CAUSTIC RECOVERY FROM HIGHLY ALKALINE DENIM MERCERIZING WASTEWATERS USING MEMBRANE TECHNOLOGY

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submitted by **CİHANGİR VAROL** in partial fulfillment of the requirements for the degree of **Master of Science in Environmental Engineering Department, Middle East Technical University** by,

Prof. Dr. Canan Özgen
Dean, Gradute School of **Natural and Applied Sciences**

Prof. Dr. Göksel N. Demirer
Head of Department, **Environmental Engineering**

Prof. Dr. Ülkü Yetiş
Supervisor, **Environmental Engineering Dept., METU**

Examining Committee Members:

Dr. Haluk Çeribaşı
Environmental Engineering Dept., METU

Prof. Dr. Ülkü Yetiş
Environmental Engineering Dept., METU

Prof. Dr. Levent Yılmaz
Chemical Engineering Dept., METU

Prof. Dr. Nalan Kabay
Chemical Engineering Dept., Ege University

Prof. Dr. Filiz B. Dilek
Environmental Engineering Dept., METU

Date:

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

Name, Last Name : Cihangir Varol

Signature :

ABSTRACT

CAUSTIC RECOVERY FROM HIGHLY ALKALINE DENIM MERCERIZING WASTEWATERS USING MEMBRANE TECHNOLOGY

Varol, Cihangir
MSc., Department of Environmental Engineering
Supervisor: Prof. Dr. Ülkü Yetiş

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Recovery of caustic solution from mercerizing wastewaters of a denim producing textile mill was performed by using membrane technologies. A comprehensive characterization study was conducted to develop the treatment scheme. Highly alkaline and warm condition of wastewater has induced using membranes made of Polyethersulfone (PES). Conducted pretreatment applications such as microfiltration, flocculation and centrifuge have been found unsuccessful to improve further treatment capacities. Hence recovery studies which are UF, NF and pilot-system membrane applications have been implemented without any pretreatment. Effects of TMP and CFV on UF and NF processes were investigated and optimum operating conditions have been defined. UF has accomplished almost complete caustic solution recovery beside high COD and color retentions 84 % and 94 % under 4.03 bar TMP and 0.79 m/s CFV at 20±2 ^{0}C. Because of higher capacity of NF membranes also in acid and alkali recovery area, NF process has been studied in addition to UF. NF has also provided nearly complete NaOH recoveries with 92 % COD and 98 % color retentions under 4.03 bar TMP and 0.79 m/s CFV at 20±2 ^{0}C. Furthermore temperature effect was also studies by repeating the same processes at 40±2 ^{0}C considering the real operating conditions. Temperature has affected the system performance positively with regards to flux increases with insignificant loses in recovery and retention capacities. Lastly a pilot plant study has been conducted and it was found successful despite some operational difficulties due to high inorganic content and temperature of wastewater.

Keywords: Caustic, Mercerization Wastewater, Membrane, Alkaline Recovery, Textile Industry

ÖZ

YÜKSEK ALKALİ DENİM MERSERİZE ATIKSULARINDAN MEMBRAN TEKNOLOJİSİ İLE KOSTİK GERİ KAZANIMI

Varol, Cihangir
Yüksek Lisans, Çevre Mühendisliği Bölümü
Tez Yöneticisi: Prof. Dr. Ülkü Yetiş

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Denim üretimi yapan bir tekstil fabrikasının merserizasyon atık sularından kostik soda geri kazanımı gerçekleştirilmiştir. Arıtım tasarılarını geliştirmek amacıyla kapsamlı bir karakterizasyon çalışması yürütülmüştür. Atık suyun oldukca alkali ve sıcak yapısı çalışmalarda Polyethersulfone (PES) bazlı membran kullanımına yöneltmiştir. İleriki aırıtımlardaki verimi artırmak amacıyla yürütülmüş mikrofiltrasyon, flokülasyon ve santrifüj ön arıtım uygulamaları başarısız bulunmuştur. Bu yüzden çalışılmış UF, NF ve pilot sistem membran uygulamaları her hangibir ön arıtım olmadan gerçekleştirilmiştir. UF ve NF çalışmaları transmembran basıncı ve yatay geçiş hızının etkileri bakımından incelenmiş, en verimli çalışma koşulları belirlenmiştir. UF prosesi en iyi 20±2^{0}C de 4.03 bar transmembran basıncı ve 0.79 m/s yatay geçiş hızında %84 renk ve %94 KOİ giderimiyle birlikte başarılı kostik çözeltisi geri kazanımı sağlamıştır. Permeat kalitesini artırmak amacıyla yüksek arıtım kapasitesi yanında asit ve alkali geri kazanımı alanındaki avantajlarıda düşünülerek NF prosesi çalışılmıştır. NF prosesi de en iyi olarak 20±2^{0}C de 4.03 bar transmembran basıncı ve 0.79 m/s yatay geçiş hızında başarılı kostik çözeltisi geri kazanımı sağlamış, %92 renk ve %98 KOİ giderimlerine olanak sağlamıştır. Bu çalışmalara ek olarak bu membran proseslerde sıcaklığın etkisi çalışılmıştır. Gerçek çalışma koşulları değerlendirilip 40±2^{0}C de arıtım çalışmaları tekrarlandığında;

sıcaklığın akı üzerindeki olumlu etkisinin yanında, geri kazanım ve giderim oranlarında az miktarlarda kayıplara yol açtığı görülmüştür. Son olarak bir pilot sistem çalışması yürütülmüş ve yüksek inorganic içeriği ve sıcaklık kaynaklı işletim problemlerine rağmen oldukça başarılı olduğu görülmüştür.

Anahtar kelimeler: Kostik, Merserizasyon Atıksuyu, Membran, Alkali Geri Kazanımı, Tekstil Endüstrisi

To My Parents

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ABBREVIATIONS

BOD	Biochemical Oxygen Demand
CFV	Cross Flow Velocity
COD	Chemical Oxygen Demand
MF	Microfiltration
MWCO	Molecular weight cut-off
NF	Nanofiltration
PES	Polyethersulfone
PTFE	Polytetrafluoroethylene
PVA	Polyvinyl alcohol
PVDF	Polyvinylidene fluoride
RO	Reverse Osmosis
TDS	Total Dissolved Solids
TMP	Transmembrane pressure
TSS	Total Suspended Solids
UF	Ultrafiltration
Be	Baume

CHAPTER 1

INTRODUCTION

1.1 General

Cloth has been the second main necessity of human being after food. Producing fibers and then processing them to make clothes constitutes fundamental milestones of the textile industry. This mandatory need makes the textile industry develop faster through the ages with increasing population and living standards. Therefore, the textile industry has taken its place near the largest export and import markets of countries.

Turkey has been an important contributor to the World textile industry in terms of both raw material and production since 16th and 17th centuries. Relations with the European Union have influenced the Turkish textile industry positively and helped Turkey to get its place among the World's largest textile exporters.

Typically textile processing starts with yarn formation continues with fabrication of this yarn and finally ends with dyeing and finishing stages. Dyeing and finishing called as "wet processing" are the most important production phases of the textile industry. Wet processes improve the value of fabric in appearance, durability and serviceability considering consumer needs. However, these processes are responsible for making the textile industry such a highly water and chemical intensive sector. In a typical textile facility; 200-400 L of water is consumed to produce 1 kg of fabric [1] and therefore large quantities of wastewaters are generated.

Textile wastewaters are highly colored and mainly constitute inorganic and organic contaminants at high concentrations [2]. Moreover these wastewaters are highly variable in both quality and quantity as the textile industry is primarily dependent on trends in product base. Therefore chemicals or additives used in processes shows serious alterations with time. There are nearly 8000 coloring and 6900 additive contaminants which contribute to organic and inorganic pollution in textile effluents [3].

Textile companies often face shortage of water resources not only because of water scarcity but also discharge limits [4]. These facts have shifted considerations toward water saving and recovery alternatives for the textile industry [2], [3] and implied that treating textile wastewaters in an end of pipe approach is unsuitable.

In general, it is accepted that membrane processes are realistic solutions for the treatment of textile wastewaters targeting at recovery [5]. Traditionally used methods (e.g. biological degradation with activated sludge) are insufficient not only for obtaining the required water quality [4] but also for water and chemical recovery.

Mercerization is one of the major finishing processes of cotton textile production where caustic (NaOH) is the main chemical used. This process is generally applied to increase dye affinity, luster and strength of fiber. Wherever it is applied, mercerization process is followed by an intensive hot water rinsing or washing process to remove excess caustic. As a result, a highly alkaline (60-70 g/L NaOH) and relatively hot wastewater which includes various other organic and inorganic impurities is generated.

Wastes from mercerizing processes bring problems of wastewater with a highly alkaline content and high amount of caustic soda losses for textile mills [6]. However, there is an opportunity of recovering caustic from these wastewaters. There are two types of caustic recovery methods from mercerizing wastewater in practice. One of them is a staged evaporation technique which has been applied since 1900 for both woven and nonwoven industries. This process provides complete recovery of the caustic in the wastewater. Although there are good examples of this system, it becomes unsuitable for some manufacturers due to operational difficulties arising from wide range of chemicals applied. For example surfactants which are used in almost all of the textile processes or its by-products may results in foaming problems in boiling thanks. These problems have induced the development of membrane based caustic recovery methods from mercerizing wastewaters. Beside wider usage area of membranes in textile wastewater treatment, it has proven its applicability in caustic recovery purposes also. Yet, caustic recovery by membrane processes does not provide full recovery of the caustic or NaOH existing in alkaline wastewaters. A caustic containing permeate that is subjected to be a proceeding evaporation step, is produced from the feed to the membrane recovery system.

UF is accepted as a caustic recovery method by membrane technology. Although it has been applied for recovering caustic from mercerizing process effluents [7], it is generally regarded as satisfactory for the removal of particles and macromolecules, generally further treatment is needed for decolorization purposes. On the other hand, NF is applicable for the separation of low molecular weight organic compounds and divalent salts and hence for decolorization. It provides a particular softening effect too [8]. This makes the usage of NF a better alternative for caustic recovery purposes. In a few of recent investigations, NF has been applied successfully to recover caustic from mercerizing process effluents from both cotton and polyester fabric manufacturing [9], [10]. Although they have achieved successful caustic recoveries, membrane performances were not assessed according to any pollutant parameters such as COD or color removal. Moreover, only one type of NF membrane was evaluated in both of these studies. In addition to all, due to nature of the mercerizing processes, treatment options should also be evaluated in high temperature conditions. However, none of these studies investigates the effect of temperature on membrane performance.

1.2 Objective and Scope of the Study

The objective of this study is to evaluate caustic recovery from mercerizing wastewaters by membrane processes with the ultimate goal of producing a caustic stream at reusable concentrations (22% NaOH). After membrane separation, further processing (evaporation) is to be applied using waste heat from stack gases for the production of a caustic stream at the desired concentration. Therefore, the goal in this investigation is to produce a purified caustic stream from mercerizing wastewaters.

In the present study, for the purpose of caustic solution recovery, applicability of membrane technology which is a new but becoming a prevalent technology in this area has been investigated. With this intend, UF and NF processes have been studied. Furthermore some pretreatment options prior to these membrane processes were evaluated using finishing wastewater samples obtained from a cotton textile mill.

The textile mill in which the present study weas conducted is one of the largest textile producers in the World located in Kayseri-Turkey. Fiber and fabric production, dyeing and finishing are the main processes of a textile production. The mill performs all these production stages; such that 20.000 meters of fiber is produced and 12 million meters fabric dyeing and finishing is applied in a year. Such a huge production capacity constitutes an important environmental threat with high level of water and chemical consumption. Caustic is one of the most frequently applied and exhausted chemical by washing after dyeing and especially after finishing operations in the mill. The two major cost items arising from caustic consumption are indicated as the cost of caustic itself and also the cost of neutralization applied to this waste during waste treatment. According to the mill, the estimated monthly total cost is about US$ 250,000 and hence caustic solution recovery and reuse should be investigated due to both environmental and also economical reasons.

This research strikes into caustic solution recovery from finishing wastewater subject basically in 3 stages. In the first part of the study, caustic containing wastewaters of the interested mill are characterized. By means of the characterization study major sources of caustic discharge of the mill are revealed. These sources are mainly the rinsing effluents after denim mercerization processes. Effluents from these stages of production reach up to nearly 60 - 70 g/L NaOH concentrations. Furthermore, they are highly colored (4000 – 10000 Pt-Co) and high in temperature (40 – 50^{0}C). Stating from where and in which conditions the caustic will be recovered, available techniques and researches conducted about alkaline recovery is investigated. This study forms the second part of the study which has accorded the advantage of setting the best alternative for recovering purpose for the specified mill. Membrane processes have been decided to be the best alternative for this mill. Because, recently, studies about chemical recovery and reuse are being shifted to membrane processes due to the technological progress in this area.

Within the scope of the present study; first of all, several pretreatment alternatives are tested for the specified wastewater. MF is evaluated primarily for the pretreatment studies. Beside commonly used microfiltration membranes, different kind of membranes which are known as highly durable to alkaline working conditions are evaluated. In the light of pretreatment studies, UF process is studied first to evaluate caustic solution recovery. Within the context of UF experiments COD and color retentions are also evaluated beside the main purpose caustic recovery. Considering the studies reported in the Literature in this area and also the caustic recovery systems used in practice, evaluation of NF is considered necessary. COD and color retentions by NF process beside caustic recovery are also evaluated. Bearing in mind real operating conditions of mercerization operations, temperature effect on these processes are also evaluated. After evaluating caustic recovery performance of membrane processes under laboratory conditions, a pilot plant study is also conducted. This study is carried out within the finishing unit of the mill by means of a ready pilot plant manufactured by a membrane company to recover caustic solution from the alkaline finishing effluents. Pilot plant studies were cooperated with the mill itself and finally a performance evaluation of this system is performed.

CHAPTER 2

BACKGROUND

2.1 TEXTILE INDUSTRY

The textile manufacturing is a comprehensive process which produces or process fiber, yarn or fabric to generate clothes, home furnishing and industrial goods. A typical textile processing flow chart is given in Figure 2.1. As briefly described in Chapter 1, in general, fibers are produced or received by textile mills. Then fibers converted into yarns. After that yarn is transformed into fabric or related products; and these produced materials are dyed and finished at various stages of production. With this approach it can be summarized that textile industry includes mainly the production of yarn, fabric, and finished goods [11].

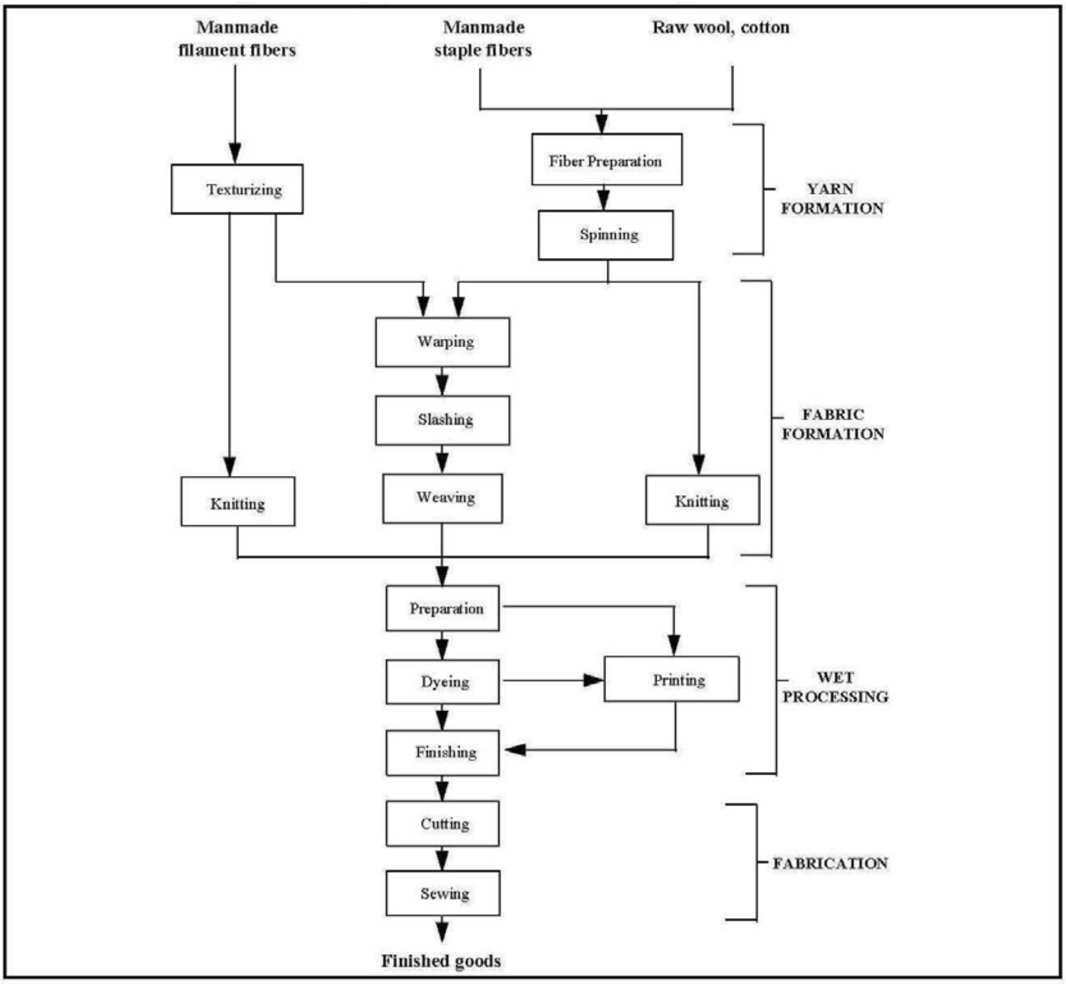


Figure 2.1 Typical textile processing flow chart

In the following sections, major steps of textile production are explained.

2.1.1 Yarn Formation

Textile fibers are bind together by grouping and twisting operations to transform into yarn. Most of the textile fibers are processed by spinning processes. However, the processes leading to spinning are depended on the type of fiber whether it is natural or manmade. Natural fibers are constituted by animal and plant fibers as cotton and wool etc. Before transforming into yarn, fibers should be passed from a series of preparation steps including opening, blending, carding, combing, and drafting. Manmade fibers may be processed into filament yarn or staple-length fibers (similar in length to natural fibers) so that they can be spun. Filament yarn may be used directly or following further shaping and texturizing [11].

2.1.2 Fabric Formation

Weaving and knitting are the two major methods in fabric manufacturing. Fabric formation processes for flat fabrics can be seen in Figure 2.2 [11].

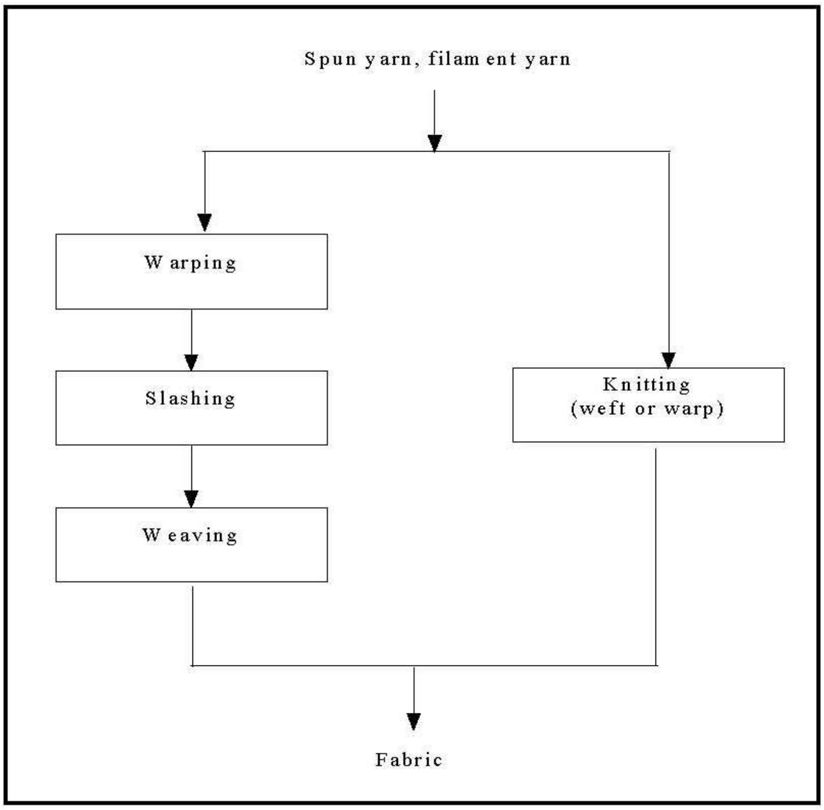


Figure 2.2 General fabric formation processes

Weaving is one of the most common processes used to create fibers. By weaving process, yarns are assembled together on a loom and a woven fabric is obtained. Lubricants and oils can be used to lubricate the loom.

Knitting is also a mechanical process and by this process yarns are knotted together with a series of needles. Mostly mineral oils are used to lubricate the needles and machinery [6].

2.1.3 Wet Processing

Wet processes are the essential processes which prepare woven and knit fabrics for being apparel or other finished goods. Therefore, these fabrics first should be passed from some wet processing stages. Wet processing improves fabrics in terms of appearance, durability, and serviceability. Wet processing mainly includes four stages, which are fabric preparation, dyeing, printing and finishing, for converting fabrics into finished consumers' goods. These steps can be followed by the Figure 2.3 [11].

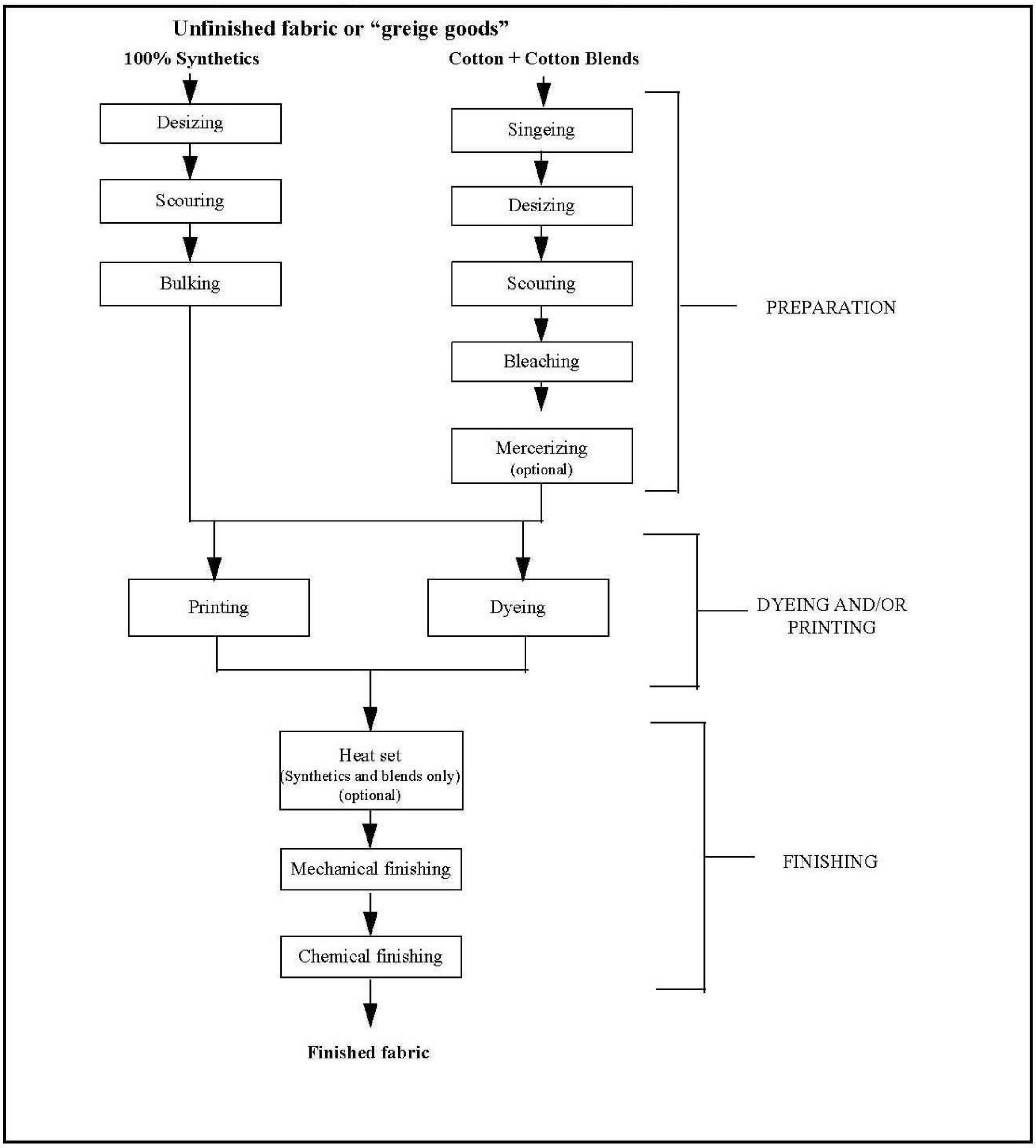


Figure 2.3 Typical wet processing steps for fabrics

2.1.3.1 Fabric Preparation

Pretreatment of fabric is mainly done for improving the wetting capacity and adsorption, dye take-up capacity, purity of the fabric, to lighten and for better material development [12]. According to the dyeing scheme, position of the pretreatment can change. Moreover, the techniques used for pretreatment is depended on the conditions of fabric, such as kind of fiber, form of fiber or amount of fiber to be treated [6].

There are mainly five pretreatment processes; i) singeing, ii) desizing, iii) scouring, iv) mercerizing, and v) bleaching. Singeing is a dry process which removes fiber ends protruding from yarns or fabrics. This removal is provided by passing the fibers over a flame or heated copper plates. If a smooth end product is desired, singeing is an essential process. Desizing is another preparation step used to remove previously applied sizing materials. Sizing should be applied before weaving and knitting operations. However, for preventing the sizing materials react with chemicals which are going to be applied in further processes, desizing is necessary. In order to remove impurities from fibers or yarns, a cleaning process named as Scouring is applied. Mainly alkaline solutions (sodium hydroxide), in some cases solvent solutions are used in this process. Bleaching is also a chemical pretreatment process to eliminate matters which effect whiteness adversely from fibers or yarns. By several bleaching agents such as hydrogen peroxide and sodium hypochlorite fibers or yarns are decolorized and prepared for dyeing or printing processes [11].

Mercerization is a kind of alkaline treatment applied for attaining a permanent shining and good handling of cotton in both pretreatment and finishing steps of production. Figure 2.4 shows in which production stages mercerizing is applied and its effects on fabric.

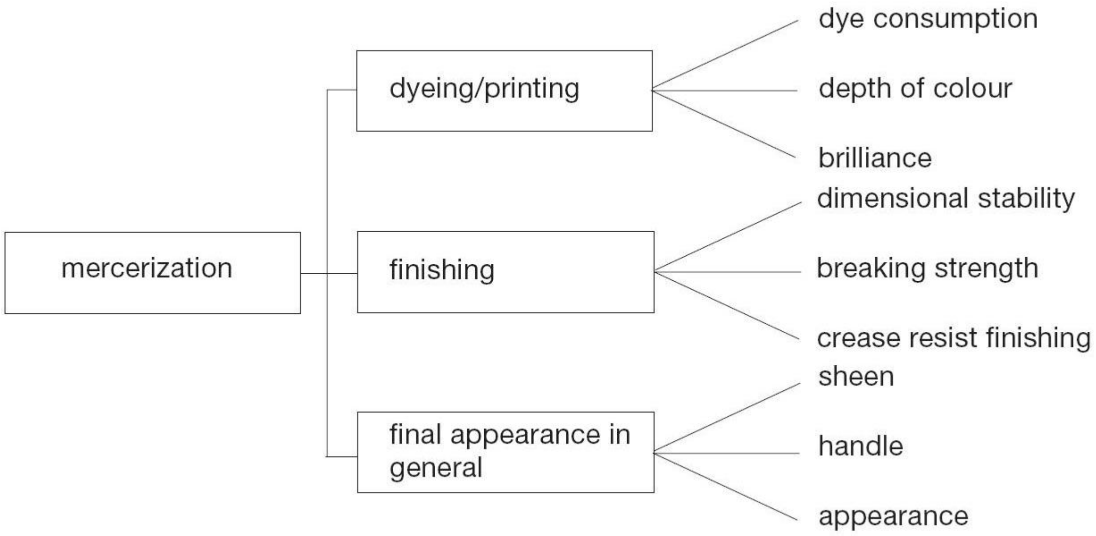


Figure 2.4 Effects of mercerization **[12]**

With mercerization “appearance is improved through increased luster, a deepening of the color and the production of a transparent look, the feel of the fabric is improved through a resulting soft hand and improved smoothness, and strength and elongation are also improved, along with the addition of good stretching ability” [13]. In Figure 2.5 and 2.6 effect of mercerization on fiber structure can be seen.

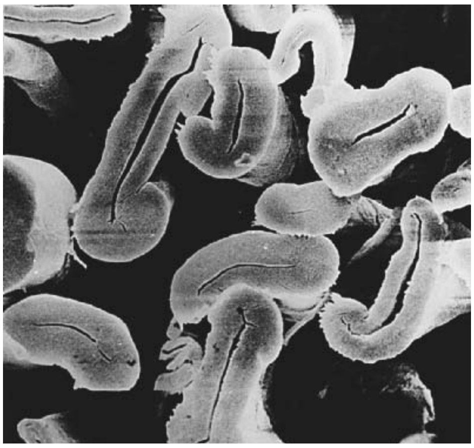


Figure 2.5 Electron microscope image of natural (untreated) cotton fibers in section magnified x 2200 **[12]**

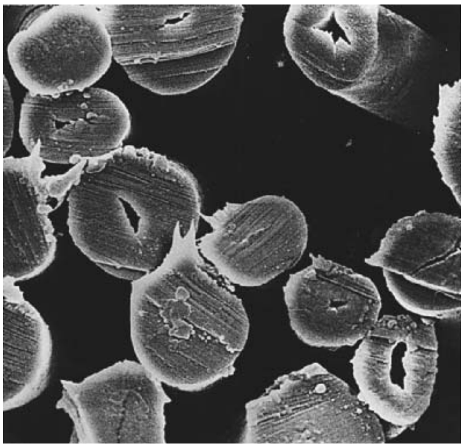


Figure 2.6 Electron microscope image of mercerized cotton fibers in section magnified x 2200 **[12]**

There are mainly two methods for mercerizing of cotton fibers. Conventionally mercerizing process is called as alkaline treatment because the fabric is treated with sodium hydroxide (NaOH) in other words "caustic" solution. Mercerization with caustic can be divided as mercerization with or without tension. Most commonly fabric is treated by 270 - 300 g/L caustic solution under tension for less than 1 min. In this common method temperature is tried to be kept between 5-18^{0}C, since the reaction between caustic and fiber is exothermic. Furthermore caustic mercerization can be applied at hot temperatures also. This method has an increasing usage area in the field of cotton mercerization. In both of these methods tension is required. However there is also another way for the application for caustic mercerization. In this way caustic is applied without tension at 20 – 30°C temperature within lower concentration caustic (145 – 190 g/L). This process is also called as slack mercerization, causticizing or caustification [6], [12]. There is also another mercerization technique with ammonia. Cotton in yarn or fabric formation is treated by anhydrous liquid ammonia in ammonia mercerizing. Although its results are similar to caustic mercerizing, it does not have a wide usage area [6].

In terms of chemical processes of mercerization following parameters are the most important ones;

- Caustic concentration
- Provenance
- Machinery and ambient temperature
- Time period of application
- Tension

Concentration of caustic is the most important performance determinant parameter of mercerization. There are optimum mercerization bath caustic soda concentrations depending on many variables. However concentration is the most difficult parameter that should be kept constant during operation. For example, when the mercerization in fabric pretreatment step is considered, the amount of caustic applied is very important for further dying process efficiency. Because caustic is one of the major factor in mechanism of fibers to absorb dye molecules. With the advantage of high affinity of caustic to fibers, it becomes more difficult to washout caustic and also dye after mercerization. Therefore to be able to provide effective dyeing, concentration of caustic is very important. Such that from studies at normal temperatures, the concentration of caustic solution should not be less than 24^0 Be (210 - 220 g/L) to guarantee complete mercerization [13].

2.1.3.2 Dyeing

Dyeing is an operation for coloring the textile material at various stages of production by applying dye using a wide variety of dyestuff, methods and equipments. As continuous and batch processes dyeing can be performed in two ways. In batch dyeing, textile and an amount of dye is leaved in a machine until equilibrium is reached. According to the type of fiber and affinity of dye to the fiber, dye molecules enter to the fiber over a period of time. Generally this process is accelerated by auxiliary chemicals and batch conditions. Also, by heat and chemicals fixation of dye molecules is enhanced. Finally, washing stage is applied to remove unfixed dye and chemicals [11].

Continuous dyeing is also a padding application but includes a moving system which is arranged according to the type of dyeing. Dye application and dye fixation is provided by chemicals and heat while the fabric is rolled. Then, it usually ends with washing stages. In continuous dyeing, there is more chance of the dye molecules to be fixed on the textile material than batch dyeing. Knowing that which dyeing process requires how much dye is important in deciding the effectiveness of the system in terms of energy and chemical savings and pollution prevention [11].

2.1.3.3 Printing

In printing, the purpose is the same with dyeing, but it differs from dyeing with its local coloring application. Printing is provided by means of machines with variety of techniques. There are four basic steps in textile printing; which are color paste preparation; dispersion of dye or pigment in a printing pasta, printing; application of dye or pigment to the textile, fixation; drying of the fiber with steam or hot air, and finally after treatment operation; includes washing and drying of the fabric [6].

2.1.3.4 Finishing

Finishing is the final step in the textile production. It has the capacity of adding some important features to the textile considering the end-use purposes. There are two types of finishing processes which are mechanical and chemical finishing. Physical treatments such as brushing or ironing are called as mechanical finishing and help to increase the luster and feel of textiles [11]. Chemical treatments such as easy-care, water-repellent, softening and flame retardant can bring in variety of properties. Although finishing in general takes place after dyeing process, it can change with production. While some finishing processes applied before dyeing, some can take place within a dyeing process. Generally in many of chemical finishing applications, the process is ended with drying, curing and cooling steps [6].

As discussed before, mercerization is one of the most frequently applied chemical finishing processes. By means of mercerization at this stage of production, fabric has been exposed to caustic second time. However purpose of mercerization at the finishing stage is generally to provide some good handle properties. Since the yarn or fabric at the finishing stage of production has been already processed by the various pretreatment and treatment processes, the textile which is going to be caustified is different. Therefore application method may differ from other mercerizing operations.

2.2 TEXTILE WASTEWATERS

There are thousands of textile plants in the World which apply wet processes and discharge large quantities of wastewater to the environment. These wastewaters are either treated on site, or in municipal wastewater treatment plants. In some cases, these wastewaters are discharged without treatment. The major pollutant parameters in the textile wastewaters are solids, biochemical oxygen demand (BOD), chemical oxygen demand (COD), nitrogen and phosphate, temperature, toxic chemicals such as phenols, heavy metals, pH, alkalinity and acidity, oils and grease, sulfides and coliform bacteria [14].

In the proceeding sections, wastewater generation in different textile manufacturing stages is discussed.

2.2.1 Sources of Wastewater in Textile Industry

Weaving, dyeing, printing and finishing are the major textile production steps and each of these produces waste in different characteristics. Although the process effluents are the major waste sources, generalization of these wastes is highly difficult. Because textile wastes are highly dependent on the processes and these processes are frequently changing according to new demands [14].

Textile wastewaters can be described as colored, having high BOD and COD values with high solids content and also as highly alkaline waters at high temperatures. These are generated from mainly rinsing operations after production processes. In textile processes 85% of the dyes and most of the auxiliary chemicals are removed by the washing stages [15]. They include both fiber origin and processing chemicals origin pollutants. Therefore, type of fibers, finishing operations, process chemicals and recycle procedures are the main factor defines characteristics and amount of wastewater. This makes the characterization and generalization of wastewaters difficult for textile effluents [14]. Before giving detailed information about major sources of textile wastewaters, general characteristics of textile effluents can be summarized in Table 2.1.

Bleaching process is one of the major processes that generate effluents including dissolved solids as inorganic and organics at small amounts. Cotton bleaching can result some suspended solids in the effluent [14]. Furthermore, bleaching agents such as caustic soda, hydrogen peroxide and sodium hypochlorite are the responsible for highly alkaline effluents from this process.

Table 2.1 General characteristics of textile effluents **[16]**

Process	**Composition**	**Nature**
Sizing	starch, waxes, carboxymethyl cellulose, polyvinyl alcohol	High in BOD and COD
Desizing	starch, glucose, carboxymethyl cellulose, polyvinyl alcohol, fats and waxes	high BOD, COD, suspended solids, dissolved solids
Scouring	caustic soda, waxes, grease, soda ash, sodium silicate, fibres, surfactants, sodium phosphate	dark coloured, high pH, high COD, dissolved solids
Bleaching	hypochlorite, chlorine, caustic soda, hydrogen peroxide, acids, surfactants, sodium silicate, sodium phosphate	alkaline, suspended solids
Mercerizing	caustic soda	high pH, low COD, high dissolved solids
Dyeing	various dyes, mordants, reducing agents, acetic acid, soap	strongly coloured, high COD, dissolved solids, low suspended solids, heavy metals
Printing	pastes, starch, gums, oil, mordants, acids, soaps	highly-coloured, high COD, oily appearance, suspended solids
Finishing	inorganic salts, toxic compounds	slightly alkaline, low BOD

Desizing is another major waste generating process that produces both dissolved and suspended solids including effluent also with oil and grease content. With this contribution, desizing constitutes nearly half of the total solid load in the total textile waste stream. As a treatment approach desizing wastewaters generally goes under a separation process of sizing material from the effluent in a kind of recycle system. With such a system, sizing material is extracted from rinsing water of the desizing process, so that it can be reused. A hyperfiltration procedure can be applied for the separation process. So that, undissolved part of the sizing material could be departed from the degraded portion for concentrating and finally reusing it [14].

Dyeing relatively has a higher pollution load capacity in terms of both visible and invisible pollutant content according to other production processes. In dyeing processes, used various additives and complexing agents beside dyestuff material under alkaline conditions at high temperatures generate high amounts of organically and inorganically polluted waste streams. Dye preparation kitchen is one of the emission sources of dyeing. With cleaning process of dye preparation tanks, a discontinuous and low-concentrated wastewater is generated. Batch dyeing results both continuous and discontinuous waste loads but at considerable concentrations. Discontinuous waste load is generated during washing of dyeing tanks. However, the rinsing operations after dyeing application produce continuous and also concentrated effluents. Continuous dyeing has a lower pollution capacity than discontinuous. Waste generation occurs when the dye baths are being drained or rinsing tanks are being washed [6].

As discussed before there are two types of finishing methods which are mechanical and chemical finishing. For mechanical finishing waste water emission is negligible. However, chemical finishing has a substantial contribution on waste water characteristic of textile mill. Like dyeing processes, there are different effects of continuous and discontinuous finishing. Since there is not any washing application in continuous finishing processes, the only chance of contribution to water pollution is via system loses and machine cleanings. As predicted, the amount of waste is too small, but the concentrations reach high values. Moreover, some of these wastes can be non-biodegradable and toxic. According to the processes and chemicals applied, type of pollutant differs. Some of the important pollutants produced in finishing processes are as follows;

- ethylene urea and melamine derivatives in their "not cross-linked form" (cross-linking agents in easy-care finishes)
- organo-phosphorous and polybrominated organic compounds (flame retardant agents)
- polysiloxanes and derivatives (softening agents)
- alkyphosphates and alkyletherphosphates (antistatic agents)
- fluorochemical repellents [6].

Discontinuous or batch finishing is generally applied for yarn and wool carpet industry. Pollution load is highly interrelated with ability of fiber to absorb finishing chemicals. Because remaining solution after the batch process will be discharged and the fraction of chemical which is not used in the process will become a pollutant. The main processes which contribute to pollution are application of mothproofing agents (emissions of biocides) and the low level of exhaustion of softeners (emissions of poorly biodegradable substances) [6].

Caustic soda is the most frequently used scouring chemical for cotton fibers. Moreover surfactant and sodium phosphate residues with also cotton waxes can be found in scouring waste effluents. These make scouring effluent highly alkaline and colored with high dissolved solids, oil and grease content. The cotton impurities are responsible for a small amount of suspended solids within a biodegradable structure.

Although mercerization can be called as another step of finishing processes, it should be evaluated separately in terms of wastewater characteristics. Caustic alkali is the main chemical that occurs in mercerization waste streams. This chemical is responsible for the high pH values (12-13). Beside this, because of strong alkali and high temperature, fiber ceases solids and dye absorbed in previous processes results in high dissolved solid content in the waste stream. Although these materials are not in a structure which contributes to BOD load much [14], produced strongly alkaline and colored effluent constitutes important environmental problems and also affects further treatment mechanisms negatively. Moreover, because of high alkalinities wastewaters including mercerizing effluents necessitate neutralization applications due to discharge regulations.

2.2.2 Textile Wastewater Treatment

Substances which are critical and hazardous for the environment are defined by the regulations and strategies are proposed to minimize these substances. However, these proposals have to be integrated into processes and production steps of textile. Figure 2.7 explains the general treatment approach for a textile plant. It shows the formation steps for a fabric to become a textile product. By the way, it gives an idea about precautions and activities to prevent pollution. Legal prohibitions or cost saving purposes of chemicals defines the type of precaution. Beside that the treatment options can change according to the type of the product [17].

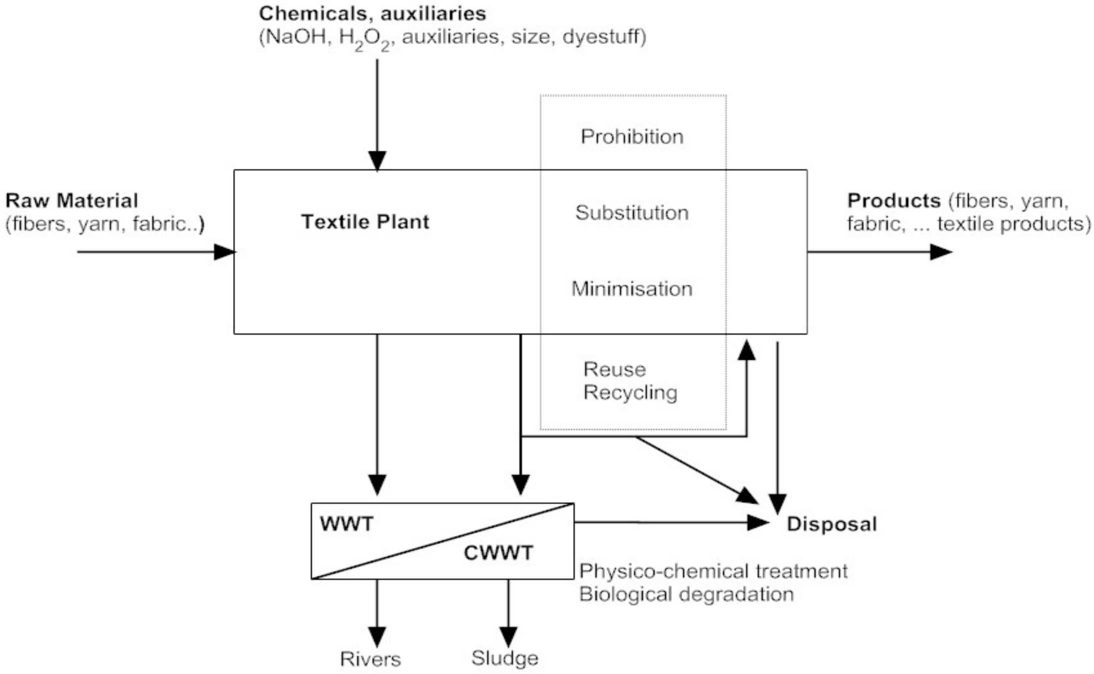


Figure 2.5 Flow structure of a textile plant with treatment options **[17]**

General approaches for the management of textile wastes can be grouped according to sources and production stages of wastes. These management approaches are;

- Replacement and minimization
- Optimization of Processes
- Separation and Recycling
- Final Treatment.

In the proceeding sections, the above-mentioned approaches are described in detail.

2.2.2.1 Replacement and Minimization

Replacement and minimization can be taken as a primary treatment option for hazardous chemicals and substances used in the textile industry. As a result hazardous chemicals can be substituted with less hazardous ones, for example [17];

- Man-made fiber preparation agents with improved environmental performance,
- Mineral oils substitution for wool and knitted fabrics,
- Selection of sizing agents with improved environmental performance,
- Minimizing sizing agent add-on by pre-wetting the warp yarns,
- Use of compact spinning like techniques allow reduced load of sizing agents,
- Minimizing residues of organochlorine, organophosphate and synthetic pyrethroid ectoparasiticides in raw material by substitution,
- Selection of textile dyes and auxiliaries to their waste water relevance,
- Substitution for hazardous surfactants,
- Selection of biodegradable/bioeliminable complexing agents in pretreatment and dyeing processes,
- Selection of antifoaming agents with improved environmental performance [6].

Applying these replacement and minimization options not only decreases chemical load of the total wastewater but also makes easier the further treatment applications.

2.2.2.2 Optimization of Processes

Optimization applications during the production steps are another treatment option for textile wastes. It is more economical and beneficial for the final treatment [17]. General processes for optimization can be given as follows;

- Chemical system evaluations
  - Solution preparation system evaluations
  - Water pre-treatment studies
- Auxiliary process optimization
  - Heat exchanger temperature optimization
  - Hot water/steam system analysis
  - Compressed air analysis
- Product flow optimization
- Process simplification
- Energy conservation audits
  - Thermal efficiency of process piping and vessels
  - Plant-wide energy use profiling
  - Water reuse studies [18]

2.2.2.3 Separation and Recycling

Separation and recycling is the final option before treatment application. Although textile industry is one of the most water and chemical consumer, it also has the highest capacity for intensive water recycling approaches and chemical recovery options [19]. Both limits about water resources and also regulations make recycling process essential for industries [20].

During the processes like dyeing, printing or finishing variant chemical is added to the textile material. Types and amount of dyes, detergents, sulphide, compounds, solvents, heavy metals and inorganic salts changes drastically composition of wastewater [19]. High amount of these chemicals are released at the rinsing stages and conveyed to the general waste treatment plant. Activated sludge system is commonly applied for textile wastewaters. However effluent quality from these plants does not meet reuse criterion. Moreover, there is a risk that high amount of persistent pollutants remains untreated with biological systems [21]. As a result, any kind of separation and recycling will not only provide conservation of resources, but it will also improve performance of further treatment units [22]. Some examples of separation and recycling are as follows;

Waters that do not expose to pollution can be directly reused; for example, system cooling waters;

- countercurrent washing of textile; for example, rinsing processes,
- treatment of wastewater from one source for reuse in another process,
- recycling of materials, by-products or energy in the same process,
- total wastewater treatment and its reuse [1].

2.2.2.4 Final Treatment

Whatever intermediate process is applied, remaining wastewater has to be discharged to a receiving body. Therefore, in order to obey the discharge limitations final wastewater treatment is applied. There are different final treatment options for textile wastewaters. With detergents, enzymes, dyes, acids, sodas and salts contents these wastes are highly variable in strength and quantity depending on the mill [23]. As aerobic or anaerobic, biological treatment is the most applied treatment process in textile industry. Moreover in order to increase efficiency physical and chemical treatments such as adjustment of pH, temperature, sedimentation, and flocculation are applied [17]. General textile wastewater treatment methods and their efficiencies are summarized Table 2.2.

Table 2.2 Evaluation of Various Technologies for the Treatment of Textile Effluents **[22]**

Process	Stage	Performance	Limitations
Fenton oxidation	Pre-treatment	Full decolorization; low capital and running costs	
Electrolysis	Pre-treatment	Full decolorization; cheap	Foaming and electrode lifespan
Foam flotation	Pre-treatment	Removes 90% color and 40% COD; cheap, compact	
Membrane Filtration	Main-or post-treatment	High performance; reuse of water, salts, and heat	Handling and disposal of concentrate stream
Biodegradation			
- Activated sludge	Main treatment	Removes bulk COD, N	High residual COD, N, color, surfactants
- Sequential anaerobic aerobic	Main treatment	Better removal of COD, color, and toxicants	High residual color and COD
- Fixed-bed	Main treatment	Better removal of COD, color	
Coagulation Flocculation	Pre, main or post treatment	Full decolorization; water reuse	Not always effective; sludge disposal
Fungi/H_2O_2	Main treatment	Full decolorization	
O_3	Post-treatment	Full decolorization; water reuse	Expensive; aldehydes formed
Sorption (carbon, clay, biomass)	Pre-or post treatment	New sorbents are effective and cheap; water reuse	High disposal or regeneration costs
Photocatalysis	Post-treatment	Near-complete color removal; detoxication	Only as final polishing step

Among these treatment alternatives membrane processes that are used in this thesis are explained in the following section.

2.3 MEMBRANE PROCESSES

Membrane processes have been used in treatment of textile wastewaters for a long time. They have proven their applicability for the variable and strongly polluted textile industry effluents. Moreover, membrane processes are being applied for recovery purposes in textile industry. Currently, there are many applications of membrane systems for chemical and water recoveries such as size, caustic or indigo dye recovery [7].

Choosing the appropriate membrane system and technology for the specific wastewater is an important issue. However, if the previous studies about textile industry are investigated, generally a kind of pretreatment method is applied before membrane unit. Beside that pretreatment is necessary and also more efficient with respect to chemical cleaning for preventing and detaining fouling mechanism in further membrane operations [24]. By pretreatment performance of the membrane is improved and less operational costs are achieved. Especially due to high solids content of the textile wastewaters membrane fouling is unavoidable if pretreatment is not applied [25]. Therefore to prevent membrane fouling and also deterioration pretreatment is necessary [8], [26].

Membrane is a kind of tool for separation of two phases or chemicals in a selective attitude. Although membranes are thought to be a newer separation method, it has a wide application area with continuing improvements. Currently there are variable membranes with different structures such as homogenous or heterogeneous, symmetric or asymmetric, solid or liquid, positive, negative or neutral charge. With this discrepancy transport phenomenon within these membranes can be affected with variety of conditions such as pressure or temperature gradient or electrical field or concentration [27].

Today water sources are more limited and valuable. This makes industries the highest raw water consumers use their sources much more efficiently. Current investigations show that treating wastewaters generated from processes for its reuse instead discharging to the waste stream is the best option for industries. Pressure driven membrane processes are more satisfying than the classical techniques for reuse and recovery purposes [28].

2.3.1 Principles of Membrane Processes

Membrane processes can be considered as segregation of a stream into permeate which is the portion of this stream that can pass through the semi-permeable membrane structure and retentate which involves part of the stream rejected [29]. This separation process needs to a kind of driving force. It could be pressure, concentration or temperature difference in the system. Performance of the process is highly related with this force to some extent. Moreover, characteristic of the membranes are also a significant factor in process efficiency. When stating the type of the process, structure or material of the membrane is highly determinant. In some cases electrical potential difference can be a driving force, when the transportation through the membrane occurs by charged particles. In Table 2.3 classification of different membrane processes is summarized with respect to their driving forces [29].

Table 2.3 Classification of membrane processes according to their driving forces **[29]**

Pressure Difference	Concentration (activity) Difference	Temperature Difference	Electrical Potential Difference
Microfiltration Ultrafiltration Nanofiltration Reverse Osmosis Piezodialysis	Pervaporation Gas Separation Vapour Permeation Dialysis Diffusion Dialysis Carrier-Mediated Transport	Thermo-Osmosis Membrane Distillation	Electrodialysis Electro-Osmosis Membrane Electrolysis

2.3.2 Pressure Driven Membrane Processes

The common feature of all pressure driven membranes is the pressure difference that is used to passing solvent through the membrane to differentiate it into permeate and retantate or concentrate. In various pressure driven membrane processes purpose is both concentrating and purifying a dilute solution. During this filtration process retained soluble or insoluble content is depended on the membrane properties which are defined according to solute characteristics. For example particle size or chemical properties of solute states the required membrane pore size.

Pressure driven membranes can be classified as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) according to characteristics of the membrane, size and charge of the retained particles and pressure exerted on the membrane [29]. When we compare these processes pore size of the membrane decreases from ultrafiltration to reverse osmosis. As a result size of the particle retained by the membrane gets smaller also. However, as the pore size decreases, required pressure gradient increases because of higher resistances. As discussed before structure of the pressure driven membrane shows discrepancies such as most microfiltration membranes are in asymmetric structure build up with a top layer thickness in the order of 1 µm. Whereas ultrafiltration, nanofiltration and reverse osmosis membranes have an asymmetric as well with a thin, relatively dense toplayer (0.1 – 1.0 µm) supported by a porous substructure (≈ 50-150 µm) [29]. In Table 2.4, comparison of the pressure driven membranes is summarized.

Table 2.4 Comparison of various pressure driven membrane processes **[30]**

Microfiltration	Ultrafiltration	Nanofiltration/ Reverse Osmosis
separation of particles	separation of macromolecules (bacteria, yeasts)	separation of low MW solutes (salts, glucose, lactose, micropollutents)
osmotic pressure negligible	osmotic pressure negligible	osmotic pressure high (≈ 1-25 bar)
applied pressure low (<2 bar)	applied pressure low (≈ 1-10 bar)	applied pressure high (≈ 10-60 bar)
symmetric or asymmetric structure	asymmetric structure	asymmetric structure
thickness of separating layer symmetric ≈ 10-150 μm asymmetric ≈ 1 μm	thickness of actual separating layer ≈ 0.1-1.0 μm	thickness of actual separating layer ≈ 0.1-1.0 μm
separation based on particle size	separation based on particle size	separation based on differences in solubility and diffusivity

Due to adsorption, pore blocking, precipitation and cake formation mechanisms accumulation of retained materials on the membrane surface becomes irreversible [29]. In which mechanism fouling will occur is highly depended on the type of the wastewater. Membrane fouling during the filtration of textile effluent is caused by the adsorption of organic compounds present in the wastewater [5]. This irreversible deformation of the membrane induces membrane fouling with a continuous flux decline.

In order to have better process designs, amount of flux decline due to fouling mechanisms should be evaluated. However, fouling depends on variety of chemical and physical parameters such as concentration, temperature, pH, ionic strength and specific interactions. Therefore, fouling mechanism is not an easily definable issue.

Concentration polarization is another phenomena cause flux decline during membrane processes. It occurs due to higher concentrations at the membrane surface due to rejected material accumulation than bulk solution [31].

2.3.2.1 Microfiltration

MF is a low-pressure cross-flow membrane process which is for separating colloidal and suspended particles in range of 0.05-10 microns. It is generally used for clarification purposes and similar to conventional coarse filtration [32]. In terms of process efficiency; high porosity and narrow pore size distribution for microfiltration membranes are better.

Although MF membranes can be prepared from many types of materials such as polymers or inorganic materials; they are generally made from a thin polymer film with a uniform pore size and a high pore density of approximately 80% [33]. There are two types of synthetic polymeric membranes as hydrophobic and hydrophilic polymeric membranes. Some of the hydrophobic and hydrophilic membranes can be seen in Table 2.5. Furthermore, pore size in MF membranes can be controlled better by inorganic membranes which show high chemical and thermal resistance [29].

Table 2.5 Two classes of polymeric membranes

Hydrophobic Polymeric Membranes	Hydrophilic Polymeric Membranes
Polytetrafluoroethylene (PTFE, teflon)	Cellulose esters
Poly(vinylidene fluoride) (PVDF)	Polycarbonate (PC)
Polypropylene (PP)	Polysulfone/poly(ether sulfone) (PSf/PES)
Polyethylene (PE)	Polyimide/poly(ether imide) (PI/PEI)
	(aliphatic) polyamide (PA)
	Polyetheretherketone (PEEK)

Flux decline is a common problem for MF applications mainly due to concentration polarization and fouling mechanisms. In order to decrease the flux decline, selection of membrane process is important. There are two types of microfiltration application which are dead-end and cross-flow filtration. Dead-end operation is a more common microfiltration application. In this process feed flow is perpendicular to the membrane surface. This creates a filter cake on the membrane surface due to accumulation of particles with time. As the thickness of this cake layer increases, rate of the permeate flux decreases. This situation necessitates cleaning or replacement of the membrane. In cross-flow operation, forming of cake layer is reduced to some extent. In this process feed flows parallel to the membrane surface. By means of driving force filtered particles forms permeate. Meanwhile species which cannot pass through the membrane surface forms retantate stream of the process. This part of the stream can also be further treated. Moreover adsorption on the membrane surface is an important problem in terms of fouling. Therefore selection of membrane material gets more important. For example hydrophobic membranes have more chance of fouling due to their non-wettability property. As a result flux decline and fouling in microfiltration processes cannot be exactly prevented. This makes a chemical cleaning unavoidable.

In many industrial applications, for large particle (> 0.1μm) filtration requirements microfiltration is preferred. Today, dead-end operation is the most widely applied technique. For large scale industries cross-flow microfiltration systems are used [29].

2.3.2.2 Ultrafiltration

UF constitutes the membrane process between MF and NF. UF is used to separate lower molecular weight particles from the macromolecules with a membrane pore size of 0.001 – 0.5 µm. Although MF and UF have the same filtration principle, UF differs from microfiltration with its structure. UF membranes have an asymmetric structure with a much denser top layer. This structure results a higher hydrodynamic resistance. As microfiltration, polymeric materials are preferred more for UF membranes. UF membranes are chosen in variety of industry for the separation of high molecular components from low molecular ones. Some of UF membrane materials are listed below.

- Polysulfone/poly(ether sulfone)/sulfonated polysulfone
- Poly(vinylidene fluoride)
- Polyacrylonitrile (and related block-copolymers)
- Cellulosics (e.g. cellulose acetate)
- Polyimide/poly(ether imide)
- Aliphatic polyamides
- Polyetheretherketone [29]

When selecting suitable UF membrane, cut-off becomes an important parameter. Cut-off is the molecular weight which is 90% rejected by the membrane. However cut off parameter as alone is not enough to determine the separation characteristics of membrane. Shape and flexibility of the molecules in the solute and their interaction with membrane material should be taken into consideration. Concentration polarization and fouling is also important performance indicator for UF process. Therefore chemical and thermal resistances of the membrane materials become a serious matter. Furthermore physical conditions such as membrane process system design affect the fouling event [29].

2.3.2.3 Reverse Osmosis and Nanofiltration

NF and RO are basically similar processes by which low molecular solutes such as inorganic or small organic solutes are separated from solvents. Much denser and hydrologically resistant membranes are used. This structure requires more pressure gradients. The pressure used in the reverse osmosis range from 20 to 100 bars and in NF from about 10 to 20 bars [29]. In NF membrane material is much more related to process efficiency than MF and UF.

Generally NF membranes have MWCO between 200 and 1000. Whereas reverse osmosis membranes have denser MWCO values about 100. Despite this, both of these semi-permeable membranes do not have definable pores [34]. Although they are both pressure driven systems, reverse osmosis has a better efficiency in terms of separation of dissolved substances.

2.3.3 Polarization Phenomena and Membrane Fouling

Membrane performance is the primary factor for the separation process efficiency. Several mechanisms such as adsorption, gel layer formation or plugging of the pores can affect membrane performance. Concentration polarization and fouling phenomena are the most prevailing determinants of this performance. In order proceed the system in an efficient and economic way, measures should be taken. However it is better to evaluate concentration polarization and fouling separately [29].

2.3.3.1 Concentration Polarization in Pressure Driven Processes

From the nature of the filtration process, while permeable part of the solvent passes through the membrane another stream permeate starts to be formed. Concentration of this accumulation increases as the process continues. As a result concentration polarization phenomenon which is the result of convection and back diffusion from the membrane surface is constituted [30].

Due to concentration polarization the retention could be lower than it is expected. By the way in the presence of macromolecular particles, concentration polarization could have a positive effect on retention of low molecular solutes. Furthermore the negative effect of polarization on the flux is unavoidable due to additional resistance to the driving force [29].

2.4 CAUSTIC RECOVERY FROM MERCERIZING WASTEWATERS

In textile production as mentioned before various chemicals and additives are used to process fibers for improving process efficiency or providing some features to the fibers. Basic chemicals used in textile processing are alkali, acids, salts and solvents [35]. There are various techniques used for the separation of these valuable materials from wastewater by membrane filtration, chemical precipitation, and adsorption by activated carbon and evaporation. Among these membrane applications are the only one separates impurities without any chemical addition [9]. There are many examples of recovery and reuse applications of chemicals due to environmental and economical reasons.

Porter has conducted a study about the recovery of polyvinyl alcohol (PVA) and hot water from textile wastewater [15]. In this study, membrane based methods to recover PVA which is one of the sizing process chemicals used in high amounts were examined. Moreover, it has been emphasized that by recovering PVA, due to the cleaning affect of membrane operation, hot process wastewater effluent will be also reusable.

Eun Jong Son has implemented two different studies about recovery of caustic soda from mercerizing of cotton [9] and polyester fabrics [10]. In both of the studies NF process with SelRO MPT-34 membrane module of Koch Membrane Company has been used to separate caustic from wastewater. Quality of feed and permeate, flux behavior and caustic recovery were the main performance evaluation parameters of these studies. In conclusion, although the systems used for membrane operations differ in capacities, they have achieved caustic recoveries between 86 – 96 %.

Schlesinger has implemented a study about the evaluation of different NF and UF membranes for the separation of hemicelluloses from the viscose fiber production process liquors [36]. All of these membranes used to evaluate recovery potential are polyethersulfone based membranes. Since the wastewater containing hemicelluloses is highly alkaline (200 g/L NaOH) and high in temperature, membranes used in the study were chosen as stable to these difficult operating conditions. In conclusion, it has been stated that all the membranes tested have achieved successful separation of hemicelluloses and caustic.

Caustic is one of the most frequently used chemical in the textile industry for dyeing and especially finishing purposes. As discussed before due to harmful effects when disposed to environment and economical reasons caustic should be recovered. Caustic recovery becomes economic when caustic use exceeds 11,300 tons per year of 100% cotton goods or 22,700 tons per year of 50/50 cotton polyester fabrics [37]. Therefore for the big textile mills which apply wet processes and especially mercerization caustic recovery is highly recommended.

There are two types of alkali recovery techniques;

- Caustic recovery by evaporation
- Caustic recovery by membrane technology

Rinsing waters from washing stages of caustification process can be recovered by evaporation technique. Caustic in rinsing water does not have high concentrations (40 - 50 g NaOH/L) to be reused in the process. With a multi staged evaporation technique weak caustic can be concentrated up to reusable values. After concentrating caustic soda it should be purified. Depending on the process from which caustic is going to be recovered by simple sedimentation or oxidation/flotation with injection of hydrogen peroxide purification can be provided. In Figure 2.5 an example of a three stage evaporation process can be seen [6].

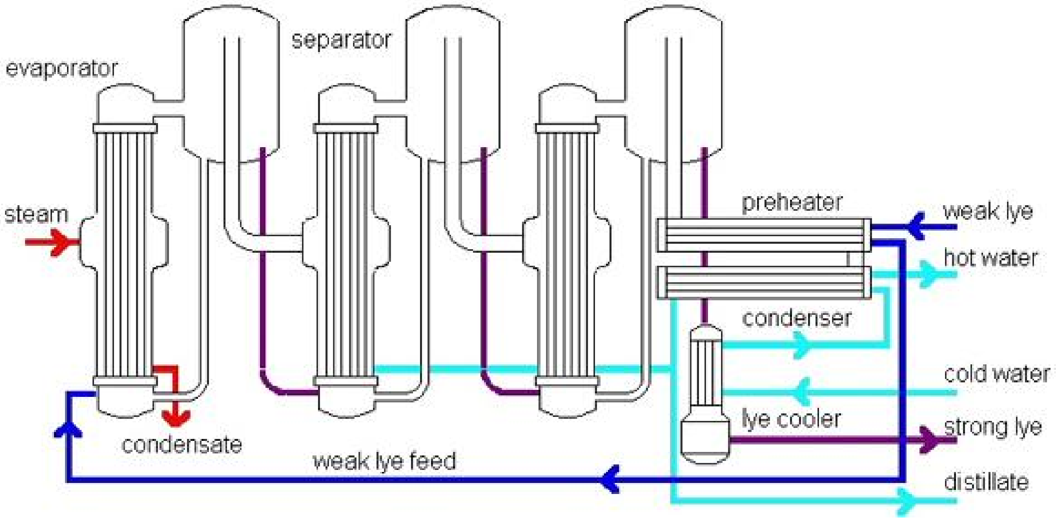


Figure 2.6 Representation of a 3 stage evaporation system

Evaporation method has the disability of recovering contaminated caustic solutions. Although there are various techniques for recovery of water and chemicals, membrane filtration has the capability of recovering raw materials by eliminating impurities without need of additional chemicals [9]. In salt and alkali recovery area NF systems are successful for separation of water, sodium hydroxide and monovalent ions from large organic compounds [10]. Membrane systems have an increasing tendency to be applied in textile alkaline recovery purposes. The same waste stream with evaporation is applied to membrane system. There are various membrane systems which provide 100% caustic recovery. After application of membrane filtration, pure and concentrated caustic soda is obtained. However recovered concentration is not enough to be reused in the process again. Therefore membrane systems are generally supported by a following evaporation unit to increase concentration of the caustic soda up to reusable values. However, due to nature of the process and extreme corrosiveness of caustic soda solutions makes membrane operation more difficult [36]. As a result resistant membranes should be preferred for caustic recovery purposes.

CHAPTER 3

MATERIALS AND METHODS

3.1 Experimental Methods

3.1.1 Characterization of the Wastewater

Experimental studies started with the characterization of the caustic wastewater that originates from mercerization processes. As indicated before, there are a number of different mercerizing lines in the plant, of which two most commonly used are Over-Dye and Pad-Steam. Throughout the study, several samples were taken from Flat-Optic process of these two caustic discharging mercerizing lines of the mill to characterize caustic mercerizing effluents. Commons schematic representation of these mercerizing lines is given in Figure 3.1.

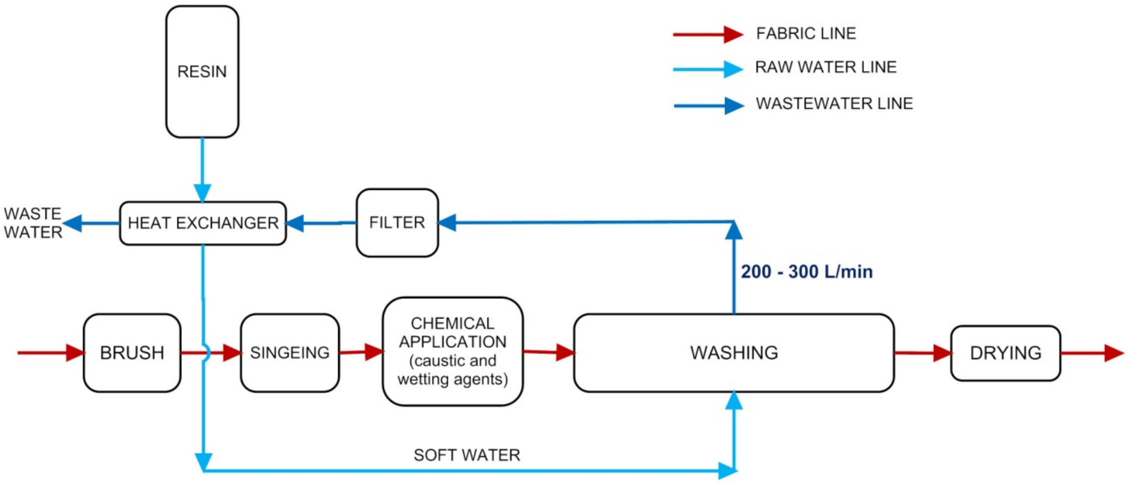


Figure 3.1 General flow diagram of a denim mercerizing line

Caustic effluents are generated from each post-rinsing or washing tanks and they together form the total wastewater of that mercerizing processing line. Therefore, sampling was done for both rinsing tanks effluents separately and for the total discharge channel. At the inlet of discharge channel, the plant uses a coarse drum filter so the sampling was done on the effluent from this filtration stage. These samples collected were analyzed in terms of some general water quality parameters such as pH, conductivity, TSS, TDS, COD, color, alkalinity, turbidity and NaOH content. Based on the results of these characterization studies, wastewater discharge locations of mercerizing units where further treatability studies will be conducted have been defined.

3.1.2 Pretreatment Experiments

Within the context of pretreatment evaluations flocculation, centrifugation and MF processes were applied. In flocculation, 500 mL glass beakers were employed with a conventional jar-test apparatus (Aqua Lytic, Germany). In these batch tests, wastewater samples taken from the first two rinsing tank effluents of the mercerizing machinery were mixed and placed in jars and mixed slowly at 30 rpm for 45 min at room temperature (20±2^{0}C).

Considering the results obtained from flocculation experiments, the application of centrifugation as pretreatment was evaluated. Caustic wastewater samples taken from the first two rinsing tank effluents of the mercerizing machinery were mixed and centrifuged at 2500 rpm for 30 min by a Hettich Universal, USA centrifugation device. In both of these pretreatment alternatives, settleability of highly alkaline mercerizing wastewaters were experienced.

MF experiments were applied at two stages. At the first stage, a dead-end conventional vacuum filtration unit operated at 25 in Hg vacuum level was used. In order to evaluate filterability of the wastewater, different pore sized; 1.2, 8 and 20-25 μm cellulose acetate microfiltration membranes were applied at room temperature (20±2^{0}C) and the wastewater samples taken from the first two rinsing tank effluents of the mercerizing machinery were mixed and utilized. At the second stage of the MF studies, a computer based controlled filtration unit was used for filtering the same wastewater sample. The system was also a dead-end operated unit as schematically represented in Figure 3.2.

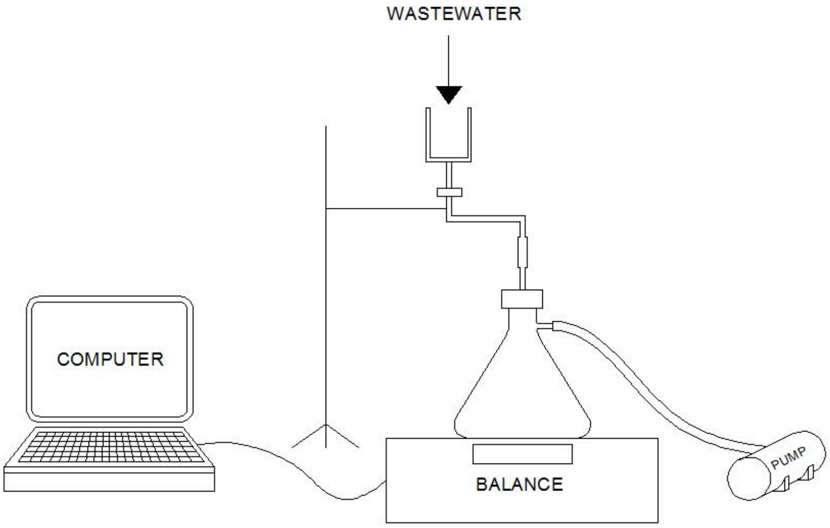


Figure 3.2 Computerized dead-end MF unit

In addition to the MF membranes given above, by taking the wastewater characteristics into consideration, alternative MF membranes which are much more durable to difficult alkaline and thermal conditions were evaluated. For this purpose 5 and 10 µm pore sized PTFE and PVDF membranes were applied at room temperature (18±2°C). With further researches PES found as the most suitable membrane material for caustic recovery purposes. After that 5 and 10 µm pore sized PES membranes were obtained and their performances were tested at the same system and conditions. All of the used membranes used throughout the study and their specifications are summarized below in Table 3.1.

Table 3.1 General specifications of the MF membranes used

Filter	Material	Pore Size (μm)	Effective Membrane Area (m^2)	Maximum Operating Temperature (^0C)
Whatman 41	Cellulose Acetate	20-25	$1.7x10^{-3}$	-
SCWP04700	Nitrocellulose	8	$1.7x10^{-3}$	75
RAWP04700	Nitrocellulose	1.2	$1.7x10^{-3}$	75
LCWP04700	Unsupported PTFE	10	1.7x10-3	260
SVLP04700	PVDF	5	1.7x10-3	85
S50WP320F5 S99WP320F5	PES	5 and 10	1.7x10-3	130

3.1.3 Caustic Recovery Experiments

Throughout the caustic recovery studies cross-flow UF and NF tests were carried out.

3.1.3.1 UF Experiments

In UF experiments, non pretreated but coarsely filtered wastewater samples were used. Prior to UF, wastewater samples were passed through a 500 μm pore sized metallic strainer for coarse filtration purposes. Based on the experience gained during pretreatment tests, it was decided to use a PES structured UF membrane in this part of the study. General specifications of the chosen membranes for UF tests can be seen in Table 3.2.

UF experiments were performed in total-recycle mode in a cross-flow plate and frame module, DSS LabStak M20 membrane filtration system (Figure 3.3) with a total membrane area of 0.036 m^2. In this operation mode, both permeate and retentate are recycled back to the feed tank. The membrane filtration system is equipped with a temperature controlling mechanism; so that during filtration operation temperature is kept constant at 18±2^{0}C within the filtration module. The filtration module owns a 6 – 6.5 L feed tank volume and also 2 – 2.5 L in the tubes of installation.

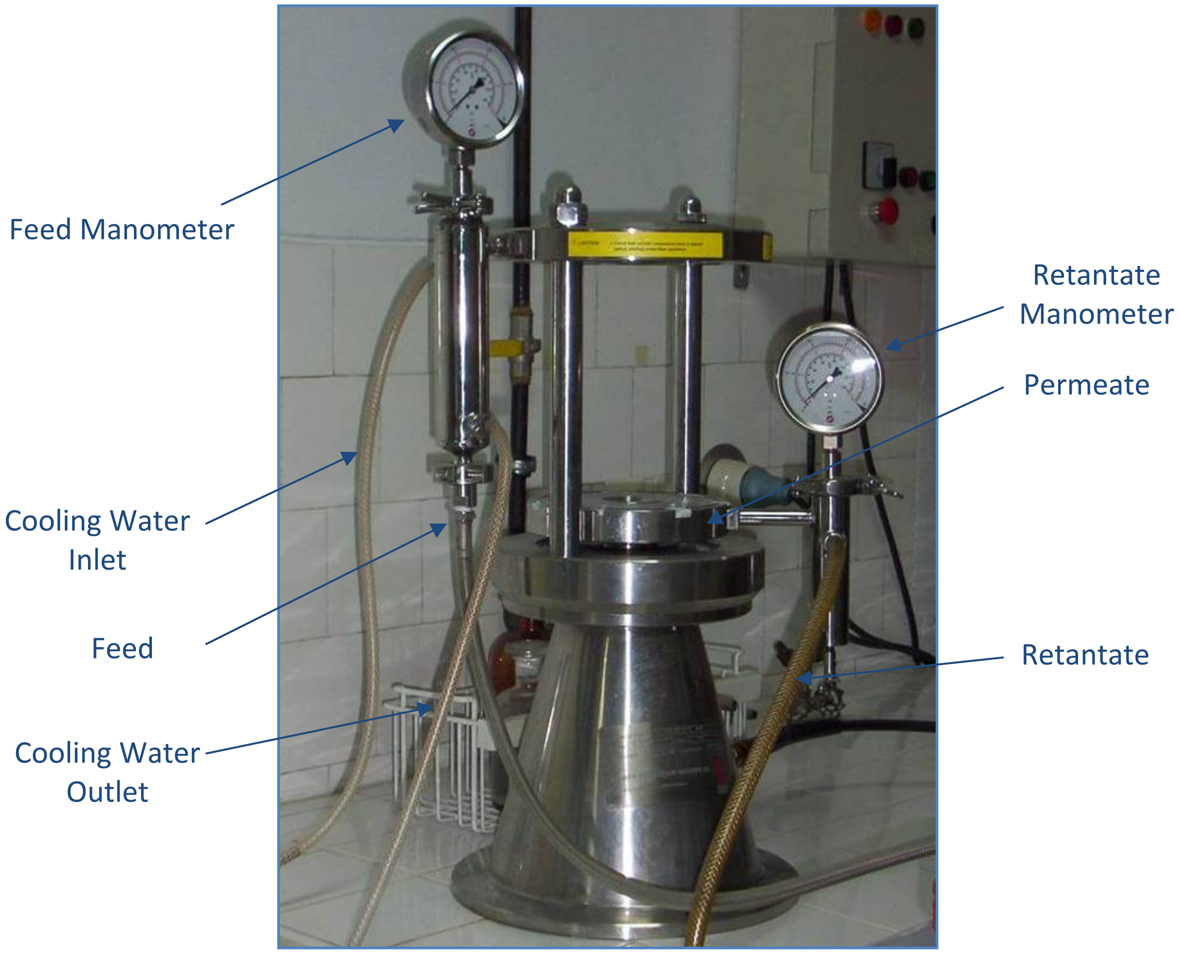


Figure 3.3 DSS LabStak M20 Membrane Module

Throughout the experiments, permeate flow rate was recorded manually to monitor permeate flux. This was continued until a steady permeate flux rate was reached. In addition, in order to evaluate the system performance COD, color, pH, conductivity and NaOH content parameters were measured both in feed and permeate samples taken at different time intervals of the membrane operation.

3.1.3.2 NF Experiments

Wastewater that is going to be used in NF experiments was only coarsely filtered as in UF. For this purpose three types of NF membranes were tested on this wastewater. General specifications of the NF membranes are given in Table 3.2.

Table 3.2 Characteristics of membranes used in caustic recovery experiments

Membrane	Material	Maximum temperature, °C	Nominal MWCO (g/mol)	Max. pressure (bar)	pH Range	Type
MF-45	Fluoropolymer	60	0.45 μm	1.5	1 – 11	MF
GR95PP	Polyethersulfone on polypropylene	75	2000	10	1 – 13	UF
NP010	Polyethersulfone Hydrophilized	95	1000	40	0 – 14	NF
NP030	Polyethersulfone Hydrophilized	95	500	40	0 – 14	NF
MPT-34 /MPF-34	Polyethersulfone on polypropylene	70	300	35	0 – 14	NF

NF studies were performed with the membrane module as in UF experiments. Moreover, the same operational conditions and performance indicating parameters were controlled. Being different from UF studies, a concentration-mode membrane study was performed additionally. Furthermore to see the effect of temperature wastewater is heated up to 45 – 50^0C and provided to be kept constant by means of a heater in the feed tank of the module. Both concentration mode and high temperature studies have provided better understanding about the real conditions of caustic recovery.

Throughout the NF studies, optimum operating conditions and the most effective membrane was determined for caustic recovery. For this purpose, the effects of different TMP's and cross-flow velocities were investigated. Attempted operational conditions relative to membrane type can be summarized in Table 3.3.

Table 3.3 Applied operational conditions during NF studies

Membrane	TMP (bar)	CFV (m/sec)	Temperature (^{0}C)
GR95PP	2.38	0.79	20 ± 2
GR95PP	4.03	0.42	20 ± 2
GR95PP	4.03	0.79	20 ± 2
GR95PP	6.23	1.40	20 ± 2
NP030	4.03	0.79	20 ± 2
NP010	4.03	0.79	20 ± 2
NP010	4.03	0.79	40 ± 2
NP010	4.03	0.40	40 ± 2
NP010	4.03	0.40	20 ± 2
NP010	4.03	1.40	20 ± 2
NP010	6.23	0.79	20 ± 2
MPT-34	4.03	0.79	20 ± 2

3.1.3.3 Pilot Plant Studies

This study was conducted in the finishing unit of the textile mill using a SelRO MPT-34 pilot plant system (Figure 3.4) manufactured by KOCH Membrane Systems. Since it is manufactured for acid and caustic recovery and specifically caustic recovery from textile wastewaters, the membrane of the pilot plant system that is MPT-34 membrane (tubular) is durable to high alkaline, acidic and temperature conditions. Allowed operating conditions of the system are given in Table 3.4.

Table 3.4 Operating information of SelRO MPT-34 Pilot System

Pilot Plant	SelRO MPT-34
Typical Operating Pressure	15-35 bar
Maximum Operating Temperature	70 ^{0}C
Allowable pH - Continuous operation	0 – 14

Pilot plant was set up and connected to the first rinsing tank of one of the most frequently used mercerizing machinery (Over-Dye). Instead of diverting rinsing effluent directly to the pilot system, manual feeding of the wastewater was applied, since the system capacity was inadequate for the total flow. Besides since the pilot system does not have its own prefiltration unit, manual filtration by means of a coarse filter was applied to remove fiber residues and other inorganic particles before introducing the wastewater into the pilot plant. During the operation of the system, when drastic decrease occurs in permeate flux due to clogging of the membrane or due to the accumulation of particulate matter on the membrane surface and/or within the membrane pores, cleaning has been applied using 1 % HNO_3 at first and then pure water.

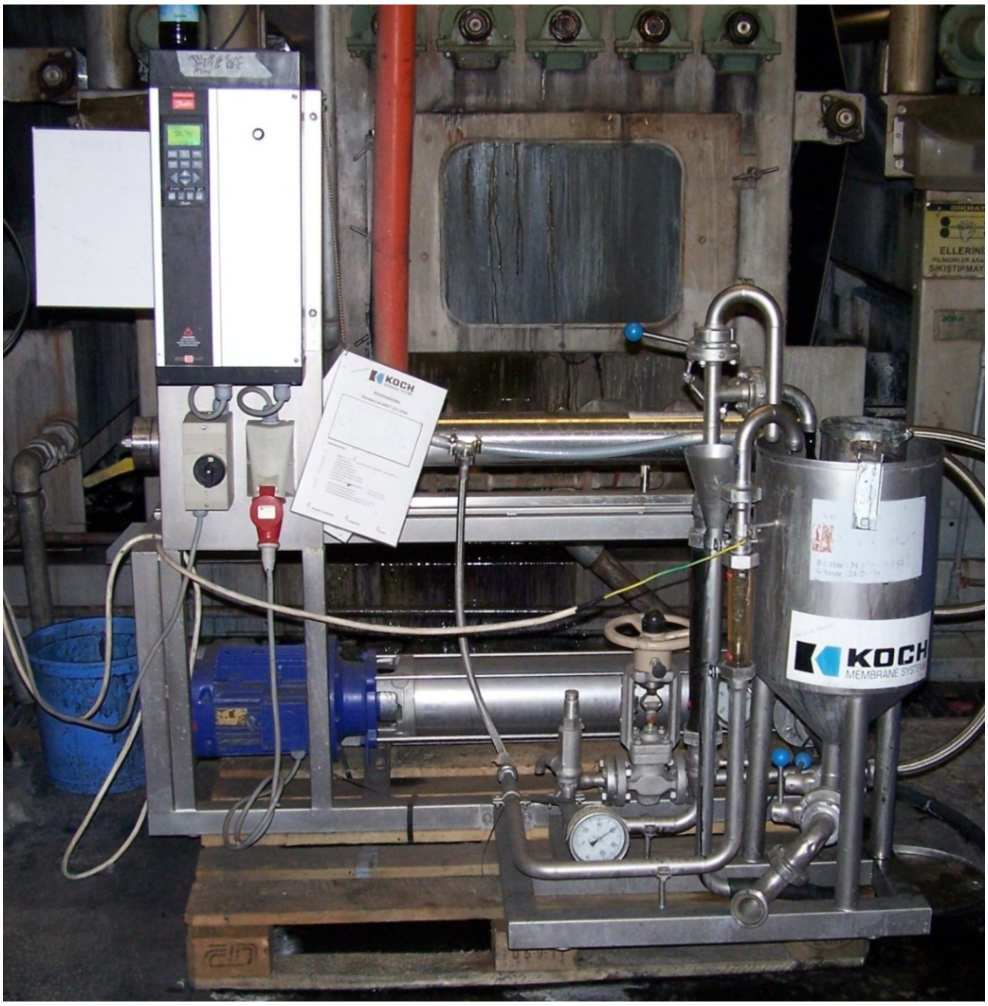


Figure 3.4 SelRO MPT34 Pilot Plant set up in the mercerizing unit of the mill

After testing the pilot plant, it was decided to investigate clogging problem of the system under laboratory conditions. For that purpose flat sheet form of the MPF-34 NF membrane which is used in the pilot system was obtained and a series of tests were performed. As a treatment scheme, this membrane was evaluated as;

- NF without pretreatment in total recycle mode like the previous NF tests and,
- MF after NF in concentrated mode.

Unlike the previous studies MF process was investigated under a high TMP prior to NF using MF-45 membrane. Table 3.2 presents the characteristics of MPF-34 and

MF-45 membranes. Operating conditions of these experiments are summarized in Table 3.5.

Table 3.5 Treatment scheme and operational conditions of MPF-34 NF experiments

Membrane		TMP (bar)	CFV (m/sec)	Temperature (^{0}C)
MPF-34	NF	4.03	0.79	20 ± 2
MF-45 + MPF-34	MF	1.73	-	20 ± 2
	NF	4.03	0.79	20 ± 2

3.2 Analytical Methods

COD HACH Sension 378 pH-conductivity-dissolved oxygen meter was used for pH and conductivity measurements. Color measurements were conducted by a HACH DR-2000 Model spectrophotometer and applying USEPA approved HACH Method #8000. A wavelength of 455 nm was employed for the calibration of the spectrophotometer with Pt-Co standard solution. COD measurements were done by using the same spectrophotometer and following the same method at the wavelength of 620 nm for high COD concentrations and at 420 nm for low COD concentrations. In turbidity measurement, a HACH Model 2100A turbidimeter was used. For total solids (TSS) content determination gravimetric analysis were applied. Particle size distribution of the mixed finishing wastewater was determined by a Malvern Nano ZS90 unit at the METU Central Laboratory. In order to evaluate caustic content of the wastewater, NaOH and alkalinity measurements were done. Alkalinity measurements were conducted according to Standard Methods (2320 B-titrimetric method) [38]. For NaOH determinations, first Na values were measured by Standard Methods with a Jenway Flame Photometer device. Since there is no other Na compound except NaOH, caustic content has been calculated directly from the measured Na concentrations by the following formula;

$$\mathrm{A} = \frac{\mathrm{B} * 40}{23}$$

A : NaOH, g/L B : Na, g/L

Na = 23, O = 16, H =1

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Wastewater Characterization

Before starting to evaluate treatment options, mercerization wastewaters of the mill were characterized. Characterization studies were conducted with the effluents from the most commonly used two mercerization machineries (Over-Dye machine and Pad-Steam machines) of the mill. For this purpose, effluents from each post rinsing tank of these two machineries or mercerizing process lines and the mixed wastewater from these lines (after a coarse filtration unit) were collected and characterized separately. Five different samples were taken at different times and analyzed for their constituents. Table 4.1 presents the general characteristics of these mercerizing effluents in the mill.

As can be seen from Table 4.1, the finishing wastewaters are heavily loaded with organic matter, suspended solids, dissolved solids and color. These wastewaters are produced at very high volumes (200-300 L/min) like the other major units of textile production .This heavy pollution load is mainly due to many different chemicals applied during mercerizing processes and also previous dyeing processes. Table 4.2 also indicates that wastewaters coming from different post-washing stages of these mercerization processes are highly variable in characteristics. Marcucci et al., have indicated that finishing wastewater quality is highly affected by the used variant type of dyes, detergents, sulfate compounds, heavy metals and inorganic compounds [21]. Therefore any change in previous production steps affects directly the mercerizing process and its resulting waste characteristics.

Table 4.1 General wastewater characteristics of washing stages of the denim mercerizing processes

Washing Stages	1	2	3	4	5	6	7	After Filtration
pH	12.3	12.1	11.8	11.7	11.4	11.1	8.9	11.3
Conductivity	150	60	20	13	9	5	1	18
TSS	1632	793	248	172	144	131	40	132
TDS	61947	23043	8348	5186	4279	3154	1151	6236
Alkalinity	41163	15002	4920	3204	2246	1216	382	4196
Color	10113	7059	3689	3651	3568	3078	844	2994
Turbidity	879	584	534	561	406	379	138	289
COD	8524	5202	2296	2080	2330	2007	542	1863
NaOH	67.5	34.7	6.3	2.8	1.9	1.4	-	-

(Unit for conductivity mS/cm, color Pt-Co, turbidity NTU, NaOH g/L, alkalinity mg/L $CaCO_3$ and TSS, TDS, and COD mg/L.)

Table 4.2 Variable characteristics of mercerizing process final effluents

Parameter	Minimum	Maximum
pH	6	12.8
Conductivity, mS/cm	2.5	26
COD, mg/L	706	6755
Color, Pt-Co	1179	6775
Alkalinity, mg/L $CaCO_3$	310	6140
TSS	58	467
Turbidity	154	488

As can be seen from Table 4.1 as we move along the post-washing stages of the mercerization line, pollution load in the wastewater decreases and nearly 80 % of the total load from finishing is discharged from the first two rinsing tanks. More importantly, more than 85 % of NaOH discharged from mercerizing process is in the wastewater from the first two stages of washing (water consumption and hence wastewater discharge from each post-washing tank are equal in volume). Based on this observation, it was thought that the wastewater mixture from the first two rinsing tanks would be tried to be treated for the alkali recovery instead of using the whole system effluent, considering the possible cost of the full-scale NaOH recovery system to be installed in the mill. It was also considered that this would be better in terms of performance of the recovery system too. Thus all pretreatment and treatment studies were run with the wastewater mixture originating from the first two post-washing tanks of the finishing mill.

For a further analysis of wastewater characteristics, particle size distribution was also analyzed and the results presented in Figure 4.1 were obtained. As can be depicted from the figure, the particles in the wastewater are mainly in the size range of 255-1000 nm; although, there are also particles in the range of 5000-6000 nm. But these larger particles are not high in intensity when compared with the other ones. From this distribution intensity based average pore size appeared to be 570.4 nm.

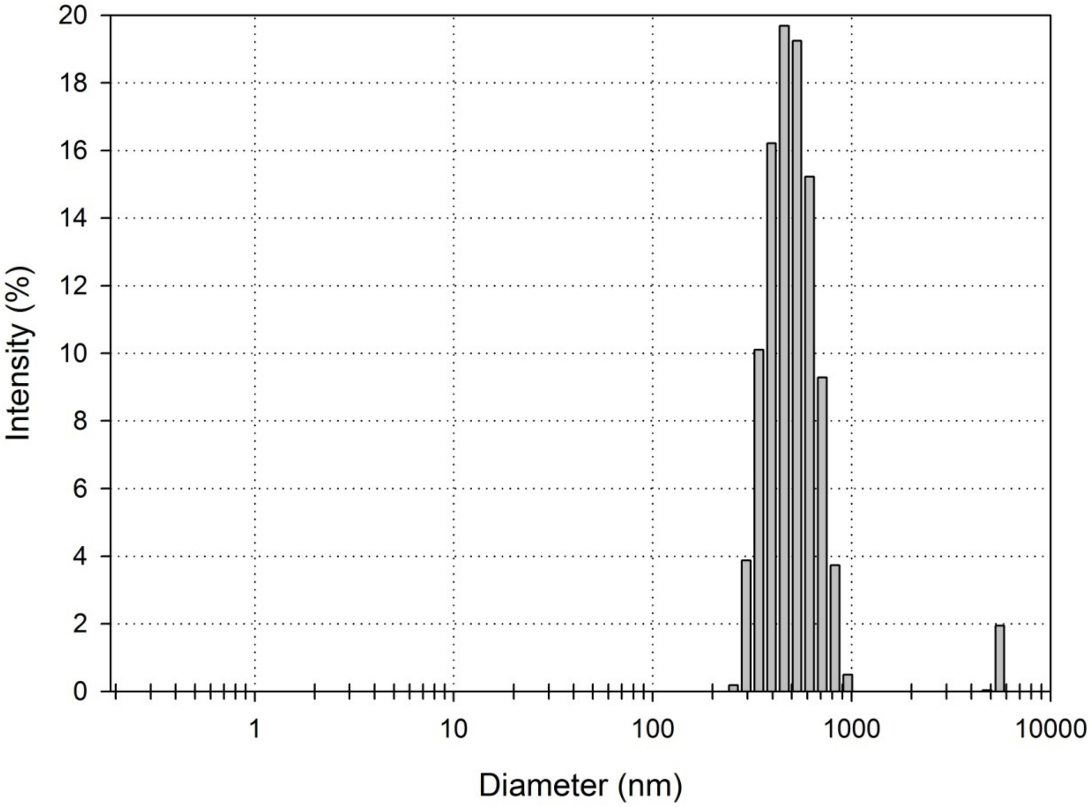


Figure 4.1 Particle size distribution of the mixed mercerizing wastewater

4.2 Pretreatment

When a NF alternative is going to be applied; biological degradation, coagulation/flocculation, MF and UF are the most frequently applied pretreatment options [39]. In this study, three different pretreatment alternatives were evaluated. The first alternative evaluated was MF. MF studies were conducted at two stages. At the first stage, MF is applied via conventional vacuum filtration unit at the vacuum level of 25 inHg and three different pore sized membranes were tested (1.2, 8 and 20-25 μm). Wastewater used in this series of MF tests was with pH of 12.4, color of 4250 Pt-Co and conductivity of 39.80 mS/cm.

When 1.2 and 8 μm sized membranes were used, there occurred immediate clogging and no filtrate were collected (no relevant data is present as there occurred direct clogging). This result indicated that wastewater filtered contains particles which are fine and sufficient enough to clog both the pores of the sizes 1.2 and 8 µm and also possibly larger ones too. When the membrane with the average pore size 20-25 µm was used, filtration lasted only for 30 seconds. After that time, there was no filtrate flow coming out. This observation implied that the finishing wastewater contains particles that cause sudden clogging of the 20-25 µm membrane surface due to high solids content of the wastewater and also due to the presence of particles which are of the sizes above 20-25 µm. As presented in Table 4.1, the wastewater filtered in this filtration test was with a TSS content of 2425 mg/L.

At the second stage of the MF study, a computerized dead-end filtration unit was used and two sets of experiments were run. In this filtration system, the mass of filtrate collected is recorded on a computer for every 2 seconds. As the filter medium, two different kinds of membranes made from Polyvinylidene fluoride (PVDF) and Polytetrafluoroethylene (PTFE) of the pore sizes 5 and 10 µm, respectively were utilized. Both of these membranes are durable to highly alkaline and thermal conditions.

Filtration experiments with each membrane were repeated seven times in order to produce reproducible data. The experimental results of seven parallel MF experiments run with the two membranes are presented in Figure 4.2 and Figure 4.3.

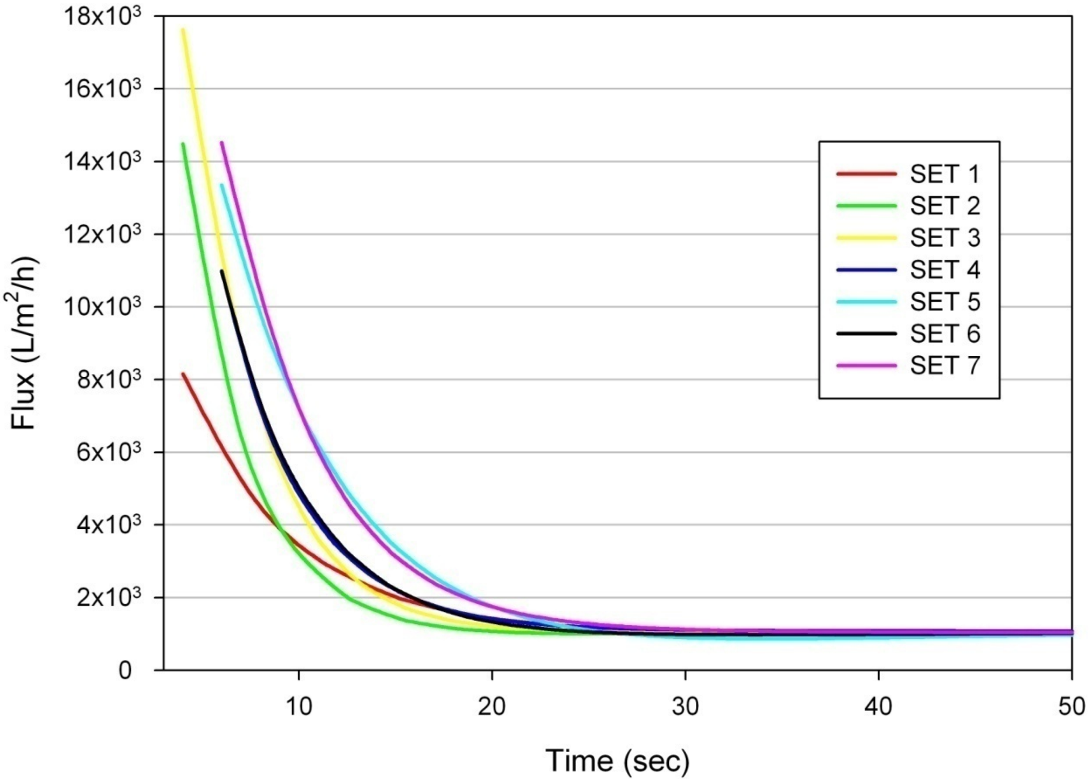


Figure 4.2 Filtration results for 5 μm PVDF MF membrane (ΔP = 0.925 bars)

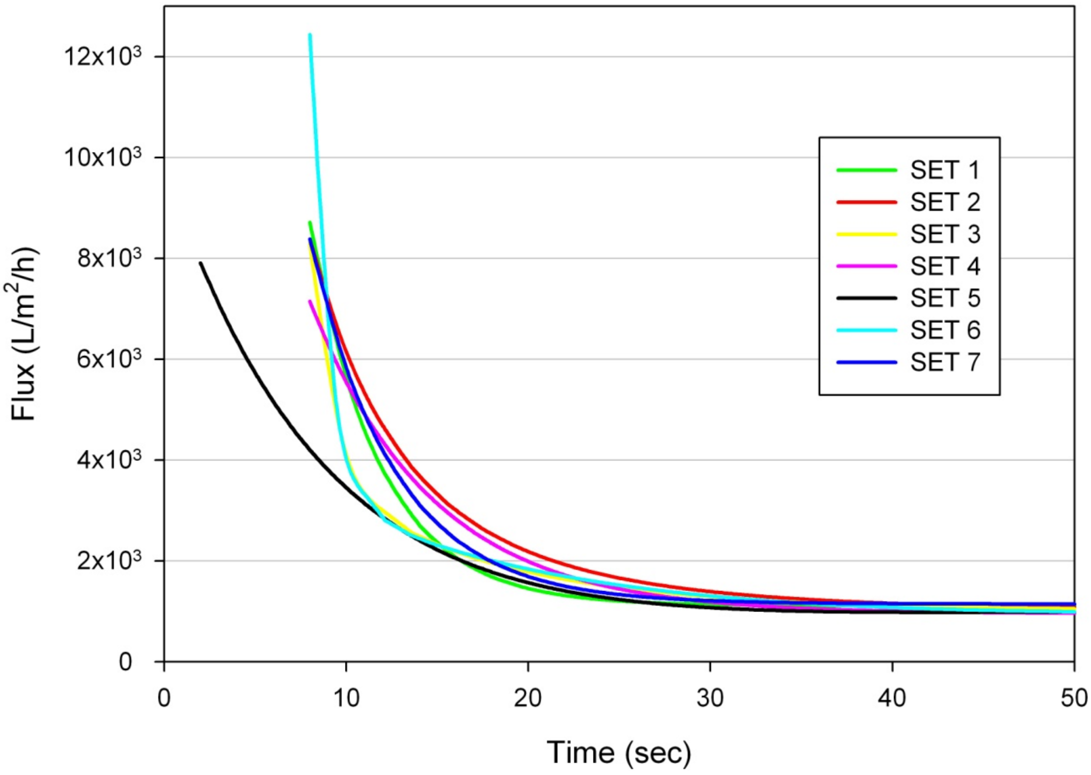


Figure 4.3 Filtration results for 10 μm PTFE MF membrane (ΔP = 0.925 bars)

From Figure 4.2 and 4.3, it is clearly seen that both membranes run into clogging problem within a very short time interval (about 10 sec) after the start of the filtration cycle. This rapid clogging mainly originated from the heavy particulate load of the wastewater. The filtrate flux from both membranes was very rapid at the start and there was linear decrease with time until about 10th second. After 10th second, the decrease in flux was relatively gradual until almost complete clogging at about 20th second.

These filtration tests carried out with 5 µm PVDF and 10 µm PTFE membranes have indicated that although these membranes are durable to alkaline conditions, they experience rapid flux declines with finishing wastewater and this makes the usage of 5 µm PVDF and 10 µm PTFE membranes inefficient as a MF alternative.

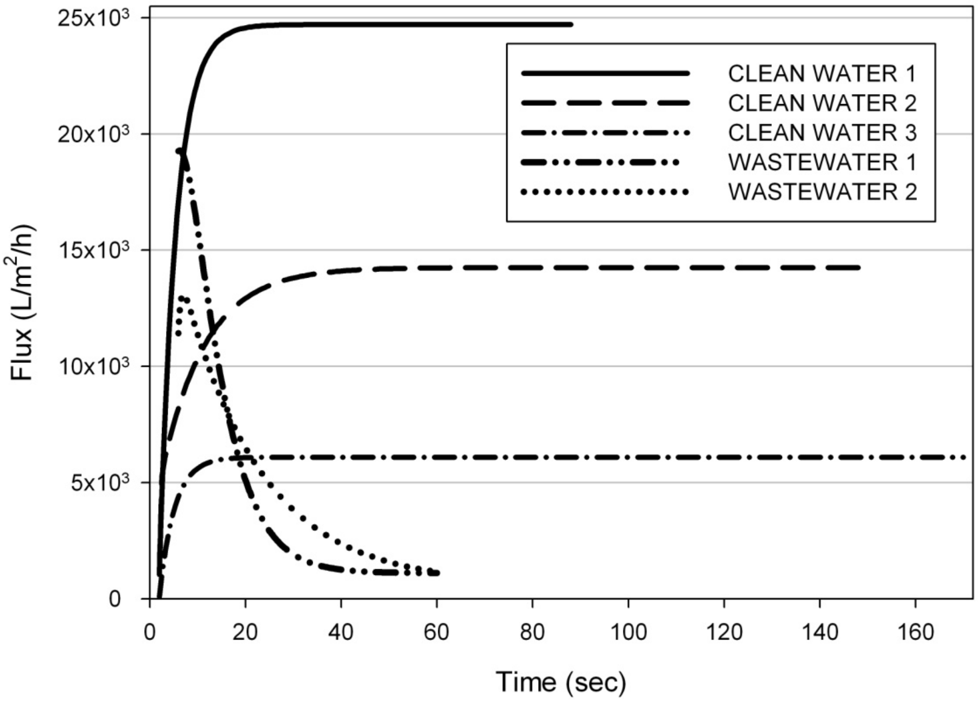
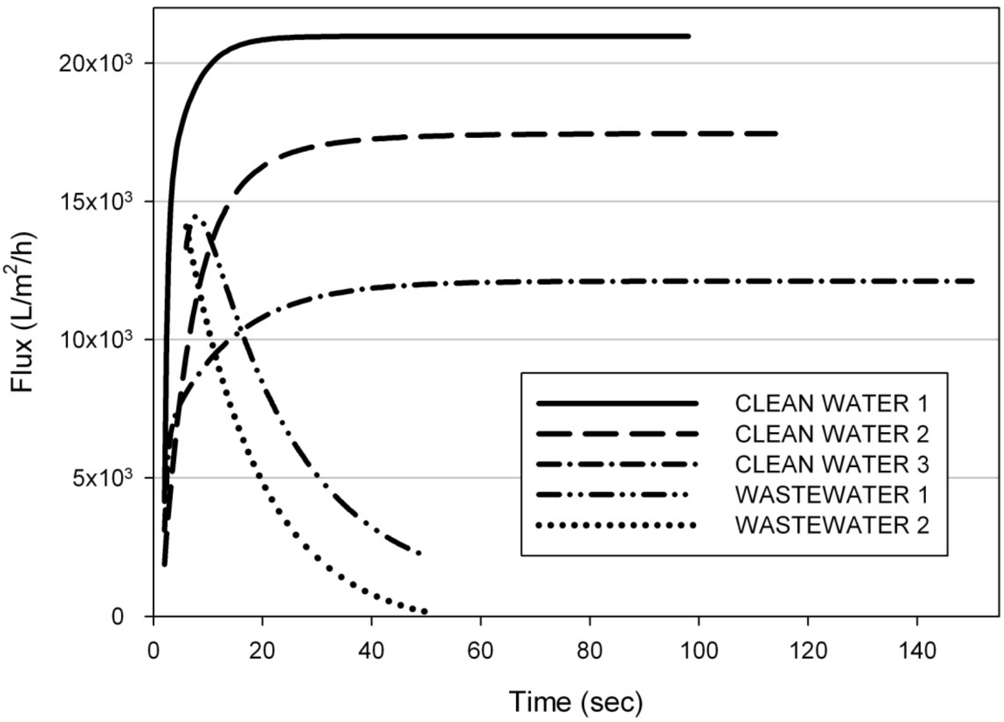


Figure 4.4 Clean water and wastewater flux development for 5 µm PES MF membrane (ΔP = 0.925 bars)

Subsequently, polyethersulfone (PES) based membranes which are hydrophilic and resistant to very high temperatures (135^{0}C) were tested. For this purpose two different pore sized (5 and 10 µm) PES structured MF membranes were applied. As being different from previous MF experiments, clean water fluxes were also evaluated, before and after filtrating wastewater in order to assess fouling behavior. These filtration tests were run at a pressure difference of 0.925 bar and the results presented in Figures 4.4 and 4.5 for the 5 and 10 µm PES membranes were achieved.



CLEAN WATER 1 -> Flux of virgin membrane with clean water

WASTEWATER 1 -> Membrane flux with wastewater

CLEAN WATER 2 -> Membrane flux with clean water following wastewater filtration

WASTEWATER 2 -> Membrane flux with wastewater following second clean water filtration

CLEAN WATER 3 -> Membrane flux with clean water following second wastewater filtration

Figure 4.5 Clean water and wastewater flux development for 10 µm PES MF membrane (ΔP = 0.925 bars)

A quick look at Figures 4.4 and 4.5 directly indicates that there occurs very rapid clogging of the 5 and 10 µm PES membranes with the wastewater and the permeate fluxes from these membranes are well below the initial clean water fluxes.

At the start, clean water fluxes from 5 and 10 µm virgin membranes reached to their steady values of about 25 L/m^2-h and 21 L/m^2-h, respectively within a similar short time period of about 20-30 sec. However, after being used for wastewater filtration, these clean water fluxes decreased to 14 and 17.5 L/m^2-h for 5 µm and 10 µm membranes respectively. These results have indicated that clogging or fouling of 5 µm membrane is more severe as compared to 10 µm membrane. As a confirmation of this observation, the clean water flux from the 5 µm membrane after its second usage for wastewater filtration was lower than that for 10 µm membrane. The total decrease in clean water flux from 5 µm PES membrane after its two consecutive usage was about 75%, while that for 10 µm membrane was only 45 % (Table 4.3). These values designate the serious clogging problems with this wastewater. Consequently, wastewater filtration with these membranes presented very rapid flux decline with time. For both membranes, a time period of 10 sec was sufficient to reach almost complete clogging and to experience a drastic decrease in filtration rate. The wastewater flux from 5 µm virgin membrane was about 14.5 L/m^2-h while that from 10 µm was 19.7 L/m^2-h. This result was somehow unusual as one expects to get a higher filtrate flow from a coarser membrane. One should not forget that 5 and 10 µm membranes are quite similar in pore size and are MF membranes that might have a certain pore size distribution resulting in such an unexpected observation. The wastewater filtered is heavily loaded with suspended solids and the size distribution of particles is another major parameter influencing filtration rate.

Table 4.3 Clean Water Fluxes and Flux Declines from 5 and 10 µm PES membranes

Membrane	CW Flux			% decrease	
	CW1	CW2	CW3	After 1st WW Filtration	After 2nd WW Filtration
5 µm	24.8	14.5	6.2	42	57
10 µm	22.8	19.7	13.5	14	31

Nevertheless, the clear finding from this series of filtration tests along with the previous microfiltration trials is that MF pretreatment option is not a successful option for the pretreatment of finishing wastewater.

4.3 Precipitation

Getting ineffective results from prefiltration studies have induced investigation of other pretreatment options and in this framework flocculation was considered as the second pretreatment alternative. During a flocculation period of 45 min at 30 rpm any flocculation mechanism was observed. Because of charged high variety of inorganic and organic content originated from sizing, spinning, weaving, desizing, dyeing or scouring, no stability has been reached.

After testing the applicability of flocculation as a pretreatment alternative and finding it unsuccessful, centrifugation was considered as the third alternative and a centrifugation study was conducted. However, even 30 minutes of centrifugation at a rotational speed of 2500 rpm was not satisfactory and did not provide a considerable precipitation of settleable material and color removal.

All above findings have indicated that centrifugation and flocculation have been found also not satisfactory to be applied for the pretreatment of finishing wastewaters. Looking the consequences of applied pretreatment alternatives, it was decided to continue the evaluation of recovery alternatives without any pretreatment.

4.4 UF Experiments

In membrane applications, generally MF processes are used as a pretreatment for UF and NF processes [40]. However characteristics of the wastewater investigated in the present study for caustic recovery brought about the failure of MF as a pretreatment alternative. Eun Jong Son has reported that when the wastewater was filtered from 10, 100 or 500 µm filters prior to membrane unit, it was realized that effect of filter size on permeate flux is minor. Therefore it was stated that filtering only visible materials which are fiber and lint for a textile wastewater will be enough to avoid instant membrane fouling [9]. Results of the studies conducted for pretreatment purposes leaded to the idea of applying UF process without any pretreatment. However, only simple coarse filtration with a strainer has been applied to the raw finishing wastewater for eliminating visible textile residues.

UF experiments were performed in total-recycle mode using a cross-flow plate and frame module with a PES UF membrane coded as GR95PP having a MWCO of 2000. Two sets of experiments were performed with this membrane. Firstly, a UF test was conducted at 4.03 bar TMP and 0.42 m/s CFV and the steady-state results summarized in Table 4.4 were obtained. In the second part of the studies, TMP and CFV were varied in order to investigate their possible influences on the performance of UF in caustic recovery and also in the removal of wastewater constituents.

Table 4.4 Steady state performance of GR95PP UF membrane at 4.03 bar TMP, 0.42 m/s CFV and 20 ± 2^0C

	Color (Pt-Co)	COD (mg/L)	NaOH (g/L)	pH	Conductivity (mS/cm)
Feed	10250	16110	32	13.24	144
Permeate	517	2885	32	13.26	150
Retention	94.9%	82.1%	N.A.	N.A.	N.A.

Table 4.4 shows the successful operation results of UF system in terms of caustic separation with significant color and COD removal. Since the NaOH is the main contributor to the alkalinity and conductivity, there is no significant change in pH and conductivity values was observed. Figure 4.6 shows the 2nd hour feed and permeate samples of the UF process applied at 4.03 bar TMP, 0.42 m/s CFV and 20 ± 2^0C.

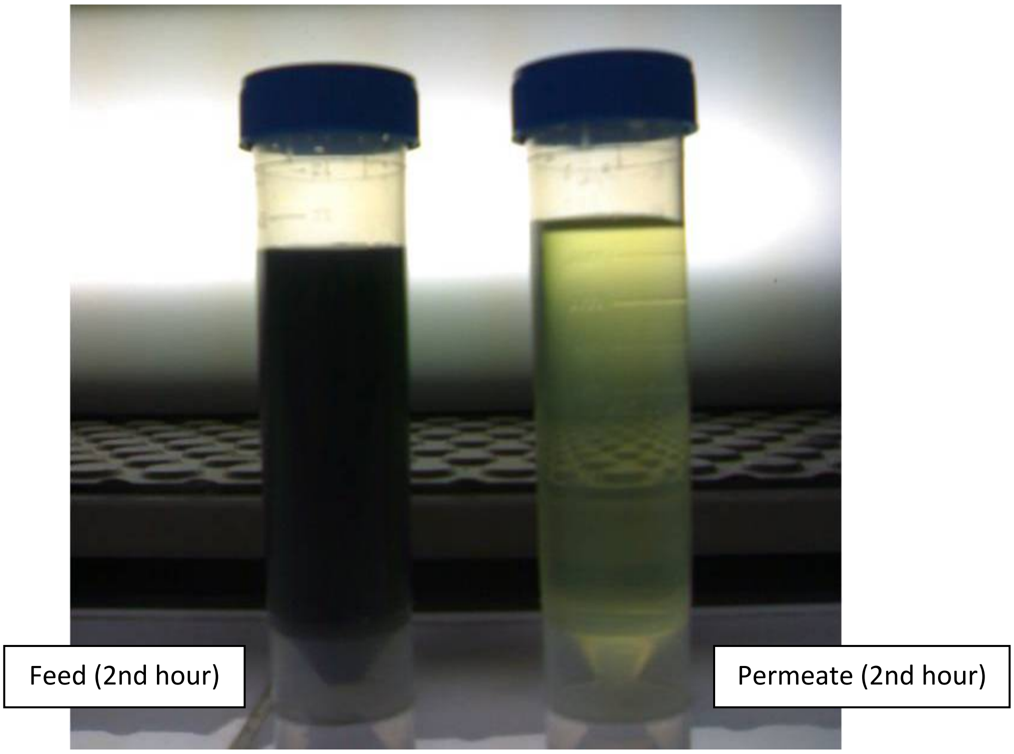


Figure 4.6 2nd hour feed and permeate samples of UF process with GR95PP at 4.03 bar TMP, 0.42 m/s CFV and 20 ± 2^{0}C

All above findings have indicated that UF process without any pretreatment except a coarse filtration is successful in caustic recovery. However this process cannot be found satisfactory when color and COD retentions were considered. These two parameters are evaluated taking into account the reusability of this permeate in the production processes. As can be seen from Table 4.4 the permeate from UF process contains 517 Pt-Co color and 2885 mg/L COD. This indicates that the permeate cannot be used in the finishing process without further treatment as it is highly colored and contains high amount of COD causing organic matter.

In order to evaluate possible improvement in the UF performance, in the second part of the UF experiments; the effects of CFV and TMP on the permeate quality were investigated and the results presented in Table 4.5 and 4.6 were achieved. In investigating the effect CFV, TMP was kept at 4.03 bar and the CFV was varied as 0.42 and 0.79 m/s. On the other side, to investigate the effect of TMP; CFV was constant at 0.79 m/s and TMP was varied from 2.38 and 4.03 bar. Furthermore, behavior of the system was also examined in a different condition by increasing both CFV and TMP, which were 1.40 m/s and 6.23 bars respectively.

Table 4.5 Effect of TMP on UF process efficiency of GR95PP UF membrane at steady state

Operating Conditions	COD Retention,%	Color Retention,%	NaOH g/L	Flux L/m^2-h
ΔP =2.38 bars CFV = 0.79 m/s	91.98	92.82	32	6.72
ΔP = 4.03 bars CFV = 0.79 m/s	83.84	93.86	32	13.55
ΔP = 6.23 bars CFV = 1.40 m/s	87.77	94.83	32	11.11

Table 4.6 Effect of CFV on UF process efficiency of GR95PP UF membrane at steady state

Operating Conditions	COD Retention,%	Color Retention,%	NaOH g/L	Flux L/m^2-h
ΔP = 4.03 bars CFV = 0.42 m/s	83.95	94.96	32	11.44
ΔP = 4.03 bars CFV = 0.79 m/s	83.84	93.86	32	13.55
ΔP = 6.23 bars CFV = 1.40 m/s	87.77	94.83	32	11.11

As seen from the steady state results, increase in TMP and CFV have resulted in higher fluxes with lower COD and color retentions and caustic separations (Table 4.5 and 4.6). On the other side, a comparison of the magnitude effects of CFV and

TMP, show that TMP has influenced the system performance more than CFV. Effect of TMP and CFV on flux values can be seen in Figure 4.7 and Figure 4.8.

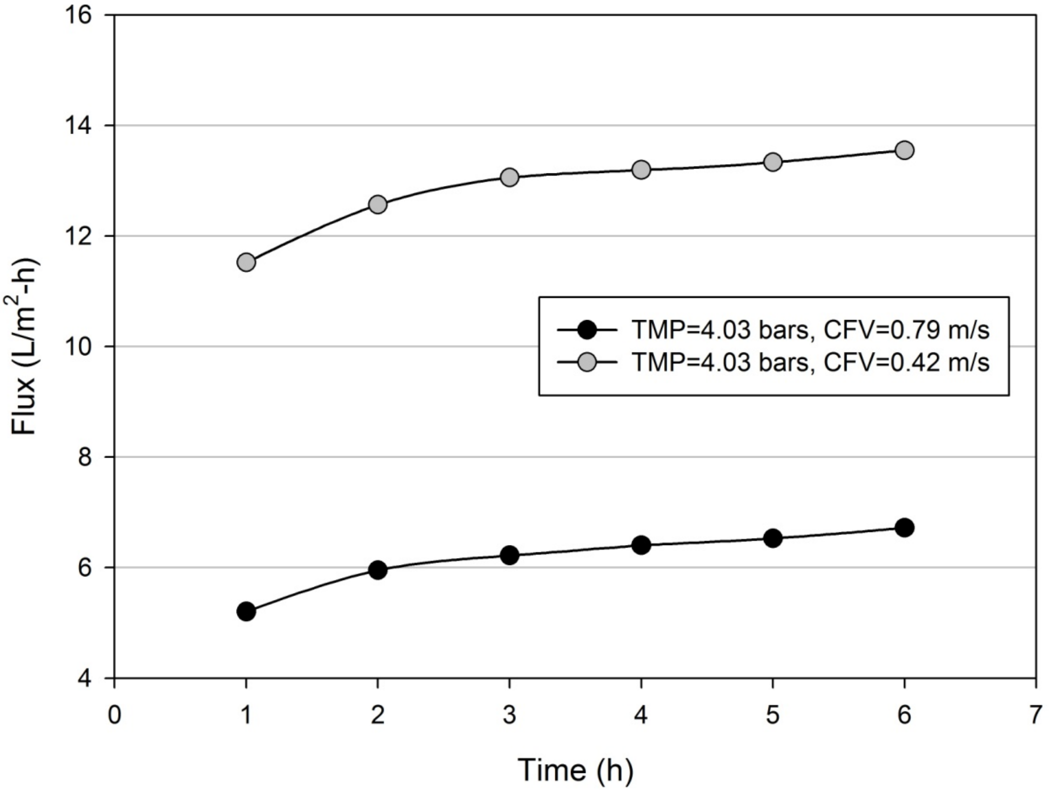


Figure 4.7 Effect of TMP on Flux for the GR95PP UF Membrane

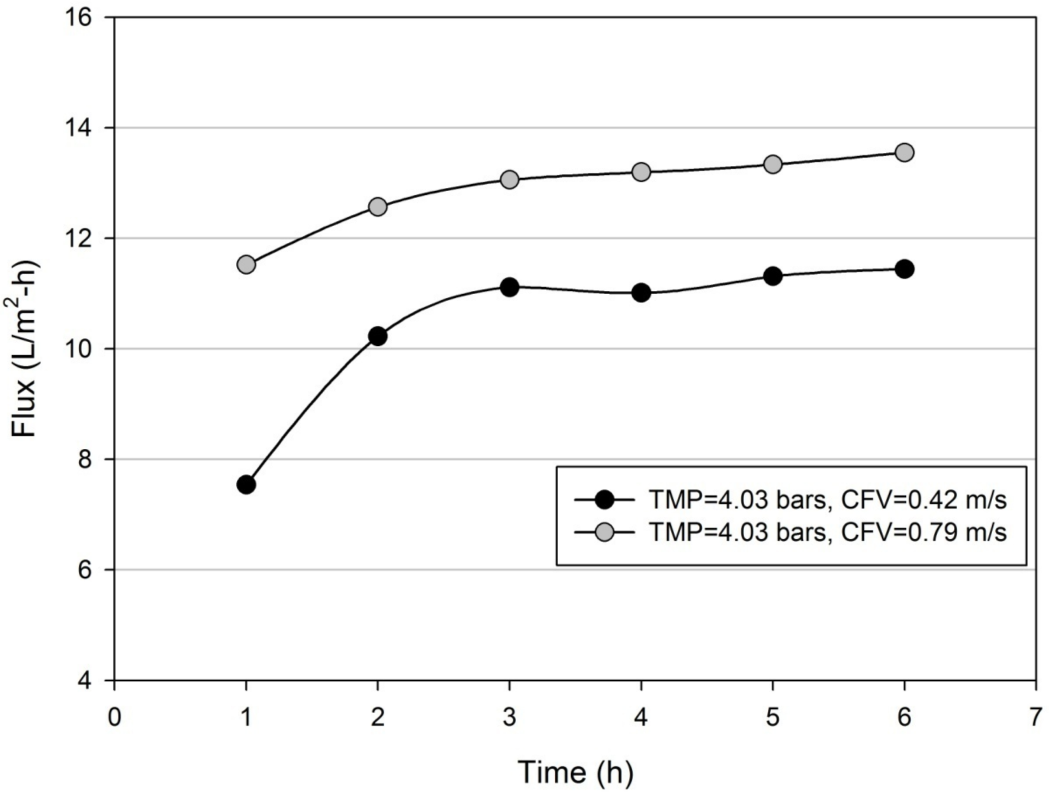


Figure 4.8 Effect of CFV on Flux for the GR95PP UF Membrane

In a recent study, S. Barredo-Damas investigated the effect of CFV on COD removal from textile wastewaters by a number of UF membranes and reported that for all UF membranes tested there was no influence of CFV on COD removal. It was also stated that due to higher solid deposition chance on the membrane surface at low cross flow velocities, lower fluxes are expectable [41]. This behavior was similar in terms of color removal efficiency. If the effect of TMP is analyzed it is obviously seen that flux increases drastically up to a point (Figure 4.7). This point has been 6.23 bars TMP for this experiment. The reason why flux increases when the pressure is increased is that membrane resistance is brought down and then flux increases with the increased driving force [42]. However after a point thickness of the filter cake starts to increase with an increased convection of solute to the membrane surface [43]. Then flux decreases with increased TMP. Beside that Ahmad has reported a research which investigated the effect of pressure on dye rejection with UF process. It was stated that as the TMP was increased, dye rejection has slightly decreased beside the increased flux [44]. In summary when the operation of the system is taken into consideration higher fluxes are more desirable unless an obvious reduction in retentions is observed. So that 4.03 bar TMP and 0.79 m/s CFV was accepted as the most efficient UF condition for the mentioned wastewater.

4.5 NF Experiments

In this series of experiments, two different NF membranes (NP010 and NP030) were tested at different operating conditions in order to evaluate the performance of NF in the recovery of caustic and to select the best membrane among these two alternatives. Characteristics of the NF membranes used are presented in Table 3.2. The wastewater used in NF experiments was not pretreated except a coarse filtration as in UF experiments with the characteristics depicted in Table 4.4.

Firstly NP010 and NP030 membranes were tested at the same conditions of 4.03 bar TMP and 0.79 m/s CFV at 20±2^{0}C, in order to compare the performances of these two membranes and the results presented in Table 4.7 were obtained. As can be depicted from this table, these two NF membranes were quite similar in performance and they both provided successful NaOH separation along with more than 90 % COD rejection. NP030 membrane rejected 90.47 % of the feed COD while NP010 rejected more; 92.37 % of it. Color removals by these two NF membranes were similar and 98.45 and 97.65 % for NP030 and NP010 membranes, respectively. However, in terms of permeate flux; NP010 was much better in performance than NP030 membrane. The permeate flux from the NP010 membrane was more than three times greater than that from the NP030 membrane. When the particle size distribution of the wastewater (Figure 4.1) is considered, MWCO parameters of these membranes (Table 3.2) could be the main reason for this flux difference.

Table 4.7 Comparative performances of NP030 and NP010 NF membranes at steady state

Membrane	Operating Conditions (ΔP in bar, CVF in m/s)	Final permeate quality			Retention (%)		Flux L/m^2-h
		COD (mg/L)	Color (Pt-Co)	NaOH (g/L)	COD	Color	
NP030	$\Delta P = 4.03$ CFV = 0.79	1535	119	32	90.47	98.45	6.02
NP010	$\Delta P = 4.03$ CFV = 0.79	1229	176	32	92.37	97.65	20.62
	$\Delta P = 4.03$ CFV = 0.42	2278	238	31	85.06	94.91	18.26
	$\Delta P = 4.03$ CFV = 1.40	1843	209	32	88.20	95.78	25.16
	$\Delta P = 6.23$ CFV = 0.79	2210	245	31	85.64	94.56	18.96

The operational conditions that had been maintained during the above mentioned NF tests were identical to those maintained during UF tests. This was a deliberate selection for the purpose of comparison. The target was to select either UF or NF for the recovery of caustic from the finishing effluent from the mill. Figure 4.9 presents the performances of GR95PP UF and NP010 and NP030 NF membranes in a comparative way. As can be depicted easily, these three membranes are equal in performance in terms of NaOH recovery. But, as regards COD and color retentions, NF membranes are superior to UF membrane. Meanwhile, different NF membranes provided different performances. While NP010 was better in color retention, NP030 was more efficient in terms of COD retention.

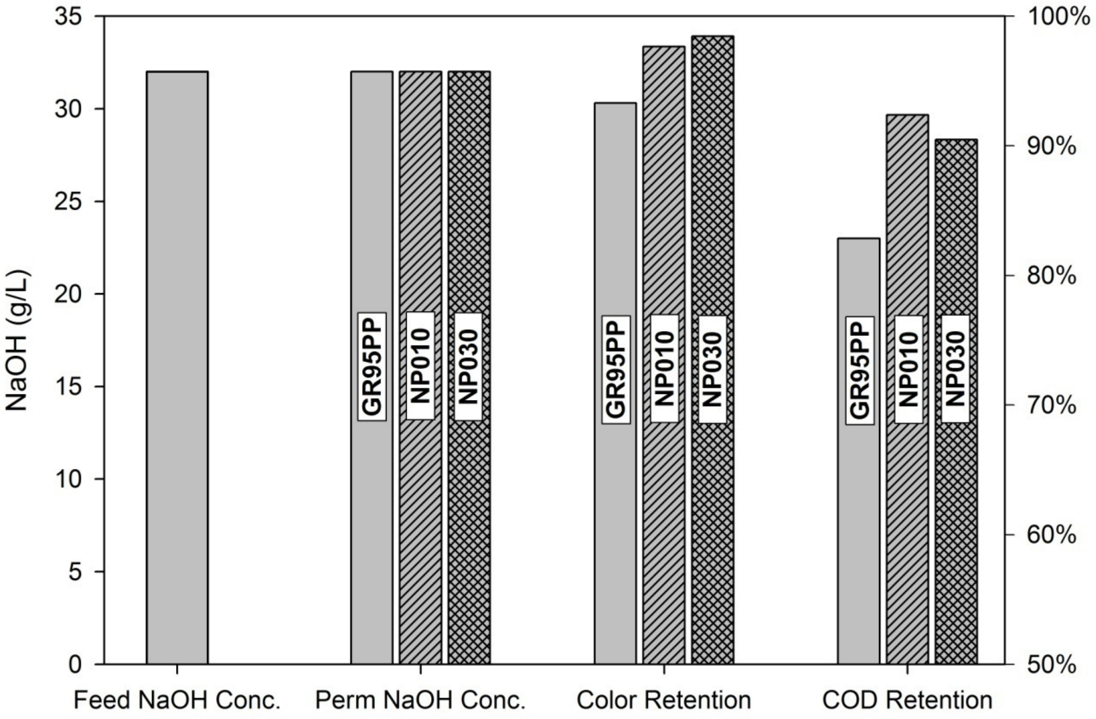


Figure 4.9 Comparison of GR95PP (UF), NP010 (NF) and NP030 (NF) membranes at 4.03 bars TMP and 0.79 m/s CFV at 20±2^{0}C for steady state

Nevertheless, when evaluating membrane performances and selecting the most appropriate membrane, permeate flux is obviously of the primary concern. Time dependent permeate flux data for the tested NP010 and NP030 NF membranes and also GR95PP UF membrane is presented in Figure 4.10. As stated before, during all these NF and UF tests, the operational conditions were kept constant. Wastewater temperature was 20±2^{0}C, TMP was 4.03 bars and CFV was 0.79 m/s.

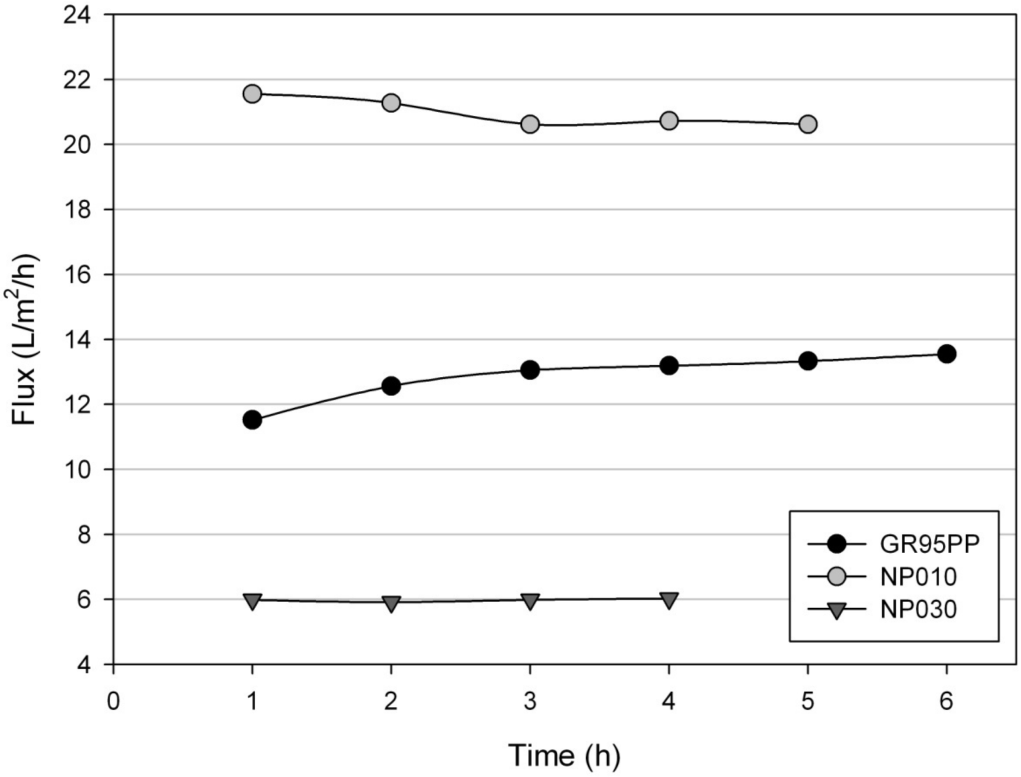


Figure 4.10 Flux comparisons of GR95PP (UF), NP010 (NF) and NP030 (NF) membranes at 4.03 bars TMP and 0.79 m/s CFV at 20±2^{0}C

When the time-variation of permeate flux from NP010 and NP030 membranes data presented in Figure 4.10 is evaluated, it is right away seen that the tested NF membranes perform drastically different and permeate flux from NP010 membrane having 1000 g/mol MWCO is much higher than that from NP030 membrane having 500 g/mol MWCO. Moreover, permeate flux from NP010 NF membrane is even higher than that from GR95PP UF membrane. This instantly recognizable advantage of the NP010 membrane in terms of permeate flux makes it a better choice among the tested membranes.

After finding out that NP010 is the most appropriate membrane for caustic recovery, the effect of operational parameters on the performance of this membrane was evaluated. Because rejection and permeate flux are the two most important performance parameters [45], the effect of operational parameters; TMP and CFV on rejection and permeate flux were evaluated for this membrane. A lower and a higher CFV than the previously tested TMP of 0.79 m/s was maintained and permeate flux data presented in Figure 4.10 was achieved. Similarly, TMP was varied and the experimental findings given in Figure 4.11 were obtained.

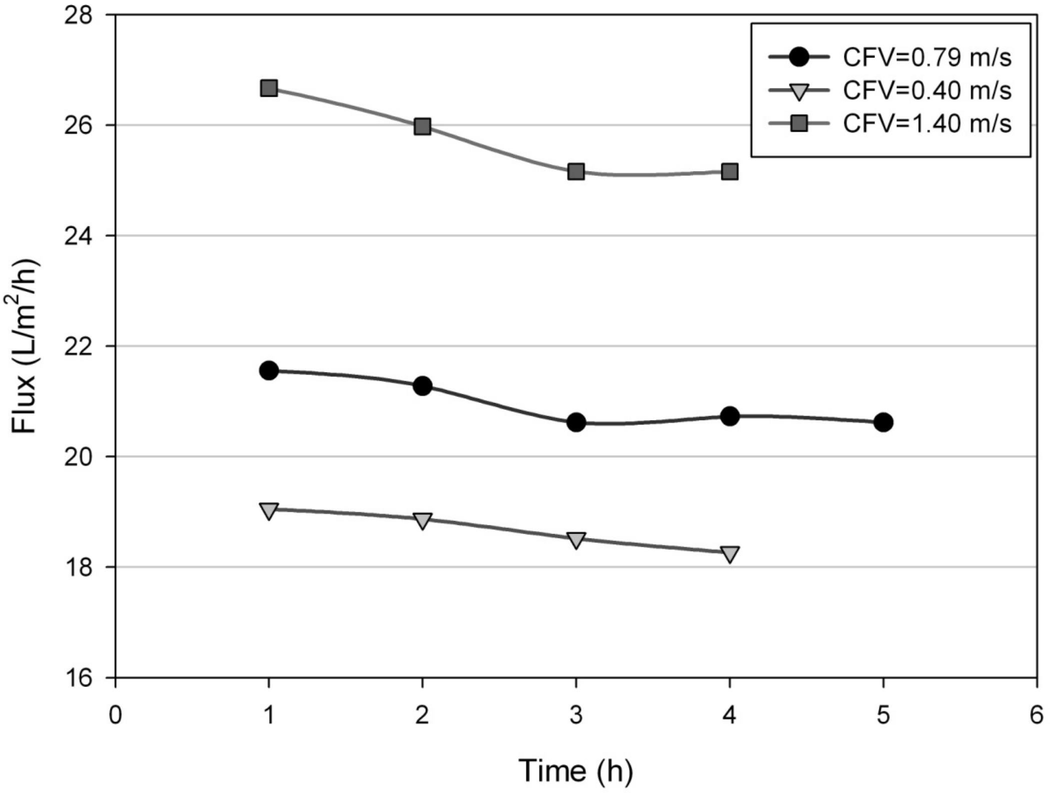


Figure 4.11 Effect of CFV on NF permeate flux when TMP=4.03 bars at 20±2^{0}C

As shown in Figure 4.11, NF CFV variations affected the system performance in the same manner as UF in terms of flux decline. Such that as the cross flow velocity increased from 0.40 to 1.40 m/s, steady-state permeate flux increased from 18.3 L/m^2-h to 25.2 L/m^2-h. In other words, with a three-fold increase in CFV, there was about 50 % increase in permeate flux. In the meantime, increasing CFV from 0.40 m/s to 0.79 m/s, caused only a 18 % increase in permeate flux; it increased from 18.3 L/m^2-h to 21.6 L/m^2-h. In addition, increasing CFV also increased the flux decline and also the time to reach steady state. The initial flux at the highest CFV tested was much greater than its steady state value; while that at the lowest CFV tested was slightly greater than that at steady state. It is known that higher velocities are the main reason for the distortion of filter cake that forms on membrane surface during filtration operation. Therefore permeate flux increases by an increase in CFV by this reducing effect on the cake resistance [46]. In agreement with this, Koyuncu has also reported that dye deposition and concentration polarization are one of the main reasons for flux declines at low cross-flow velocities [45]. Based on the results obtained under different CFV conditions, it can be concluded that NF using NP010 membrane at a high CFV is useful to extent the membrane cleaning cycles and hence to provide a longer membrane service life.

Although dyeing is mainly applied before mercerization steps, due to higher alkaline conditions and high temperature, fabric ceases its dye content at every post-rinsing or washing step of mercerization process. This fact further supports the above-mentioned argument that relates flux decline to the deposition of dye particles over the surface of the membrane. Characterization of the first post-rinsing tank wastewater of the indigo dyeing process as reported by Uzal [47] and the first post-rinsing tank wastewater of the mercerization process of the same textile mill in which caustic recovery studies conducted is compared in Table 4.8. As can be depicted, the wastewater from the first post-rinsing tank after mercerization is much higher in pollution load as compared to the wastewater from the first post-rinsing tank after indigo dyeing. The mercerization wastewater is with a COD of 8524 mg/L while dyeing wastewater is with a COD of only 1547 mg/L. More importantly, color in the mercerizing wastewater is more than twice that in the dyeing wastewater. Therefore, it is likely to have dye deposition and concentration polarization problems that are encountered in NF of dyeing wastewater [47] in the NF of mercerizing wastewaters.

Table 4.8 Comparison of the first rinsing tank effluents from indigo dyeing and mercerizing processes of the textile mill

Wastewater Source	pH	COD (mg/L)	Color (Pt-Co)	Alkalinity (mg/L $CaCO_3$)
Indigo Dyeing 1st Post – rinsing	11.2	1547	4824	4000
Mercerizing 1st Post - rinsing	12.3	8524	10113	41163

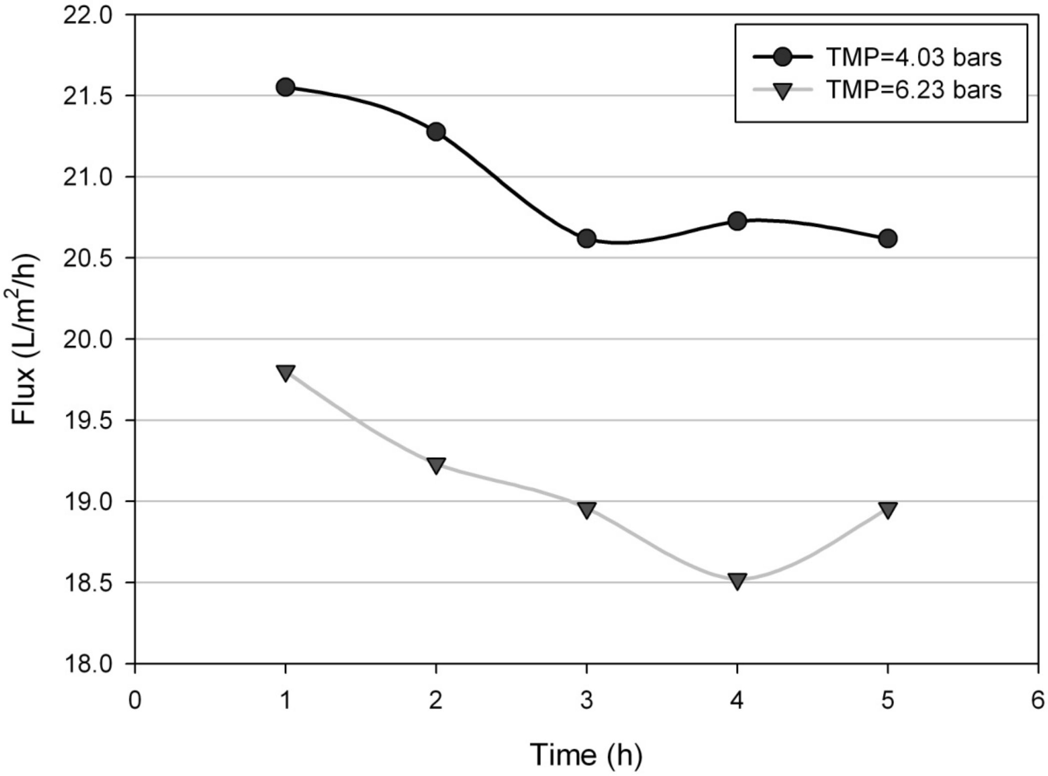


Figure 4.12 Effect of TMP on NF (NP010) permeate flux when CFV=0.79 m/s at 20±2^{0}C

TMP is one of the most important operational parameter that determines membrane performance. In order to evaluate how TMP does affect the flux behavior of NF process, the system was operated with the selected NP010 NF membrane at the TMP's of 4.03 and 6.23 bars and the flux decline was followed. The results obtained are presented in Figure 4.12. As can be depicted from this figure, although the flux decline trend was quite similar, permeate flux at 4.03 bar TMP was greater than at 6.23 bar. In general higher permeate fluxes are expected at higher TMP; as increasing pressure difference affect filtration driving force through the membrane or increase it [48]. However the results are contrary to this general expectation. As can be seen, steady-state permeate flux at 4.03 bar TMP is about 1.6 L/m^2-h higher than that at 6.23 bars. Similarly, initial flux observed at 4.03 bar TMP (21.5 L/m^2-h) is well above that observed at 6.23 bar (19.8 L/m^2-h). This unexpected result was attributed to the particle deposition on the membrane surface. Satyanarayana reported that deposition mechanisms on membrane surface come into existence faster at higher pressures [49]. These retained solutes on the membrane surface reduce flux by forming a second boundary layer as a result of concentration polarization.

After assessing the flux behavior of NP010 NF membrane with different TMP and CFV, rejection, which is the secondary performance indicator of a membrane filtration system performance, was evaluated in terms of color and COD. Figure 4.13 summarizes the steady state COD and color retentions along with NaOH recoveries for various CVFs and TMPs tested for the NP010 NF membrane.

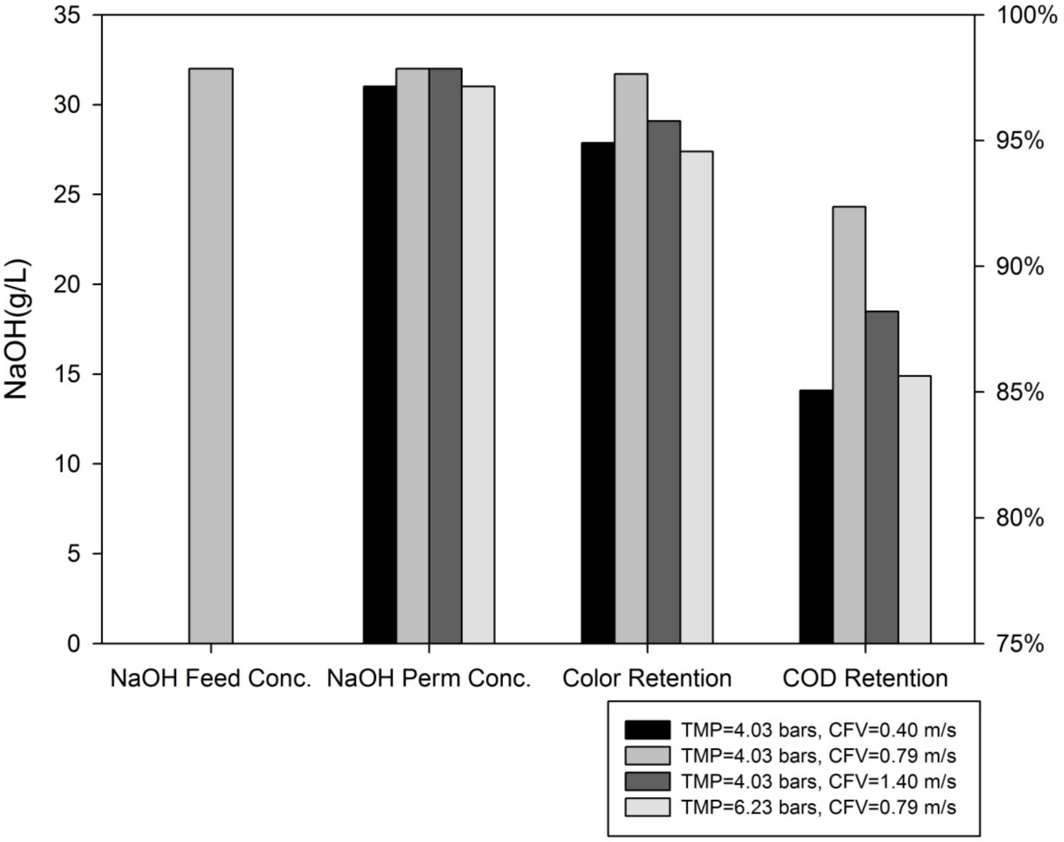


Figure 4.13 Effect of TMP and CFV on NaOH recovery, Color and COD retentions at steady state (membrane: NP010 and T = 20±2^{0}C)

As seen from Figure 4.13 for all the experimental conditions, membrane filtration using NP010 membrane provided successful caustic separations. When the COD and color retentions are also considered, it is immediately seen that NF with NP010 membrane provides the best performance at a TMP of 4.03 bar and a CFV of 0.79 m/s. What is also seen from Figure 4.13 is that the greatest effect of operational parameters is on COD retention and the effect on color retention is not that large. Such that increasing CFV for the same TMP increased COD and color retentions until it reaches to 0.79 m/s. After that point increasing velocity more, affected the system inversely. If TMP effect is examined, it can be seen that increasing the pressure from 4.03 to 6.23 bars at the same CFV (0.79 m/s) resulted in a slight increase in COD and a slight decrease in color retention (Figure 4.13). Generally rejection is expected to increase with the increase in flux due to convective transport. By the way concentration polarization, which cause decrease in retentions, starts to increase with pressure [46]. As a result, possibility of both pressure side effects concentration polarization and convective transport could have prevented considerable changes in COD and color retentions.

Real operating conditions of mercerizing or caustification processes in the textile mill was discussed before. It was emphasized that rinsing operations after alkaline processes are applied at very high temperatures (80-90 ^{0}C) to remove impurities coming from previous production stages and to provide a resistant silk shine and good handle features to the fabric. On account of this high temperature, temperature effect on NF performance was investigated in order to better evaluate caustic recovery and to generate results applicable under real operating conditions of the textile mill,.

NP010 NF membrane was again used to investigate the effect of temperature on membrane filtration process in terms of flux, NaOH recovery, COD and color retentions. Two different CFVs (0.79 and 0.40 m/s) were applied at the same TMP (4.03 bars) at 40^{0}C. Considering the process conditions at the mill, 40^{0}C was chosen as the elevated temperature to work with. In the process, rinsing waters are generated at the temperature of 80-90^{0}C and then cooled down to 40-45^{0}C by passing thru heat exchangers. Flux behavior of NP010 membrane at 40±2^{0}C is shown in Figure 4.14.

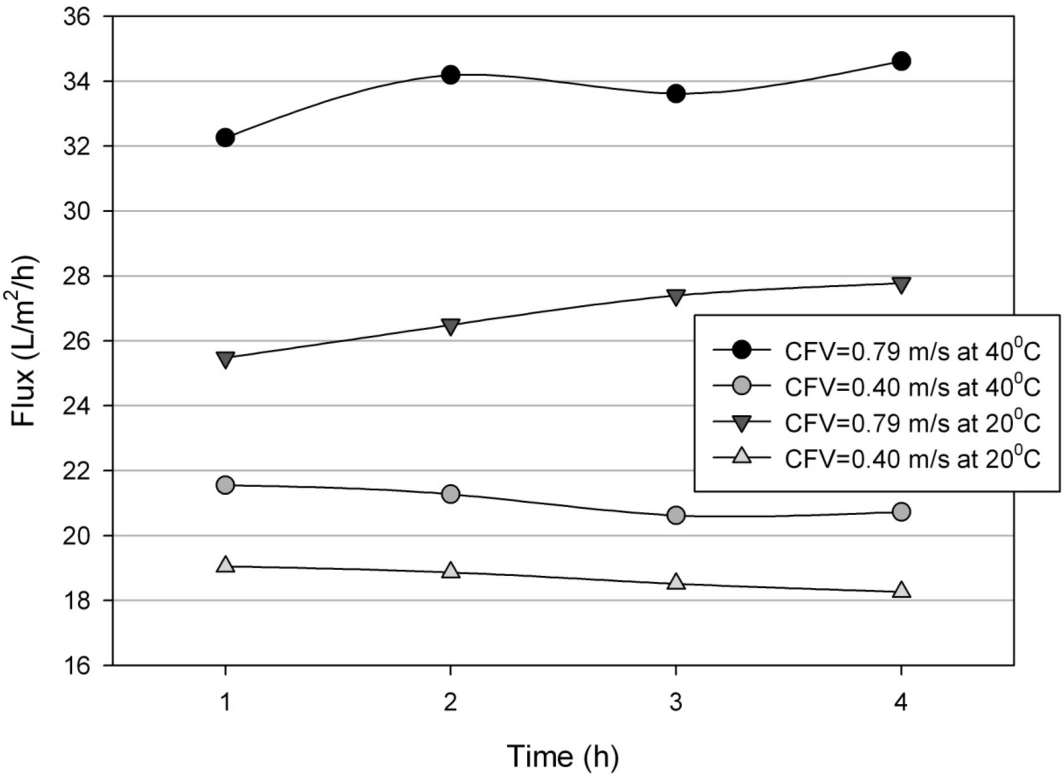


Figure 4.14 Effect of temperature on permeate flux at TMP = 4.03 bars for CFV = 0.79 & 0.40 m/s

As shown in Figure 4.14, increasing the feed temperature from 20 to 40^0C has improved the permeate flux for both cross-flow velocities. There occurred about a 50 % increase in permeate flux when the temperature was increased from 20 to 40° at the cross-flow velocity of 0.79 m/s. However, the increase in permeate flux with temperature was much less at the cross-flow velocity of 0.40 m/s. Due to decreasing effect of temperature on viscosity, increasing in permeate flux is an expected phenomena [50]. Schlesinger reported a strong influence of temperature on NF permeate flux of various NF and UF membranes such that flux is doubled by increasing temperature from 20 to 49^0C [36]. Temperature has also an effect on retention mechanism of membrane processes. Effect of temperature on COD and color retentions can be compared by the Figure 4.15. As can clearly be seen, the optimum performance is at the temperature of 40 °C at a CFV of 0.79 m/s when the flux and retention parameters are considered together.

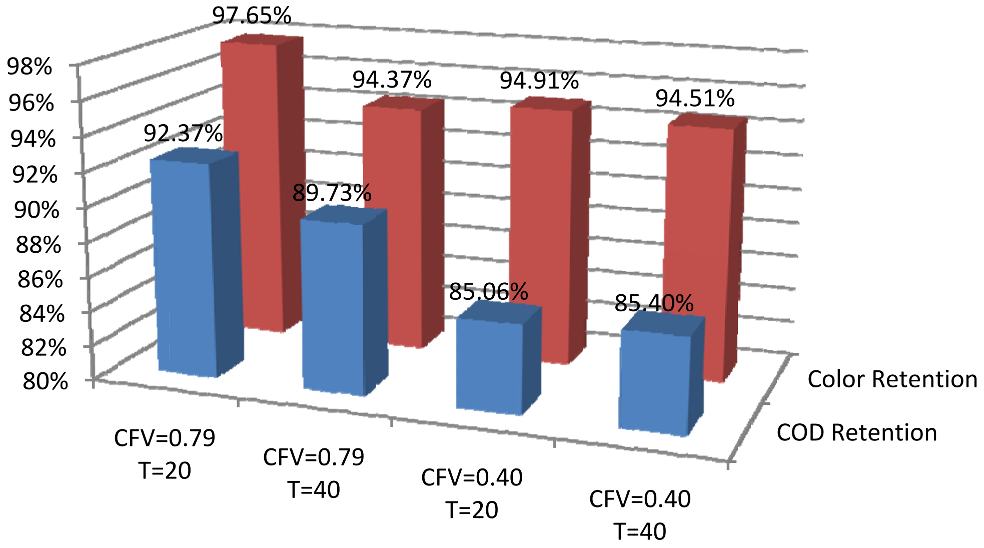


Figure 4.15 Effect of temperature on NF retentions
for CFV = 0.79 and 0.40 m/s at TMP = 4.03 bars with NP010 NF membrane

4.6 Pilot Plant Studies

Caustic recovery pilot plant work was initially conducted by the mill's technical staff and observed that SelRO MPT-34 pilot plant system faces an immediate clogging problem and therefore operational difficulties. Thereafter, the present study was conducted and the time dependent variation in the performance of the system was monitored. As presented in Table 4.9, the recovery tests with SelRO MPT-34 pilot plant system was more successful in terms of caustic separations with a 98% COD and 99% color retentions than that achieved under laboratory conditions.

Table 4.9 Caustic recovery test results by SelRO MPT-34 pilot plant at TMP = 20 bar

Time (hour)	Temperature (^{0}C)	Feed NaOH (g/L)	Permeate NaOH (g/L)
t = 1	70	44	16
t = 2	90	68	52
t = 3	95	60	58
t = 4	98	64	60

As seen from the results, the system reaches up to 80% caustic recovery after a 2 hours period as proportional to volumetric recovery of the system. After this time on, the caustic recovery became stable making the pilot system successful. However, the system was found to be not applicable practically as the permeate flux was very low or almost null by this time and there was a serious increase in the temperature (Table 4.9). Since there is no cooling system in the pilot plant, the system temperature had reach up to 98 ^{0}C after a short time period. As denoted in Chapter 3, allowed operating temperature of this system is 70 ^{0}C. However, when the rinsing process temperature (70 – 80^{0}C) of the mercerizing operation is considered, overheating of the membrane after a short time is unavoidable unless there is a cooling system. Furthermore, in extended use of organic membranes at highly alkaline conditions, 60^{0}C should not be exceeded [36]. Thus, it is not concern to say that the result obtained from this study do make a complete simulation of the real scaled system as there is no cooling system within the tested pilot plant.

Temperature rise was not in fact the only operational difficulty with the pilot plant system. There was very rapid decline in permeate flux from the system due to heavy solids load in the feed or in the mercerizing effluent. As mentioned before, the pilot system does not have its own prefiltration unit. However when the high inorganic and fiber residue content of mercerizing wastewater is considered, at least a coarse filtration seems to be necessary. In the present study, a very coarse filtration of about 5 mm has been applied. But, as it is too coarse, it was not satisfactory in decreasing the solids load to the pilot system. Figure 4.16 shows the coarse filtration apparatus added to the system and how much fiber residue is collected on it in half an hour time.

Figure 4.16 SelRO MPT-34 Pilot system feeding tank coarse filtration unit

Results obtained from pilot studies have leaded to the investigation of eliminating the existing clogging problem. Flat sheet type MPF-34 NF membrane has been used to evaluate the problem under laboratory scale conditions and to assess the possible improvement in membrane fouling with the application of microfiltration to reduce clogging.

Microfiltration studies had been found unsuccessful for different kind of membranes (Table 3.1) pore sized from 1.2 to 25 μm at 25 mm Hg pressure. Therefore it was decided to apply a high-pressure MF process with a tighter membrane (0.45μm) prior to NF process. Table 4.10 shows the steady state recovery and retention performances of NF and MF+NF applications.

Table 4.10 NF and MF+NF tests results with MPF-34 and MF-45 membranes at steady state and 20 ± 2^0C

Membrane and operating conditions		COD (mg/L)	Color (Pt-Co)	NaOH (g/L)
	Feed	17890	8600	41
MPF-34 TMP = 4.03 bar CFV = 0.79 m/s	Permeate Quality	498	26	41
	Retention, %	**97.22**	**99.70**	
	Feed	11780	7370	24
MF-45 TMP = 1.73 bar	Permeate Quality	2350	1288	24
	Retention, %	**80.05**	**82.53**	
MPF-34 TMP = 4.03 bar CFV = 0.79 m/s	Permeate Quality	210	14	24
	Retention, %	**94.78**	**99.43**	

When the MPF-34 is applied in total recycle mode like the previous NF tests, it was seen that caustic separation is satisfactory. Meanwhile, COD and color retentions reach considerably higher values than the previously applied NF experiments (Table 4.7). Providing such permeate qualities at very low organic content and nearly colorless states promotes the reuse of caustic solutions.

Another application of MPF-34 is executed under concentrated mode conditions. Beside that a high-pressure MF application is incorporated with NF application as a pretreatment option. Results of MF+NF application should be evaluated in terms of mainly two points. One of them is the effect of MF process on NF permeate flux values. Figure 4.16 gives the variation of permeate flux of NF with and without prefiltration.

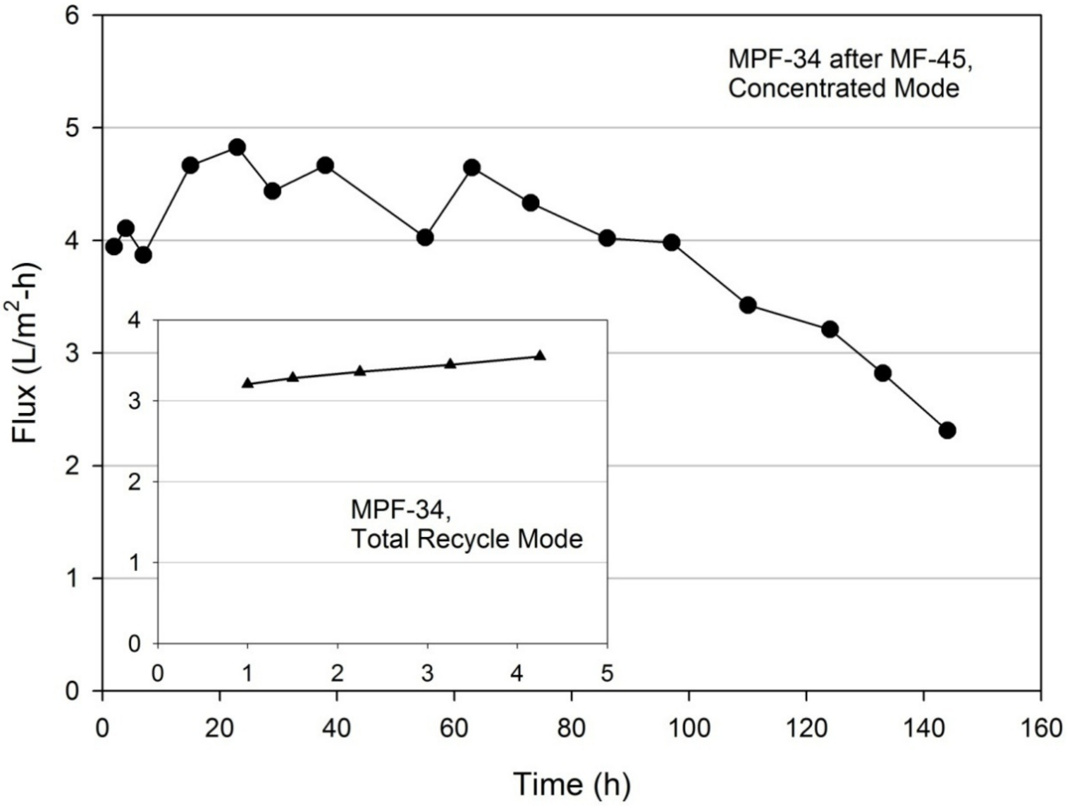


Figure 4.17 Permeate flux variations with time of MPF-34 and MF-45+MPF-34 NF processes at 20 ±2 ^{0}C

Figure 4.16 gives the time variation of NF permeate flux from MPF-34 membrane with and without MF application. Although process durations highly differ from each other; an increasing effect of MF process on permeate flux can be observed in Figure 4.16. Starting from the beginning of NF process, MF application has influenced the permeate fluxes positively but not higher than 15%. There was an increasing trend in permeate flux until 23th hour. After that time, membrane fouling was observed to start resulting in a decrease in permeate flux.

Second effect of MF on NF that should be evaluated is the effect on NF recovery and retention capacities. There was no increasing effect of MF on NF was observed with respect to retention and recovery capacities (Table 4.10). However, as another barrier to wastewater, MF+NF application has yielded lower COD and color parameters. As a result high-pressure MF process can be incorporated with the NF operation in order to decrease cleaning cycles and in addition to this final permeate quality will be increased.

CHAPTER 5

SUMMARY

This study is conducted to develop a new caustic recovery process alternative for a denim producing textile mill located in Kayseri – Turkey. The tests have been carried out with the mercerization process rinsing effluents of the mill and the membrane processes have been applied.

Experimental studies have been performed basically in at three stages. At the first stage of the study, mercerization process rinsing process effluents have been characterized. Then at the second stage of the study to improve treatment efficiency of membrane processes some kind of pretreatment alternatives have been evaluated. At the last stage of the study UF and NF membrane operations have been applied to accomplish the recovery purpose. After the completion of lab scaled experiments, a pilot plant study was also conducted to observe process under real conditions. In the proceedings paragraphs, the results of these studies are summarized.

In the characterization studies carried out separately for both total finishing effluent and rinsing effluents, both wastewaters were found as highly alkaline with a comparatively high pollution load in terms of COD, color, conductivity and solids content. It has been observed that there was a drastic decrease in the caustic content and consequently pollution content of the wastewater from rinsing tanks. Such that the effluents from the first two rinsing tanks were found to constitute 80% of the total wastewater load. Thus, caustic recovery studies were carried out with the wastewater generated from these first two rinsing tanks.

In the pretreatment studies first of all membrane prefiltration methods have been applied. None of a wide range of microfiltration membranes from ordinary ones to special ones which are durable to highly alkaline conditions has shown satisfactory performance. In both of the simple and computerized dead end microfiltration experiments carried out at 25 mmHg operating pressure sudden clogging of membranes has been observed in less than 1 min. Furthermore all the membrane types which were cellulose acetate, PVDF, PTFE and PES have shown similar results in terms of clogging problems. As a result it was concluded that usual prefiltration methods which are mostly applied before membrane operations are not proper for mercerizing effluents.

Flocculation and centrifugation were the other applied pretreatment alternatives. Both of these methods have been inefficient due to the same reason with prefiltration such that fiber residues have made removal mechanisms of these processes unsuccessful.

UF studies which were applied without any pretreatment except a coarse filtration have been successful in terms of caustic recovery and COD and color retentions. Despite all the UF tests carried out under different operational conditions have provided successful caustic soda recovery, performances in terms of COD and color retentions and also permeate fluxes were different. TMP of 4.03 bars and CFV of 0.79 m/s at 20 ± 2^0C have been found as the optimum operating condition for the UF of caustic finishing wastewater. It has resulted in a purified caustic permeate with 93.86% color and 83.84% COD retentions and 13.55 L/m^2 permeate flux. When the effect of TMP and CFV on permeate flux was investigated it was seen that increasing both TMP and CFV has influenced flux positively. However if the results were evaluated in terms of COD and color retentions, it can be concluded that increase in TMP and CFV has yielded decrease in retentions. Meanwhile, when it is considered that observed decrease in retention capacity is very low, high TMP and CFV for this system are much more preferable.

NF process which has been evaluated by means of two different membranes has been found also as successful in caustic recovery. It provided 94.91% color and 85.06% COD retention with 18.26 L/m^2 permeate flux at the same operational conditions with UF. In spite of slightly higher COD and color retentions, NP010 has been found more successful achieving 3 times higher permeate fluxes than NP030. When the performance evaluation was done under different operating conditions 4.03 bars TMP and 0.79 m/s CFV at 20 ± 2^0C has been found as the most efficient. Although almost the same caustic recoveries have been obtained, increase in TMP and CFV have influenced system performance negatively. When the effect of temperature was evaluated by increasing feed temperature from 20 to 40^0C, higher fluxes with lower recovery and retentions capacities have been acquired. At higher CFV this reduction in recovery and retention capacities beside serious increase in flux can be seen more clearly.

Pilot-scale studies which were conducted with a SelRO MPT-34 membrane unit have been found successful in terms of caustic separations with higher COD and color retentions than the laboratory-scale experiments. However, due to the lack of cooling within the pilot-scale system and also prefiltration, rapid heating and clogging problems were encountered. Therefore, the pilot-scale system could typically be operated for only 4 hours until there was no permeate flow.

CHAPTER 6

CONCLUSIONS

Based on the results obtained in this study; in general, it can be concluded that the treatment of caustic finishing wastewater by a combination of UF and NF treatment results in an effluent quality that can be recycled into the finishing process after evaporation. The dissolved and suspended substance are almost completely retained and concentrated, while the purified caustic passes through the membrane. As much as 95% or more of the caustic is recovered, while its concentration remains unchanged.

The other conclusions drawn from the present study are as follows:

1. All the findings from the laboratory pretreatment tests revealed that MF, flocculation and centrifugation are not effective and efficient pretreatment methods for caustic finishing wastewater from denim textile production.

2. The laboratory tests with GR95PP UF membrane having a MWCO of 2000 have shown that UF is successful in providing a relatively clean caustic solution with 93.86% color and 83.84% COD retentions. As the permeate from GR95PP is still high in color (513 Pt-Co) and COD (2590 mg/L), it appears that it is essential to have further purification of it.

3. Further purification of the permeate from UF via NF using NP010 and NP030 membranes was satisfactory providing a clean permeate or caustic solution. Among these two NF membranes, NP010 membrane was better providing a higher permeate flux along with 94.9% and 85.06 % color and COD removals, respectively.

4. Over the range of temperature studied, the NF of the permeate from UF revealed that the permeate flux increases seriously with an increase in temperature.

5. Pilot-scale tests with the SELRO MPT-34 unit were successful in terms of caustic purification and recovery. The system provided high COD and color retentions of 98 % and 99 % respectively producing a permeate or caustic solution with a COD of 498 mg/L and color of 26 Pt-Co. However, the operation of the pilot-scale system was disturbed by rapid clogging and temperature rise problems.

6. When the laboratory filtration system was operated with the NF membrane MPF-34 employed in the SELRO MPT-34 unit, it was seen that high-pressure MF prior to NF has increased permeate flux by only 15%.

CHAPTER 7

RECOMMENDATIONS

An overall evaluation of the findings from laboratory-scale and pilot-scale tests reveals that the flux decline and temperature increase problems observed during pilot-scale tests should be further investigated. Additional prefiltration tests seem to be essential for a better removal of suspended solids prior to NF. A wide variety of MF membranes operated under a wide variety of operational conditions may produce better results and therefore may lessen flux decline problem during NF.

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APPENDIX A

Table A1. RAW DATA OF NF MEMBRANE EXPERIMENTS

Membrane : GR95PP Type : UF

Operating Conditions

	Feed	Retantate	Pump
Pressure (bar) :	5.00	5.00	5.25
Temperature (^{0}C) :	20 ± 2		
TMP (bar) :	4.03		
CFV (m/s) :	0.42		

Clean Water Experiment

Time (h)	Flux (L/m^2-h)
1	33.09
2	25.86
3	19.15
4	15.41
5	13.55
6	12.23
7	10.83
8	10.59
9	10.20

Wastewater Experiment

Time (h)	Flux (L/m^2-h)	NaOH (g/L)	Feed COD (mg/L)	Perm COD (mg/L)	Feed Color (Pt-Co)	Perm Color (Pt-Co)
1	7.54	32	18856	2590	8750	538
2	10.22	32	17565	2687	9960	535
3	11.11	32	18005	2337	8905	521
4	11.01	32	17590	2243	9200	529
5	11.31	32	17456	2725	9875	520
6	11.44	32	16110	2585	10250	517

Membrane : GR95PP Type : UF

Operating Conditions

	Feed	Retantate	Pump
Pressure (bar) :	3.50	3.20	4.90
Temperature (^{0}C) :	20 ± 2		
TMP (bar) :	2.38		
CFV (m/s) :	0.79		

Clean Water Experiment

Time (h)	Flux (L/m^2-h)
1	16.39
2	12.66
3	10.70
4	9.48
5	8.81
6	8.47
7	8.26

Wastewater Experiment

Time (h)	Flux (L/m^2-h)	NaOH (g/L)	Feed COD (mg/L)	Perm COD (mg/L)	Feed Color (Pt-Co)	Perm Color (Pt-Co)
1	5.20	32	28240	2173	7050	524
2	5.95	32	24890	2375	8900	544
3	6.22	32	27100	2615	7500	542
4	6.40	32	25680	2345	7500	556
5	6.53	32	22560	2690	7875	558
6	6.72	32	24985	2480	7850	564
7	6.68	32	27155	2178	7855	564

Membrane : GR95PP Type : UF

Operating Conditions

	Feed	Retantate	Pump
Pressure (bar) :	7.20	7.20	7.00
Temperature (^{0}C) :	20 ± 2		
TMP (bar) :	6.23		
CFV (m/s) :	1.40		

Clean Water Experiment

Time (h)	Flux (L/m^2-h)
1	28.57
2	25.64
3	24.69
4	23.81
5	23.81

Wastewater Experiment

Time (h)	Flux (L/m^2-h)	NaOH (g/L)	Feed COD (mg/L)	Perm COD (mg/L)	Feed Color (Pt-Co)	Perm Color (Pt-Co)
1	9.45	32	18990	2380	7350	379
2	9.96	32	20120	2330	7425	396
3	10.50	32	17700	2268	7125	395
4	10.82	32	19920	2433	7300	399
5	10.94	32	20070	2538	7485	394
6	11.11	32	20073	2455	7678	397

Membrane : GR95PP Type : UF

Operating Conditions

	Feed	Retantate	Pump
Pressure (bar) :	5.20	4.80	6.40
Temperature (^{0}C) :	20 ± 2		
TMP (bar) :	4.03		
CFV (m/s) :	0.79		

Clean Water Experiment

Time (h)	Flux (L/m^2-h)
1	45.45
2	35.09
3	29.85
4	27.03
5	25.64
6	24.39

Wastewater Experiment

Time (h)	Flux (L/m^2-h)	NaOH (g/L)	Feed COD (mg/L)	Perm COD (mg/L)	Feed Color (Pt-Co)	Perm Color (Pt-Co)
1	11.52	32	15800	2660	7575	499
2	12.56	32	16340	2780	7350	516
3	13.05	32	16380	2950	7600	500
4	13.19	32	12800	2670	8050	494
5	13.33	32	15900	2570	7925	516
6	13.55	32	16025	2590	8365	513

Membrane : NP030 Type : NF

Operating Conditions

	Feed	Retantate	Pump
Pressure (bar) :	5.20	4.80	6.40
Temperature (^{0}C) :	20 ± 2		
TMP (bar) :	4.03		
CFV (m/s) :	0.79		

Clean Water Experiment

Time (h)	Flux (L/m^2-h)
1	18.25
2	16.95
3	17.24
4	17.09
5	17.39

Wastewater Experiment

Time (h)	Flux (L/m^2-h)	NaOH (g/L)	Feed COD (mg/L)	Perm COD (mg/L)	Feed Color (Pt-Co)	Perm Color (Pt-Co)
1	5.99	32	16540	1490	6950	110
2	5.92	32	16480	1495	7250	118
3	5.99	32	16540	1500	7350	135
4	6.02	32	16107	1535	7675	119

Membrane : NP010 Type : NF

Operating Conditions

	Feed	Retantate	Pump
Pressure (bar) :	5.20	4.80	6.40
Temperature (^{0}C) :	20 ± 2		
TMP (bar) :	4.03		
CFV (m/s) :	0.79		

Clean Water Experiment

Time (h)	Flux (L/m^2-h)
1	37.04
2	39.22
3	40.00

Wastewater Experiment

Time (h)	Flux (L/m^2-h)	NaOH (g/L)	Feed COD (mg/L)	Perm COD (mg/L)	Feed Color (Pt-Co)	Perm Color (Pt-Co)
1	21.55	32	13030	1405	6875	191
2	21.28	32	14340	1505	7000	172
3	20.62	32	14540	1400	7000	205
4	20.73	32	15980	1350	7100	182
5	20.62	32	16110	1229	7475	176

Membrane : NP010 Type : NF

Operating Conditions

	Feed	Retantate	Pump
Pressure (bar) :	5.15	4.85	6.10
Temperature (^{0}C) :	40 ± 2		
TMP (bar) :	4.03		
CFV (m/s) :	0.79		

Clean Water Experiment

Time (h)	Flux (L/m^2-h)
1	71.43
2	74.63
3	76.92
4	78.13
5	78.13
6	78.13

Wastewater Experiment

Time (h)	Flux (L/m^2-h)	NaOH (g/L)	Feed COD (mg/L)	Perm COD (mg/L)	Feed Color (Pt-Co)	Perm Color (Pt-Co)
1	32.26	32	9760	1525	6000	357
2	34.19	32	11090	1898	6225	305
3	33.61	32	12730	1895	6125	288
4	34.62	32	15070	1445	6175	247

Membrane : NP010 Type : NF

Operating Conditions

	Feed	Retantate	Pump
Pressure (bar) :	5.10	4.90	5.10
Temperature (^{0}C) :	40 ± 2		
TMP (bar) :	4.03		
CFV (m/s) :	0.42		

Clean Water Experiment

Time (h)	Flux (L/m^2-h)
1	72.46
2	111.11
3	104.17
4	100.00

Wastewater Experiment

Time (h)	Flux (L/m^2-h)	NaOH (g/L)	Feed COD (mg/L)	Perm COD (mg/L)	Feed Color (Pt-Co)	Perm Color (Pt-Co)
1	25.48	32	14390	2263	5063	241
2	26.49	32	13640	2375	5013	289
3	27.40	32	15590	2350	5150	285
4	27.78	32	16470	2405	5188	281

Membrane : NP010 Type : NF

Operating Conditions

	Feed	Retantate	Pump
Pressure (bar) :	5.10	4.90	5.20
Temperature (^{0}C) :	20 ± 2		
TMP (bar) :	4.03		
CFV (m/s) :	0.42		

Clean Water Experiment

Time (h)	Flux (L/m^2-h)
1	37.04
2	36.70
3	36.70

Wastewater Experiment

Time (h)	Flux (L/m^2-h)	NaOH (g/L)	Feed COD (mg/L)	Perm COD (mg/L)	Feed Color (Pt-Co)	Perm Color (Pt-Co)
1	19.05	32	15050	2063	4725	268
2	18.87	32	15190	1990	4975	261
3	18.52	32	16470	1920	4663	220
4	18.26	32	15240	2278	4675	238

Membrane : NP010 Type : NF

Operating Conditions

	Feed	Retantate	Pump
Pressure (bar) :	7.10	6.90	7.20
Temperature (^{0}C) :	20 ± 2		
TMP (bar) :	6.03		
CFV (m/s) :	0.79		

Clean Water Experiment

Time (h)	Flux (L/m^2-h)
1	70.42
2	68.49
3	70.42

Wastewater Experiment

Time (h)	Flux (L/m^2-h)	NaOH (g/L)	Feed COD (mg/L)	Perm COD (mg/L)	Feed Color (Pt-Co)	Perm Color (Pt-Co)
1	19.80	32	15930	2120	4500	291
2	19.23	32	14450	2150	4550	247
3	18.96	32	16710	2073	4600	260
4	18.52	32	14700	2185	4388	259
5	18.96	32	15390	2210	4500	245

Membrane : NP010 Type : NF

Operating Conditions

	Feed	Retantate	Pump
Pressure (bar) :	5.20	4.80	8.40
Temperature (^{0}C) :	20 ± 2		
TMP (bar) :	4.03		
CFV (m/s) :	1.36		

Clean Water Experiment

Time (h)	Flux (L/m^2-h)
1	43.48
2	43.48
3	43.96

Wastewater Experiment

Time (h)	Flux (L/m^2-h)	NaOH (g/L)	Feed COD (mg/L)	Perm COD (mg/L)	Feed Color (Pt-Co)	Perm Color (Pt-Co)
1	26.67	32	15410	1908	4625	171
2	25.97	32	15310	2010	5088	211
3	25.16	32	15290	1848	5063	213
4	25.16	32	15620	1843	4950	209

Membrane : MPT-34 Type : NF

Operating Conditions

	Feed	Retantate	Pump
Pressure (bar) :	5.10	4.90	6.50
Temperature (^{0}C) :	20 ± 2		
TMP (bar) :	4.03		
CFV (m/s) :	0.79		

Clean Water Experiment

Time (h)	Flux (L/m^2-h)
1	6.73
2	7.09
3	7.27
4	7.49
5	7.49

Wastewater Experiment

Time (h)	Flux (L/m^2-h)	NaOH (g/L)	Feed COD (mg/L)	Perm COD (mg/L)	Feed Color (Pt-Co)	Perm Color (Pt-Co)
1	3.21	41	17410	510	8225	51
2	3.28	41	16940	525	8075	37
3	3.36	41	16420	505	8500	40
4	3.44	41	17710	502	8350	29
5	3.55	41	17890	498	8600	26

Membrane : MF-45 Type : MF

Operating Conditions

	Feed	Retantate	Pump
Pressure (bar) :	2.80	2.60	4.80
Temperature (^{0}C) :	20 ± 2		
TMP (bar) :	1.73		
CFV (m/s) :			

Clean Water Experiment

Time (h)	Flux (L/m^2-h)
1	454.55
2	416.67

Wastewater Experiment

Time (h)	Flux (L/m^2-h)	NaOH (g/L)	Feed COD (mg/L)	Perm COD (mg/L)	Feed Color (Pt-Co)	Perm Color (Pt-Co)
1	81.08	24	7490	1520	6390	980
2	71.43	24	7370	1470	6125	1070
4	57.47	24	7650	1460	6588	1005
5	53.19	24	7805	1560	6980	995
6	49.02	24	8900	1695	7600	1305
7	47.62	24	8700	1560	7495	1245
8	45.87	24	9050	1565	8885	1345
9	45.05	24	9635	1745	9050	1465
10	45.05	24	10160	1880	10005	1540
11.5	42.02	24	11130	1890	9870	1590
14.5	38.17	24	12890	2140	9805	1600
23	26.46	24	11780	2350	9675	1690

Membrane : MPT-34 (after MF-45) Type: NF

Operating Conditions

	Feed	Retantate	Pump
Pressure (bar) :	5.10	4.90	6.50
Temperature (^{0}C) :	20 ± 2		
TMP (bar) :	4.03		
CFV (m/s) :	0.79		

Wastewater Experiment

Time (h)	Flux (L/m^2-h)	NaOH (g/L)	Feed COD (mg/L)	Perm COD (mg/L)	Feed Color (Pt-Co)	Perm Color (Pt-Co)
2	3.94	24	3120	258	1080	5
4	4.11	24	5500	308	2470	15
7	3.87	24	2980	185	1250	25
15	4.66	24	3575	193	1220	7
23	4.83	24	3355	175	1395	8
29	4.44	24	3605	218	1545	17
38	4.66	24	4040	208	1605	23
55	4.03	24	4315	190	1820	21
63	4.65	24	4540	225	1900	23
73	4.33	24	4785	263	2005	20
86	4.02	24	4890	290	2165	49
96	3.98	24	4405	230	2655	4
108	3.42	24	4275	210	2940	7
122	3.21	24	4305	190	2760	12
131	2.82	24	3910	220	2890	18
142	2.31	24	3990	210	2455	14