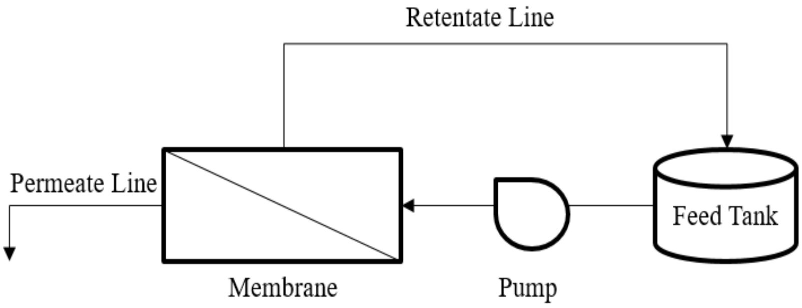

Figure 3.12: Concentrate Mode

3.5.2.1 Cross-Flow NF Experiments

During cross-flow NF experiments, filtration of 1500 mL feed solution was performed till steady state permeate flux or decided VRF was reached. During that period, permeate flux was measured at every 20 minutes. When considered necessary, measurement interval was decreased to 10 minutes. Flux was assumed to reach steady state if measurements were almost same for an hour. Average of flux values measured during the period, in which the flux measurements confirmed the steady state, and the flux measured at the point that VRF got up to decided level set as raw water flux, Jrw.

At TRM, samples were taken from permeate line at every hour. After steady state was reached, two permeate samples were collected.

During NF experiments at CM, samples were taken from both permeate and retentate lines to obtain instant removal percentages of TOC, color, and conductivity. The amount of retentate sample was minimized to 3-4 mL for conducting analysis without any distraction on VRF calculations. For this purpose, conductivity was measured directly from the feed bottle.

3.5.2.2 Cross-Flow Pretreatment Experiments

Same sampling and flux monitoring procedure were followed during cross-flow UF at 2.65 bar with CM. As different from NF, UF of 1750 mL feed till VRF of 2.5 was conducted to collect 1050 mL of permeate. The measured flux at the final VRF was taken as filtration flux.

3.5.2.3 Dead-End Experiments

Dead-end UF and MF test were conducted with dead-end filtration by 400 mL stirred cell at 100 rpm. Membranes, 0.45 µm PES MF and 150 kDa PES UF, were evaluated at 0.2 and 0.5 bar, respectively, using 255 mL wastewater samples. Sampling procedure was same with other filtration experiments but flux was measured continuously with 2-minute intervals by weighing the collected permeate in a graduated cylinder. Same with cross-flow pretreatment, the measured flux at the decided VRF was taken as the filtration flux.

3.5.3 Membrane Cleaning and Storage

After filtration, basically, UPW fluxes of membranes were tested without cleaning, after physical cleaning and after chemical cleaning of membrane to complete membrane fouling analysis. All these flux measurements were done at filtration pressure and all membranes were stored in in 0.25% sodium bisulfite solution after each step of experimental procedure was completed.

After cross-flow NF, raw water was fully drained off from the membrane filtration system. Then, UPW water was applied at filtration TMP and CF for 5 minutes to obtain permeance flux without any cleaning of membrane (J_{cwf}). This measurement was not repeated even the read value had been changing in 5 minutes. It was assumed that this change during measurement was risen from cleaning of membrane as a result of applying UPW. So, the very first measurement was taken as J_{cwf} not to see any effect of membrane cleaning on flux. After measurement was completed, system was emptied.

Membrane was cleaned physically with 1500 mL of UPW at CF of 114.3 mL/s without pressure for 30 minutes. By high CF, physically reversible portion of membrane fouling was swept away. Then, UPW permeate flux was measured to obtain J_{cwp}.

Physical cleaning was followed by chemical cleaning of membrane for the determination of the sustainability of membranes to be used for the treatment of dyeing effluent (Ong et al., 2012). Same process with chemical cleaning done before filtration was applied. After all, UPW flux of chemically cleaned membrane was measured.

For all experiments, water fluxes after filtration without cleaning, after physical and chemical cleaning were measured in same manner. Only for dead-end experiments, filtration cell was filled several times with UPW to reach flux measurement with insignificant error. Besides that, physical cleaning of membranes after dead-end and cross-flow pretreatment filtration differed from cross-flow NF as seen from Table 3.8. Chemical cleaning after filtration was same with followed procedure for membrane preparation previously shown in Table 3.6.

Table 3.8: Physical Cleaning of Membranes

	Membranes	**UPW Volume (mL)**	**Time (min)**	**Condition**
Dead-End	MF	300	30	Stirring at 300 rpm
	UF	300	30	
Cross-Flow	UF	1500	30	CF of 114.3 mL/s
	NF	1500	30	

After all experiments, used membranes were stored in 0.25% sodium bisulfite solution.

3.6 Analytical Methods

Collected WW samples were analyzed in terms of TOC, color, turbidity, conductivity, and pH. For all parameters, measurements of samples were repeated at least three times to overcome the measurement errors. The average of closest three measurements were taken as the value. Also, the standard deviation of these values was calculated. Treatment efficiencies were criticized in terms of removal percentages calculated by using following equation.

$$R = (\frac{Cf - Cp}{Cf}) \times 100$$

Where;
R= Removal percentage
C_f= Feed concentration
C_p= Permeate Concentration

TOC measurements were completed with Shimadzu 5000A model TOC analyzer applying high temperature (680°C) catalytic combustion technique where the sample was injected onto a reaction chamber filled with oxidative platinum catalyst in an oxygen richened atmosphere. Total carbon and inorganic fraction of it were measured separately to obtain difference corresponding TOC by the instrument.

Color contents of samples were determined by measuring absorbance at the wavelengths of 436, 525 and 620 nm using Varian Cary 100 model UV-VIS spectrophotometer calibrated with UPW. Reading absorbance values at different wavelengths was done to be able to monitor yellow, red, and blue colors and their shades which give absorbance at wavelengths between 400-500, 500-600 and 600-700 nm, respectively. Spectral adsorption coefficient (SAC) values were calculated with absorbance values by using the formula given below.

$$SAC(\lambda) = \left(\frac{A}{d}\right) * f$$

Where;

SAC= Spectral Absorption Coefficient (m^{-1})
A= Absorbance (cm^{-1})
d= Spectral Band (mm)
f= Conversion Constant

HACH 2100Q model portable turbidimeter was used to measure the turbidity of samples according to the Standard Method No. 2130B. Calibration was permanently repeated with 800, 100 and 20 NTU standard solutions and corrected with 10 NTU standard solution.

Conductivity and pH of samples were measured with different probes of HACH SensION 378 Multimeter by following the Standard Method No. 2510B and No. 4500-H^+, respectively. Calibration of device for pH was repeated with buffer standard solutions with pH 4, 7, and 10.

3.7 Flux Decline Analysis

Flux was the primary parameter monitored during experiments for the examination of membrane behaviors during and after filtration. All flux measurements during compaction and filtration at TRM were achieved by 10-sec-weighing by an automated scale device connected to a computer for few minutes at every 10 or 20 minutes till steady state. During filtration at CM, continuous monitoring of permeate flux was achieved also by 10-sec-weighing till decided VRF and data were processed in 2-minute intervals. Formula related to flux was given below.

$$J = \frac{Q_p}{A}$$

Where;
J= Flux (L/m^2h)
Q_p= Permeate flow (L/h)
A= Effective surface area of membrane (m^2)

During NF, the osmotic pressure caused by the salinity of feed solution was at very significant level. Osmotic pressure decreased the effective driving force resulting in lowered filtration flux (Aouni, et al., 2012) meaning that the permeate flux critically decreased and the relation between permeate flux and osmotic pressure was stated as linear (Aouni, et al., 2001). As it is also stated by Aouni et al. (2012), osmotic pressure does not cause any resistance increase to mass transfer. In another study conducted by Aouni et al. (2005), it was explained that the osmotic pressure caused by high salt content of feed does not result in any membrane fouling because its contribution in flux decline is completely reversible. Following formulas of permeate flux and normalized permeate flux (Kim et al., 2016) are used to derive a third equation for the calculation of filtration flux which would be obtained in case of no osmotic pressure decreasing the effective driving force.

$$J = K(TMP - P_O)$$

Where;

J= Filtration flux (L/m^{2}h)

K= Raw water permeability coefficient of membrane (L/m^{2}hbar)

TMP= Transmembrane pressure (bar)

P_O= Osmotic pressure of feed solution (bar)

$$Js = \frac{TCFs(Pfs - \pi fs)}{TCFa(Pfa - \pi fa)} Ja$$

Where;

J_a= Permeate flux at actual conditions (L/m^{2}h)

J_s=Permeate flux at standard conditions (L/m^{2}h)

TCF_a= Temperature correction factor at actual conditions

TCF_s= Temperature correction factor at standard conditions

π_{fa}= Feed osmotic pressure at actual conditions (kPa)

π_{fs}= Feed osmotic pressure at standard conditions (kPa)

As in the previous formula, raw water permeability was calculated by using measured permeate flux during filtration as the J value, and the muplication of the calculated raw water permeability and the TMP was designated as the $J_{corrected}$ which would be the observed filtration flux value in case of no osmotic pressure decreasing the effective driving force. So, the following formula was derived from previous one with mentioned designations. The steps of derivation are given in Appendix B.2

$$Jcorrected = Jmeasured(\frac{TMP}{TMP - Po})$$

Where;

$J_{corrected}$= Osmotic pressure corrected permeate flux (L/m^{2}h)
$J_{measured}$= Measured permeate flux (L/m^{2}h)
TMP= Transmembrane pressure (bar)
P_O= Osmotic pressure of feed solution (bar)

Descriptions of measured fluxes in their order at experiments were given at Table 3.9. All these measurements were conducted at feed temperature of 24±0.5°C. All UPW flux measurements during CF experiments were run at 58.9 mL/s of CF rate even the NF would be operated at 103.2 mL/s of CF rate for the investigations on possible effects of different experimental conditions.

Table 3.9: Flux Descriptions

Flux	**Definition**
J_{cwi}	Initial UPW flux of virgin/clean membrane measured before filtration at filtration TMP
J_{rw}	Raw water flux measured at steady state or decided VRF
J_{cwf}	UPW flux measured after filtration without any cleaning of membrane
J_{cwp}	UPW flux measured after physical cleaning of membrane
J_{cwc}	UPW flux measured after chemical cleaning of membrane
Normalized Flux	Raw water flux divided by initial UPW flux
Corrected Flux	The flux which would be obtained in the absence of osmotic pressure

By using measured flux values before, during and after filtration, resistance calculations were done with the formula given below.

$$R = \frac{TMP}{\mu \times J}$$

Where;

R= Resistance (m^{-1})

TMP=Trans Membrane Pressure (bar)

μ= Viscosity of Water

J=Flux (L/m^2h)

Definitions of resistances and formulas used to calculate them were given at Table 3.10. Example related to these calculations is also given in Appendix B.1.

Table 3.10: Definition and Formula of Resistances

Resistance	Definition	Formula
R_{mem}	Membrane's subsistent resistance	$Rmem = \frac{TMP}{\mu \times Jcwi}$
R_{tot}	The summation of R_{mem}, R_f and R_{cp}.	$Rtot = \frac{TMP}{\mu \times Jrw}$
R_f	Resistance caused by fouling	$Rf = \left(\frac{TMP}{\mu \times Jcwf}\right) - Rmem$
R_{cp}	Resistance caused by concentration polarization	$Rcp = Rtot - (Rmem + Rf)$
$R_{ph\text{-}irr}$	Physically irreversible fouling resistance	$Rph - irr = \left(\frac{TMP}{\mu \times Jcwp}\right) - Rmem$
$R_{ch\text{-}irr}$	Chemically irreversible fouling resistance	$Rch - irr = \left(\frac{TMP}{\mu \times Jcwc}\right) - Rmem$

CHAPTER 4

RESULTS AND DISCUSSION

Experimental studies were designed to reach the optimal conditions and configuration for the treatment of the real reactive dyeing wastewater taken from three sequential baths following dyeing of fabric with the purpose of clean water recovery as briefly narrated before in Section 3.2 (Study Approach) and showed by Figure 3.3, Figure 3.4, and Figure 3.5. The success criteria of filtration were both treatment efficiency in terms of removal of TOC, conductivity, and color, as well as flux decline/recovery and membrane fouling behavior. Results related to direct NF experiments (Figure 3.4) are given under Section 4.1. Following section (Section 4.2) covers both selection of pretreatment option and UF pretreatment prior to NF. Beside performance of NF after pretreatment, comparative results with direct NF application are detailed in Section 4.3.

During experiments, three different wastewater samples were used as stated in Section 3.1. The pollutant load ranges of samples in terms of TOC, conductivity, and color are given in Table 3.2. Feed values of all experiments were given in Appendix D. Each filtration was performed with different membrane piece except for studies on selection of pretreatment option.

4.1 Treatment of Reactive Dyeing Effluent by Direct NF Application

Under this section, performance of direct NF application was tested at 3 different TMPs (4, 10 and 14 bars) and 2 different CFs (58.9 and 103.2 mL/s). The main purpose was the matching optimal TMP and CF during the NF of reactive dyeing effluents. The conditions providing the highest removal rates in terms of conductivity and TOC besides, color permeate values closest to complete retention were set as most successful (Section 4.1.1). Also, the correlation between the operational conditions and the membrane fouling behaviors was investigated to support designated optimal TMP and CF (Section 4.1.2). These experiments were conducted at TRM to obtain continuous influent to filtration unit needed for long filtration periods till the steady state. In addition to TMP and CF, the effects of VRF, so the change in pollutant load of feed mixture, on performance of NF at optimal operating conditions were studied to simulate real treatment systems demanding lower concentrated stream (Section 4.1.3). This set of experiments were carried out with effluent mixture, named as WW#1 (Table 3.2).

To perform more factual simulation of real systems and to support observations on the relationship of NF performance with TMP and CF, wastewater sample taken from reactive dyeing achieved with a different recipe was treated with direct NF. Another reason behind NF of different recipe effluent was to understand how the pollutant load influencing the optimal operating parameters. (Section 4.1.4) During different recipe studies, experiments conducted by WW#2 (Table 3.2), provided at second sampling, were compared with experiments conducted by WW#1 at same operating conditions.

4.1.1 Effect of TMP and CF on Treatment Performance of NF Membrane

The priority was given to the treatment performance of NF membrane, NF90, during its direct application only after coarse filter. The indication of a successful treatment was high TOC, conductivity, and color retentions which given below with this order.

When TOC removal performance of NF90 membrane was considered, it was observed that the increase in TMP enhanced the TOC retention for both CFs as the purification ability of NF90 membrane increased with the increase in the TMP. At lowest TMP (4 bar), dominant mechanism was caused by the concentarion difference between two sides of membrane as the osmotic pressure was critically high which is discussed in the subsequent sections. With the increase in TMP, influence of osmotic pressure decreased and higher rejection rates were achieved with the pressure-driven filtration. On the other hand, insignificant differences were observed by increasing the CF (Figure 4.1).

During direct application of NF, feed TOC value stayed at 466.07±71.95 mg/L. As seen from Figure 4.1, at TMP of 4 bar, high permeate TOC values were observed beside the variation during the filtration was higher compared to other TMPs. The removal percentages of 92±1 and 90±1 were able to decrease the TOC values only to the levels of 42.93±5.03 and 48.52±5.60 mg/L at CFs of 58.9 and 103.2 mL/s, respectively. Low retention levels pointed out that TMP of 4 bar was not high enough for NF of WW#1. By increasing TMP of 4 bar to 10 bar, 8 percent increase in TOC removal rate was obtained. When TMP was maximized to 14 bar, close to 99% TOC retention was achieved for both CFs and lower permeate TOC value of 6.07± 0.62 mg/L was able to be reached with NF at 14 bar and lower CF.

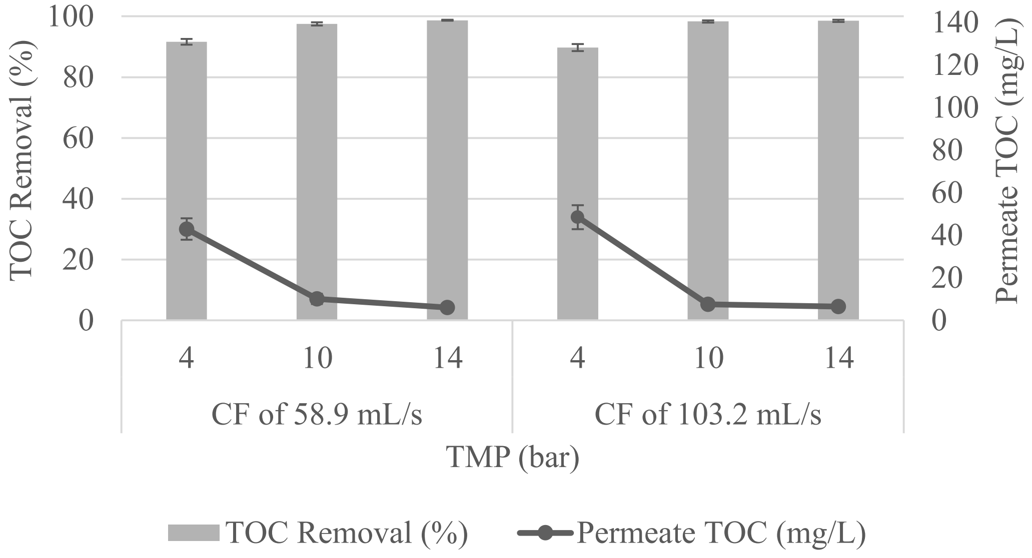

Figure 4.1: TOC Removal Percentages and Permeate TOC Values Reached at Different TMPs and CFs

NF90 membrane showed very successful performance in terms of conductivity removal which was crucial for clean water recovery from reactive dyeing effluents because of the high salt content of the wastewater by its nature. Typical NaCl rejection rate of NF90, 90-96 % (Hildebrand et al., 2013), couldn't be achieved by 4 bar TMP at both CFs. It was suspected that the TMP of 4 bar was insufficient because of the extent of the osmotic pressure caused by high salt (conductivity) content of the feed solution. It was focused on in following chapter (Section 4.1.2) including the analysis on NF flux.

With the increase in TMP, satisfying results were obtained and feed conductivity (14.45±0.03 mS/cm) was able to be decreased below 1 mS/cm at 10 and 14 bar. Same conductivity retentions of 93±1% was obtained for both low and high CFs at 10 bar. The conductivity removal was close to 96% at 14 bar. Eventually, the effluent quality reached to the levels of 0.66±0.02 and 0.59±0.12 mS/cm for CF of 58.9 and 103.2 mL/s, respectively, where these conductivity values were considered the same.

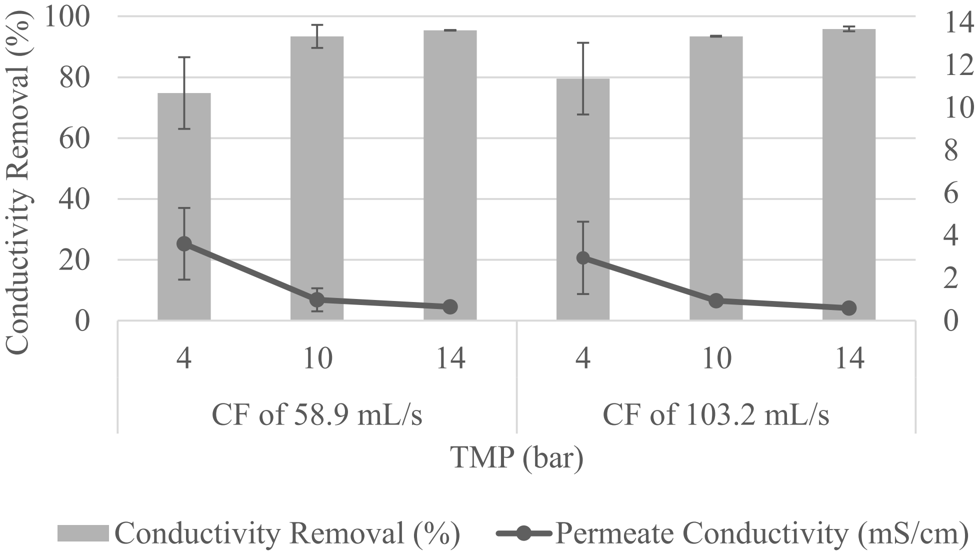

Figure 4.2: Conductivity Removal Percentages and Permeate Conductivity Values Reached at Different TMPs and CFs

Decolorization performance of NF90 was examined at three different wavelengths which are 436, 525, and 620 nm to be able to monitor removal of different reactive dyes with color shades giving absorbance at different wavelength ranges as mentioned before in previous sections. Results clearly showed that the retentions of different colors were different from each other. It was convinced that indicated decolorization performance was directly linked to different molecular weights of used dyes. Used dyes (Reactive Orange S3R, Reactive Deep Red SB6 and Remazol Ultra Navy Blue) were with molecular weights around 550, 700 and 900 g/mol, respectively. These dyes were giving absorbances at wavelengths between 400-500, 500-600 and 600-700nm, respectively.

The feed SAC values were 161.99±0.48, 186.13±0.44, and 35.92±0.21 m^{-1} at 436, 525 and 620 nm, respectively. At all TMPs and CFs, permeate absorbance of direct NF were found very close to zero at all wavelengths. So, almost complete decolorization was reached for all conditions. The measured absorbance values of permeate samples were very small for the instrument detection even the used UV-VIS spectrophotometry was competent to read values with up to four decimals. Although these very small and close absorbance values, the conversion factor used to convert absorbance to SAC unit made the standard deviation profile of measurements appear more significant than they really are.

When all wavelengths were considered, lower CF was found as preferable because no significant improvement in treatment efficiency was gained with higher CF (Figure 4.3,Figure 4.4 and Figure 4.5). Lowest decolorization performance was observed at 4 bar TMP and 103.2 mL/s in terms of all wavelengths, whereas removal percentages were at a lower level at 620 nm for all operating conditions.

In addition to these results, the feed and permeate sample photos given in Appendix C demonstrated that NF90 membrane showed a satisfying decolorization performance.

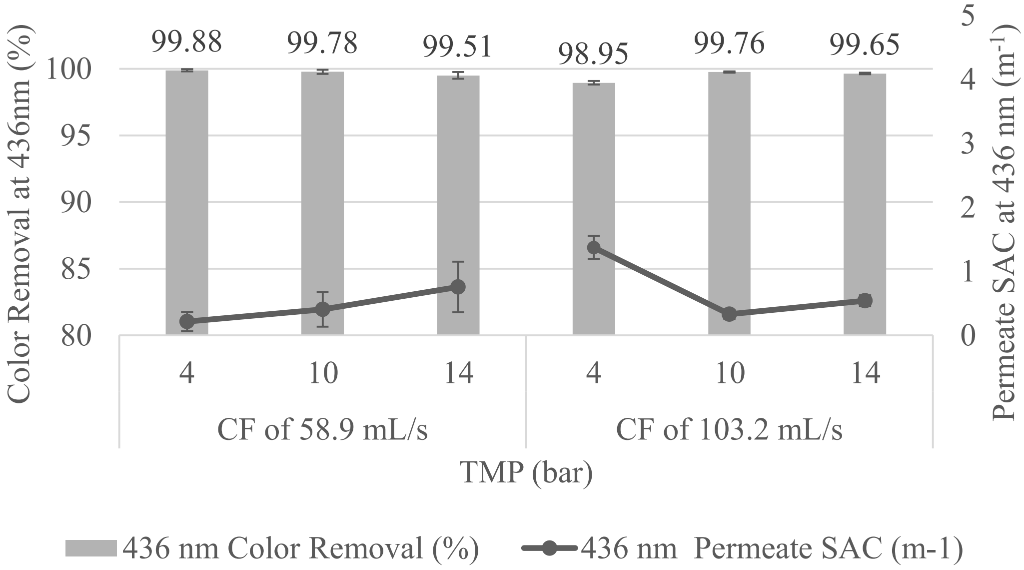

Figure 4.3: Color Removal Percentages and Permeate SAC Values Reached at Different TMPs and CFs (436 nm)

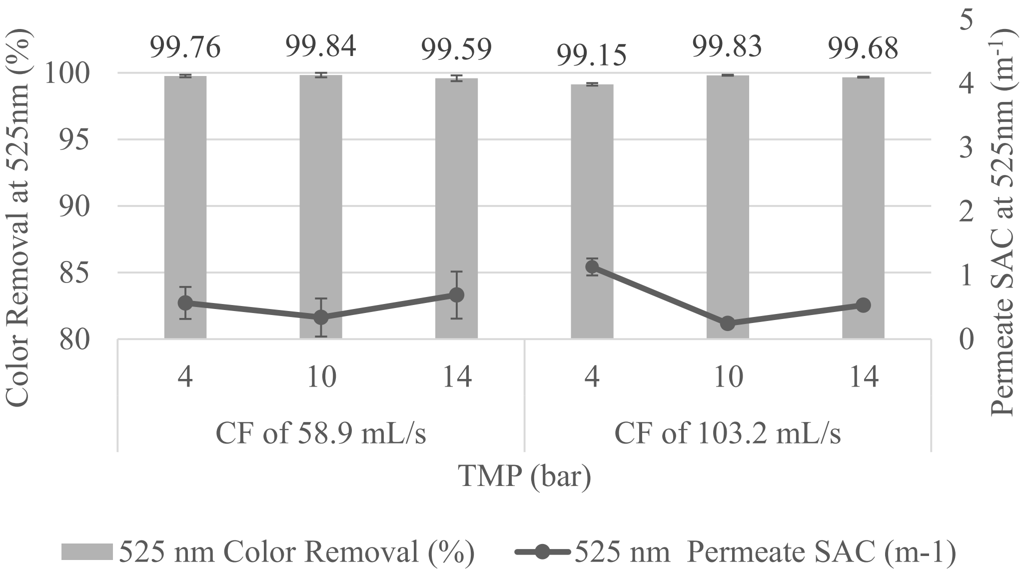

Figure 4.4: Color Removal Percentages and Permeate SAC Values Reached at Different TMPs and CFs (525 nm)

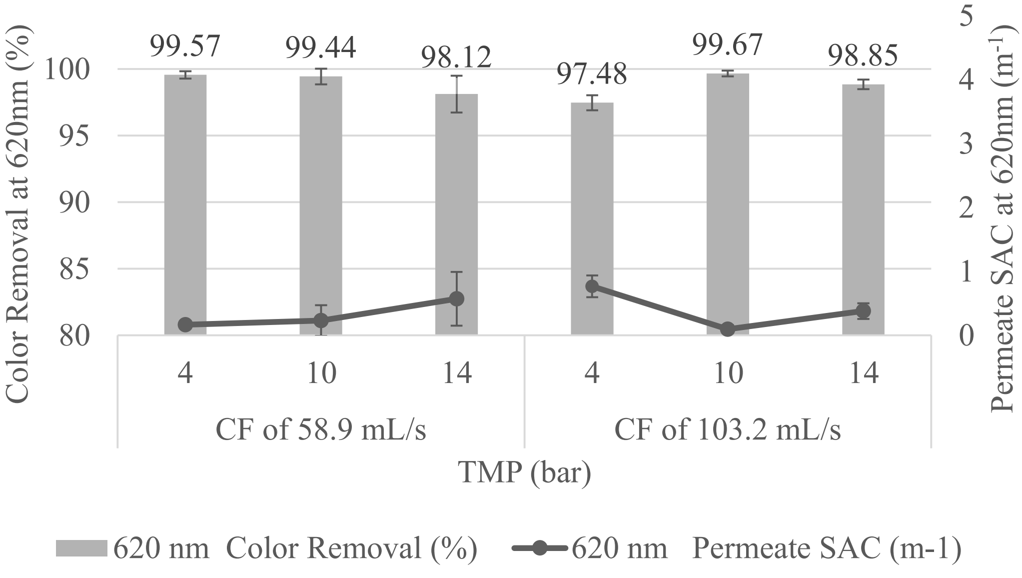

Figure 4.5: Color Removal Percentages and Permeate SAC Values Reached at Different TMPs and CFs (620 nm)

Regarding these findings on treatment performance of single stage NF, no significant improvement was provided by increasing the CF. The reason behind this was seen as that the CF was not increased to levels high enough to reach any improvement. Besides that higher CFs than tested ones would be disadvantageous especially regarding the operating costs.

In terms of TOC and conductivity retentions, the highest rates were reached by TMP of 14 bar where close to zero permeate color values were obtained same as in case of other TMPs.

4.1.2 Effect of TMP and CF on Flux Decline and Fouling Behavior of NF Membrane

A membrane treatment system is needed to provide an effective and sufficient removal performance at a long-life period while maintaining reasonable permeate fluxes in order to be considered as successful. The lifetime of a membrane is directly proportional to its fouling behavior and cleanability so, during the studies on clean water recovery from reactive dyeing effluents, the membranes were tested with respect to flux decline, fouling behaviors, and flux recovery in addition to analysis on their treatment efficiency.

Under this section, the effects of operating parameters such as TMP and CF on pure water flux before and after filtration, filtration flux, flux decline and recovery were analyzed along with resistances due to concentration polarization and fouling. The flux measurements, normalized and corrected flux calculations and resistance analysis were completed as it was explained in detail in Section 3.7. These analyses were done in a comparative way between both experiments conducted at different TMPs and same CF rate beside the ones at same TMP and different CF rates.

When ultra-pure water and filtration fluxes were taken into consideration, no clear evidence of any change in measured fluxes caused by different CF rates was appeared. The increase in CF rate did not contribute any increase in filtration flux which might be expected due to less concentration polarization and cake layer formation by means of possible sweeping effect of higher CF rate. The filtration and normalized flux profiles depicted in the following three figures (Figure 4.6, Figure 4.7, and Figure 4.8) demonstrate that the flux curves of NF tests conducted at same filtration pressure but different CFs overlapped. The observed variations between these curves were associated with conducting each experiment with a different piece of membrane. In the mentioned three figures, the results of NF experiments at 4, 10 and 14 bar were detailed individually.

The initial UPW fluxes of two different virgin NF90 membranes (J_{cwi}) were found as 23.91 and 25.71 L/m^{2}h. These values were declined to 1.29 L/m^{2}h at the very beginning of NF at 4 bar TMP for both CFs. As the filtration approached to the steady state condition, monitored very low raw water flux even got closer to zero at the flux decline rates of 80 and 70 percent and, at the end, J_{rw} values became 0.26 and 0.39 L/m^{2}h at CFs of 58.9 and 103.2 mL/s, respectively. The raw water flux was not sufficient at any point of filtration because the osmotic pressure of 3.23 bar (calculations on related osmotic pressure data were given in Appendix B.2) was quite close to filtration pressure and so, critically significant. The results of calculations on osmotic pressure corrected fluxes given in Table 4.1 showed that the filtration flux would be four times higher in the absence of osmotic pressure corresponding to the corrected fluxes of 1.34 and 2.05 L/m^{2}h at lower and higher CFs, respectively. The sharpest increase in flux after filtration without any cleaning was appeared at 4 bar experiments. At both CFs, physical and chemical cleaning processes achieved same advances in UPW flux, after which J_{cwc} values of 22.71 and 23.31 L/m^{2}h were able to be reached.

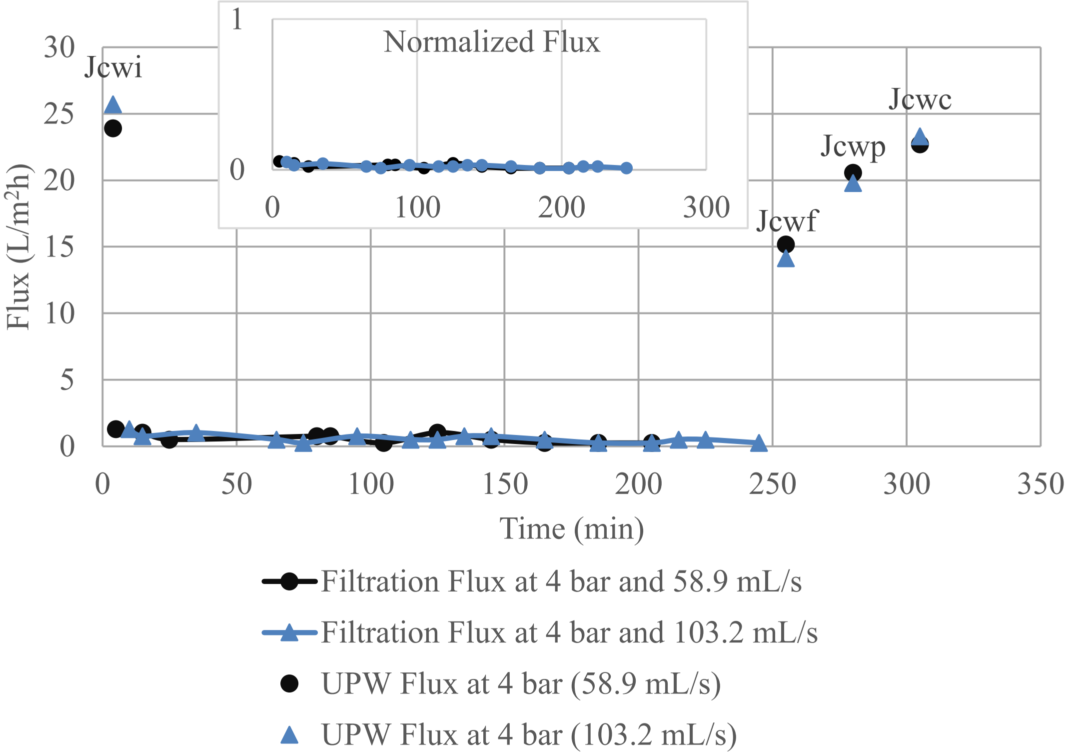

Figure 4.6: Change in Raw Water Flux with Time during NF and UPW Fluxes of NF90 Membrane at TMP of 4 bar

For all TMPs, NF90 membrane was tested by two experiments at CFs of 58.9 and 103.2 mL/s. During single stage NF studies, only at TMP of 10 bar and CF of 58.9 mL/s, the experiment was repeated with a new piece of membrane to check the reproducibility of the experiments. As it was precisely expected, the increase in TMP caused increase in both UPW and filtration flux. The NF90 membrane pieces used during NF at lower CF had higher initial UPW fluxes (66.34 and 68.40 L/m^{2}h) than the one used during NF at high CF (58.37 L/m^{2}h) (Figure 4.7). Filtration flux profile of NF at low CF Test 1 and NF at high CF were shown over each other. On the other hand, some variations were noticed between raw water fluxes of Test 2 and the others. The significance of osmotic pressure was lower at TMP of 10 bar but still it was at a considerable level. The calculated osmotic pressure corrected fluxes (Table 4.1) were 48-53 percent higher than the monitored filtration flux at steady state. Different from NF experiments at 4 bar, the flux decline curves were apparent especially during first test of NF at CF of 58.9 mL/s and NF at CF of 103.2 mL/s. Part of flux decline due to fouling on/in the NF membrane was able to be recovered with cleaning steps. The J_{cwf} values (42.94, 48.34, and 37.03 L/m^{2}h) were raised to 47.06, 52.71, and 44.23 L/m^{2}h with physical cleaning. Only 8 to 10 percent of flux decline could not be recovered by chemical cleaning of membranes.

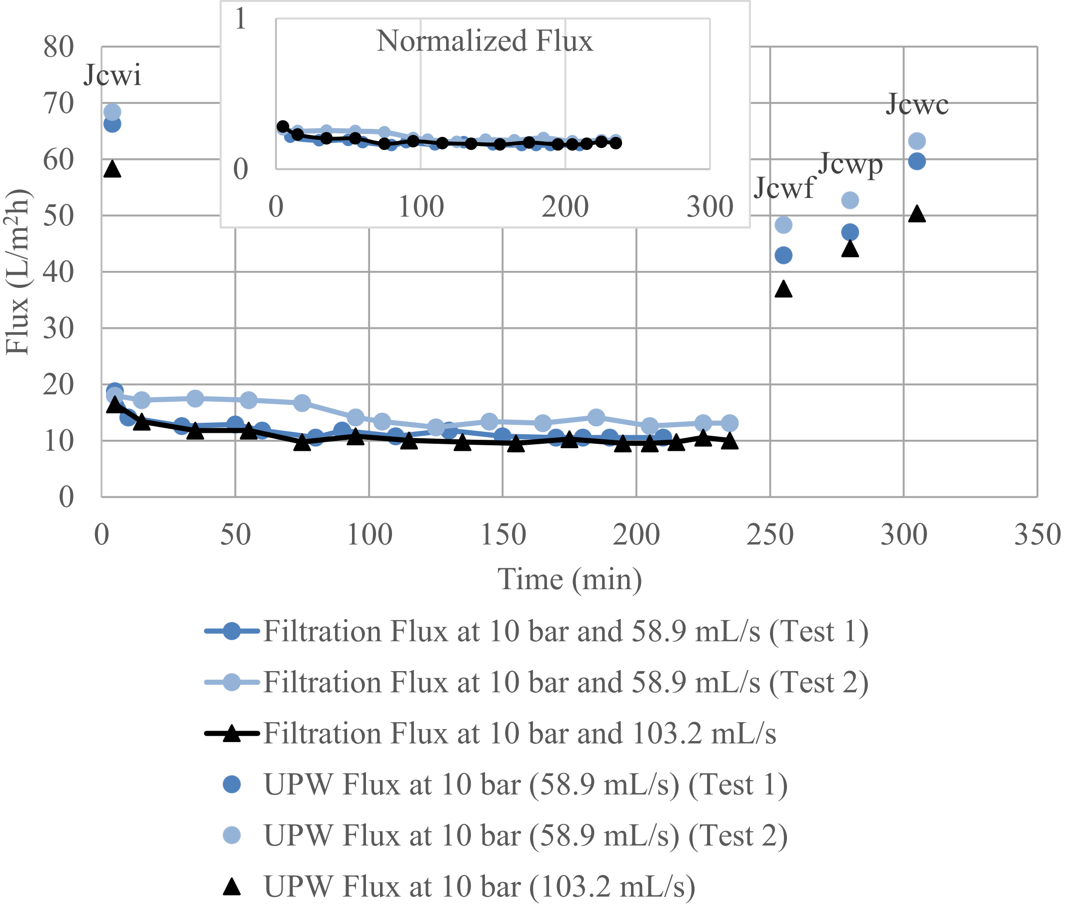

Figure 4.7: Change in Raw Water Flux with Time during NF and UPW Fluxes of NF90 Membrane at TMP of 10 bar

Two different piece of NF90 membrane with similar initial UPW fluxes of 94.37 and 92.06 L/m^{2}h were tested at TMP of 14 bar for different CFs (Figure 4.8). During 14 bar NF at lower CF, flux decline became relatively gradual after 80 minutes and it was considered that the steady state was reached after two hours. Even though, filtration flux profile of NF conducted at TMP of 14 bar and higher CF got steady after 3 hours, the flux decline rates were similar for both CFs (32 %). The raw water fluxes at the very beginning of filtration (30.86 and 32.40 L/m^{2}h at the 10th minute of NF) and after steady state (21.12 and 23.71 L/m^{2}h) were quite close to each other and to the J_{cwi}, in addition to overlapping overall flux decline curves. These values revealed TMP of 14 bar provided more feasible permeation rates which were two times higher than J_{rw} values reached at TMP of 10 bar. This finding was explained by that the effect of 3.23 bar osmotic pressure was not significant for the TMP of 14 bar. The differences between the J_{rw} and corrected flux had been sharper at TMP of 4 and 10 than 14 bar where it was found that the conductivity content of the feed solution decreased the filtration flux at a rate of 25 and 23% at CFs of 58.9 and 103.2 mL/s.

The UPW fluxes before cleaning processes were same but after, achieved flux recovery percentages were lower for the NF90 membrane used to conduct NF at TMP of 14 bar and CF of 103.2 mL/s. UPW flux decline of 39%, which appeared after NF, was recovered by 32 and 19 percent with physical cleaning of the NF90 membranes used at CFs of 58.9 and 103.2 mL/s, respectively. The difference between flux recovery rates was associated with that the higher CF had already avoided a part of fouling on the membrane. When compared to NF90 membranes used at 4 and 10 bar TMPs, chemical cleaning step achieved lower flux recovery at 14 bar.

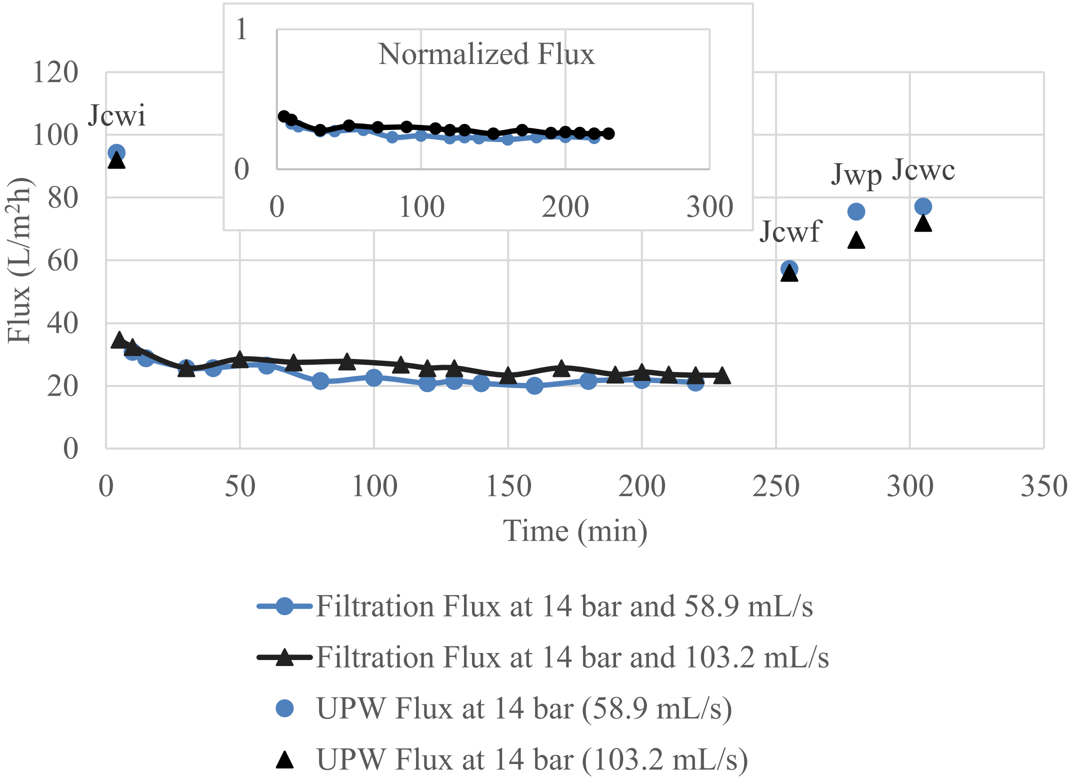

Figure 4.8: Change in Raw Water Flux with Time during NF and UPW Fluxes of NF90 Membrane at TMP of 14 bar

During all direct NF experiments, UPW flux decline, calculated as the percent difference between J_{cwi} and J_{cwf}, was quite similar (37±4%). However, the NF90 membrane reacted differently to physical and chemical cleaning procedures during experiments conducted at different TMPs. So, the total flux recovery rates were varied. As the TMP was increased, the lower recovery percentages were attained where the irreversible portion of fouling, which was thought to be linked with the permanent pore clogging, got larger.

While interpreting the previous figures on flux profiles of single stage NF tests, the effect of osmotic pressure at different TMPs was mentioned separately for each TMP by addressing Table 4.1. By looking at the whole table, a more apparent profile about the change in the significance of osmotic pressure effect on the filtration flux was seen. It was clear that, raising the 4 bar TMP to 10 bar lessened the effect of osmotic pressure by approximately 90 percent and its influence was minimized by increasing TMP to 14 bar.

Table 4.1: Osmotic Pressure Corrected Fluxes of Direct Application of NF

	CF of 58.9 mL/s				**CF of 103.2 mL/s**		
	4 bar	**10 bar (Test1)**	**10 bar (Test2)**	**14 bar**	**4 bar**	**10 bar**	**14 bar**
J_{rw} (L/m^{2}h)	0.26	10.59	13.22	21.12	0.39	9.89	23.71
Corrected Flux (L/m^{2}h)	1.34	15.63	20.26	27.45	2.05	14.59	30.83
Flux Increase (%)	422.76	47.62	53.30	29.94	432.19	47.62	30.05

It was stated before that the different pieces of membranes could show slightly different flux profiles meaning difference in inherent resistances (Table 4.2). Single stage NF experiments operated with these membrane pieces concluded in pressure-dependent R_{tot} values which was the summation of membrane fouling and concentration polarization resistances. Whereas, this was not resulted from increase in the fouling related resistances because there was no direct correlation between fouling resistance and TMP. The increase in CF rate resulted in higher values of R_f. The lowest fouling resistance values were observed during two NF experiments conducted at TMP of 10 bar and CF of 58.9 mL/s. In the summation of R_f and $R_{cp+\pi}$, the concentration polarization resistance was dominant where it was not possible to calculate the resistance due to concentration polarization separately from the effect of osmotic pressure on the driving force. It was because the related calculation done by using the difference between the steady state filtration flux and the UPW flux after filtration without any cleaning where the J_{rw} was under the influence of both in addition to fouling and the J_{cwf} was only affected by extent of fouling. When compared to R_f, $R_{cp+\pi}$ was extremely high especially at TMP of 4 bar. As the TMP was raised, it was reduced.

The lowered flux resulting from the concentration polarization was reversed by diminishing the concentration difference during UPW flux measurement. Besides that, the remaining flux decline due to fouling was tried to be recovered by physical cleaning, at first. Better recovery results were achieved at TMP of 4 bar of both CFs (Table 4.3). Some portion of physically irreversible fouling could be eliminated by chemical cleaning procedure where the chemically irreversible fouling resistance values were lower than the resistance due to physically irreversible fouling especially at the TMP of 10 bar. As the TMP increased, higher chemically irreversible fouling related resistance values were observed where TMP rise enlarged the extent of permanent fouling.

In total, higher irreversible fouling values were obtained at higher CF. So, it was found that the filtration TMP affected the reaction of NF90 membrane to chemical cleaning and the extent of physical cleaning was correlated with the CF at which the filtration was conducted.

When these findings were considered together with the fact that the filtration flux at 4 bar of TMP was at impracticable levels, optimal operational conditions were designated as TMP of 14 bar and CF of 58.9 mL/s with respect to filtration flux, flux decline/recovery and membrane fouling, similar with the treatment efficiency.

Table 4.2: Analysis on Resistances at Different Experimental Conditions

Resistance (10^{13} m^{-1})	**CF of 58.9 mL/s**				**CF of 103.2 mL/s**		
	4 bar	**10 bar (Test1)**	**10 bar (Test2)**	**14 bar**	**4 bar**	**10 bar**	**14 bar**
R_{mem}	6.02	5.43	5.26	5.34	5.60	6.17	5.47
R_{tot}	560.01	33.98	27.24	23.86	373.34	36.42	21.26
R_f	3.47	2.96	2.18	3.45	4.58	3.55	3.52
$R_{cp+\pi}$	550.51	25.60	19.79	15.07	363.16	26.69	12.27
$R_{ph\text{-}irr}$	0.98	2.22	1.57	1.33	1.67	1.97	2.09
$R_{ch\text{-}irr}$	0.32	0.61	0.43	1.19	0.58	0.98	1.53

Table 4.3: Physically and Chemically Irreversible Portions of Membrane Fouling

Irreversible Fouling (%)	**CF of 58.9 mL/s**				**CF of 103.2 mL/s**		
	4 bar	**10 bar (Test1)**	**10 bar (Test2)**	**14 bar**	**4 bar**	**10 bar**	**14 bar**
Ph-irr Fouling	28.20	75.21	71.72	38.45	36.51	55.48	59.52
Ch-irr Fouling	9.17	20.56	19.60	34.59	12.58	27.44	43.38

4.1.3 Effect of VRF on NF Performance during CM Filtration

Single stage NF performance at the optimum TMP and CF designated above was tested by CM experiments at VRF of 2.5 to see possible effects of pollutant load variations as dyeing mill effluent composition, so its load, is highly fluctuating. From 1750 mL of WW#1, 1050 mL of permeate was collected to reach intended VRF. VRF was set by considering the required amount of clean water recovery in addition to the inside and feed volume of filtration system. The retention percentages were calculated by using instant feed and permeate values at related VRF for all parameters.

Figure 4.9 represents the variation in TOC retention performance of NF90 membrane during CM filtration till 2.5 VRF. Feed TOC raised to the 614.80 mg/L from 259.44 mg/L when VRF reached to 2.5. Permeate quality and retention in terms of TOC improved with the increase in VRF till 1.52 at which best performance was obtained (7.56 mg/L permeate TOC value). After this point, permeate value increased to 9.55 mg/L and the removal rate at VRF of 2.05 (98%) stayed very close the one at VRF of 1.52. Filtration at a VRF higher than 2.06 was found impracticable for TOC removal due to critical decrease in instant and total permeate quality.

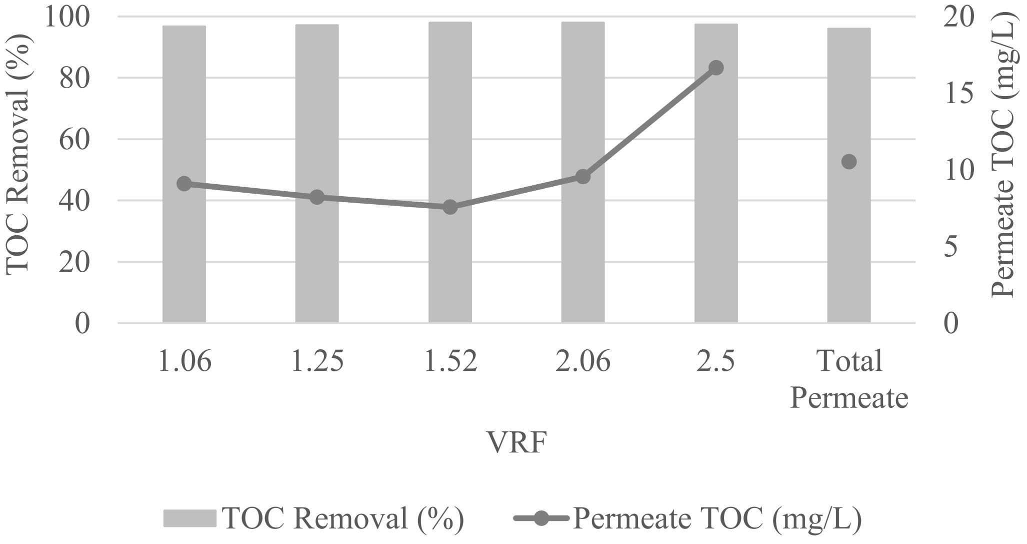

Figure 4.9: Change in TOC Removal Percentages and Permeate TOC Values with the Increase in the VRF

As detailed in Section 4.1.2, feed conductivity causing osmotic pressure is very influential on filtration flux by reducing the extent of TMP. This is supported by Figure 4.10 which clearly demonstrates the inverse correlation between the filtration flux and feed conductivity. As expected, feed conductivity increased from 14.52 mS/cm to 32.00 mS/cm with the increase in VRF. So, the beginning osmotic pressure of 3.28 bar multiplied by 2.2 and reached to levels around 7.23 bar at 2.5 VRF. This increase in conductivity, so the osmotic pressure, contributed in 95% decline in filtration flux.

While decreasing the filtration flux, permeate conductivity was increased by the increased feed conductivity (Figure 4.11). After VRF of 2.06, effluent conductivity quality had become much worse and out of the range of 800-2200 µS/cm needed for water reuse (Table 2.4). Until 2.06, the rate of increase in permeate quality was lower compared to the rate after this VRF. Not only the permeate conductivity but also the removal rate was reduced (Figure 4.11) while the rate of increase in feed conductivity was also raised as seen from Figure 4.10. Initial retention of 95% dropped below 84% corresponding to 0.79±0.00 and 5.12±0.03 mS/cm, respectively.

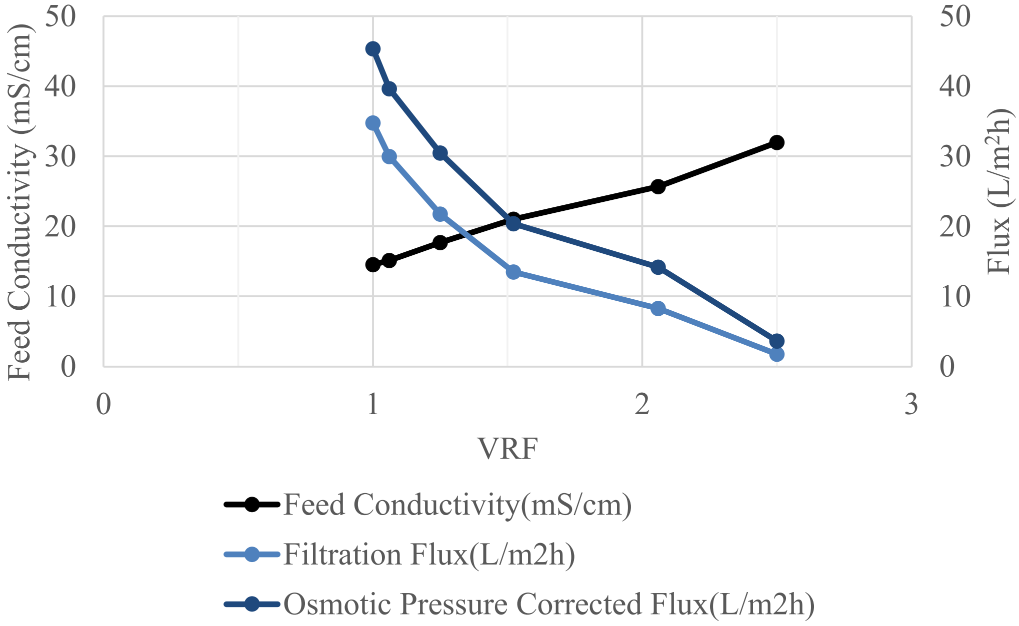

Figure 4.10: Feed Conductivity and Filtration Flux of CM Filtration

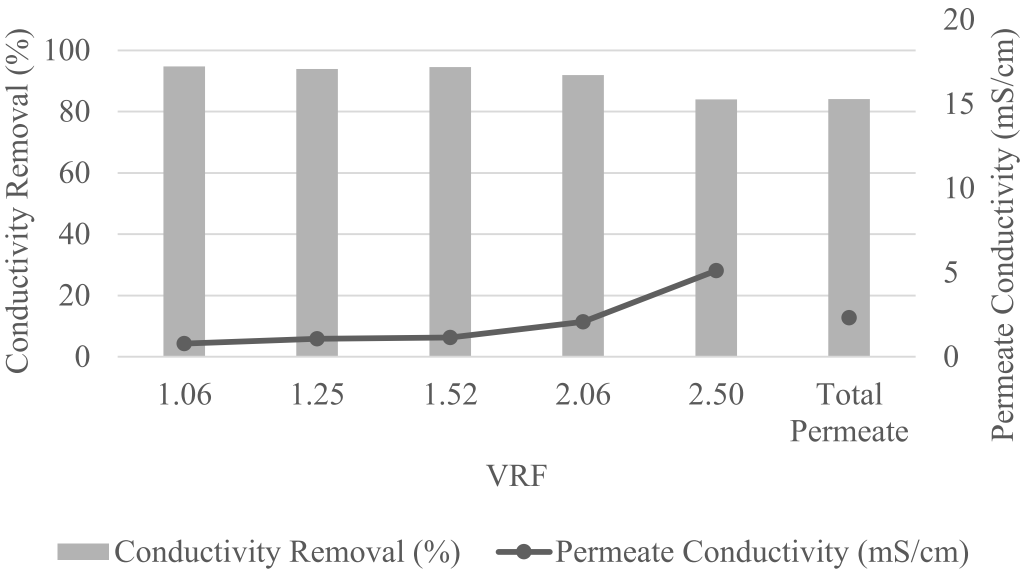

Figure 4.11: Change in Conductivity Removal Percentages and Permeate Conductivity Values with the Increase in the VRF

For all wavelengths, permeate color quality showed exactly same trend with permeate TOC content. Initial feed SAC values (134.64, 131.36, and 33.76 m^{-1}at wavelengths of 436, 525, and 620 nm, respectively) were multiplied by almost 2.5 at 436 and 525 nm, and 2.2 at 620 nm when VRF reached to 2.5. Even for the VRF of 2.5 at which point higher SAC values (1.37±0.02, 1.73±0.02, and 0.33±0.02 m^{-1}at 436, 525, and 620 nm, respectively) were obtained, nearly complete decolorization was achieved. Moreover, absorbance values of permeate samples taken at VRF of 1.52 and 2.06, and the total permeate were under the detection limit of the instrument, as a result, the retention found as 100 percent for all wavelengths. The color retentions obtained at other points were above 99%.

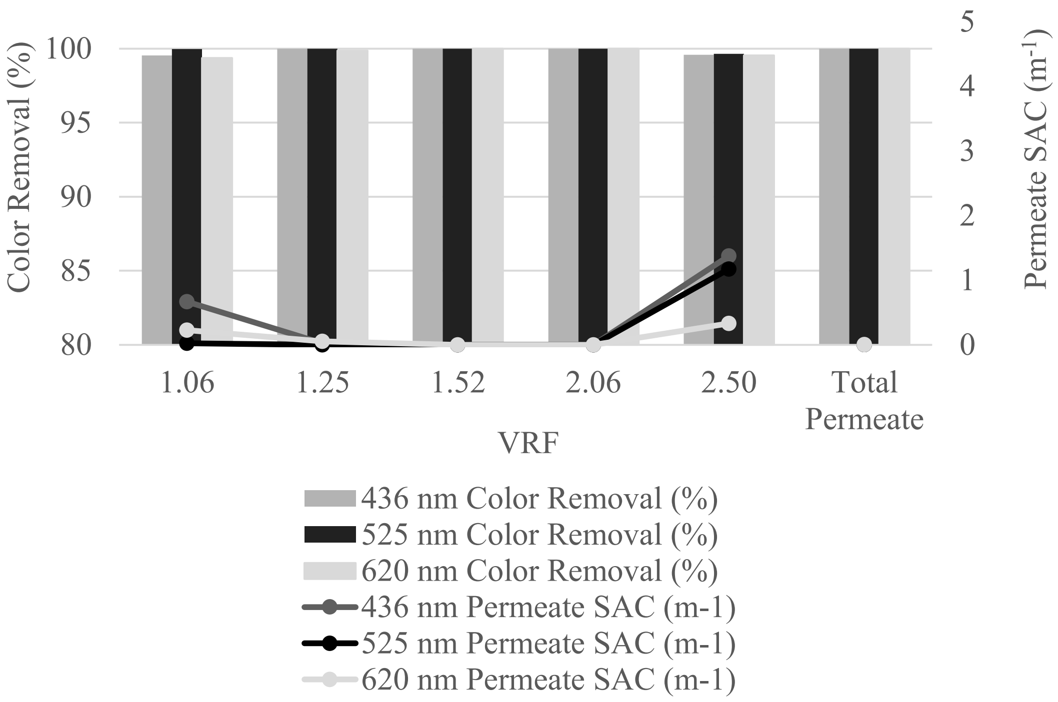

Figure 4.12: Change in Color Removal Percentages and Permeate SAC Values with the Increase in the VRF

When retentions of all parameters were considered, VRF of 2.06 was decided as the highest implementable VRF. Especially for TOC and conductivity, permeate quality declined by VRF increase after 2.06. Likewise, permeate SAC values also increased at following VRFs but water quality in terms of color still stayed acceptable.

At the very beginning of filtration, J_{cwi} value decreased to 27.65 and 34.40 L/m^{2}h at Test 1 and Test2, respectively which were quite similar to filtration flux of 30.86 L/m^{2}h at the 10th minute of TRM NF at the same conditions (14 bar TMP and 58.9 mL/s CF). As the time passed and VRF increased, the filtration flux declined and J_{rw} was found as 2.84 and 2.41 L/m^{2}h when the VRF reached to 2.5 corresponding flux decline of 90 and 93% at Test 1 and 2, respectively. Increased feed concentrations, especially in terms of conductivity, were the reasons behind the continuous decline of filtration flux because the increase in the salt concentration difference between both sides of membrane caused higher osmotic pressure, lowering the effective filtration pressure, extent of which had been demonstrated before in Figure 4.10. Pure water flux right after filtration without any cleaning displayed that the flux decline was caused not only by concentration polarization via solutes on membrane surface but also the fouling on/in the membrane.

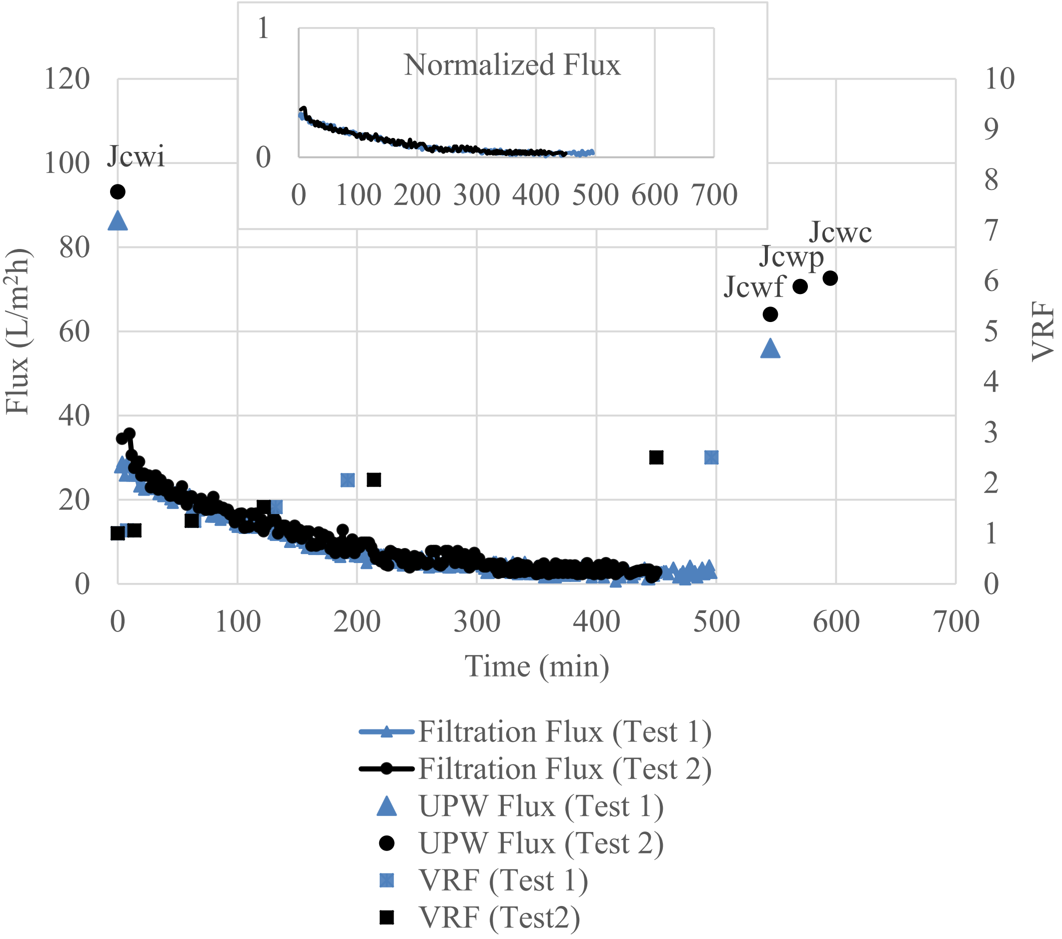

Figure 4.13: Timely Variations in Raw Water Flux and VRF during CM Filtration and UPW Fluxes of NF90 Membrane at TMP of 14 bar

The contribution of chemical cleaning was not large as much as physical cleaning which can be deduced from J_{cwp} and J_{cwc} values shown in Figure 4.13. In other words, fouling on the membrane could be drawn away by the application of physical cleaning to a certain extent. But, the NF90 membrane reacted same with the reactions during other direct NFs conducted at 14 bar and TRM, and the resistance values due to physically and chemically irreversible fouling at CM experiments were also found as very close to each other.

Even though the fouling resistance observed during CM experiments were lower than the TRM filtration at the same TMP and CF, both of physically and chemically irreversible fouling resistances were higher as the Table 4.5 shows what percentages of fouling could not be reversed by physical or consecutive chemical cleaning procedures. After CM filtration, the reaction of NF90 membrane to physical cleaning was much more limited and, as it has already been mentioned, the chemical cleaning procedure showed same performance with other experiments conducted at same TMP. So, the pure water flux recovery was at a lower rate, and physically and chemically irreversible fouling resistances were both greater compared to the TRM experiments resulting from permanent fouling as a result of that the absorption of dye molecules by membrane increased as the color of feed solution got concentrated with the increase in VRF. The difference between the amount of dye adsorption at TRM and CM filtrations at 14 bar and 58.9 was visible Also, to see the effect of cleaning procedures on mentioned dye adsorption, a NF90 membrane used during Test 1 was not subjected to any cleaning. It was observed that there is an obvious difference between membranes before and after cleaning.

Table 4.4: Analysis on Resistances Obtained during CM Experiments

Resistance (10^{13} m^{-1})	**CM (Test 1)**	**CM (Test 2)**	**TRM**
R_{mem}	5.83	5.41	5.34
R_{tot}	177.45	208.79	23.86
R_f	3.16	2.46	3.45
$R_{cp+\pi}$	168.46	200.92	15.07
$R_{ph\text{-}irr}$	-	1.72	1.33
$R_{ch\text{-}irr}$	-	1.53	1.19

Table 4.5: Physically and Chemically Irreversible Portions of Membrane Fouling Obtained during CF Experiments

Irreversible Fouling (%)	**CM (Test 1)**	**CM (Test 2)**	**TRM**
Ph-irr Fouling	-	69.96	38.45
Ch-irr Fouling	-	62.15	34.59

4.1.4 Effect of Change in Wastewater Characteristics due to Difference between Dyeing Recipes

NF90 membrane and the operating conditions were tested with WW#2 collected from lighter shade dyeing applied with different recipe but quite similar dyes (Table 3.1) to perform more factual simulation of real systems. As seen from Table 3.2 on wastewater characterization, pollutant load of WW#2 was almost 28 and 35 percent of WW#1 in terms of TOC and conductivity. As the WW#2 was with lighter shade, feed SAC values at wavelengths of 436, 525 and 620 nm were 27, 41 and 46 percent of the ones of WW#1.

The lowest permeate TOC value of 4.82±0.37 mg/L was reached at 10 bar TMP and 58.9 mL/s even the removal percentages were quite same at all tests (94±2%). Feed conductivity of 5.10±0.02 mS/cm was decreased to 0.33±0.02 corresponding to removal rate of 93%. Better results could be obtained by increasing TMP to 10 bar, and so, decreasing the influence of osmotic pressure. Permeate conductivity was taken to 0.15±0.03 mS/cm as a result of 97±1 percent removal.

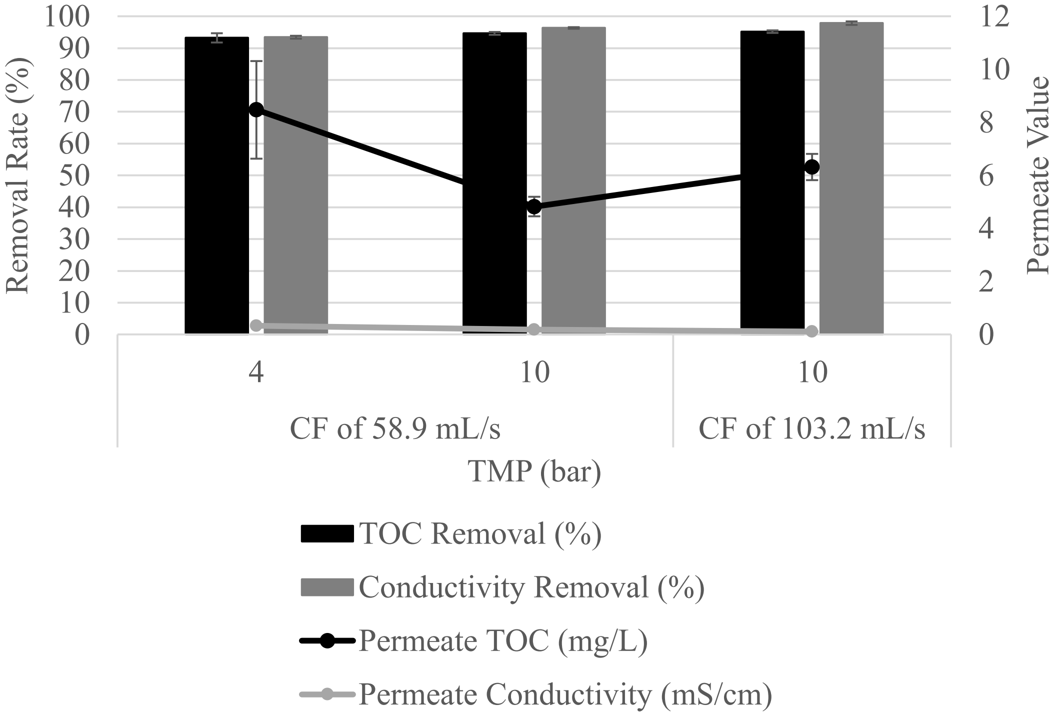

Figure 4.14: TOC and Conductivity Removal Performance Reached during NF of WW#2 at i) 4 bar and 58.9 mL/s, ii)10 bar and 58.9 mL/s, and iii)10 bar and 103.2 mL/s

Even though the feed color content of WW#1 was at a lower level, NF90 membrane's decolorization performance during the filtration of WW#2 quite similar with the filtration of WW#1. The highest color retentions were reached at TMP of 10 bar and CF of 58.9 mL/s and SAC values of 0.31±0.14, 0.35±0.10 and 0.22±0.10 m^{-1} were obtained at 436, 525 and 620 nm wavelengths, respectively.

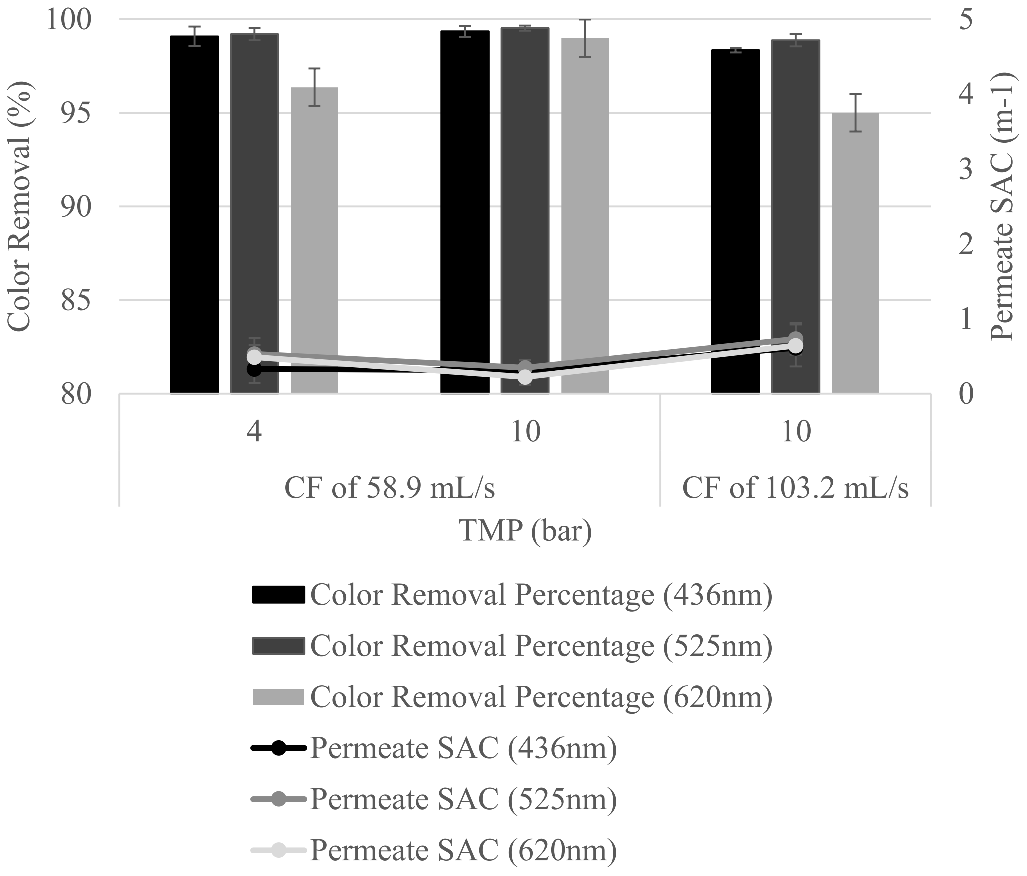

Figure 4.15: Decolorization Performance Reached during NF of WW#2 at i) 4 bar and 58.9 mL/s, ii)10 bar and 58.9 mL/s, and iii)10 bar and 103.2 mL/s

As the feed pollutant load of WW#2, especially in terms of conductivity, was at a lower level than WW#1, higher permeate flux values were reached at lower TMPs (Figure 4.16).

At TMP of 4 bar and CF of 58.9 mL/s, filtration flux was obtained as 10.90 L/m^{2}h and permeate flux increased to 34.06±2.56 L/m^{2}h by taking the TMP to 10 bar from 4 bar. The fluxes reached during filtration of WW#2 was higher than the fluxes reached during filtration of WW#1 at same TMPs. Like the previous findings, tests conducted at 10 bar show that CF have no influence on both the filtration flux and the UPW fluxes after filtration.

Feed conductivity of 5.10±0.02 mS/cm was assumed to cause an osmotic pressure level around 1.16 bar. As it was expected, the influence of osmotic pressure was higher at 4 bar. It was found that the filtration flux would be 40 and 13% percent higher in the absence of osmotic pressure.

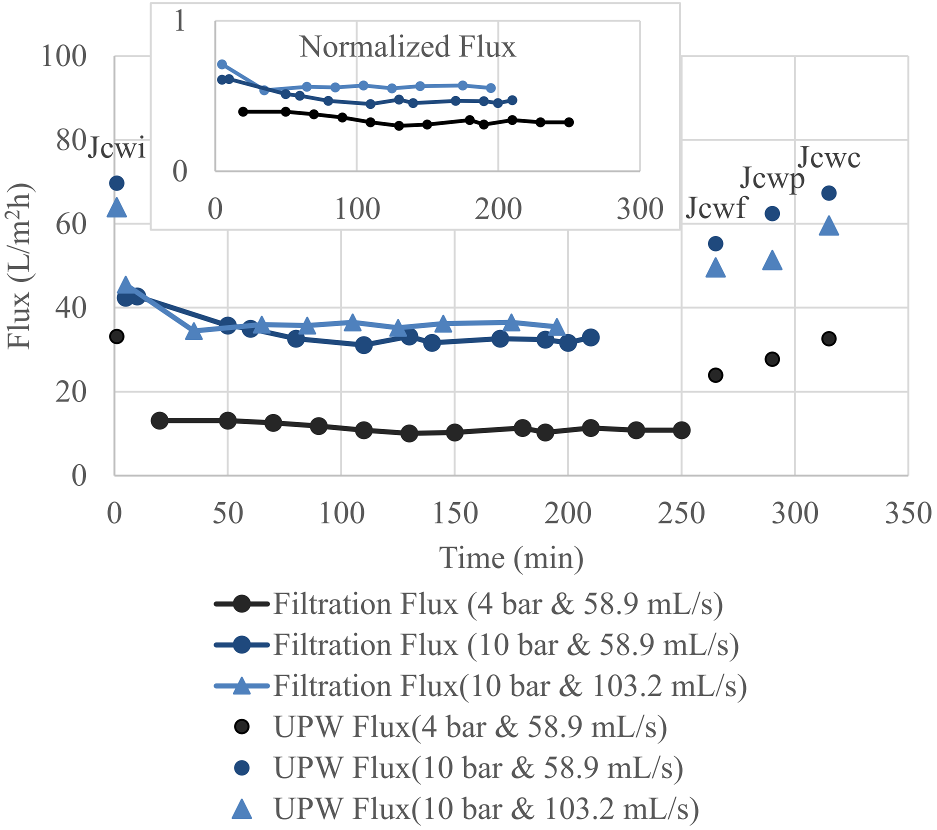

Figure 4.16: Permeate Flux Profile during NF of WW#2 and UPW Fluxes of NF90 Membrane before and after Filtration

Table 4.6: Osmotic Pressure Corrected Fluxes of Direct Application of NF with WW#2

	TMP of 4 bar CF of 58.9 mL/s	**TMP of 10 bar CF of 58.9 mL/s**	**TMP of 10 bar CF of 103.2 mL/s**
J_{rw} (L/m^2h)	10.90	32.25	35.87
Corrected Flux (L/m^2h)	15.29	36.46	40.56
Flux Increase (%)	40.27	13.05	13.06

Fouling related resistances were quite close each other (Table 4.7) but its physically and chemically irreversible portions were different (Table 4.8). Resulting from lower pollutant load and osmotic pressure, $R_{cp+\pi}$ was very small when compared to values obtained during NF of WW#1. Concentration polarization and osmotic pressure related resistance was higher at 4 bar and got lower as the TMP increased. Similar with the previous findings, lower values were reached at higher CF as the extent of cake layer formation decreased. Beside that, resistances due to physically and chemically irreversible fouling were higher at CF of 103.2 mL/s.

Table 4.7: Analysis on Resistances Obtained during NF of WW#2

Resistance (10^{13} m^{-1})	**TMP of 4 bar CF of 58.9 mL/s**	**TMP of 10 bar CF of 58.9 mL/s**	**TMP of 10 bar CF of 103.2 mL/s**
R_{mem}	4.34	5.17	5.62
R_{tot}	13.21	11.16	10.04
R_f	1.68	1.35	1.63
$R_{cp+\pi}$	7.19	4.65	2.78
R_{ph-irr}	0.84	0.60	1.38
R_{ch-irr}	0.07	0.18	0.41

Table 4.8: Physically and Chemically Irreversible Portions of Membrane Fouling Obtained during NF of WW#2

Irreversible Fouling (%)	TMP of 4 bar CF of 58.9 mL/s	TMP of 10 bar CF of 58.9 mL/s	TMP of 10 bar CF of 103.2 mL/s
Ph-irr Fouling	50.23	44.24	84.44
Ch-irr Fouling	4.07	13.19	25.25

The findings on that no additional enhancement due to higher CF was obtained supported the decision of setting CF to 58.9 mL/s. TMP of 10 bar was found applicable at which treatment performance was even better than the one obtained during NF of WW#1 at optimal conditions (14 bar and 58.9 mL/s). Similarly, the filtration flux was significantly higher. So, increasing TMP to higher values was not needed whereas the requirement of adjusting TMP according to feed pollutant load (especially in terms of conductivity) arose.

4.2 Pretreatment of Reactive Dyeing Effluent

It is possible to enhance the performance of NF membrane in terms of treatment efficiency, flux decline and fouling behavior with the implementation of an appropriate pretreatment method as mentioned in Section 2.2.3.3 by giving specific examples found in literature. Among all possible pretreatment methods, MF and UF processes were both pointed as rational pretreatment alternatives by many studies to overcome the limits and weaknesses of NF process. Under the light of this knowledge, to complete the process optimization on clean water recovery from reactive dyeing effluents on the basis of NF, possible improvements were investigated which might be achieved by using pretreatment prior to NF instead of direct application of NF90 membrane. At first, two different membranes, 0.45 μm MF membrane and 150 kDa UF membrane, were tested by dead-end filtration and related results were given in Section 4.2.1. After the determination of applicable pretreatment alternative, its performance in CF filtration system was evaluated in Section 4.2.2.

4.2.1 Selection of Pretreatment Option

The pretreatment selection studies were carried out with WW#3 by 400 mL stirred cell at 100 rpm. Performances of both MF and UF were tested in terms of treatment efficiency and membrane fouling behavior. For each alternative, dead-end filtration experiments till VRF of 2.75 were performed with two different pieces of membrane. One of the membrane pieces were subjected to filtration for the second time to see whether it would maintain the same effectiveness. MF and UF membranes were tested at 0.2 and 0.5 bars, respectively, and 255 mL of permeate was collected from 400 mL corresponding to VRF of 2.75. Results related to each alternative were given separately in Sections 4.2.1.1 and 4.2.1.2 followed by comparison between them (Section 4.2.1.3). Pollutant load of feed solution, namely WW#3, was given in Table 3.2.

4.2.1.1 Dead-End Performance of 0.45 µm MF Membrane

A 0.45 µm PES MF membrane was tested at 0.2 bar and 100 rpm till VRF of 2.75. In terms of TOC retention, MF membrane was only able to decrease the TOC level of 149.27±13.13 mg/L to around 119.17±7.41 mg/L. At the first filtration, different pieces showed different performances corresponding to TOC removal rates of 13±2% and 25±5%. At the second filtration conducted with the first piece which had performed lower TOC retention, the removal rate increased to 21±2%. Even though the rates were different, the permeate TOC concentrations were found to be very close. Variations in feed load slightly increased the TOC retention and did not distract the permeate quality in terms of TOC.

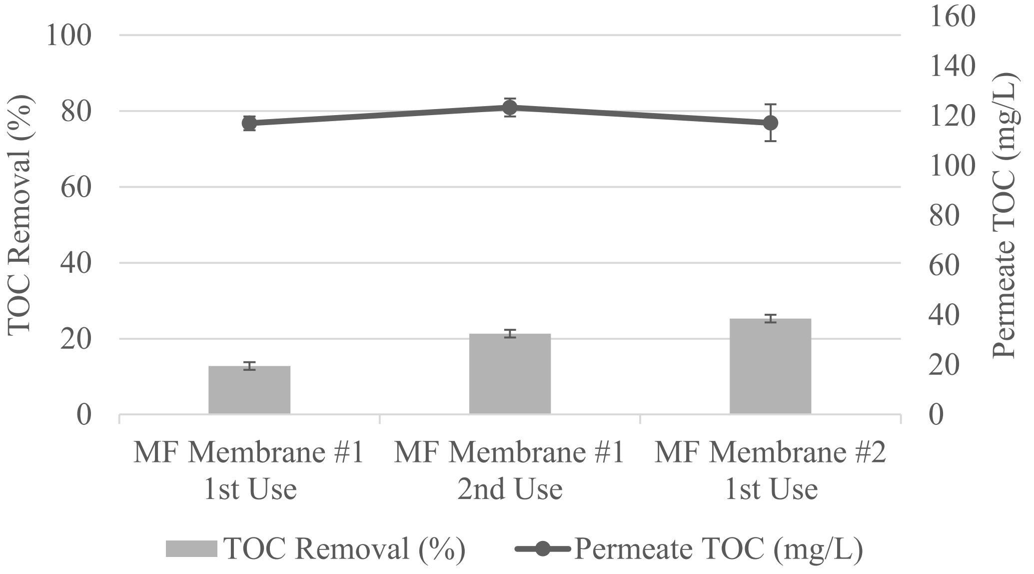

Figure 4.17: Overall TOC Retention Performance of 0.45 μm MF Membrane and Permeate TOC Values

As expected, a reasonable portion of turbidity could be removed by 0.45 μm PES MF membrane. A decline trend in the turbidity content of permeate samples taken at VRFs of 1.33, 2 and 2.75 was observed as shown in Figure 4.18 which was probably caused by continual cake layer formation despite of stirring at 100 rpm. The lowest values of turbidity were reached at VRF of 2.75 which were quite close to permeate turbidity obtained by direct NF at lower CFs.

In addition to cake layer formation, an improvement in terms of permeate turbidity between the two filtrations of the same piece of MF membrane was experienced as a possible effect of a permanent pore clogging which couldn't be removed by physical and chemical cleaning. As it can be seen from Figure 4.18, at all VRFs, better turbidity values were achieved with second use of first MF membrane compared to first filtration. The overall retentions given in Figure 4.19 supported this observation. The turbidity removal of 88±4% increased to 91±3% at second filtration of MF membrane #1. Resulting from differences between different pieces of same membrane, MF membrane #2 could reach removal percentage of 91±2 at first run. The examinations on removal of other parameters and membrane fouling behavior was conducted also to understand the extent of cake layer formation and pore clogging, suspected due to findings on turbidity retention.

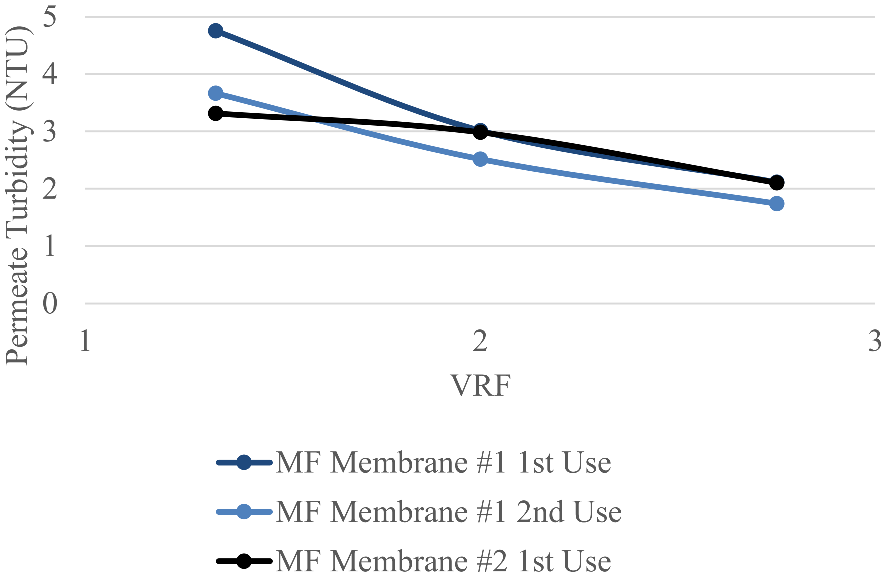

Figure 4.18: Change in Permeate Turbidity during Dead-End MF Experiments

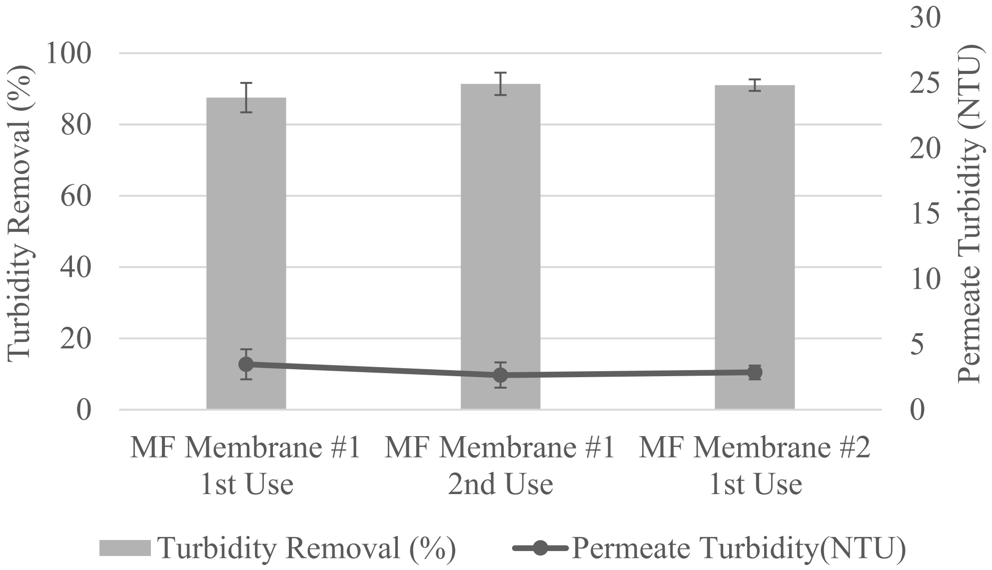

Figure 4.19: Overall Turbidity Retention Performance of 0.45 µm MF Membrane and Permeate Turbidity Values

It is obvious that it is not possible to achieve any significant conductivity removal by MF membranes. So, the feed, permeate and concentrate conductivity values were same without any evidence of retention or concentrated feed. Only a slight decrease in conductivity (2±1%) was detected at filtration conducted by MF membrane #2 which was assumed as insignificant.

For all wavelengths, very close color retentions and permeate SAC values were reached. Similar to turbidity, permeate SAC values decreased during the MF experiments referring considerable increase in instant retention rates. A significant part of color removal was achieved by the means of the suspended solid elimination beside that, in a small extent, dyes were adsorbed in/on the membrane piece during filtration.

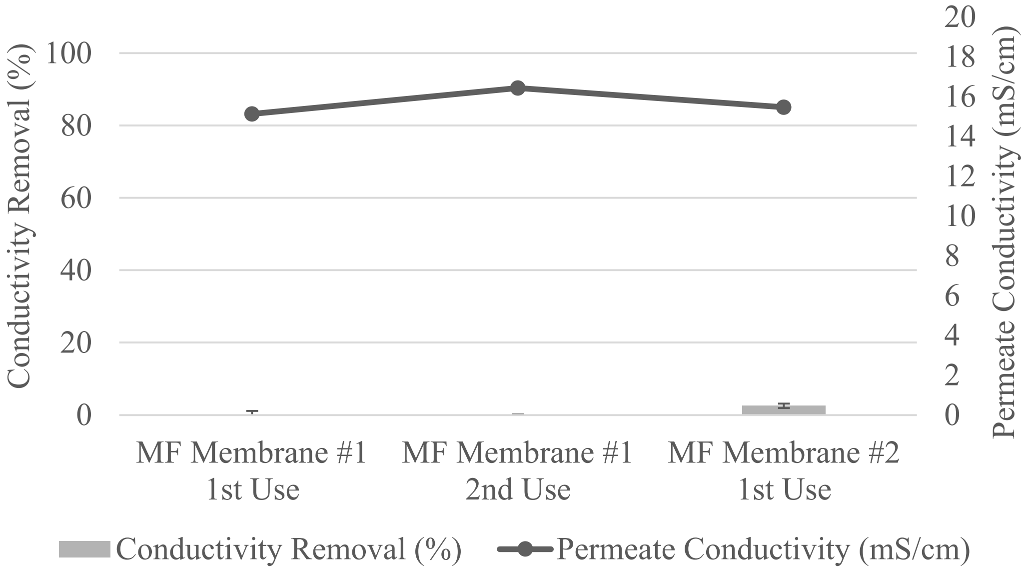

Figure 4.20: Overall Conductivity Retention Performance of 0.45 µm MF Membrane and Permeate Conductivity Values

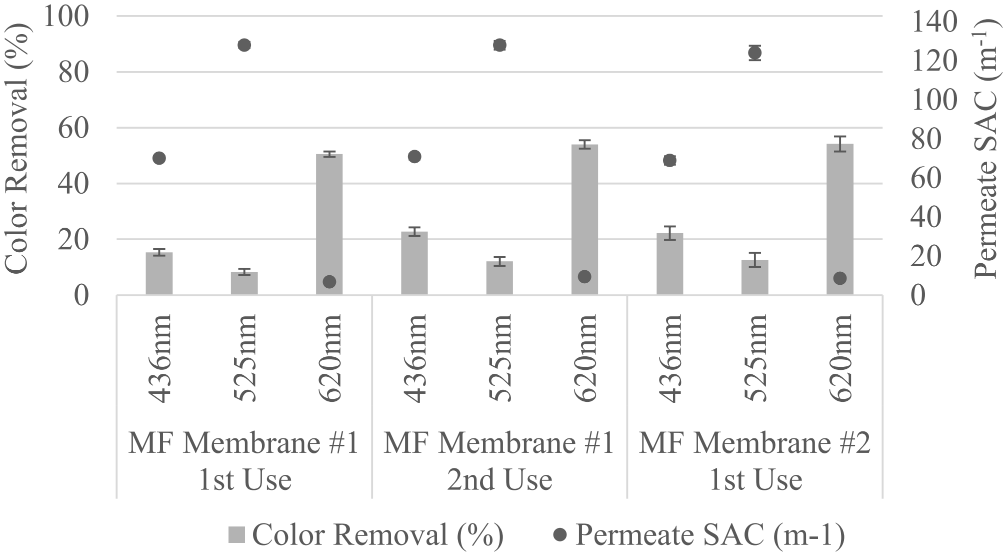

Figure 4.21: Overall Color Retention Performance of 0.45 µm MF Membrane and Permeate SAC Values

MF membranes are considered as advantageous pretreatment options when compared to UF membranes with respect to their high filtration flux at low filtration pressures, less membrane surface requirement and so, lower maintenance and operating costs. For this reason, in addition to treatment performance, flux profile of 0.45 µm MF membrane during dead-end filtration, its fouling behavior and reaction to cleaning processes were examined. Figure 4.22 demonstrates UPW fluxes of 0.45 µm MF membrane before and after filtration beside raw water flux profile during dead-end filtration till VRF of 2.75.

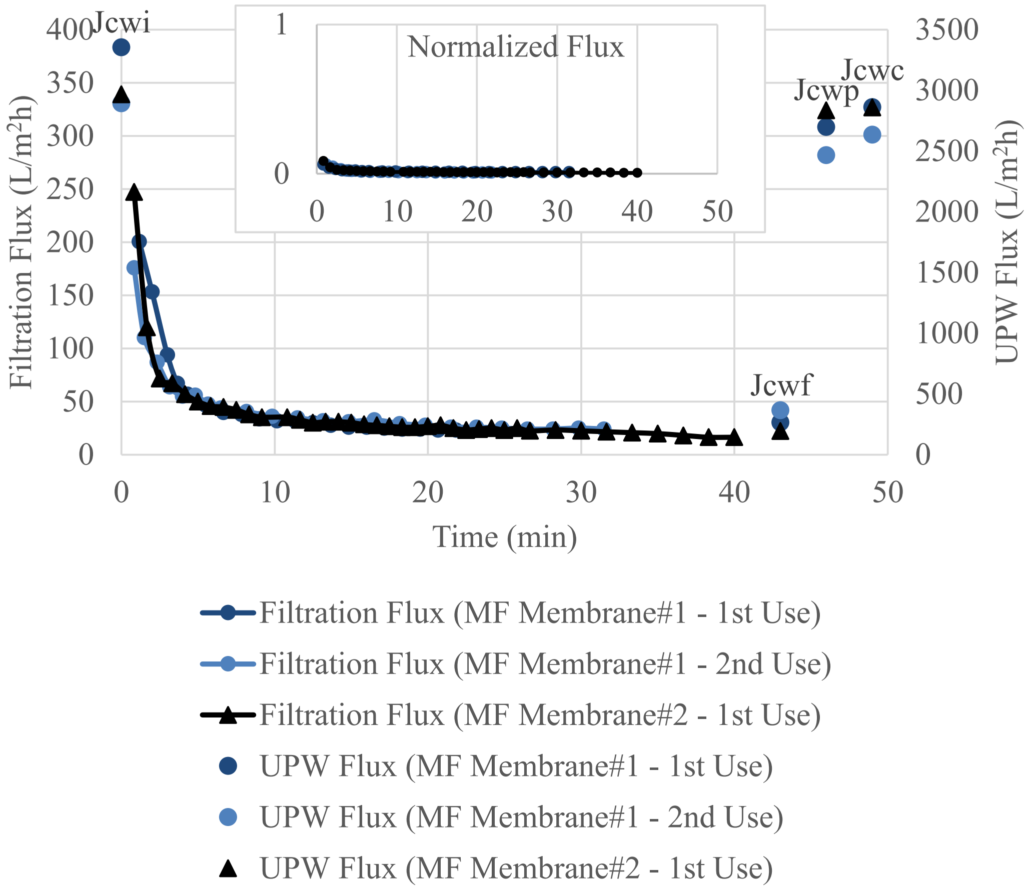

Figure 4.22: Permeate Flux Profile during Dead-End MF till VRF of 2.75 and, UPW Fluxes of 0.45 µm MF Membrane before and after Filtration

The J_{cwi} values of three different pieces of MF membranes varied from each other and the UPW flux of MF membrane at 0.2 bar before filtration was quite high as it was expected. These high flux values dramatically decreased to a range between 176 and 247 L/m^{2}h at the very beginning of the filtrations. The initial flux decline was very sharp possibly due to rapid pore blocking at critical amounts. After the fourth minute of filtration, the decline was relatively gradual which was due to the low flux that could be balanced by back diffusion.

The J_{cwi} and initial filtration flux observed at the second use of MF membrane #1 was lower than the first use. The UPW flux obtained after the cleaning applications of first use of MF membrane and obtained before second filtration was 2863 and 2893 L/m^{2}h which were considered as very similar where the UPW flux of virgin MF membrane

#1 (3355 L/m^{2}h) was higher. The UPW flux after cleaning steps (J_{cwc}) was again lower than the initial UPW flux obtained before second filtration.

On the contrary, quite close J_{rw} values (23 and 24 L/m^{2}h) were reached at the VRF of 2.75 during first and second filtration conducted by same membrane piece. With second piece, which was with lower UPW flux before filtration than the first piece, in the same manner, lower J_{rw} of 16 L/m^{2}h was obtained at 2.75 VRF. The UPW fluxes right after filtration without any cleaning was relatively close to these declined raw water fluxes when compared to UPW fluxes before filtration and after cleaning steps. The J_{cwf} values were 93±1% of UPW fluxes of virgin states of MF membranes. At second use, the ratio was obtained as 87%.

Because of its nature, the inner resistance of MF membrane was very small and both pieces were with 0.002 10^{13} m^{-1} resistance which didn't change at the second test (Table 4.9). The concentration polarization resistance was quite higher than the fouling related resistance and, by physical cleaning, big portion of obtained UPW flux decline could be reversed and two pieces reacted to cleaning similarly even though there were small differences which are seen from both the Figure 4.22 showing the flux profiles and Table 4.9 which includes resistance values. Beside very low physically irreversible resistances (so, the physically irreversible portion of fouling was quite low), the chemically irreversible fouling related resistance was even lower than these values. The resistance values of MF membrane #1 was very similar at both two experiments but lower than the ones obtained by MF membrane #2, even all resistance values were proportional to each other at each experiment.

Table 4.9: Analysis on Resistances Obtained during Dead-End MF Experiments

Resistance (10^{13} m^{-1})	**MF Membrane#1 1st Use**	**MF Membrane#1 2nd Use**	**MF Membrane#2 1st Use**
R_{mem}	0.002	0.002	0.002
R_{tot}	0.310	0.299	0.440
R_f	0.025	0.017	0.035
R_{cp}	0.283	0.279	0.403
$R_{ph\text{-}irr}$	0.001	0.000	0.000
$R_{ch\text{-}irr}$	0.000	0.000	0.000

Table 4.10: Physically and Chemically Irreversible Portions of Membrane Fouling Obtained during Dead-End MF Experiments

Irreversible Fouling (%)	**MF Membrane#1 1st Use**	**MF Membrane#1 2nd Use**	**MF Membrane#2 1st Use**
Ph-irr Fouling	2.10	2.51	0.32
Ch-irr Fouling	1.48	1.41	0.27

4.2.1.2 Dead-End Performance of 150 kDa UF Membrane

A 150 kDa PES UF membrane was evaluated as an alternative to 0.45 µm PES MF membrane to be employed as pretreatment prior to NF. Dead-end UF experiments were conducted at 0.5 bar and 100 rpm till VRF of 2.75.

There were quite a few differences between TOC removal performances of two different pieces of UF membrane. The feed TOC level of 139.33±5.20 mg/L was decreased to 93.54±6.35 and 121.67±2.87 mg/L by UF membrane numbered as #1 and #2, respectively, as shown in Figure 4.23 The first piece maintained the same TOC removal efficiency (even with a slight increase in retention) at the second run which was twice of the retention reached by the other piece. Same results obtained with two tests conducted with UF membrane#1 showed that there were no permenant pore blocking caused by filtration.

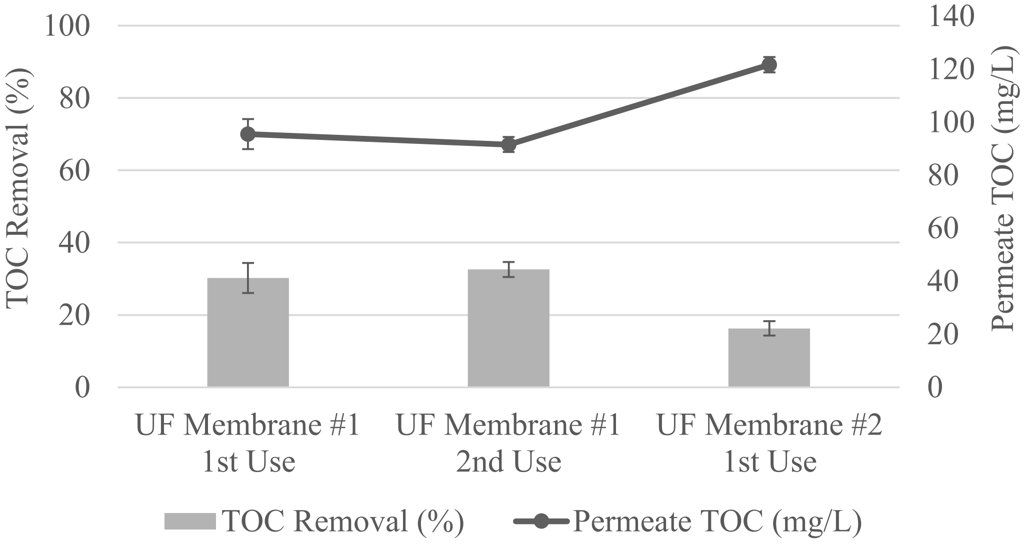

Figure 4.23: Overall TOC Retention Performance of 150 kDa UF Membrane and Permeate TOC Values

Compared to MF, lower permeate turbidity values were obtained by UF membrane which was clearly demonstrated in Figure 4.24. Similar turbidity retention rates were achieved by first and second pieces of UF membranes which were 97±1 and 96±1 percent, respectively. The highest permeate quality in terms of turbidity was 0.91±0.15 NTU. To see whether the high rates of turbidity elimination would be maintained by UF membrane #1, a second experiment was completed with this piece. However, the rate of removal reached by first filtration of first piece was decreased to 88±2% equal to 3.03±0.46 NTU. The reasons behind the efficiency loss in turbidity retention were tried to be explained while commenting on dead-end UF performance especially in terms of the analysis on filtration fluxes.

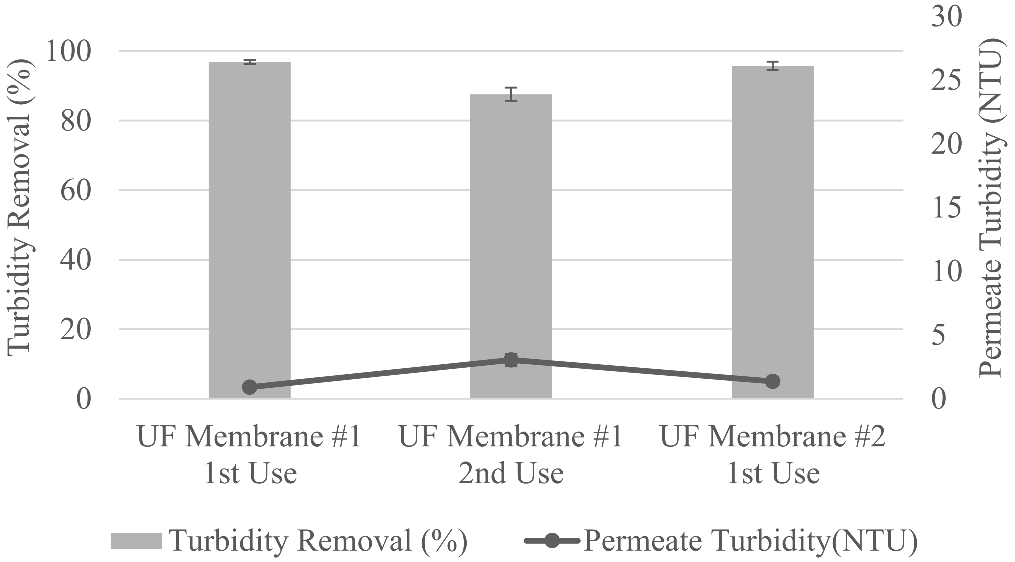

Figure 4.24: Overall Turbidity Retention Performance of 150 kDa UF Membrane and Permeate Turbidity Values

No significant conductivity removal was achieved by dead-end experiments conducted with 150 kDa PES UF membrane. As the result of almost zero conductivity retention, conductivity value remained as 15.38±0.14 mS/cm in permeate line.

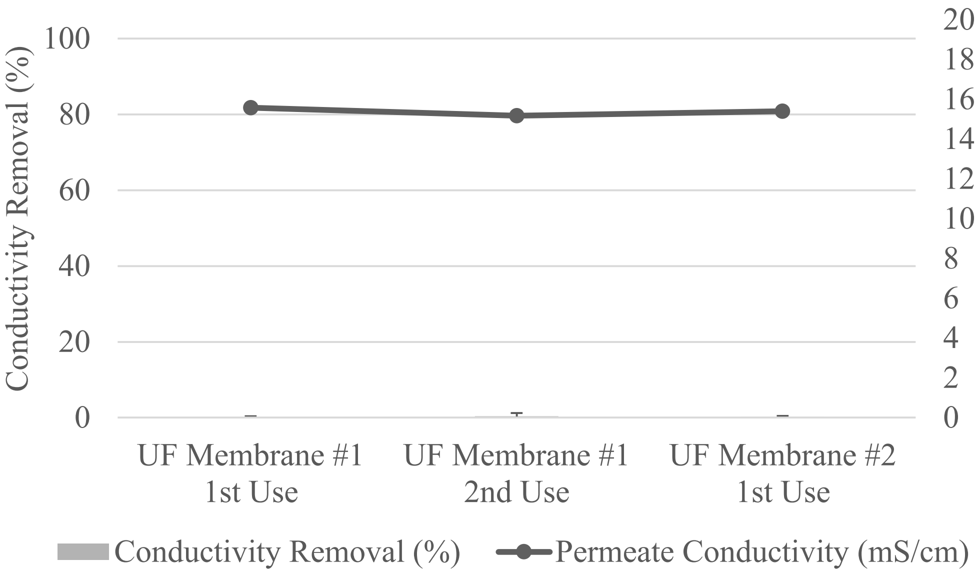

Figure 4.25: Overall Conductivity Retention Performance of 150 kDa UF Membrane and Permeate Conductivity Values

Similar with TOC, better color removal was obtained by dead-end experiments conducted with first piece of UF membrane compared to second piece at their first run. At the second filtration of UF membrane #1, the color removal performance was decreased for all wavelengths. As it was mentioned before, same difference between two filtrations of first piece was experienced for turbidity retentions. The highest color retention rates were reached by first filtration of UF membrane #1 leading to the lowest permeate SAC values of 56.87±2.26, 106.03±3.14, and 6.60±0.86 m^{-1}at wavelengths of 436, 525, and 620 nm, respectively.

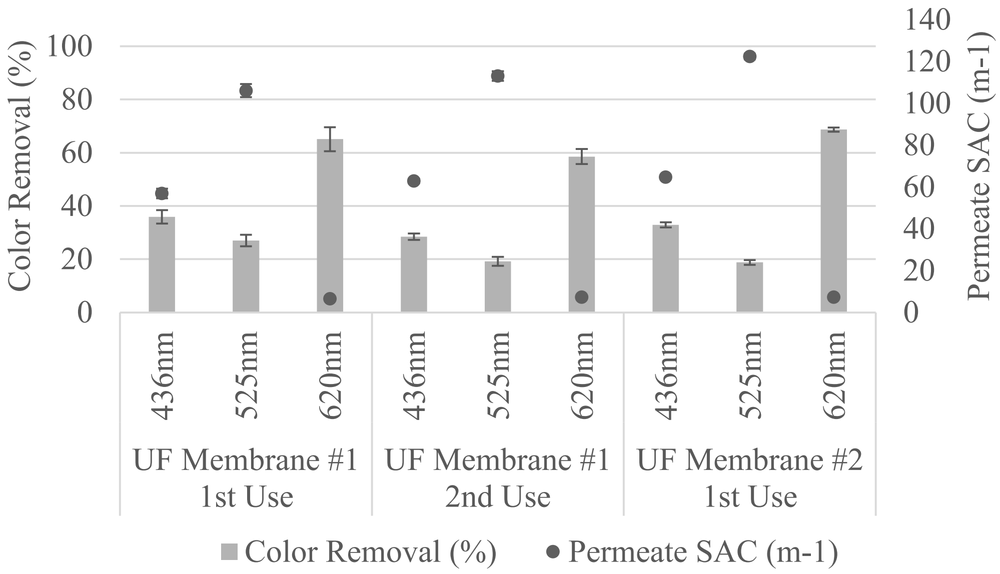

Figure 4.26: Overall Color Retention Performance of 150 kDa UF Membrane and Permeate SAC Values

150 kDa PES UF membrane was also tested in terms of flux decline/recovery and its reaction to cleaning processes. For this purpose, experiments were conducted with two different UF membrane pieces and one of the pieces were tested by second run. Filtration pressure was set to 0.5 bar for UF experiments, different from the filtration pressure of 0.3 bar at which the MF was conducted because a higher pressure was needed to reach raw water flux level which could be taken into consideration in a comparative way with MF permeate flux. Following figure (Figure 4.27) demonstrates UPW fluxes of 150 kDa UF membrane before and after filtration beside raw water flux profile during dead-end filtration till VRF of 2.75.

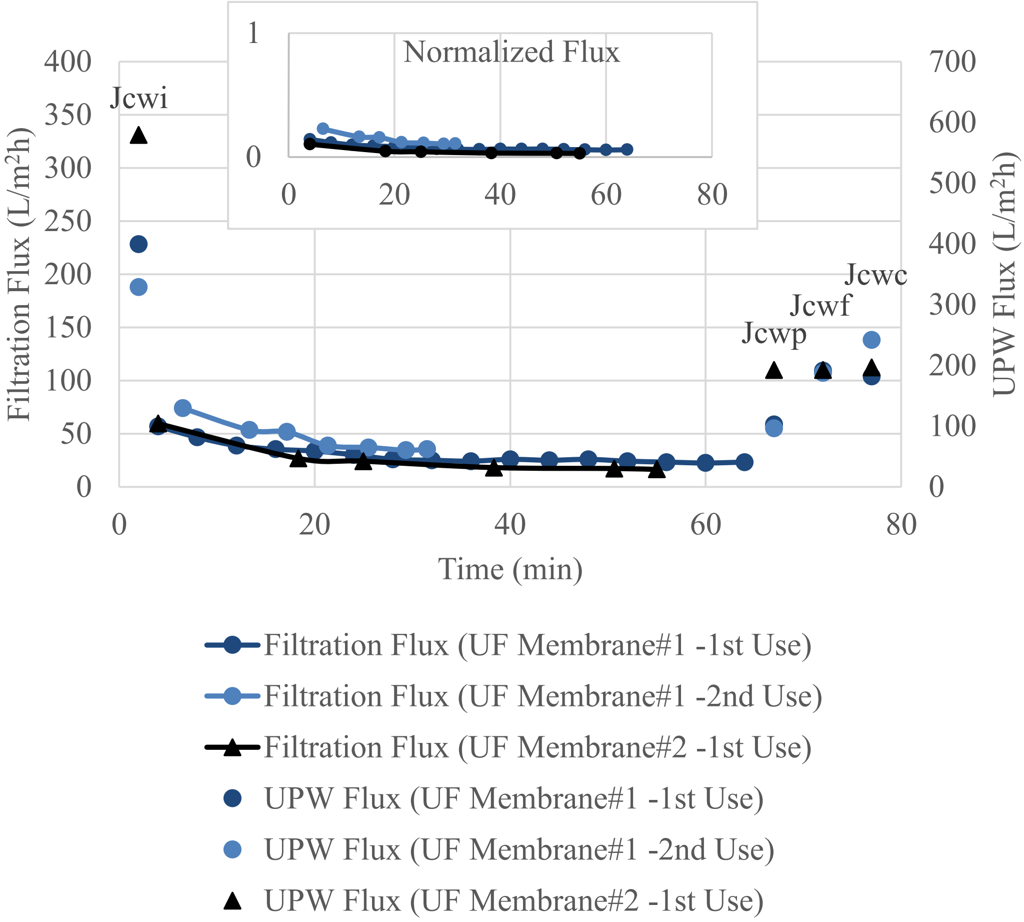

Figure 4.27: Permeate Flux Profile during Dead-End UF till VRF of 2.75 and, UPW Fluxes of 150 kDa UF Membrane before and after Filtration

The J_{cwi} values of different pieces were different from each other where 400 and 579 L/m^{2}h were the J_{cwi} values of virgin UF membrane #1 and #2, respectively (Figure 4.27). In first 20 minutes of all filtrations, decline in raw water flux was relatively sharper. After this point, no significant change in raw water permeate flux was observed. On the contrary to initial UPW fluxes, the J_{rw} of UF membrane #1 was 23 L/m^{2}h which was higher than 16 L/m^{2}h J_{rw} of UF membrane #2. The high filtration flux of UF membrane #1 was higher during the second filtration which might be caused by enlarged pore size that also led decrease in turbidity removal performance.

After filtrations conducted by first piece, UPW flux values were 102 and 96 L/m^{2}h before cleaning steps which increased to 191 and 188 L/m^{2}h after physical cleaning. The UPW flux without any cleaning and after physical cleaning obtained during experiment conducted with UF membrane #2 were equal (192 L/m^{2}h) because the UF membrane could not be cleaned physically (Table 4.12).

The UPW flux of UF membrane # 1 decreased after chemical cleaning as seen from Figure 2.1. However, this decreased UPW value of 182 L/m^{2}h raised to 329 L/m^{2}h after storage in 0.25% sodium bisulfite for two weeks. The reason behind this behavior was not investigated in the context of this study, on the other hand, this issue has been studied in detail as another section of the project enclosing current study.

The fouling related resistance of UF membrane #1 was same at both tests where obtained R_f during the experiment completed with second piece was half of these resistance values (Table 4.11). As it is given in Table 4.12, the physically and chemically irreversible portions of fouling were not consistent similar to resistances due to concentration polarization. The UF membrane did not give any loss in its filtration flux performance, even the flux decline could not be reversed at significant levels by any further cleaning with acid and base after physical cleaning.

Table 4.11: Analysis on Resistances Obtained during Dead-End UF Experiments

Resistance (10^{13} m^{-1})	**UF Membrane #1 1st Use**	**UF Membrane #1 2nd Use**	**UF Membrane #2 1st Use**
R_{mem}	0.045	0.055	0.031
R_{tot}	0.784	0.516	1.100
R_f	0.131	0.132	0.062
R_{cp}	0.608	0.329	1.006
$R_{ph\text{-}irr}$	0.049	0.041	0.062
$R_{ch\text{-}irr}$	0.054	0.020	0.061

Table 4.12: Physically and Chemically Irreversible Portions of Membrane Fouling Obtained during Dead-End UF Experiments

Irreversible Fouling (%)	**UF Membrane #1 1st Use**	**UF Membrane #1 2nd Use**	**UF Membrane #2 1st Use**
Ph-irr Fouling	37.60	31.18	100.00
Ch-irr Fouling	41.36	14.88	97.04

4.2.1.3 Comparison between Dead-End Pretreatment Experiments

The treatment performance and flux decline/recovery analyses of 0.45 µm PES MF and 150 kDa PES UF membranes, given in the previous sections of 4.2.1.1 and 4.2.1.2, were taken into consideration together to select the most appropriate pretreatment which might enhance the performance of subsequent NF application regarding many aspects such as its efficiency of purification, flux profile in addition to final product quality.

As summarized in Table 4.13 by giving the removal rates of different parameters, relatively more successful retention performance was achieved by 150 kDa UF membrane. Especially in terms of TOC and turbidity, the higher removal rates made the UF pretreatment more favorable compared to MF. It was because the single stage NF permeate TOC and turbidity were at an acceptable level but a further enhancement was still needed at designated optimal conditions. Both of tested pretreatment processes did not show a significant conductivity removal. Close to complete decolorization had been achieved by single stage NF application where the lowest color removal rate was obtained at wavelength of 620 nm at 14 bar TMP and 58.9 mL/s CF. The UF membrane presented its best decolorization performance at 620 nm which might improve the final product quality in terms of color at 620 nm as well as other wavelengths.

Table 4.13: Retention Percentages of 0.45 µm MF and 150 kDa UF Membranes

Removal Rate (%)	0.45 µm MF Membrane	150 kDa UF Membrane
TOC	19.80±5.63	26.53±5.05
Turbidity	89.96±5.46	93.40±2.31
Conductivity	-	-
Color (436 nm)	20.11±3.05	32.45±2.98
Color (525 nm)	11.04±3.18	21.69±2.87
Color (620 nm)	52.93±3.26	64.11±5.39

There was a huge difference between the initial UPW fluxes between MF and UF membrane as expected. In same manner, the raw water flux of MF membrane was quite higher than UF membrane at the very beginning of filtration. Despite this difference, the J_{rw} values obtained at final VRF were counted the same (20±3 L/m^2h). So, the flux decline during MF was sharper than UF. The required filtration pressure to obtain these results were 0.3 and 0.5 bar for MF and UF, respectively. The possibility of operation at lower filtration pressure for same filtration flux was an advantage where it also shortened the filtration time.

The reversible and irreversible portions of fouling were also considered in detail. The fouling resistances were lower than concentration polarization related resistances for both membranes. In addition to higher fouling resistances, the irreversible fouling of UF membrane was also higher than the MF.

Under the light of mentioned points especially about treatment performance, UF with 150 kDa PES membrane was decided as pretreatment prior to NF process.

4.2.2 Cross-Flow UF Pretreatment prior to NF

To verify the performance of UF membrane achieved by dead-end filtration and, also, to collect permeate required to conduct NF experiments succeeding UF pretreatment, CF application of UF was performed and replicated three times. Instead of 0.5 bar filtration pressure, 2.75 VRF and WW#3 employed during dead-end UF experiments, CF UF was conducted at TMP of 2.65 bar and VRF of 2.5 with WW#1 with higher pollutant load than WW#3 due to different dyeing recipe. By considering the limits of both the CF filtration system and UF membrane, the TMP was set as 2.65 bar beside the VRF of 2.5 was decided according to inside and feed tank volume of SEPA CF filtration system. CF was fixed to 58.9 mL/s.

150 kDa UF membrane achieved higher TOC removal rates by its CF application when compared to 27±5 percent reached at dead-end experiments. Again, both the retentions and final effluent quality in terms of TOC differed between different pieces of UF membrane. During Test1 and Test3, TOC retention decreased as the VRF ascended whereas the lowest removal rates were obtained at Test2. The permeate quality fell to the lowest level at VRF of 2.5. Overall TOC retention varied between 35 and 50 percent equal to 311.85 and 210.35 mg/L of total permeate TOC.

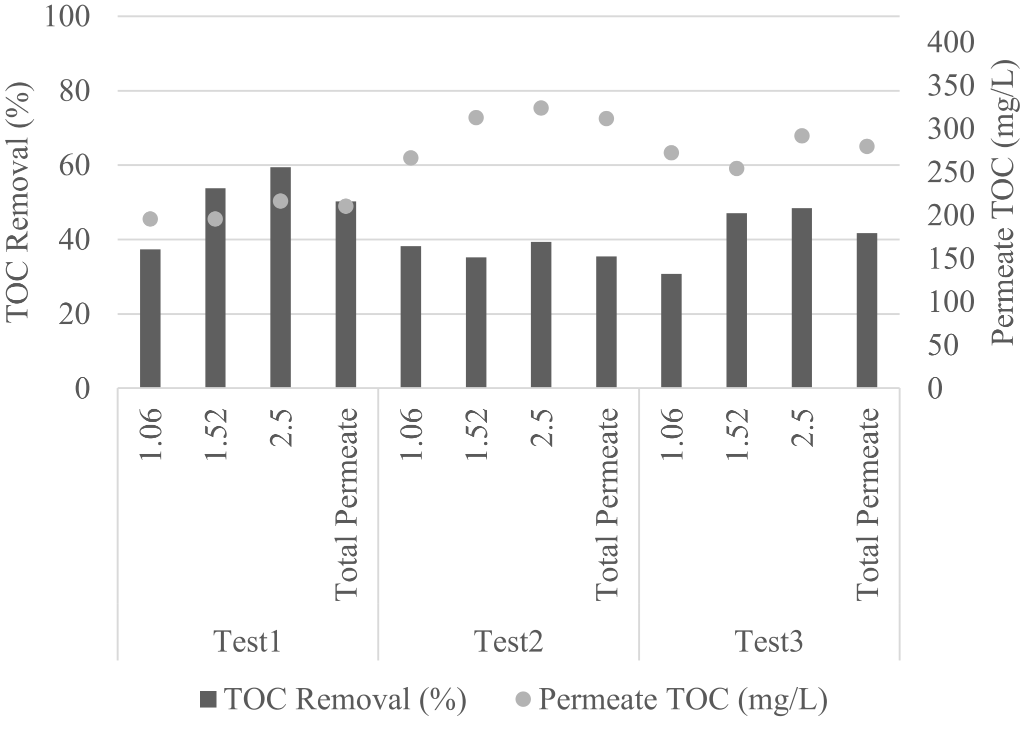

Figure 4.28: TOC Removal Performance and Permeate TOC Values during CF Filtration of 150 kDa UF Membrane

It was not expected to observe conductivity removal at a considerable level, and so, as seen from Figure 4.29, the conductivity removal did not exceed 3%.

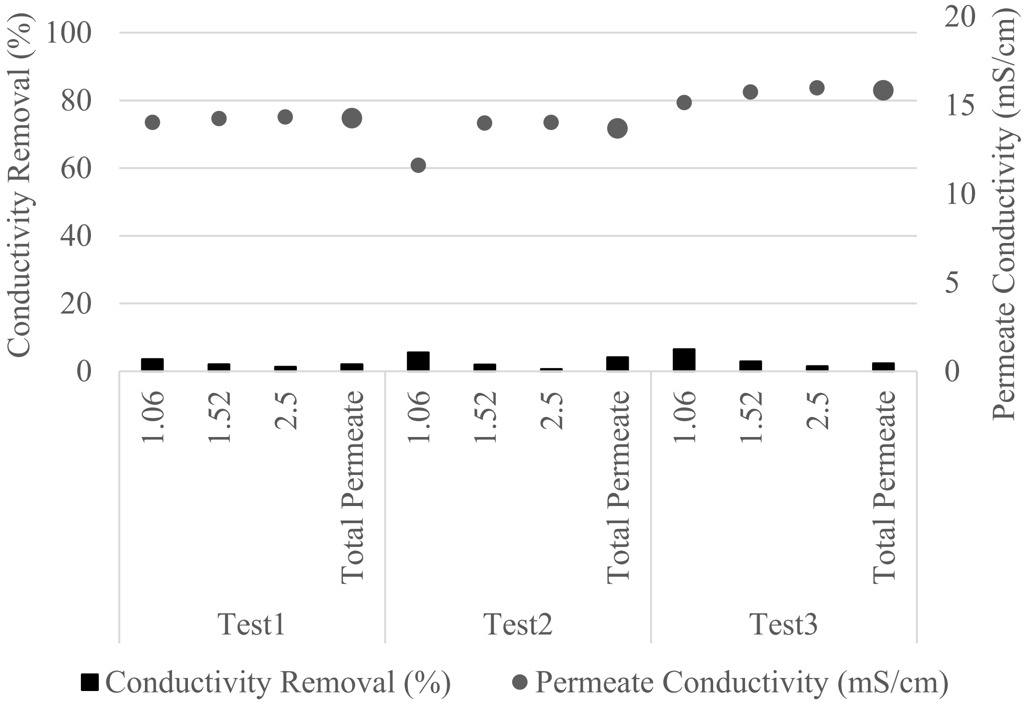

Figure 4.29: Conductivity Removal Performance and Permeate Conductivity Values during CF Filtration of 150 kDa UF Membrane

Decolorization performance of UF membrane was substantially enhanced with CF filtration system. Permeate SAC values were monitored during CF pretreatment experiments at VRFs of 1.06, 1.25, 1.52, 2.06, and 2.5 (Figure 4.31) additional to measurement of total permeate SAC and removal percentages at these VRFs were calculated as shown in Figure 4.30. For all wavelengths, color retention rates rose till VRF of 2.5 and the higher permeate SAC values were observed at this point. The highest retention percentages were obtained at VRF of 2.06. In total, decolorization ratios were obtained as 80±2, 81±3 and 88±2% at wavelengths of 436, 525 and 620 nm, respectively. When the decolorization at different wavelengths was considered, UF pretreatment was found more efficient to remove dyes with shades giving absorbance at the wavelength of 620 nm beside at other wavelengths, considerable portion of color was able to be removed. Yet, the sample photos given in Appendix C clearly testified that even the reached color removal rates were quite satisfying for an UF membrane with MWCO of 150 kDa, further treatment was critical to complete the decolorization.

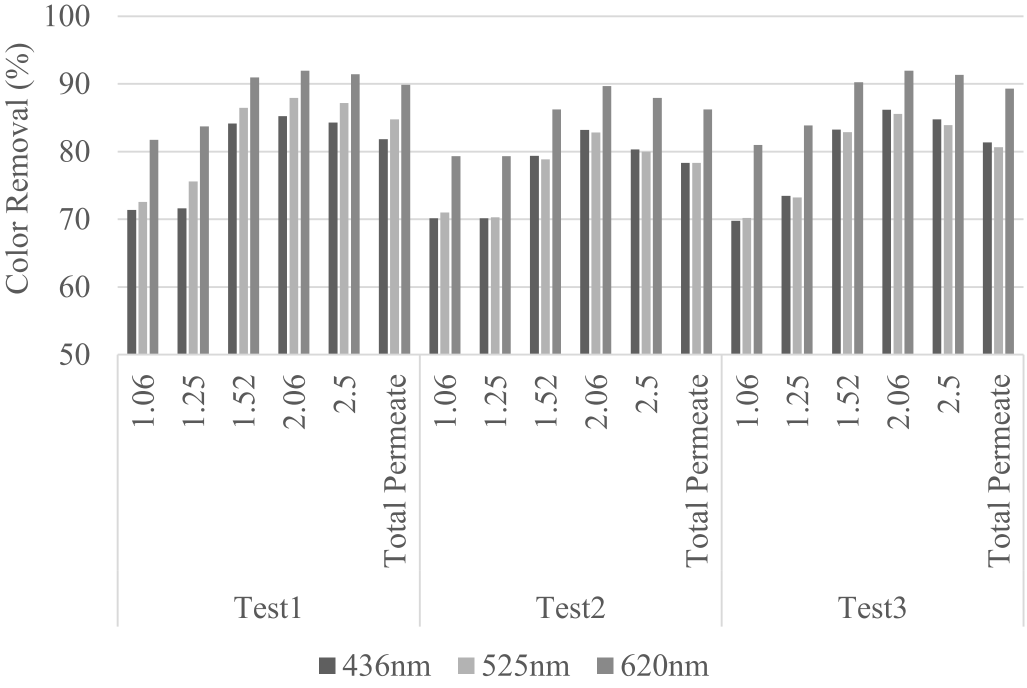

Figure 4.30: Color Removal Performance during CF Filtration of 150 kDa UF Membrane

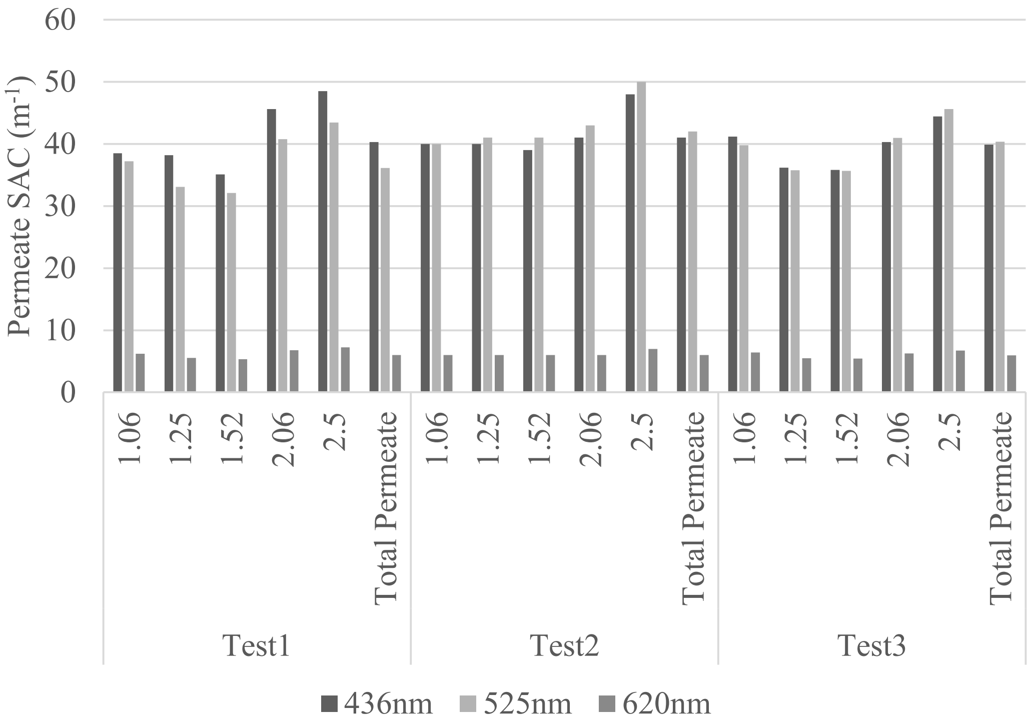

Figure 4.31: Permeate SAC Values during CF Filtration of 150 kDa UF Membrane

These results showed that retention rates in terms of TOC and conductivity achieved by CF application of 150 kDa UF membrane at 2.65 bar TMP were better than dead-end filtration at filtration pressure of 0.5 bar while decolorization performance was maintained at a satisfying level.

The initial UPW fluxes of different pieces were very close but still different from each other. The raw water fluxes were at an order directly correlated with the difference between J_{cwi} values so the normalized flux values were almost same. As depicted in Figure 4.32, permeate fluxes showed a parallel decline trend while the VRF was increasing. The flux decline was very sharp till 1.25 VRF, followed a relatively gradual path after this VRF and stayed almost steady after VRF of 2.05. The observed flux decline was mostly associated with cake layer formation and concentration polarization rather than pore blocking.

Resulting from 54, 44 and 44% decline in raw water flux during filtration, J_{rw} was observed as 88, 121 and 141 L/m^{2}h when 2.5 VRF was reached at Tests 1, 2 and 3, respectively. These values were about five times higher than the Jrw values obtained during dead-end UF at filtration pressure of 0.5 bar and 2.75 VRF. The UPW fluxes after filtration without any cleaning (J_{cwf}) were 497 and 519 L/m^{2}h meaning that the filtration caused 72 percent decrease in initial UPW fluxes (J_{cwi}) of membranes used during Tests 2 and 3.

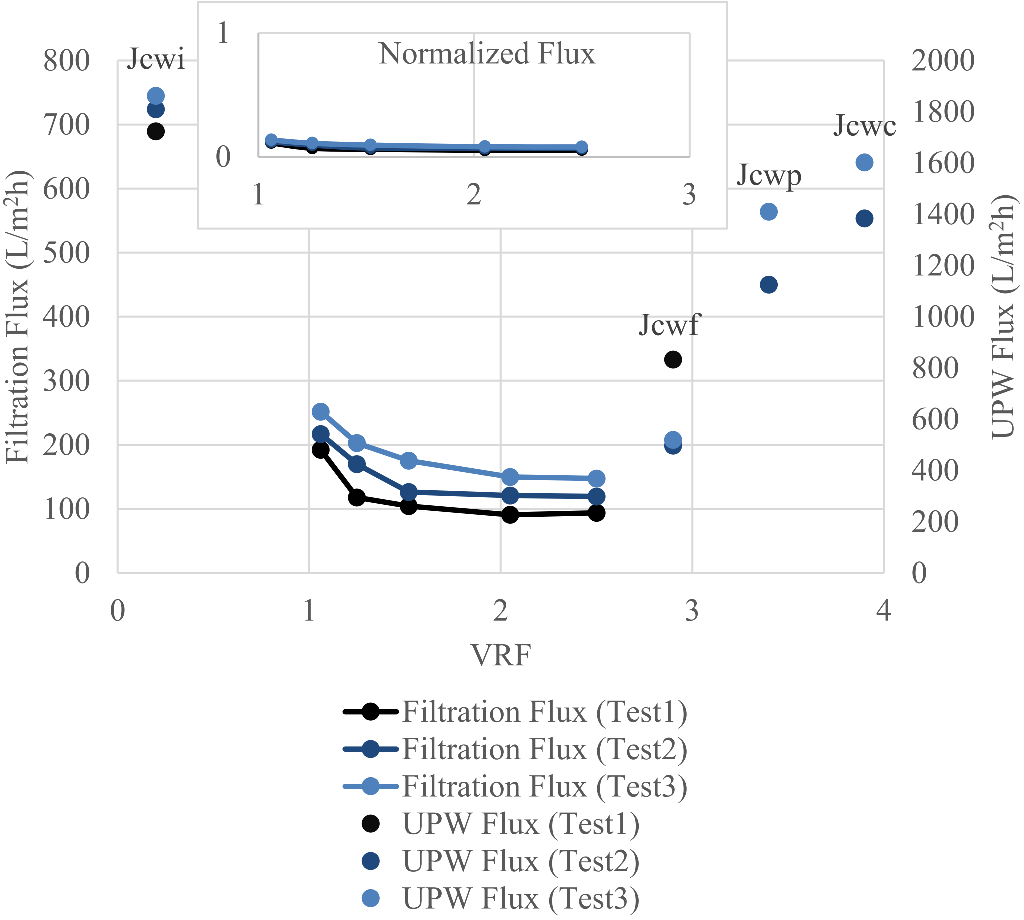

Figure 4.32: Change in Raw Water Flux with VRF during CF Filtration by 150 kDa PES UF Membrane and UPW Fluxes before and after Filtration

Unlikely to dead-end UF experiments, quite effective reactions to cleaning steps were performed by 150 kDa UF membrane during Tests 2 and 3. With physical cleaning, big portion of these declines were able to be reversed which supported that the rapid initial decline was also due to cake layer formation beside the concentration polarization was higher than the fouling as given in Table 4.14 related to resistances. The fouling and concentration polarization related resistances obtained during CF experiments were not so distant from the ones of dead-end filtration tests. As seen from Table 4.15, fouling of membranes used during Test 2 and 3 was 12 and 6 percent chemically irreversible, respectively.

Table 4.14: Analysis on Resistances Obtained during CF UF Experiments

Resistance (10^{13} m^{-1})	**UF before NF Test 1**	**UF before NF Test 2**	**UF before NF Test 3**
R_{mem}	0.056	0.053	0.052
R_{tot}	1.089	0.797	0.682
R_f	0.060	0.140	0.134
R_{cp}	0.973	0.603	0.497
$R_{ph\text{-}irr}$	-	0.032	0.017
$R_{ch\text{-}irr}$	-	0.016	0.008

Table 4.15: Physically and Chemically Irreversible Portions of Membrane Fouling Obtained during CF UF Experiments

Irreversible Fouling (%)	**UF before NF Test 1**	**UF before NF Test 2**	**UF before NF Test 3**
Ph-irr Fouling	-	23.00	12.42
Ch-irr Fouling	-	11.64	6.28

4.2.2.1 *Change in Performance of UF Pretreatment in case of Inclusion of Dyeing Bath to Feed Solution*

As stated before, the dyebath effluent was excluded due to its high pollutant load especially the high salt content. As the consequence of the inclusion of dyeing bath, feed concentrations of different parameters had increased at different rates (Table 4.16).

Table 4.16: Change in Influent of UF Pretreatment in case of Inclusion of Dyeing Bath to Feed Solution

	TOC (mg/L)	**Conductivity (mS/cm)**	**SAC (m^{-1})**		
			436 nm	**525 nm**	**620 nm**
Feed to UF (Baths2,3&4) (WW#1)	412.20± 60.84	15.33± 0.01	134.25 ±0.15	136.80 ±0.15	31.45 ±0.05
Feed to UF (Baths1,2,3&4)	478.86	32.97± 0.03	220.68 ±0.96	201.55 ±1.30	40.15 ±0.12

The effects of possible inclusion of dyeing bath to feed solution leading pollutant load change on performance of UF pretreatment were investigated under this section.

The level of feed TOC was variable during experiments. The inclusion of dyeing bath solution did not result in a dramatic load change and the feed TOC concentration was considered as in the range during the case of exclusion of dyeing bath. So, UF membrane performed TOC retention proportional with influent load change and permeate TOC level decreased to 357.06 mg/L where the permeate TOC reached to 596.50 mL/s at 2.5 VRF.

Unlike the feed TOC, pollutant load in terms of other parameters scaled up at a considerable rate. Feed conductivity concentration multiplied and reached 32.97±0.03 mS/cm, respectively (Table 4.16).

UF of wastewater mixture containing dyeing bath effluent generated permeate with conductivity content of 30.33±0.35 mS/cm. Conductivity retention rate varied between 7 to 10 percent.

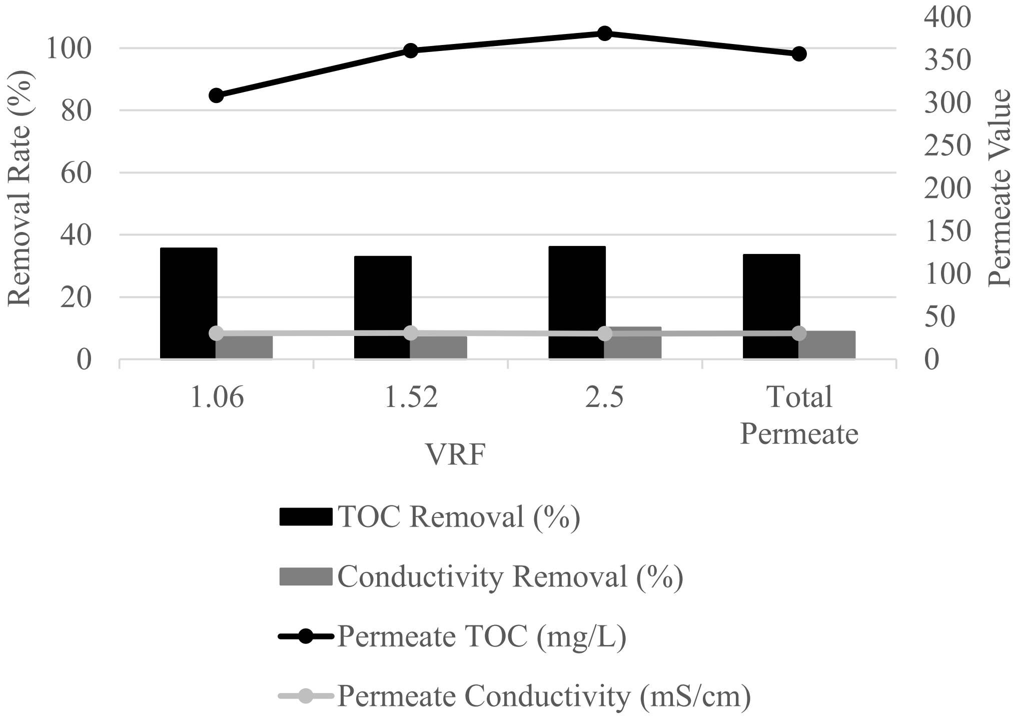

Figure 4.33: TOC and Conductivity Removal Performance of 150 kDa UF Membrane in case of Inclusion of Dyeing Bath to Feed Solution

By the addition of dyebath solution to feed mixture, feed SAC values became 220.68±0.96, 201.55±1.30, and 40.15±0.12 m^{-1} at wavelengths of 436, 525, and 620 nm, respectively. The color removal performance of UF membrane and resultant SAC values at different VRFs as it was observed during earlier UFs of WW#1, the highest and the lowest decolorization rates at all wavelengths were performed at VRFs of 1.52 and 2.5 in turn. Both the color removal rates and the permeate SAC values were deteriorated. Overall decolorization percentages reduced to 64, 63, and 77 causing 97, 91, and 53 percent higher permeate SAC values at 436, 525, and 620 nm, respectively.

The lowest permeate values were seen in the removal of colors giving absorbance at 620 nm wavelength.

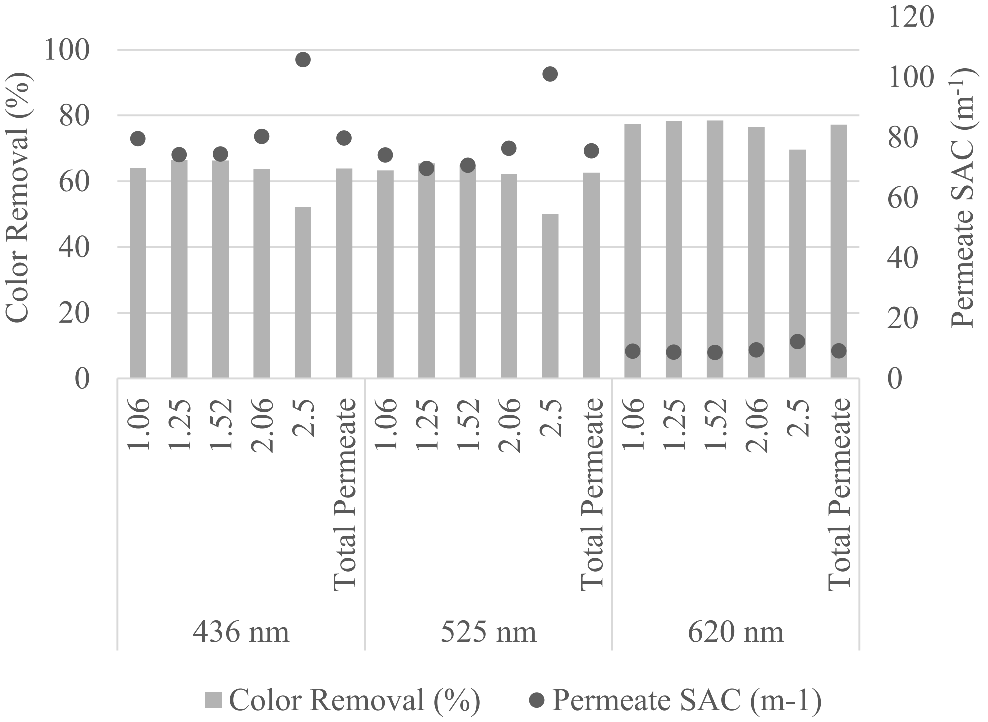

Figure 4.34: Color Removal Performance of 150 kDa UF Membrane in case of Inclusion of Dyeing Bath to Feed Solution

Even though the treatment efficiency in terms of retention rates and effluent quality had been influenced, inclusion of dye bath to feed solution mixture, namely WW#1, caused no change in neither the filtration flux nor the decline in raw water flux during filtration. Resulting from the same flux decline rate of 45%, the J_{rw} value decreased to 113 L/m^2h at VRF of 2.5 from 205 L/m^2h (Figure 4.36).

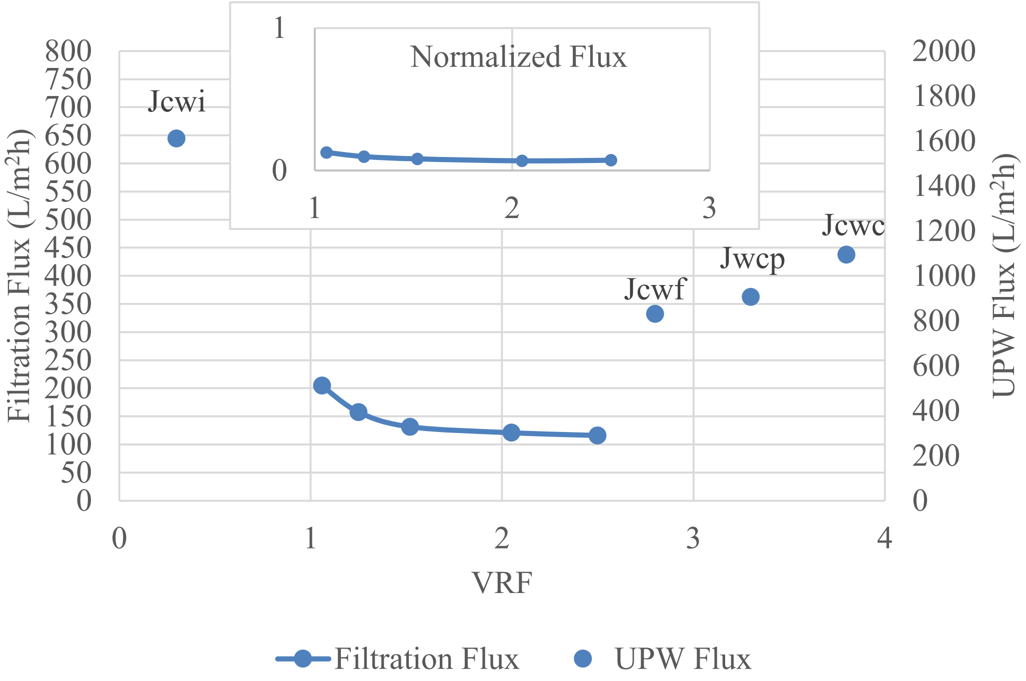

Figure 4.35: Change in Raw Water Flux with VRF during CF Filtration by 150 kDa PES UF Membrane and UPW Fluxes before and after Filtration in case of Inclusion of Dyeing Bath to Feed Solution

After filtration, the obtained J_{cwf} value was 831 L/m^{2}h which was very close to the value obtained during 1st test conducted with WW#1. Moreover, the resistances due to fouling and concentration polarization were found between the range of resistances during UF experiments in the absence of dyeing bath effluent (Table 4.17). The dye bath inclusion did only influence the reaction of UF membrane to cleaning applications. The physically and chemically irreversible fouling related resistances were increased at an important rate. Besides, only 83 and 50% of UPW flux decline could be reversed by physical and chemical cleaning, respectively (Table 4.18). This increase in irreversible fouling was linked to increase in dye adsorption in and/or on the membrane due to higher color content of feed, and permanent pore clogging.

Table 4.17: Analysis on Resistances Obtained during CF UF Experiments in case of Inclusion of Dyeing Bath to Feed Solution

Resistance (10^{13} m^{-1})	**UF before NF**
R_{mem}	0.060
R_{tot}	0.847
R_f	0.056
R_{cp}	0.732
$R_{ph\text{-}irr}$	0.046
$R_{ch\text{-}irr}$	0.028

Table 4.18: Physically and Chemically Irreversible Portions of Membrane Fouling Obtained during CF UF Experiments in case of Inclusion of Dyeing Bath to Feed Solution

Irreversible Fouling (%)	**UF before NF**
Ph-irr Fouling	82.78
Ch-irr Fouling	50.18

4.3 NF Performance after UF pretreatment

After the determination of applicable pretreatment alternative, the performance of NF after pretreatment was compared with direct application of NF to trace any improvement in membrane separation process. The main comparative studies were conducted at TMP of 14 bar and CF of 58.9 mL/s designated as optimal operating conditions (Section 4.3.1).

The changes in performance of NF caused by pretreatment was also inspected under lower pressure than optimal TMP and in case of possible inclusion of dyeing bath to feed.

4.3.1 Performance of NF after Pretreatment Under Optimal Conditions

The secondary effluent collected by UF pretreatment was subjected to NF at operating conditions designated as optimal conditions earlier. The obtained results were compared with single stage NF practice.

To understand the influence of UF pretreatment on both NF treatment performance and the final effluent quality, retention rates obtained by NF after UF alone and by sequential UF/NF were given separately. TOC and conductivity removal performances were given together in Figure 4.36.

Additional treatment provided by UF pretreatment didn’t contribute any improvement in final permeate quality with respect to its TOC content. In other words, even though the UF pretreatment could decrease the TOC level to 295.61±22.97 mg/L from 412.20±26.66 mg/L, NF permeate TOC stayed at a range 6.31±2.51 mg/L enclosing single stage NF permeate value of 6.07±0.62 mg/L. TOC retention rate of NF after UF was 98±1 percent which was almost same with 99% TOC removal sustained by direct application NF. These results indicated that NF90 membrane produces filtrate with a consistent TOC level, independently of the feed TOC load.

UF pretreatment didn’t perform any remarkable reduction in conductivity as it was expected. So, no enhancement in both conductivity removal performance and permeate quality was projected which might be achieved by affiliation of pretreatment. Conductivity of treated water was 0.83±0.13 mS/cm as the result of overall removal percentage of 95±1 which was 95% during direct application of NF.

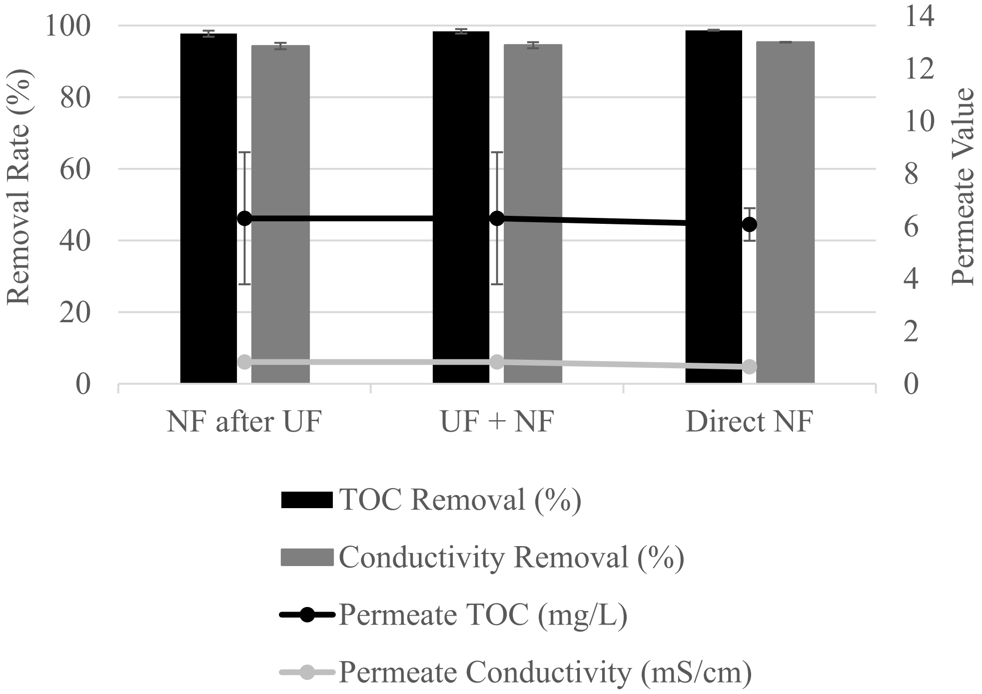

Figure 4.36: Comparison between i) NF Performance after UF pretreatment, ii) Overall Performance of UF and NF, and iii) Performance of Single Stage NF in terms of TOC and Conductivity at Optimal Conditions

The previous SAC values obtained during single stage NF were found very close to zero referring almost complete decolorization at wavelengths of 436 and 525 nm and 98±1% at 620 nm. As seen from Figure 4.37 showing decolorization performances of NF after pretreatment, sequential UF/NF treatment system and direct NF application, moderately lower color removal rates were achieved by NF90 membrane during filtration of pre-treated wastewater. On the contrary, permeate SAC values were far less (0.32±0.27, 0.26±0.27, and 0.14±0.12 at 436, 525, and 620 nm) because the overall color retention of sequential UF/NF was higher and closer to complete decolorization when compared with direct NF.

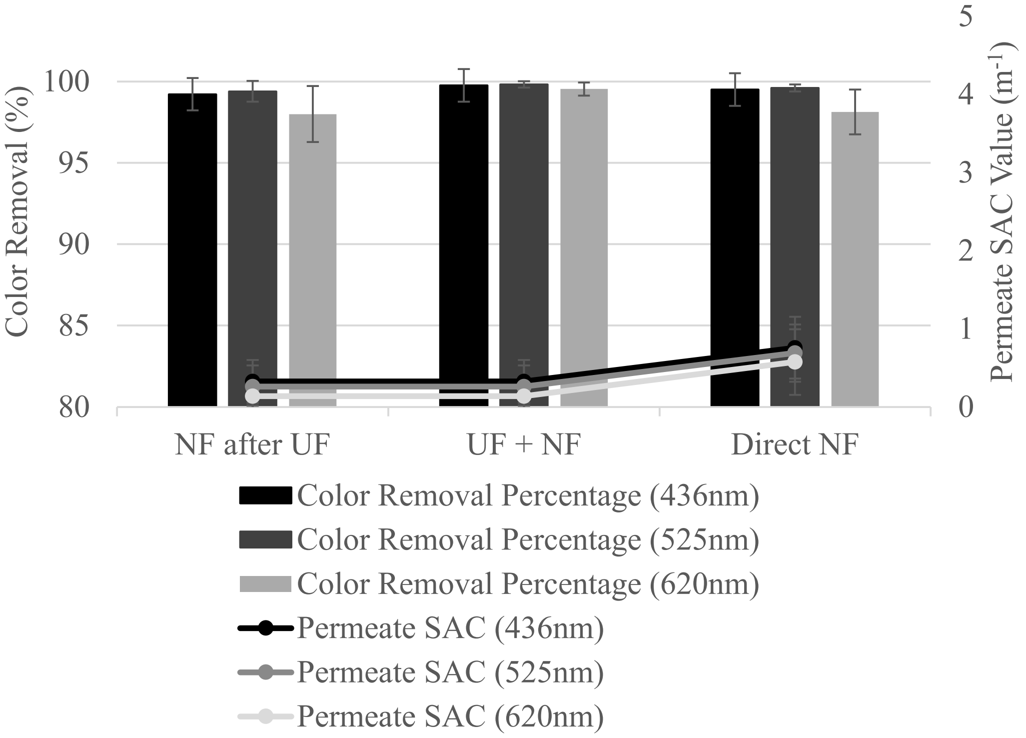

Figure 4.37: Comparison between i) NF Performance after UF pretreatment, ii) Overall Performance of UF and NF, and iii) Performance of Single Stage NF in terms of Color Removal at Optimal Conditions

Membrane fouling is the primary drawback of membrane separation systems. Especially for the treatment of textile dyeing effluents, this drawback becomes a self-limiting factor for direct NF application (Van der Bruggen et al., 2001). In many studies, it was stated that a successful pretreatment leads to longer membrane life, higher filtration flux and minimized flux decline So, to see whether any enhancement in fouling tendency of NF90 membrane could be obtained with the UF pretreatment, findings of NF after UF pretreatment were interpreted by making comparison with direct NF application at same operating conditions selected as optimal.

NF after UF pretreatment experiment was repeated with two pieces of NF90 membrane. As seen from Figure 4.38, initial UPW fluxes were normally varied for different pieces but the difference was not at a level constituting any impediment for their comparison.

The raw water fluxes at the very beginning of filtrations were in an order parallel to initial UPW fluxes. Flux variations during filtration period clearly showed that UF pretreatment provided a significant control on the permeate flux decline. Flux decline rate of 32% (obtained as the difference between the raw water flux at the very beginning of filtration and the steady state filtration flux), observed during direct NF application, was lowered with pretreatment and became 5 and 7% during 1st and 2nd test of NF after pretreatment, respectively. The enhancement in flux decline during filtration was mostly due to turbidity removal possibly achieved by UF so, the initial flux decline due to the cake layer formation during NF could be avoided. The J_{rw} values were obtained as 36.77 and 33.39 L/m^{2}h which were nearly 40 percent higher than 21.12 L/m^{2}h J_{rw} of the direct NF.

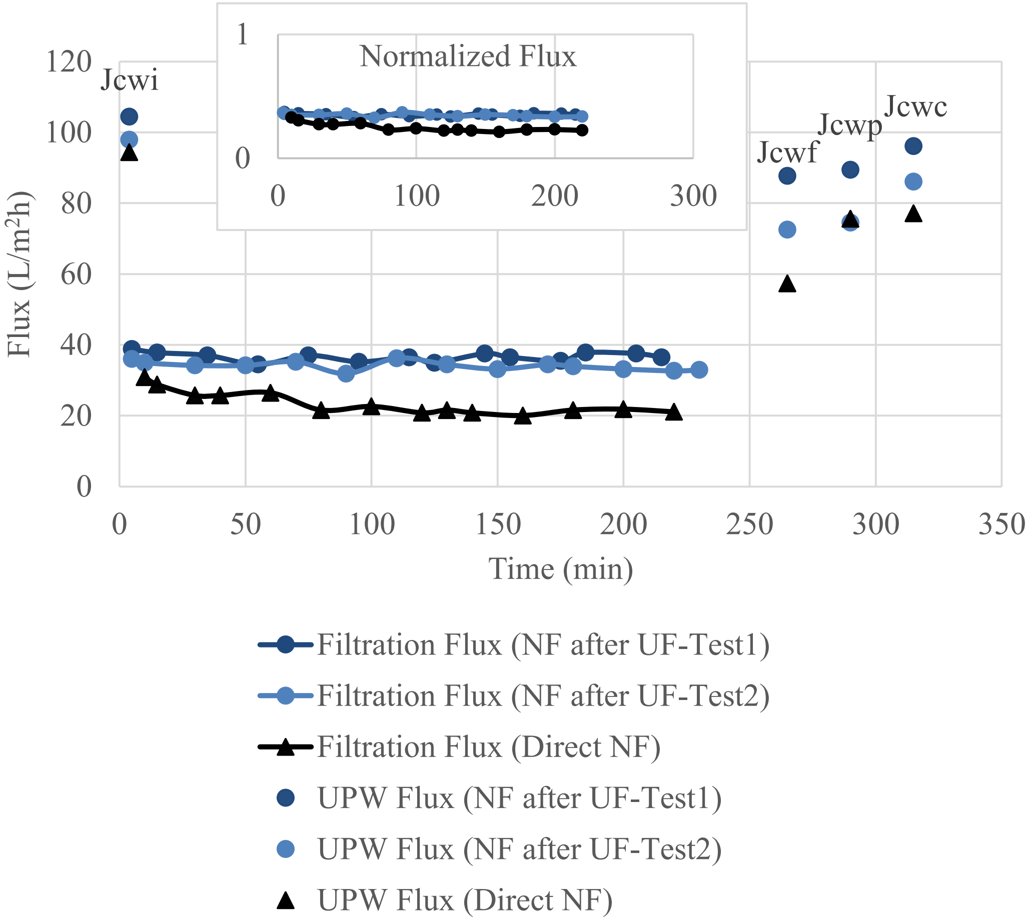

Figure 4.38: UPW and Raw Water Flux Profiles of NF after UF Pretreatment and Direct NF Conducted at Optimal Operating Conditions

Mentioned average filtration flux values were also given in Table 4.19 to be able to comment on the significance of osmotic pressure. It was seen from the comparison between obtained J_{rw} during filtrations and the calculated osmotic pressure corrected flux which would be reached in the absence of osmotic pressure that the decrease in flux due to osmotic pressure stayed at same degree independently from whether any pretreatment was employed or not.

Table 4.19: Osmotic Pressure Corrected Fluxes of NF after UF and Direct NF Conducted at Optimal Operating Conditions

	NF after UF Test 1	**NF after UF Test 2**	**Direct NF**
J_{rw} (L/m^{2}h)	36.77	33.39	21.12
Corrected Flux (L/m^{2}h)	47.24	44.53	27.45

In addition to minimized decline in raw water flux, the UPW fluxes after filtration without any cleaning showed that decline in UPW flux was also reduced. The J_{cwf} values were 87.68 and 72.51 L/m^{2}h which were 16 and 26 percent lower than initial UPW fluxes for Tests 1 and 2, respectively. The difference between the J_{cwi} and J_{cwf} had been 39 percent.

The UPW fluxes got closer after physical cleaning because the flux recovery achieved with physical cleaning was higher during direct application studies as the concentration polarization and the fouling related resistances were both greater (Table 4.20). In detail, the pretreatment decreased the obtained the R_f and $R_{cp+\pi}$ values to half of previous values. The physically irreversible fouling resistances were quite close as the permanent decline in UPW fluxes due chemically irreversible fouling differed between NF with and without pretreatment. Chemical cleaning applied to NF90 membranes (used during 1st and 2nd NF after pretreatment tests) could take the UPW flux values up to 96.17 and 86.14 L/m^{2}h which were only 8 and 12% lower than J_{cwi}, values, respectively.

Table 4.20: Analysis on Resistances of NF after UF and Direct NF Conducted at Optimal Operating Conditions

Resistance (10^{13} m^{-1})	**NF after UF Test 1**	**NF after UF Test 2**	**Direct NF**
R_{mem}	4.83	5.14	5.34
R_{tot}	13.71	15.10	23.86
R_f	0.92	1.81	3.45
$R_{cp+\pi}$	7.96	8.15	15.07
$R_{ph\text{-}irr}$	0.80	1.61	1.33
$R_{ch\text{-}irr}$	0.41	0.71	1.19

Table 4.21: Physically and Chemically Irreversible Portions of Membrane Fouling Obtained during NF after UF and Direct NF Conducted at Optimal Conditions

Irreversible Fouling (%)	**NF after UF Test 1**	**NF after UF Test 2**	**Direct NF**
Ph-irr Fouling	87.44	89.38	38.45
Ch-irr Fouling	44.89	39.11	34.59

Together with enhancement in color removal, findings on the improvements in filtration flux, flux decline during filtration and fouling tendency of NF90 membrane showed that employing UF pretreatment prior to NF accomplished the objectives about the NF performance.

4.3.2 Performance of NF after Pretreatment Under Lower TMP

The enhancements provided by UF pretreatment directed the study to the inspection of the possibility of conducting NF at lower TMPs while maintaining an efficient membrane separation process. So, NF after UF experiment was repeated at TMP of 10 bar and CF of 58.9 mL/s to see whether the pretreatment would compensate the lowered TMP especially with respect to flux decline and membrane fouling.

In terms of TOC and conductivity, the performance of NF was higher at TMP of 14 bar which could not be enhanced by UF pretreatment. Similarly, sequential UF/NF did not contribute any increase in retention rates and permeate quality when NF was conducted at 10 bar of TMP as represented in Figure 4.39. Thus, TOC and conductivity could not be decreased below 10.55±0.57 mg/L and 1.86±0.38 mS/cm, respectively.

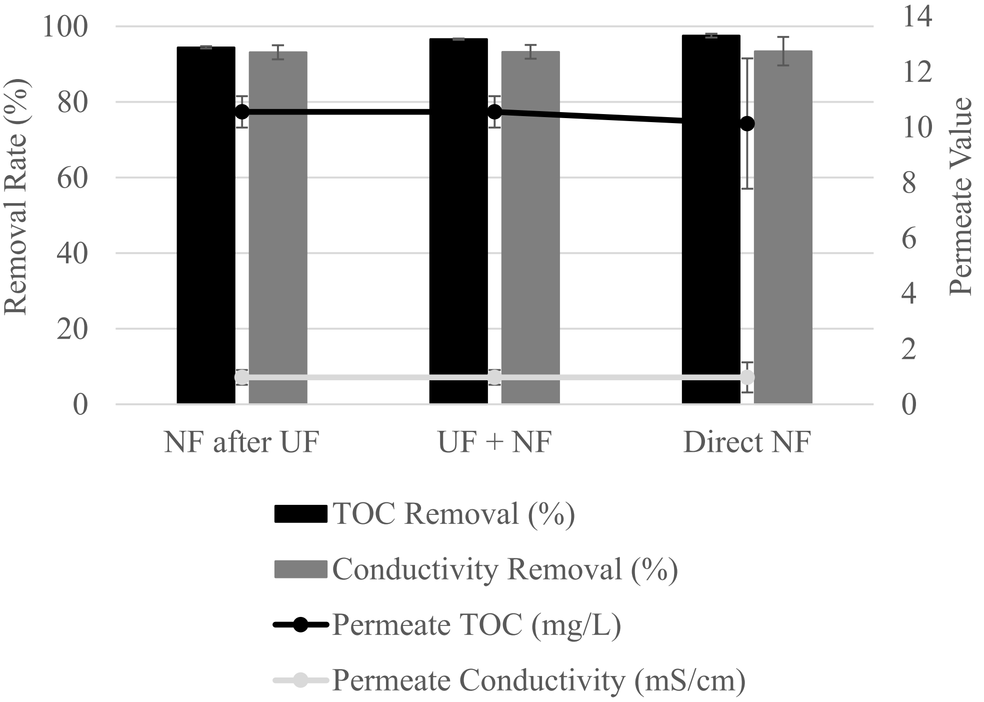

Figure 4.39: Comparison between i) NF Performance after UF pretreatment, ii) Overall Performance of UF and NF, and iii) Performance of Single Stage NF in terms of TOC and Conductivity at TMP of 10 bar

The improvements in decolorization performance achieved during experiments conducted at TMP of 14 bar could not be sustained at 10 bar for all wavelengths. Moreover, the performance of NF declined in absence of UF pretreatment. Especially for the wavelength of 620 nm, the permeate SAC value was doubled. At the other wavelengths, color contents of permeate were 1.64 times higher than the ones obtained by direct NF at TMP of 10 bar.

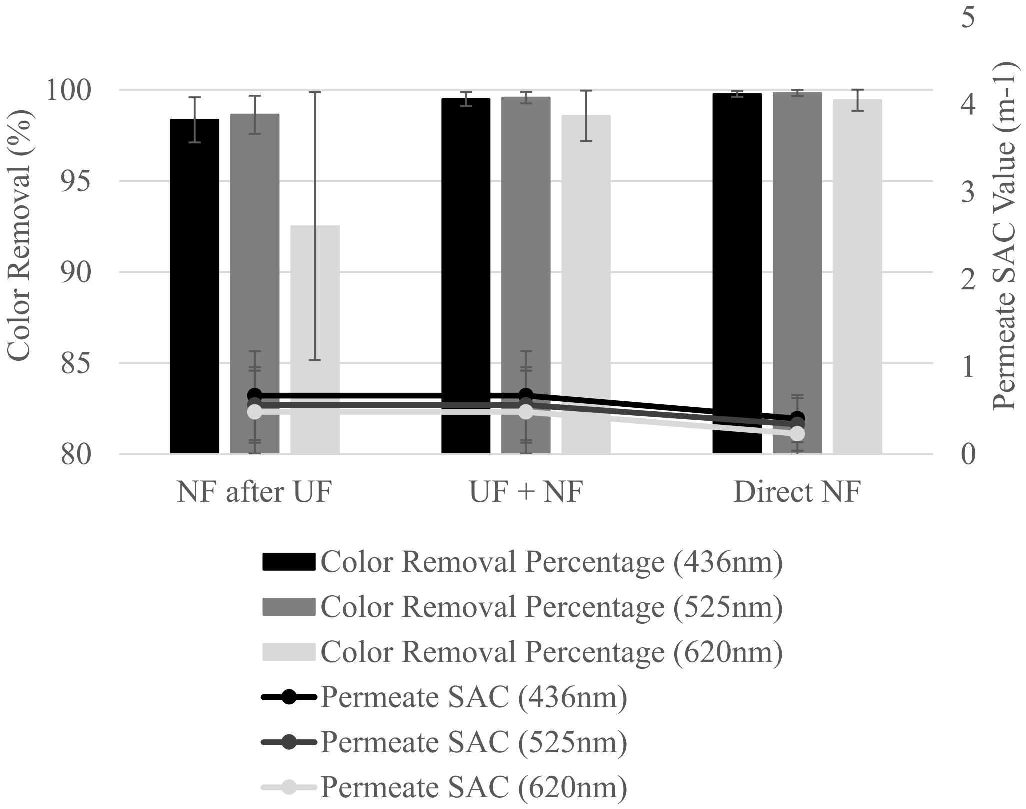

Figure 4.40: Comparison between i) NF Performance after UF pretreatment, ii) Overall Performance of UF and NF, and iii) Performance of Single Stage NF in terms of Color Removal at TMP of 10 bar

These results supported the decision of setting the TMP to 14 bar as the optimal TMP with respect to treatment efficiency. The greatest handicap of conducting NF at lower TMPs than 14 bar was the insufficient raw water flux. Experiments conducted at 14 bar TMP and 58.9 mL/s indicated that up to 40% increase in filtration flux was able to be provided by employing UF pretreatment prior to NF process. As mentioned in the beginning of this section, the main objective of conducting NF after pretreatment at TMP of 10 bar was to see whether that increase could be succeeded at lower TMPs than optimal TMP. Two tests on direct NF at 10 bar TMP and 58.9 mL/s CF were compared with the NF of secondary effluent at same operating conditions. However, the filtration flux profiles of NF with or without pretreatment lied over each other and no increase in the J_{rw} value could be achieved.

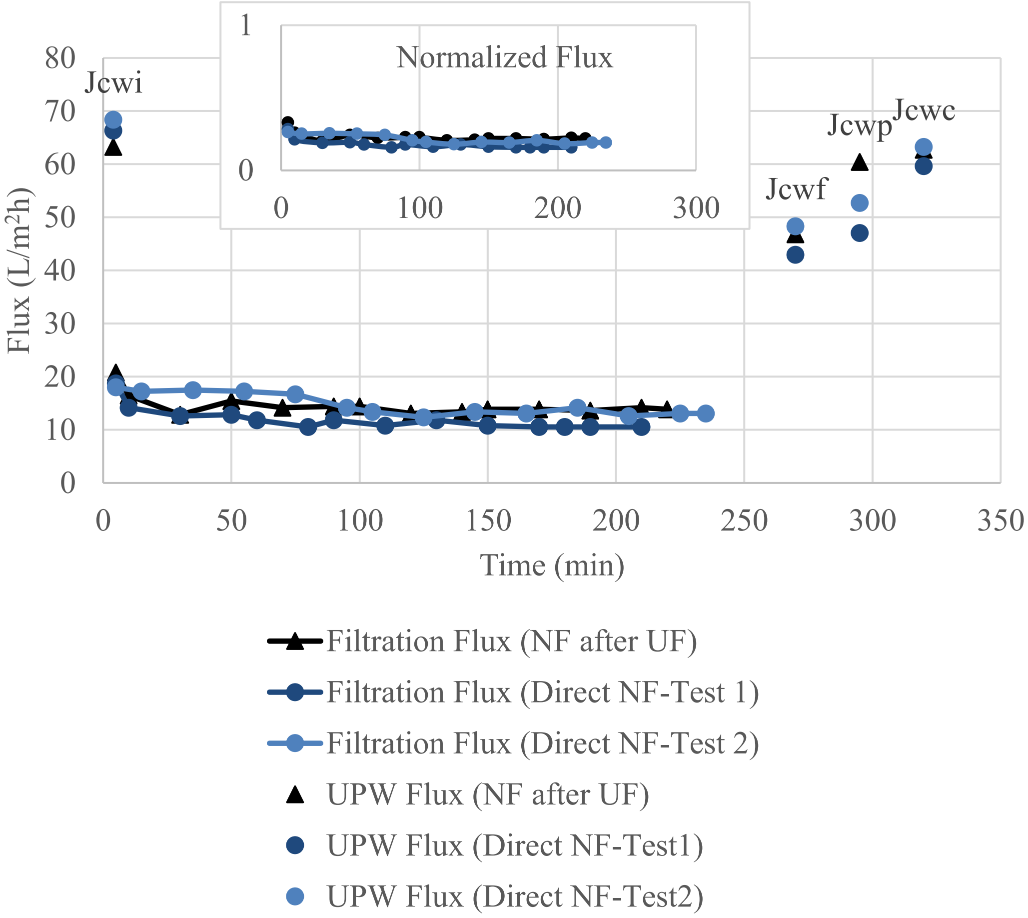

Figure 4.41: UPW and Raw Water Flux Profiles of Direct NF and NF after UF Pretreatment Applications at TMP of 10 bar

The UF pretreatment did not remove any conductivity. So, in terms of osmotic pressure corrected flux, there was no difference between NF with or without UF pretreatment at TMP of 10 bar like 14 bar. Table 4.22 includes measured filtration flux and calculations on osmotic pressure corrected flux showing that the osmotic pressure remained its influence on permeate flux without any change.

Table 4.22: Osmotic Pressure Corrected Fluxes of NF after UF and Direct NF Conducted at TMP of 10 bar

	NF after UF	**Direct NF Test 1**	**Direct NF Test 2**
J_{rw} (L/m^{2}h)	13.70	10.59	13.22
Corrected Flux (L/m^{2}h)	20.28	15.64	20.26

In same manner, the UF pretreatment did not provide any enhancement in concentration polarization and fouling related resistances at this filtration pressure (Table 4.23). The UPW flux after filtration without any cleaning was 46.80 L/m^{2}h which was quite same with the ones obtained during direct NF application (Figure 4.41). Inversely, the reaction of NF90 membrane to cleaning processes differed. After physical cleaning, UPW flux raised to 29% of J_{cwf} and became 60.43 L/m^{2}h. as the resistance due to physically irreversible fouling was only 0.27 10^{13} m^{-1} as given in Table 4.23. Moreover, the J_{cwc} was found as 62.74 L/m^{2}h equal to 0.81 percent of initial UPW flux. Eventually, the lowest resistance value due to chemically irreversible fouling attained during all NF experiments was obtained as 0.05 10^{13} m^{-1}. These findings showed that pretreatment only provided decrease in irreversible portion of fouling of NF membrane (Table 4.24) where the fouling related resistances were same.

Table 4.23: Analysis on Resistances of NF after UF and Direct NF Conducted at TMP of 10 bar

Resistance (10^{13} m^{-1})	**NF after UF**	**Direct NF Test 1**	**Direct NF Test 2**
R_{mem}	5.69	5.43	5.26
R_{tot}	26.27	33.98	27.24
R_f	2.00	2.96	2.18
$R_{cp+\pi}$	18.58	25.60	19.79
$R_{ph\text{-}irr}$	0.27	2.22	1.57
$R_{ch\text{-}irr}$	0.05	0.61	0.43

Table 4.24: Physically and Chemically Irreversible Portions of Membrane Fouling Obtained during NF after UF and Direct NF Conducted at TMP of 10 bar

Irreversible Fouling (%)	**NF after UF**	**Direct NF Test 1**	**Direct NF Test 2**
Ph-irr Fouling	13.31	75.21	71.72
Ch-irr Fouling	2.33	20.56	19.60

4.3.3 Change in Performance of NF after UF Pretreatment in case of Inclusion of Dyeing Bath to Feed Solution

The changes in performance of UF pretreatment which might be caused by possible inclusion of dyeing bath to feed solution had been investigated under the Section 4.2.2.1. As stated in that section, inclusion of dyeing bath to WW#1 caused an increase in the pollutant load of UF permeate and so, the feed solution of NF process (Table 4.25).

Table 4.25: Change in Influent of NF conducted at TMP of 14 bar following UF Pretreatment in case of Inclusion of Dyeing Bath to Feed Solution of UF

	TOC (mg/L)	**Conductivity (mS/cm)**	**SAC (m^{-1})**		
			436 nm	**525 nm**	**620 nm**
Feed to NF (Baths2,3&4)	289.39 ±25.02	14.61 ±0.01	40.86 ±0.05	41.66 ±0.02	6.49 ±0.00
Feed to NF (Baths1,2,3&4)	336.10	29.23 ±0.15	79.14 ±0.02	75.12 ±0.01	9.26 ±0.01

The experiment was conducted at 14 bar where the lower TMPs were not found efficient despite of the UF pretreatment in previous section. Resulting from the differences between feed solutions, the performance of NF at 14 bar after UF pretreatment altered in many aspects including both treatment efficiency and membrane fouling behaviors.

In terms of TOC and conductivity treatment efficiency, performance of NF90 membrane declined as seen in Figure 4.42. TOC removal percentage decreased to 94±1 and 96±1 for NF after UF alone and sequential UF/NF, respectively. The rates resulted in final effluent TOC of 19.29±4.35 mg/L which was 6.31±2.51 mg/L during the case of exclusion of dyeing bath. Similarly, NF90 membrane showed very poor conductivity removal performance. The obtained NF and overall retention rates of 76±8% and 79±7%, respectively, were quite close to the ones during the single stage NF at TMP of 4 bar where the operating TMP was insufficient for the feed conductivity level. So, the 14 bar TMP became inadequate with the increase in osmotic pressure which is directly proportional to conductivity load. Eventually, the permeate conductivity could not be decreased under 6.99±2.35 mS/cm which was critically higher than the water reuse limit given in Table 2.4.

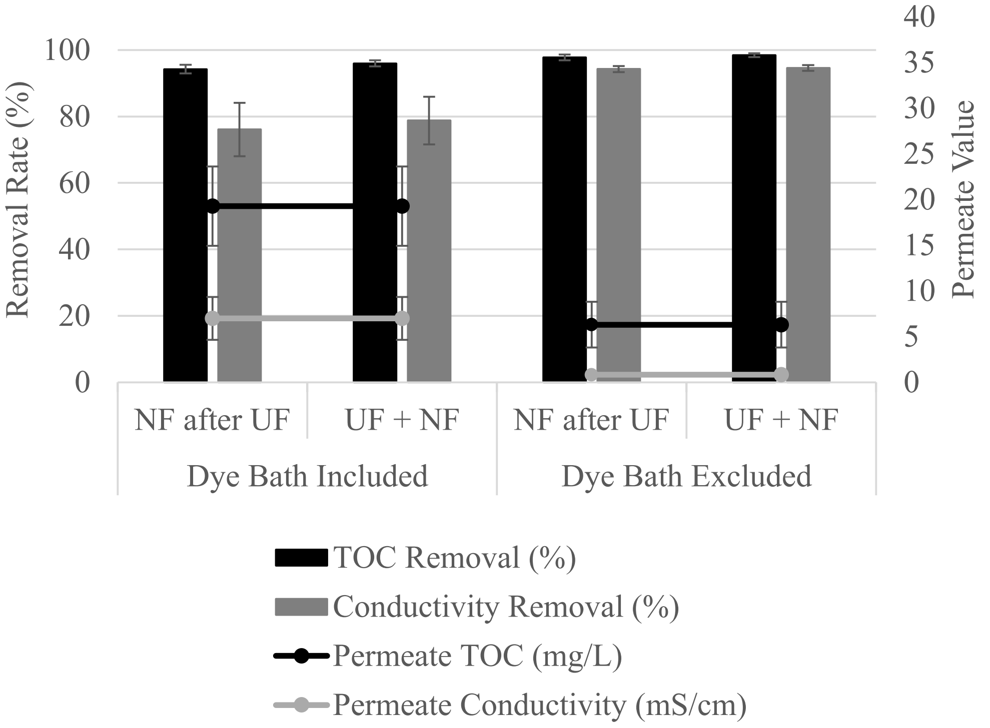

Figure 4.42: Change in TOC and Conductivity Removal Performance of NF90 Membrane in case of Inclusion of Dyeing Bath to Feed Solution

Decolorization performance of NF90 membrane had changed in terms of final effluent quality because of the increase in NF feed color values at rates of 94, 80, and 43 percent at wavelengths of 436, 525, and 620 nm in the case of inclusion dye bath to UF feed solution where the related findings were given in Figure 4.43. Besides the color retention rates were not influenced from the change in feed load. So, the permeate SAC values at 436, 525, and 620 nm were measured as 0.44±0.16, 0.52±0.17, and 0.29±0.07 m^{-1}, respectively, meaning that the permeate color values were doubled at 525 and 620 nm wavelengths.

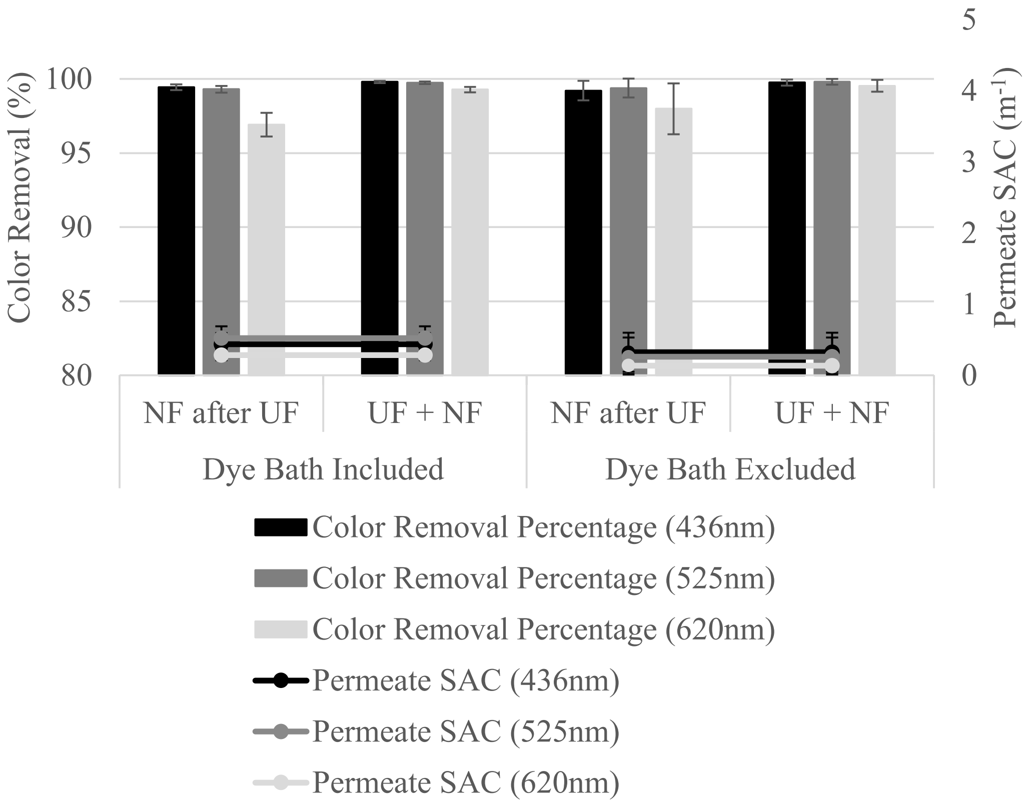

Figure 4.43: Change in Color Removal Performance of NF90 Membrane in case of Inclusion of Dyeing Bath to Feed Solution

Increase in pollutant load of feed raised both the concentration polarization, membrane fouling and the osmotic pressure. As a result of these increases, the raw water flux dramatically decreased by 85 percent corresponding permeate flux of 5.36 L/m^{2}h (Figure 4.44).

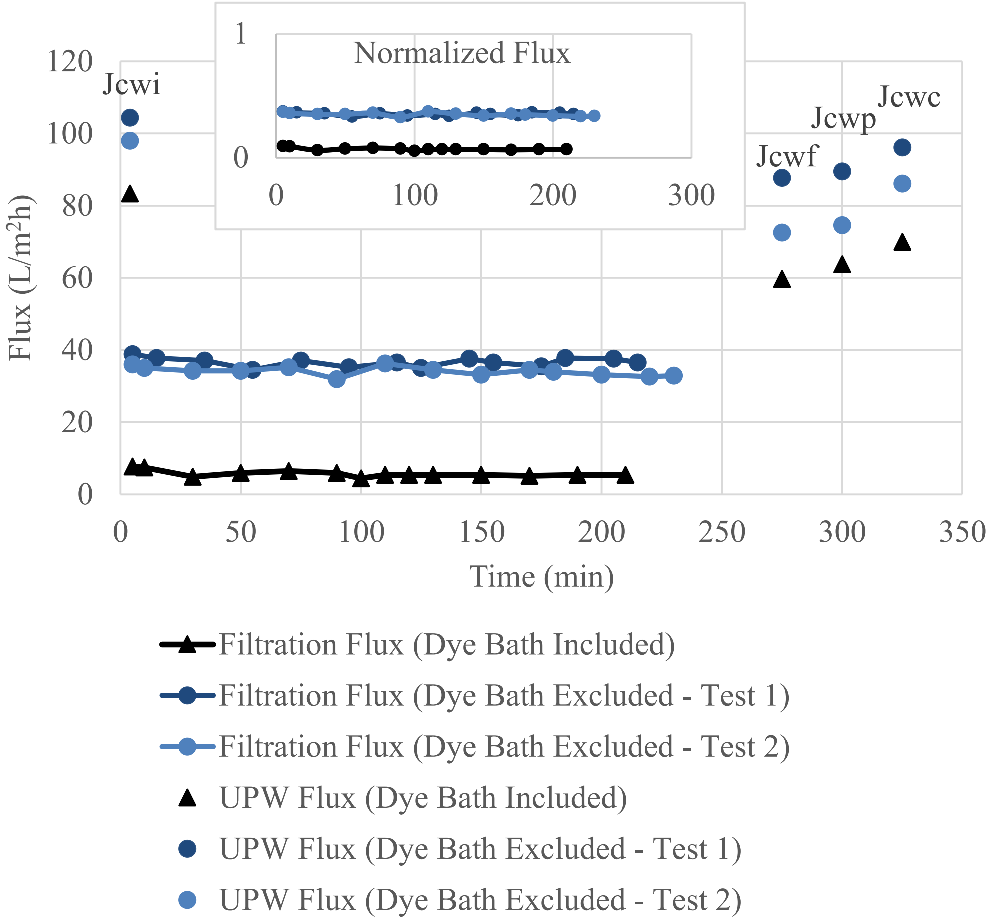

Figure 4.44: Change in UPW and Raw Water Flux Profile of NF after UF Pretreatment in case of Inclusion of Dyeing Bath to Feed Solution

The osmotic pressure multiplied due to doubled feed conductivity. To see at what degree the filtration flux was influenced by osmotic pressure which reduces the effective filtration pressure, osmotic pressure corrected flux calculations were conducted and given as in Table 4.26 to be compared with the experiments at same operating conditions in the case of exclusion of dyeing bath from feed solution mixture. The calculations revealed that the filtration flux would be 10.38 L/m^{2}h in the absence of the osmotic pressure of 6.77 bar.

Table 4.26: Osmotic Pressure Corrected Fluxes of NF after UF Pretreatment in case of Inclusion of Dyeing Bath to Feed Solution

	NF after Pretreatment		
	Dye Bath Included	**Dye Bath Excluded Test 1**	**Dye Bath Excluded Test 2**
J_{rw} (L/m^{2}h)	5.36	36.77	33.39
Corrected Flux (L/m^{2}h)	10.38	47.24	44.53
Flux Increase (%)	93.52	28.46	33.38

The other reasons behind the lowered filtration flux were thought as increase in fouling and concentration polarization. Resistance values given in Table 4.27 supported that. In detail, fouling and concertation polarization related resistances increased at different rates. As seen in Figure 4.44, the UPW before cleaning applications was 59.66 L/m^{2}h implying that the resistance due to concentration polarization value was more than 10 times of the that in the case of exclusion of dyeing bath. Fouling resistance did not show an increase at a critical level like concentration polarization. So, the contribution of membrane fouling in flux decline was still lower than osmotic pressure and concentration polarization. Physical cleaning could not recover 77 percent of membrane fouling (Table 4.28) and J_{cwf} reached to 63.77 L/m^{2}h (Figure 4.44). However, reaction of NF90 membrane to chemical cleaning application varied with the inclusion of dyeing bath to WW#1. The R_{ch-irr} value increased in a fluctuating range from 64 to 180 percent (Table 4.27).

Table 4.27: Analysis on Resistances of NF after UF Pretreatment in case of Inclusion of Dyeing Bath to Feed Solution

Resistance (10^{13} m^{-1})	**NF after UF (Dye Bath Included)**	**NF after UF (Dye Bath Excluded) Test 1**	**NF after UF (Dye Bath Excluded) Test 2**
R_{mem}	6.05	4.83	5.14
R_{tot}	93.97	13.71	15.10
R_f	2.40	0.92	1.81
$R_{cp+\pi}$	85.53	7.96	8.15
R_{ph-irr}	1.85	0.80	1.61
R_{ch-irr}	1.16	0.41	0.71

Table 4.28: Physically and Chemically Irreversible Portions of Membrane Fouling Obtained during NF after UF Pretreatment in case of Inclusion of Dyeing Bath to Feed Solution

Irreversible Fouling (%)	**NF after UF (Dye Bath Included)**	**NF after UF (Dye Bath Excluded) Test 1**	**NF after UF (Dye Bath Excluded) Test 2**
Ph-irr Fouling	77.28	87.44	89.38
Ch-irr Fouling	48.21	44.89	39.11

The obtained results during the NF after UF experiment in the case of inclusion of dyeing bath to UF feed solution mixture showed that, the pollutant load change had adverse effects on NF performance. The permeate quality level in terms of all parameters dropped. In addition, filtration flux dramatically decreased especially due to fouling, especially, concentration polarization, and doubled osmotic pressure.

Also ,the menitioned findings were taken into consideration under the light of literature, they have found highly consistent with studies conducted by NF90 membrane with lab or pilot scale systems. Among these studies, Liu et al. (2011) stated that NF permeate flux was 45 L/m^{2}h at TMP of 1.0 MPa and CFV of 0.38 m/s. The filtration flux was higher as the salinity of feed solution was way lower than WW#1 (Liu et al., 2011). In another study of Gozálvez-Zafrilla et al. (2008), salt retention rates reaching 95% was obtained with NF90 membrane by pilot scale experiments. This study also showed that NF performance can be significantly improved by employing UF prior to NF especially in terms of permeate flux with decrease in permeate COD level (Gozálvez-Zafrilla et al., 2008). In literature, many studies pointed osmotic pressure as a factor having critical influences on permeate flux as it was observed during this study. In addition to that, Hildebrand et al. (2013) stated that there were no effect of osmotic pressure on color removal efficiency of NF90 which corresponds the findings of this study.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

Experimental studies were designed to reach the optimal conditions and configuration for the treatment of the real reactive dyeing wastewater taken from three sequential baths following dyeing of fabric with the purpose of clean water recovery from reactive dyeing effluents.

A membrane treatment system is needed to provide an effective and sufficient removal performance at a long-life period while maintaining reasonable pure and raw water fluxes in order to be considered as successful. The lifetime of a membrane is directly proportional to its fouling behavior and cleanability so, during the studies on clean water recovery, the membranes were tested with respect to flux decline, fouling behaviors, and flux recovery in addition to analysis on their treatment efficiency.

During this study related to the process optimization on clean water recovery, designation of optimal TMP and CF was given priority at which the most appropriate NF could be performed. The most favorable match was tried to be find between 3 different TMPs (4, 10 and 14 bars) and 2 different CFs (58.9 and 103.2 mL/s).

TMP of 4 bar was found insufficient in terms of both TOC and conductivity removal for both CFs besides the obtained filtration flux was at impracticable levels due to osmotic pressure which changed between 3.23 and 3.48 bar during single stage NF experiments. TOC removal efficiency enhanced with the increase in the TMP but it was mostly lower at higher CF. Conductivity removal performance followed the same trend and the permeate conductivity quality improved with the increase in TMP. For all conditions, close to complete decolorization was reached even there were little differences.

Significance of osmotic pressure decreased with the increase in TMP and the filtration flux reached to 21.12 and 23.71 L/m^{2}h at 14 bar for 58.9 and 103.2 mL/s, respectively. The fouling resistances were almost same during direct NF experiments but the lowest concentration polarization was observed at the highest TMP.

CF increase did not contribute any significant improvement in treatment efficiency. In like manner, this increase did not conclude in raise in filtration flux which might be caused by lessen concentration polarization and cake layer formation by the means of possible sweeping effect of higher CF rate. So, the filtration flux curves obtained during NF at different CFs but same TMPs overlapped. The CF change had only influence on the irreversible portion of membrane fouling. Lower irreversible fouling resistances were obtained at lower CF for all TMPs.

As the result of direct NF at TRM, TMP of 14 bar and CF of 58.9 mL/s were designated as optimal conditions to conduct following NF experiments and set as reference performance to be compared with further studies.

These optimal conditions were tested with CM filtration till VRF of 2.5 to simulate real systems and see the effects of VRF (so, the pollutant load change as dyeing mill effluent composition is highly fluctuating) on the direct NF application. VRFs higher than 2.06 was found as impracticable in terms of TOC, conductivity, and color retention performance. Moreover, the permeate conductivity increased to 5.12 mS/cm that exceeds the criteria for water reuse. Even at 2.5 VRF, no change in fouling related resistances was obtained however there was a dramatic increase in concentration polarization as it was expected. The filtration flux of 21.75 L/m^{2}h at 1.25 VRF was same with the one obtained during TRM filtration. After this point, filtration flux decreased under mentioned level and continued to decline resulting from heightened feed concentrations. The filtration flux was decreased down to 8.30 L/m^{2}h at the VRF of 2.06, the maximum VRF until which NF membrane maintained a reliable treatment efficiency.

Also, to perform more factual simulation of real systems and to support observations on the relationship of NF performance with TMP and CF, wastewater sample taken from reactive dyeing achieved with a different recipe was treated with direct NF. Results revealed that TMP adjustment might be required according to feed pollutant load (especially, in terms of conductivity) to achieve similar treatment efficiency with a constant permeate flux in case of NF of effluents coming from dyeing process completed with different recipes.

In addition to optimal condition, performances of single stage NF application and sequential treatment system employing pretreatment prior to NF were compared to reach optimal configuration.

For this purpose, first, dead-end experiments were conducted with 0.45 μm PES MF and 150 kDa PES UF membranes for the selection of pretreatment option. UF was more favorable as pretreatment prior to NF compared to MF regarding TOC, turbidity, and color removal efficiencies where any significant conductivity removal could not be achieved by both option. Even, the permeate flux of MF was so higher than UF at the very beginning of filtration, the J_{rw} values obtained at final VRF were same at the final VRF. That brought the possibility of operating the MF at lower filtration pressures than the UF to obtain same filtration flux while shortening the filtration time. However, that fact does not an advantage in terms of improving NF performance. In addition, no critical aging caused by filtration and chemical cleaning was observed for both alternatives. Under the light of mentioned points especially about treatment performance, UF with 150 kDa PES membrane was decided as pretreatment prior to NF process and UF pretreatment was also tested with CF experiments at 2.65 bar while collecting permeate for subsequent NF. With UF pretreatment, 42±4 and 3±1 percent of TOC and conductivity was removed, respectively. The decolorization rates reached to 85±1, 85±2 and 91±1 percent for wavelengths of 436, 525 and 620 nm, respectively.

The J_{rw} values were 116.60±21.66 L/m^{2}h during CF UF experiments which were 4.70 times higher than the values obtained during dead-end UF.

UF pretreatment enhanced the NF performance in terms of color where the permeate TOC and conductivity values remained same. The biggest contribution of pretreatment happened in filtration flux and membrane fouling. The J_{rw} was taken up to a level 40 percent higher than the direct NF flux. The flux decline could be minimized with the employment of UF pretreatment as well the R_f and $R_{cp+\pi}$ values were halved. These results clearly showed that the projected enhancements in NF performance with the help of UF pretreatment were accomplished. Moreover, the amount of increase in filtration flux achieved with UF pretreatment emerged the idea about the inspection of the possibility of conducting NF at 10 bar TMP and 58.9 mL/s CF. Unfortunately, it was found that the pretreatment could not compensate lower TMPs. So, the increase in raw water flux experienced during the experiment at 14 bar was not attained when the NF after UF was conducted at 10 bar. Similarly, no enhancement in overall treatment efficiency was obtained when the NF of pretreated wastewater conducted at TMP of 10 bar. Only, the physically and chemically irreversible fouling was able to be reduced. It showed that conducting NF at lower TMPs without any distraction in its performance is possible only if the conductivity of feed, so the osmotic pressure, is reduced which might be achieved with pretreatment with a tighter UF membrane than 150 kDa UF membrane.

To see the reproducibility of the study, many experiments selected and repeated as they were given in previous section (RESULTS AND DISCUSSION). Direct NF at 10 bar, NF at CM, dead-end pretreatment, and UF prior to NF experiments were conducted again with virgin membrane pieces for this purpose. Findings of these tests showed that the study is quite reproducible and the obtained minor differences were caused by conducting test with different pieces of MF, UF and NF membranes.

The dyeing bath effluent had been segregated from feed solution mixture due to its high pollutant load, especially in terms of conductivity and color. So, the clean water recovery studies were conducted with the mixture of three baths following dyeing process. The UF/NF configuration that gave the most appropriate results was tested with the mixture obtained by adding dyeing bath effluent to WW#1. Inclusion of dyeing bath did not influence the retention rates and filtration flux of UF process at considerable levels. The UF permeate quality was higher proportional with the higher feed load. Osmotic pressure did not show any adverse effect on UF permeate flux as it was expected. On the contrary, performance of NF following UF was highly affected from higher influent load due to the inclusion of dyeing bath to UF feed solution. Permeate quality in terms of both TOC, conductivity and color deteriorated besides the filtration flux was decreased to impracticable levels because of doubled osmotic pressure, greater cake layer formation, and dye adsorption. So, it was proved that the decision of excluding dyeing bath effluent from feed solution mixture during the clean water recovery studies was confirmed. The segregated dyeing bath effluent was continued to be considered for studies on brackish water recovery by UF processes.

These mentioned findings pointed that the sequential UF/NF was favored as optimal treatment configuration where TMP of 14 bar and CF of 58.9 mL/s were optimal operating conditions for NF process. Treatment of WW#1 with UF/NF hybrid system at these conditions resulted in an effluent with 6.31±2.51 mg/L TOC and 0.83±0.13 mS/cm conductivity. Overall color retention rates got closest values to complete decolorization. Together with better treatment efficiency, the highest NF flux 35.08±1.69 L/m^{2}h was reached. The sequential UF/NF process at optimal conditions succeeded the minimized concentration polarization and fouling as the irreversible fouling resistances were at lowest level.

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APPENDIX A

COMPACTION FLUX PROFILES

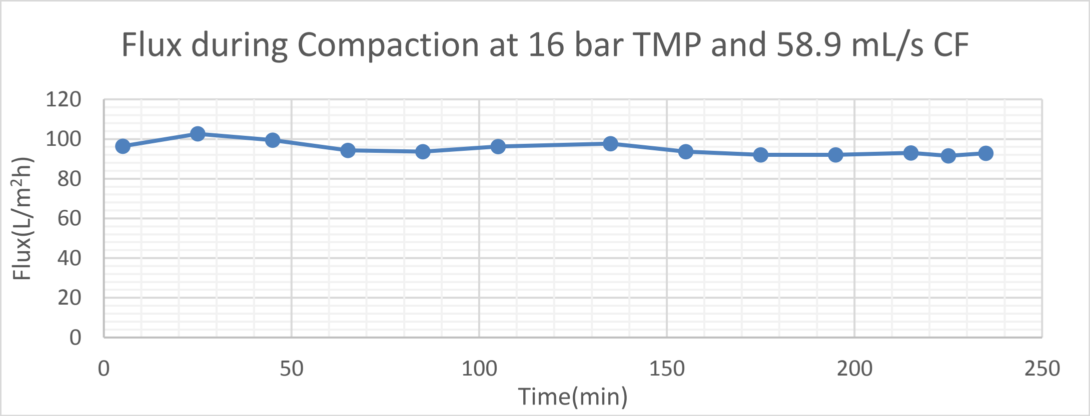

Figure A-1. Compaction Flux Profile of NF90 Membrane # 1 used during Direct NF conducted at TMP of 4 bar and CF of 58.9 mL/s

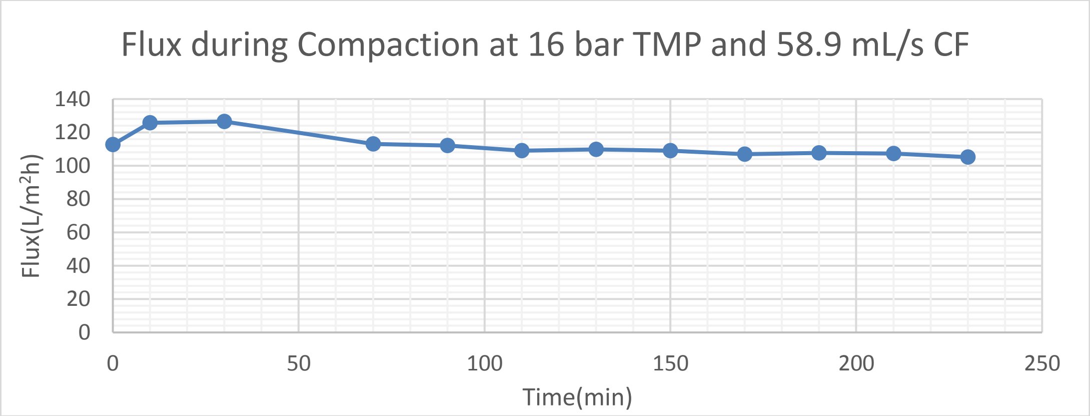

Figure A-2. Compaction Flux Profile of NF90 Membrane # 2 used during Direct NF conducted at TMP of 10 bar and CF of 58.9 mL/s (Test 1)

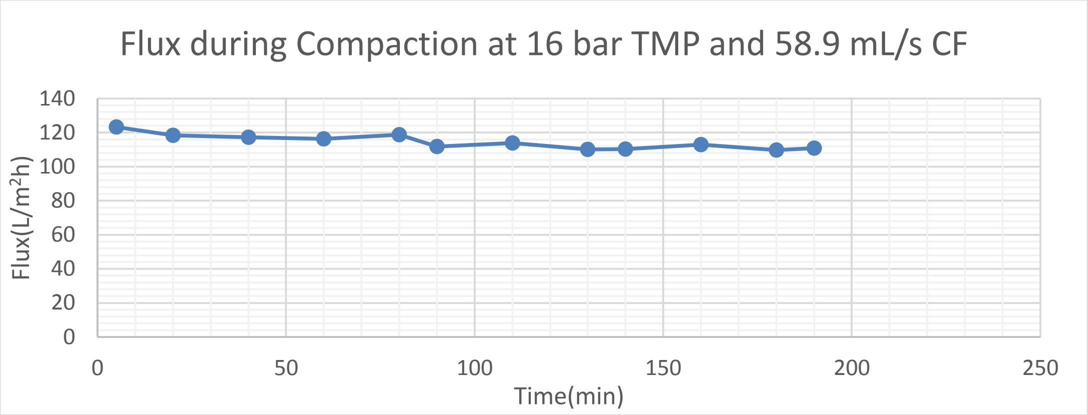

Figure A-3. Compaction Flux Profile of NF90 Membrane # 3 used during Direct NF conducted at TMP of 10 bar and CF of 58.9 mL/s (Test 2)

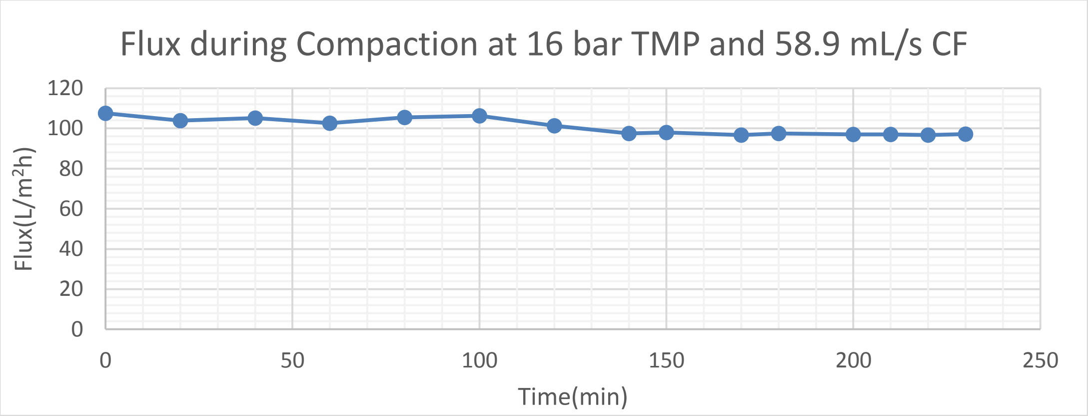

Figure A-4. Compaction Flux Profile of NF90 Membrane # 4 used during Direct NF conducted at TMP of 14 bar and CF of 58.9 mL/s

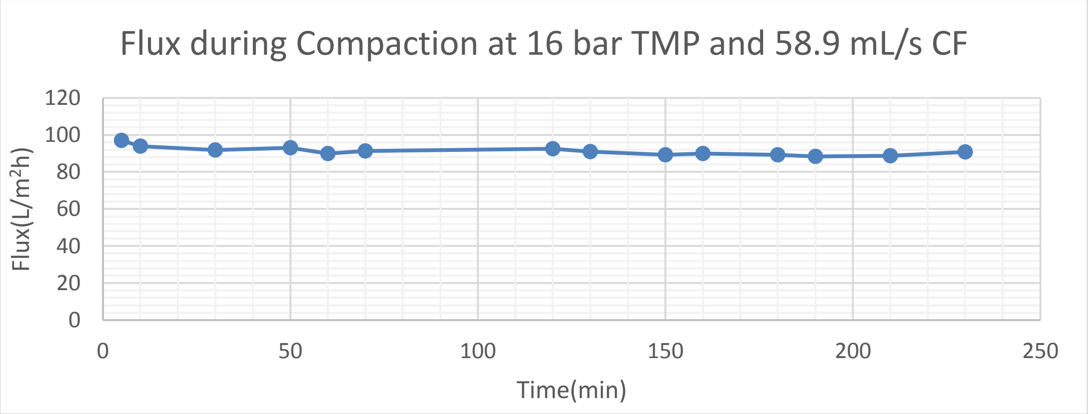

Figure A-5. Compaction Flux Profile of NF90 Membrane # 5 used during Direct NF conducted at TMP of 4 bar and CF of 103.2 mL/s

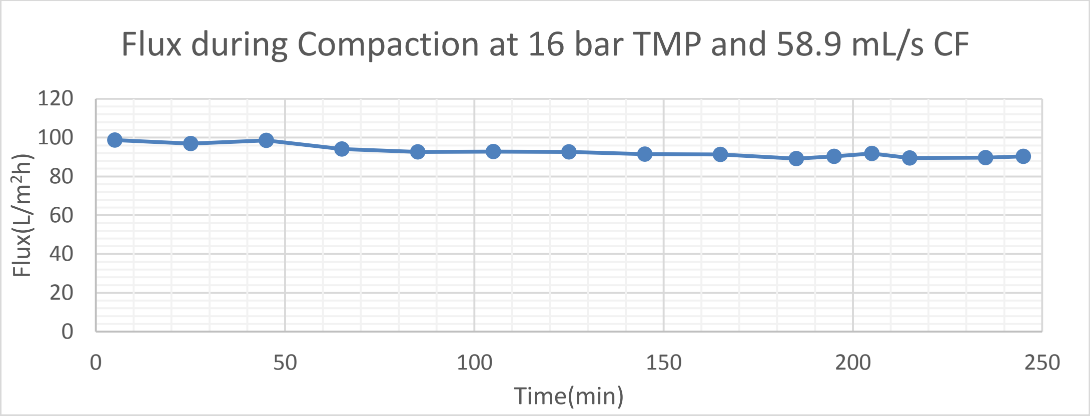

Figure A-6. Compaction Flux Profile of NF90 Membrane # 6 used during Direct NF conducted at TMP of 10 bar and CF of 103.2 mL/s

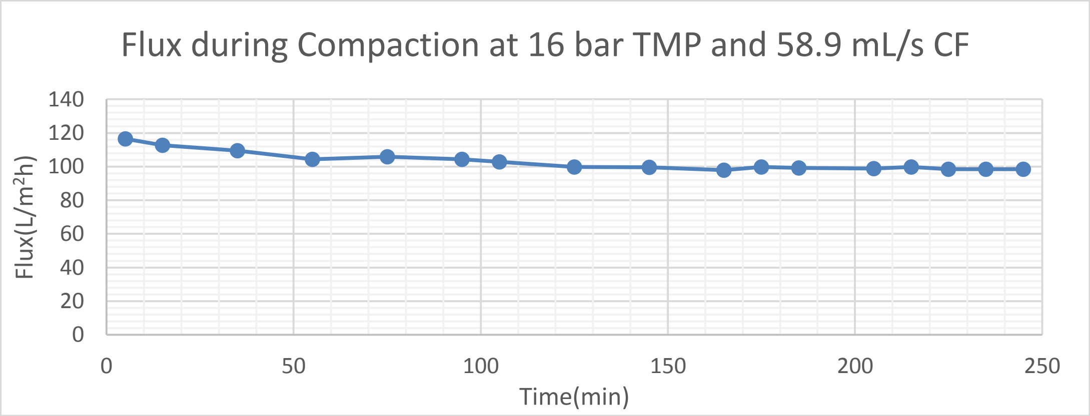

Figure A-7. Compaction Flux Profile of NF90 Membrane # 7 used during Direct NF conducted at TMP of 14 bar and CF of 103.2 mL/s

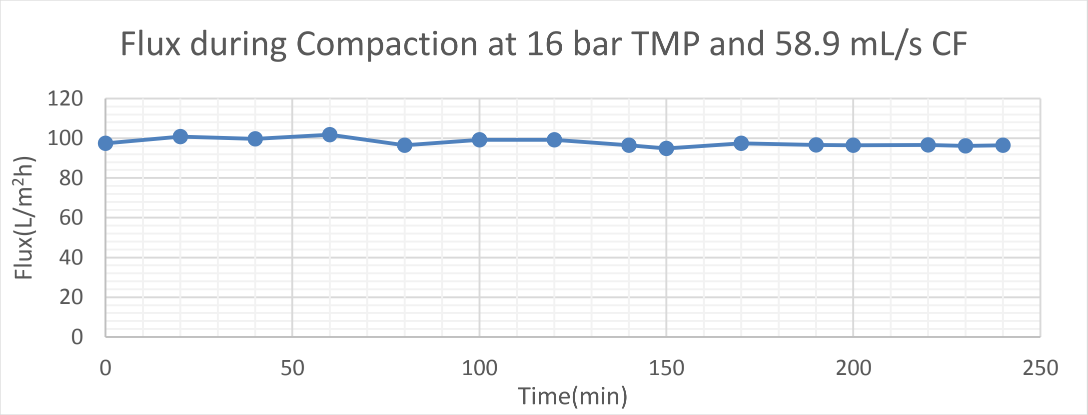

Figure A-8. Compaction Flux Profile of NF90 Membrane # 8 used during Direct NF conducted at Concentrate Mode, TMP of 14 bar and CF of 58.9 mL/s (Test 1)

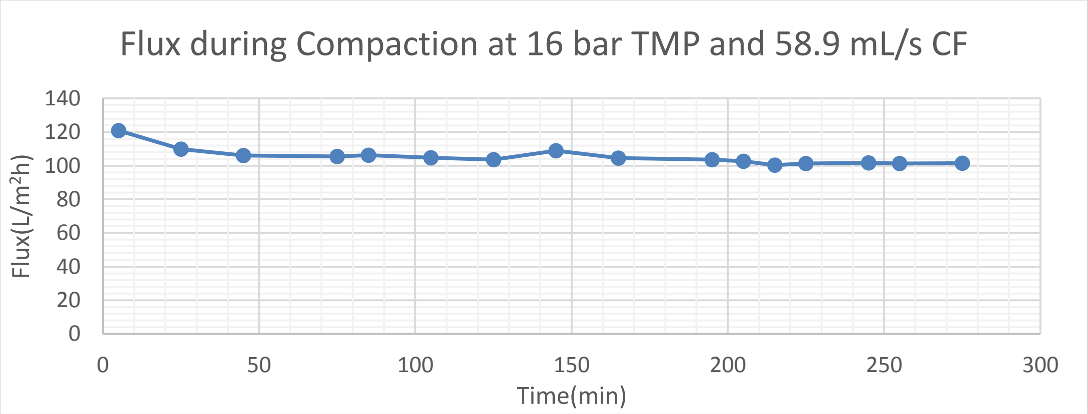

Figure A-9. Compaction Flux Profile of NF90 Membrane # 9 used during Direct NF conducted at Concentrate Mode, TMP of 14 bar and CF of 58.9 mL/s (Test 2)

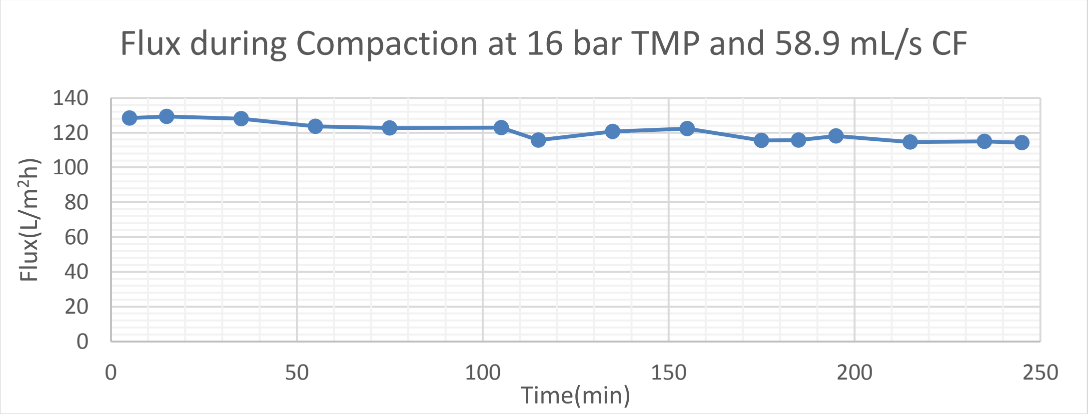

Figure A-10. Compaction Flux Profile of NF90 Membrane # 10 used during NF after Pretreatment conducted at TMP of 14 bar and CF of 58.9 mL/s (Test 1)

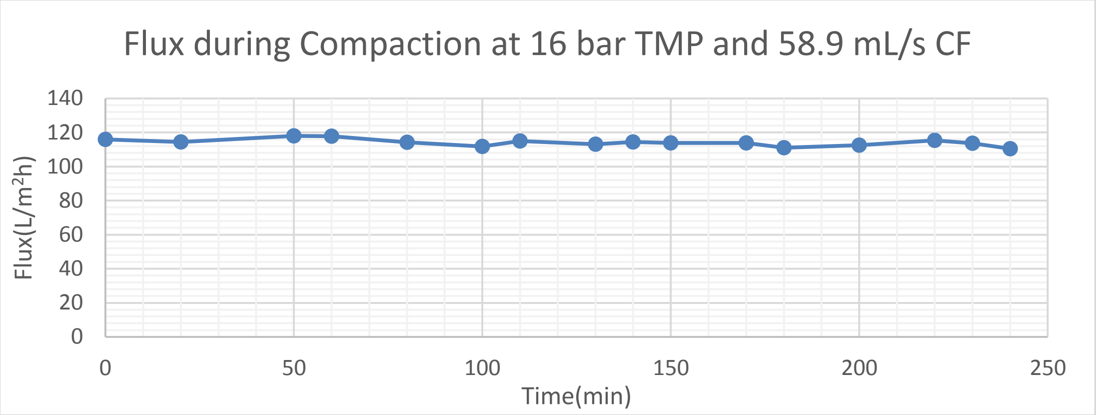

Figure A-11. Compaction Flux Profile of NF90 Membrane # 11 used during NF after Pretreatment conducted at TMP of 14 bar and CF of 58.9 mL/s (Test 2)

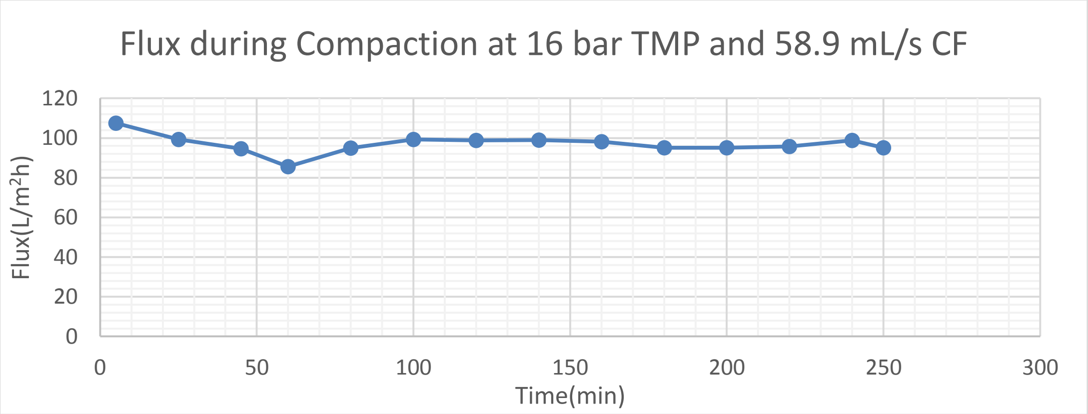

Figure A-12. Compaction Flux Profile of NF90 Membrane # 12 used during NF after Pretreatment conducted at TMP of 10 bar and CF of 58.9 mL/s

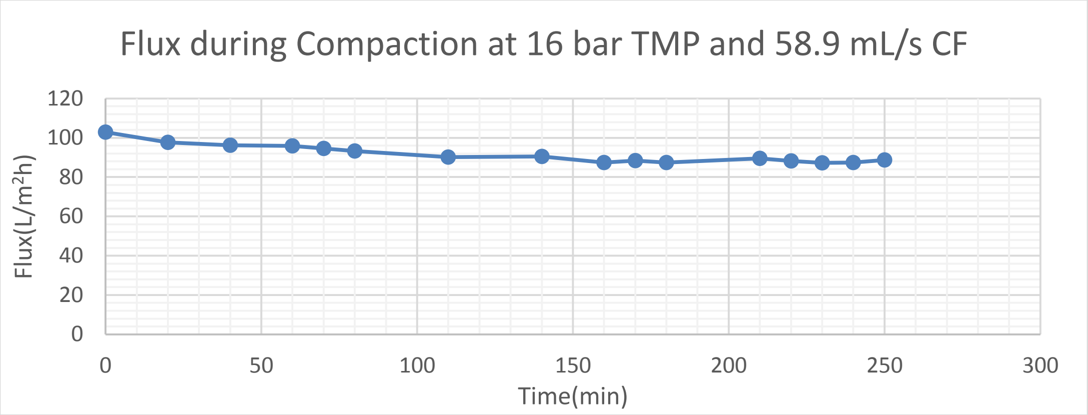

Figure A-13. Compaction Flux Profile of NF90 Membrane # 13 used during NF after Pretreatment conducted at TMP of 10 bar and CF of 58.9 mL/s in case of Inclusion of Dyeing Bath to Feed Solution

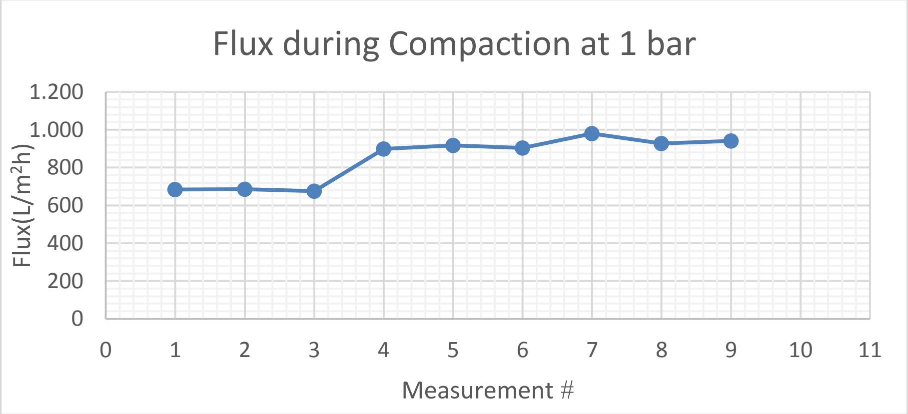

Figure A-14. Compaction Flux Profile of 150 kDa PES UF Membrane # 1 used during Dead-End UF conducted at 0.5 bar and 100 rpm (Test 1)

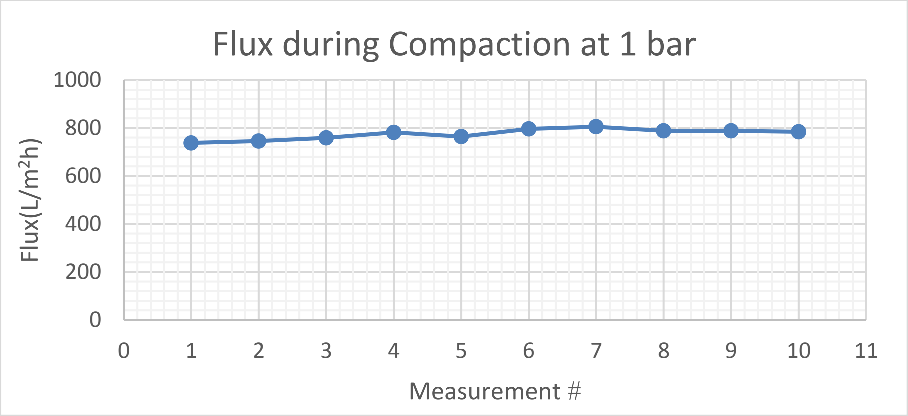

Figure A-15. Compaction Flux Profile of 150 kDa PES UF Membrane # 2 used during Dead-End UF conducted at 0.5 bar and 100 rpm (Test 2)

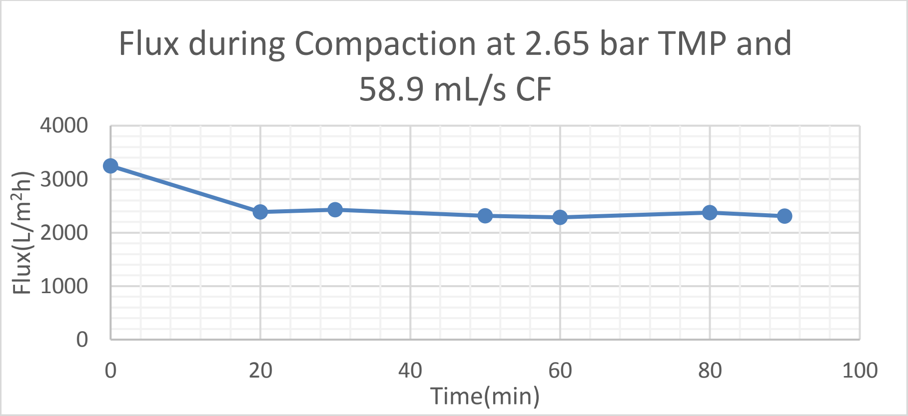

Figure A-16. Compaction Flux Profile of 150 kDa PES UF Membrane # 3 used during CF UF conducted at TMP of 2.65 bar and CF of 58.9 mL/s (CF Test 1)

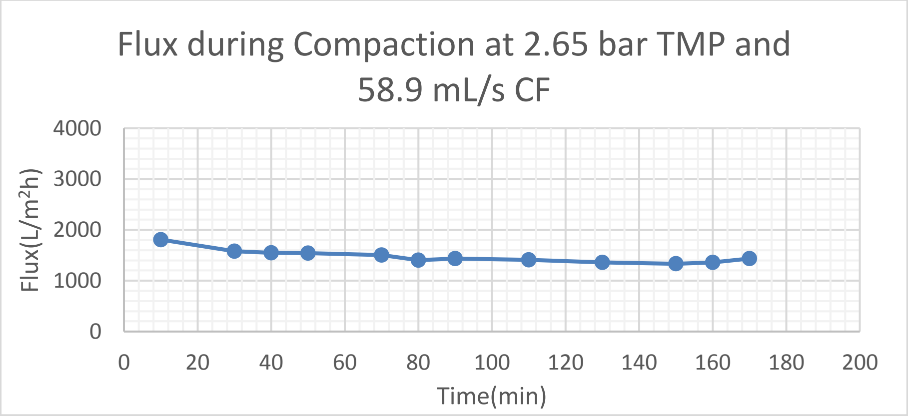

Figure A-17. Compaction Flux Profile of 150 kDa PES UF Membrane # 4 used during CF UF conducted at TMP of 2.65 bar and CF of 58.9 mL/s (CF Test 2)

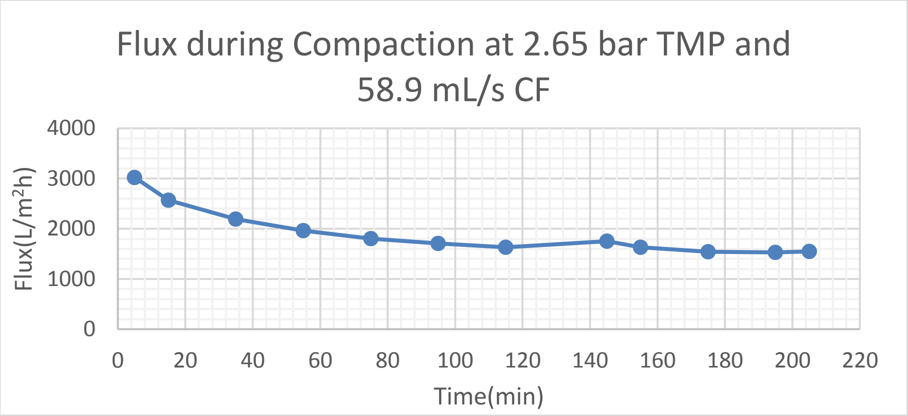

Figure A-18. Compaction Flux Profile of 150 kDa PES UF Membrane # 5 used during CF UF conducted at TMP of 2.65 bar and CF of 58.9 mL/s (CF Test 3)

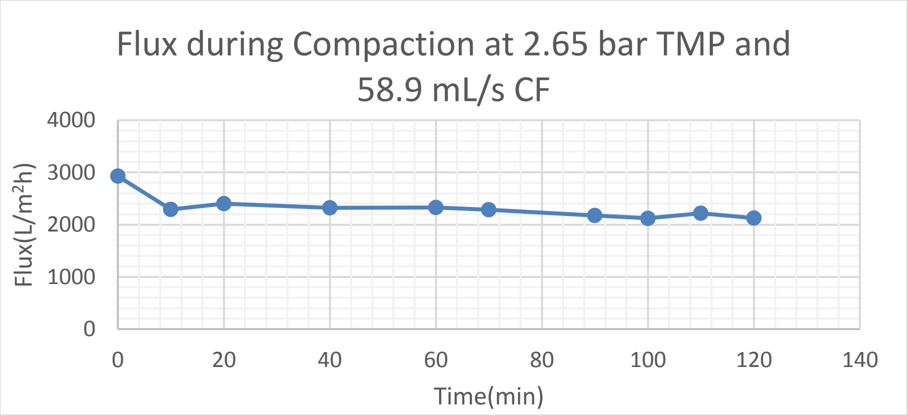

Figure A-19. Compaction Flux Profile of 150 kDa PES UF Membrane # 6 used during CF UF conducted at TMP of 2.65 bar and CF of 58.9 mL/s in case of Inclusion of Dyeing Bath to Feed Solution

APPENDIX B

CALCULATIONS AND DERIVATIONS

B.1. RESISTANCE ANALYSIS

$$R = \frac{TMP}{\mu \times J}$$

Where;

R= Resistance (m^{-1})

TMP=Trans membrane pressure (bar)

μ= Dynamic viscosity of permeate (Pa s)

J= Permeate flux (L/m^2h)

Dynamic viscosity of permeate was taken as 10^{-3} Pa s for all calculations as the viscosity of water is $0.932*10^{-3}$ Pa s at 23 °C at which temperature all experiments were conducted.

R_{mem}, R_{tot}, $R_{mem} + R_f$, $R_{mem} + R_f$, $R_{mem} + R_{ph-irr}$, and $R_{mem} + R_{ch-irr}$ were calculated by using J_{rw}, J_{rw}, J_{cwf}, J_{cwp}, and J_{cwc}, respectively. R_f , R_{cp} , R_{ph-irr} and R_{ch-irr} were found out from the relations between these calculations (Table B. 1).

Table B. 1: Relations used to Calculate R_f , R_{cp} , R_{ph-irr} and R_{ch-irr}

Resistance	
R_f	$(R_{mem} + R_f) - R_{mem}$
R_{cp}	$R_{tot} - R_{mem} - R_f$
R_{ph-irr}	$(R_{mem} + R_{ph-irr}) - R_{mem}$
R_{ch-irr}	$(R_{mem} + R_{ch-irr}) - R_{mem}$

To conclude, following formulas were used for the calculation of resistances. In addition, resistances corresponding to data set of fluxes obtained during direct NF at 14 bar and 58.9 mL/s (Section 4.1.2) given in were calculated as an example.

$$Rmem = \frac{TMP}{\mu \times Jcwi}$$

$$Rtot = \frac{TMP}{\mu \times Jrw}$$

$$Rf = \left(\frac{TMP}{\mu \times Jcwf}\right) - Rmem$$

$$Rcp = Rtot - (Rmem + Rf)$$

$$Rph - irr = \left(\frac{TMP}{\mu \times Jcwp}\right) - Rmem$$

$$Rch - irr = \left(\frac{TMP}{\mu \times Jcwc}\right) - Rmem$$

Table B. 2: Fluxes obtained during Direct NF Application at 14 bar and 58.9 mL/s

Flux	**L/m^{2}h**
J_{cwi}	94.37
J_{rw}	21.12
J_{cwf}	57.34
J_{cwp}	75.60
J_{cwc}	77.14

$$Rmem = \frac{140000}{0.001\ Pa\ s \times 94.37\ \mathrm{L}/m^2\mathrm{h}} = 5.34\ m^{-1}$$

$$Rtot = \frac{140000}{0.001\ Pa\ s \times 21.12\ \mathrm{L}/m^2\mathrm{h}} = 23.86\ m^{-1}$$

$$Rf = \left(\frac{140000}{0.001\ Pa\ s \times 57.34\ \mathrm{L}/m^2\mathrm{h}}\right) - 5.34 = 3.45\ m^{-1}$$

$$Rcp = 23.86 - (5.34 + 3.45)\ \ = 15.07\ m^{-1}$$

$$Rph - irr = \left(\frac{140000}{0.001\ Pa\ s \times 75.60\ \mathrm{L}/m^2\mathrm{h}}\right) - 5.34 = 1.33\ m^{-1}$$

$$Rch - irr = \left(\frac{140000}{0.001\ Pa\ s \times 77.14\ \mathrm{L}/m^2\mathrm{h}}\right) - 5.34 = 1.19\ m^{-1}$$

B.2. OSMOTIC PRESSURE AND CORRECTED FLUX

Even the basic information about dyeing recipes was known, certain amount and the type of salts used and other auxiliaries were not given by the dyeing mill due to their privacy principles. During experiments, as mentioned before, conductivity of samples was measured, converted to TDS, and used to estimate the osmotic pressure that caused by salt content of feed solution mixtures.

To be able to relate the conductivity and the TDS concentration of feed solution mixture, NaCl, Na_2CO and Na_2SO_4 solution mixtures with mass percentages of 0.25, 0.50 and 1.00% were prepared at 23±1°C. Their conductivity was measured by multimeter (Table B. 3) and converted to TDS and salinity by instrument as given in Table B. 4. Also, data given in Table B. 3 was used to draw Figure B. 1.

Table B. 3: Conductivity Measurements of Prepared Mixtures with Different Salts

Concentration (g/L)	**Conductivity (mS/cm)**		
	NaCl	**Na_2CO_3**	**Na_2SO_4**
2.50	4.17	3.86	3.10
5.00	8.06	7.06	5.75
10.00	15.43	12.64	10.51

Table B. 4: Conductivity, TDS and Salinity of Prepared Mixtures with Different Salts

Compound	**Mass Percentage**	**Conductivity (mS/cm)**	**TDS (g/L)**	**Salinity (o/oo)**
NaCl	0.25%	4.17	2.09	2.20
	0.50%	8.06	4.03	4.50
	1.00%	15.43	7.72	9.00
Na_2CO_3	0.25%	3.86	1.93	2.00
	0.50%	7.06	3.53	3.90
	1.00%	12.64	6.32	7.30
Na_2SO_4	0.25%	3.10	1.54	1.60
	0.50%	5.75	2.88	3.10
	1.00%	10.51	5.25	5.90
Mixture	1.00%	12.90	6.45	7.40

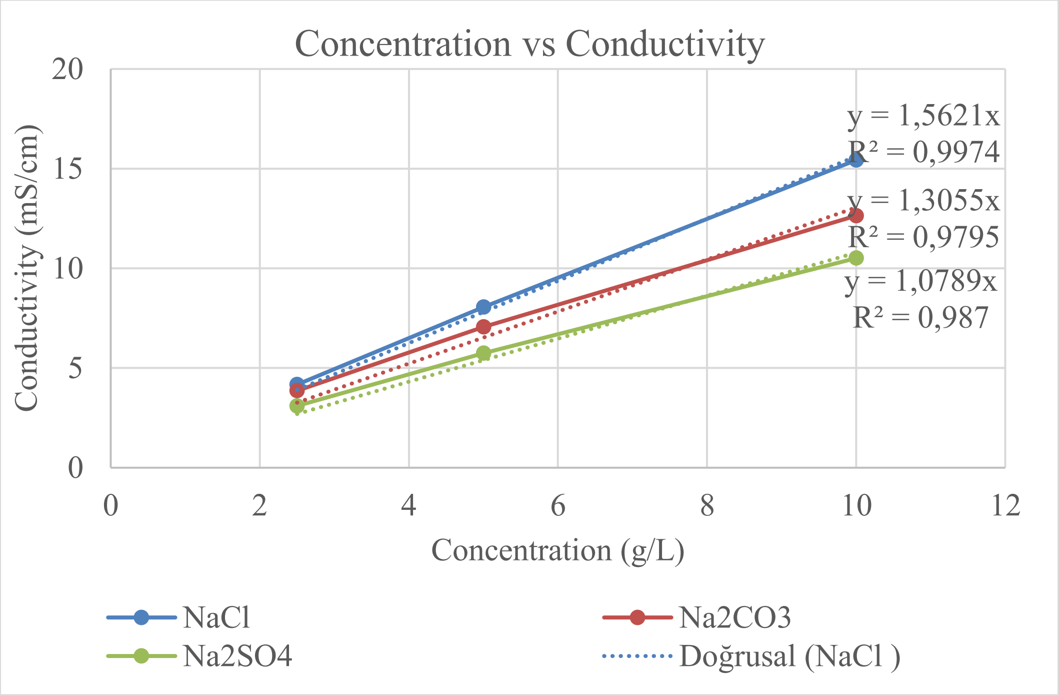

Figure B. 1: Conductivity Measurements of Solutions with Different Salt Concentrations

TDS value corresponding to 13.05 mS/cm conductitivty of WW#1 were found as given in Table B. 5 meaning that TDS of WW#1 would be 8.35, 10.00, 12.10 and 10.12 g/L if the conductivity was caused by only NaCl, Na_2CO_3, Na_2SO_4, and mixture of these salts, respectively.

Table B. 5: TDS Values in terms of Different Salts

Conductivity (mS/cm)	**TDS (g/L)**			
	NaCl	Na_2CO_3	Na_2SO_4	Mixture
13.05	8.35	10.00	12.10	10.12

On the contrary, multimeter converted conductivity of 13.05 mS/cm, measured by itself, to 6.53 g/L TDS. So, it was understood that conductivity of dyeing effluents were possibly caused not only by salts used but also substances with higher molecular weights. At the end, it was decided to use the value reached by instrumental conversion for the calculation of osmotic pressure with following formula and the salt used in recipe was assumed as NaCl because of its wide usage in reactive dyeing. Reached TDS value was used

$$\pi = R * T * \Sigma ci$$

Where;

π= Osmotic pressure (bar)
R= Universal gas constant (L bar/K mol)
T= Temparature (K)
c= Concentration of ions (mol/L)

Example:
R=8.314*102 L bar K^{-1} mol^{-1}
T=297.15 K
i=2

TDS=6.53 g/L
MW $_{\mathrm{NaCl}}$ =58.44 g/mol

So,
π=(8.314*10^2 L bar K^{-1} mol^{-1})*(297.15 K)*(2*((6.53 gL^{-1})/(58.44 gmol^{-1})))
π=5.5 bar

However, during the filtration of feed mixture solution, conductivity of which was 13.05 mS/cm, permeate flux was started to be observed at TMP of 2.95 bar as the TMP was raised gradually starting from zero. Because many assumptions were done during the calculation of osmotic pressure, manually measured osmotic pressure value was considered more reliable compared to calculated one. Osmotic pressure values during all NF experiments (Table B. 6) were calculated with direct correlation by setting this measurement as reference point.

Table B. 6: Feed Conductivity and Osmotic Pressure Values during Experiments

Experiment		**Feed Conductivity (mS/cm)**	**Osmotic Pressure (bar)**
Direct NF TRM	4 bar 58.9 mL/s	14.31	3.23
	10 bar 58.9 mL/s (Test 1)	14.27	3.23
	10 bar 58.9 mL/s (Test 2)	15.38	3.48
	14 bar 58.9 mL/s	14.27	3.23
	4 bar 103.2 mL/s	14.37	3.25
	10 bar 103.2 mL/s	14.27	3.23
	14 bar 103.2 mL/s	14.31	3.23
Direct NF CM	14 bar 58.9 mL/s (Test 1)	14.66	3.31
	14 bar 58.9 mL/s (Test 2)	14.52	3.28
Direct NF TRM Different Recipe Studies	4 bar 58.9 mL/s	5.08	1.15
	10 bar 58.9 mL/s	5.11	1.16
	10 bar 103.2 mL/s	5.11	1.16
Dead-End Experiments Selection of Pretreatment Option	0.45 µm MF Membrane#1 1st Filtration	14.89	3.37
	0.45 µm MF Membrane#1 2nd Filtration	16.42	3.71
	0.45 µm MF Membrane#2 1st Filtration	15.86	3.59
	150 kDa UF Membrane#1 1st Filtration	15.58	3.52
	150 kDa UF Membrane#1 2nd Filtration	15.23	3.44

Table B. 6: Cont'd.

	150 kDa UF Membrane#2 1st Filtration	15.44	3.49
CF UF Experiments prior to NF after Pretreatment CM	2.65 bar 58.9 mL/s (Test 1)	14.57	3.29
	2.65 bar 58.9 mL/s (Test 2)	14.43	3.26
	2.65 bar 58.9 mL/s (Test 3)	16.23	3.67
	2.65 bar 58.9 mL/s (Dyeing Bath Added to WW#1)	32.97	7.45
NF after Pretreatment Studies TRM	14 bar 58.9 mL/s (Test 1)	13.72	3.10
	14 bar 58.9 mL/s (Test 2)	15.50	3.50
	10 bar 58.9 mL/s	14.35	3.24
	14 bar 58.9 mL/s (Dyeing Bath Added to WW#1)	29.23	6.61

$$J = K(TMP - \pi_{feed})$$

Where;

J= Filtration flux (L/m^2h)

K= Raw water permeability coefficient of membrane (L/m^2hbar)

TMP= Transmembrane pressure (bar)

π_{feed}= Osmotic pressure of feed solution(bar)

In this formula, filtration flux, J, was designated as measured filtration flux and the multiplication of permeance and TMP was accepted as the filtration flux that would be obtained in the absence of osmotic pressure. So, following derivations were done to reach a formula to be used for the calculation of osmotic pressure corrected flux.

$$J_{measured} = K*(TMP-\pi_{feed})$$

$J_{measured}= K*TMP-K*\pi_{feed}$ where $J_{corrected}=K*TMP$

$$J_{measured}= J_{corrected}-K*\pi_{feed}$$

$J_{corrected} =J_{measured}+K*\pi_{feed}$ where $K=J_{measured}/(TMP-\pi_{feed})$

$$J_{corrected}=J_{measured}+(J_{measured}*\pi_{feed})/(TMP-\pi_{feed})$$

$$J_{corrected}= J_{measured}*(1+\pi_{feed} /(TMP-\pi_{feed}))$$

$$Jcorrected = Jmeasured(\frac{TMP}{TMP - \pi_{feed}})$$

APPENDIX C

FEED AND PERMEATE SAMPLE PHOTOS

Table C. 1 Feed and Permeate Sample Photos

Experiment		Feed and Permeate Photos
Direct NF TRM	4 bar 58.9 mL/s	
	10 bar 58.9 mL/s (Test 1)	
	10 bar 58.9 mL/s (Test 2)	-
	14 bar 58.9 mL/s	
	4 bar 103.2 mL/s	

Table C. 1 Cont'd.

Experiment		**Feed and Permeate Photos**
	10 bar 103.2 mL/s	
	14 bar 103.2 mL/s	
Direct NF CM	14 bar 58.9 mL/s (Test 1)	
	14 bar 58.9 mL/s (Test 2)	-
Direct NF TRM Different Recipe Studies	4 bar 58.9 mL/s	-
	10 bar 58.9 mL/s	
	10 bar 103.2 mL/s	-
Dead-End Experiments Selection of Pretreatment Option	0.45 µm MF Membrane#1 1st Filtration	
	0.45 µm MF Membrane#1 2nd Filtration	-
	0.45 µm MF Membrane#2	-

Table C. 1 Cont'd.

Experiment		**Feed and Permeate Photos**
	1st Filtration	
	150 kDa UF Membrane#1 1st Filtration	
	150 kDa UF Membrane#1 2nd Filtration	-
	150 kDa UF Membrane#2 1st Filtration	-
CF UF Experiments prior to NF after Pretreatment CM	2.65 bar 58.9 mL/s (Test 1)	
	2.65 bar 58.9 mL/s (Test 2)	-
	2.65 bar 58.9 mL/s (Test 3)	-
	2.65 bar 58.9 mL/s (Dyeing Bath Added to WW#1)	
NF after Pretreatment Studies TRM	14 bar 58.9 mL/s (Test 1)	
	14 bar 58.9 mL/s (Test 2)	-

Table C. 1 Cont'd.

Experiment		**Feed and Permeate Photos**
	10 bar 58.9 mL/s	
	14 bar 58.9 mL/s (Dyeing Bath Added to WW#1)	

APPENDIX D

FEED CHARACTERISTICS OF EACH EXPERIMENT

Table D. 1. Feed Characteristics during Direct NF at TRM

Experiment		**Feed = WW#1**					
		TOC mg/L	Turbidity NTU	Conductivity mS/cm	SAC (m^{-1})		
					436 nm	525 nm	620 nm
Direct NF TRM	4 bar 58.9 mL/s	514.00	49.43±0.93	14.31±0.00	188.70±0.36	241.10±0.24	40.60±0.15
	10 bar 58.9 mL/s (Test 1)	568.00	41.40±0.70	14.27±0.02	234.23±0.02	315.46±0.02	52.36±0.02
	10 bar 58.9 mL/s (Test 2)	333.12	42.33±0.95	15.38±0.01	137.09±0.06	134.79±0.36	34.88±0.12
	14 bar 58.9 mL/s	475.27	38.37±0.55	14.27±0.01	153.15±0.00	169.89±0.00	30.57±0.05
	4 bar 103.2 mL/s	473.40	43.10±0.26	14.37±0.01	131.15±0.02	132.59±0.02	30.40±0.07
	10 bar 103.2 mL/s	450.3	38.13±0.45	14.27±0.02	136.27±0.05	142.17±0.05	29.47±0.02
	14 bar 103.2 mL/s	448.32	44.13±0.76	14.31±0.00	153.33±0.31	166.90±0.03	33.18±0.00

Table D. 2. Feed Characteristics during Direct NF at CM

Experiment		Feed = WW#1					
		TOC mg/L	Turbidity NTU	Conductivity mS/cm	SAC (m^{-1})		
					436 nm	525 nm	620 nm
Direct NF CM	14 bar 58.9 mL/s (Test 1)	327.00	44.80±0.44	14.66±0.06	138.36±0.96	134.87±0.82	37.04±1.87
	14 bar 58.9 mL/s (Test 2)	259.44	46.30±0.24	14.52±0.00	134.64±0.09	131.36±0.10	33.76±0.09

Table D. 3. Feed Characteristics during Direct NF at TRM (Different Recipe Studies)

Experiment		Feed = WW#2					
		TOC mg/L	Turbidity NTU	Conductivity mS/cm	SAC (m^{-1})		
					436 nm	525 nm	620 nm
Direct NF TRM Different Recipe Studies	4 bar 58.9 mL/s	125.84	25.70±0.53	5.08±0.00	36.29±0.02	65.86±0.05	13.49±0.03
	10 bar 58.9 mL/s	89.88	35.53±0.72	5.11±0.00	47.74±0.01	72.48±0.01	22.27±0.04
	10 bar 103.2 mL/s	131.64	23.00±0.36	5.11±0.00	37.09±0.07	65.66±0.04	12.87±0.03

Table D. 4.Feed Characteristics during Dead-End Experiments

Experiment		**Feed = WW#3**					
		TOC mg/L	Turbidity NTU	Conductivity mS/cm	SAC (m^{-1})		
					436 nm	525 nm	620 nm
Dead-End Experiments Selection of Pretreatment Option	0.45 µm MF Membrane#1 1st Filtration	134.10	27.77±0.29	14.89±0.00	82.86±0.05	139.77±0.06	13.94±0.00
	0.45 µm MF Membrane#1 2nd Filtration	156.80	30.53±1.50	16.42±0.06	91.82±0.08	145.57±0.05	20.57±0.02
	0.45 µm MF Membrane#2 1st Filtration	156.90	31.57±1.04	15.86±0.00	88.69±0.06	141.95±0.06	18.76±0.07
	150 kDa UF Membrane#1 1st Filtration	136.90	28.97±1.45	15.58±0.22	88.74±0.11	145.26±0.10	18.90±0.01
	150 kDa UF Membrane#1 2nd Filtration	135.80	24.37±0.81	15.23±0.00	87.93±0.12	139.92±0.07	17.56±0.01
	150 kDa UF Membrane#2 1st Filtration	145.30	32.00±0.53	15.44±0.08	96.55±0.32	150.76±0.14	23.48±0.11

Table D. 5. Feed Characteristics during CF UF Experiments prior to NF

Experiment		**Feed = WW#1**					
		TOC mg/L	Turbidity NTU	Conductivity mS/cm	SAC (m^{-1})		
					436 nm	525 nm	620 nm
CF UF Experiments prior to NF after Pretreatment CM	2.65 bar 58.9 mL/s (Test 1)	312.00	44.53±0.31	14.57±0.01	134.50±0.15	135.60±0.15	33.90±0.05
	2.65 bar 58.9 mL/s (Test 2)	431.05	41.33±1.27	14.43±0.01	134.00±0.00	138.00±0.00	29.00±0.00
	2.65 bar 58.9 mL/s (Test 3)	393.35	39.83±0.60	16.23±0.01	136.28±0.14	133.48±0.11	33.85±0.22
	2.65 bar 58.9 mL/s (Dyeing Bath Added to WW#1)	478.86	77.37±1.07	32.97±0.03	220.68±0.96	201.55±1.30	40.15±0.12

Table D. 6. Feed Characteristics during NF after Pretreatment Studies

Experiment		**Feed = Permeate of UF Pretreatment**					
		TOC mg/L	Turbidity NTU	Conductivity mS/cm	SAC (m^{-1})		
					436 nm	525 nm	620 nm
NF after Pretreatment Studies TRM	14 bar 58.9 mL/s (Test 1)	307.08	3.15±0.17	13.72±0.00	42.23±0.05	43.87±0.02	6.92±0.00
	14 bar 58.9 mL/s (Test 2)	271.70	3.11±0.03	15.50±0.01	39.51±0.01	39.46±0.01	6.05±0.00
	10 bar 58.9 mL/s	190.15	3.67±0.69	14.35±0.01	41.01±0.01	41.53±0.01	6.43±0.01
	14 bar 58.9 mL/s (Dyeing Bath Added to WW#1)	336.10	4.83±0.48	29.23±0.15	79.14±0.02	75.12±0.01	9.26±0.01