

TREATMENT OF REACTIVE DYEING WASTEWATER AND RECOVERY OF
BRACKISH WATER BY APPLYING ULTRAFILTRATION

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ABSTRACT

TREATMENT OF REACTIVE DYEING WASTEWATER AND RECOVERY OF BRACKISH WATER BY APPLYING ULTRAFILTRATION

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Reactive dyeing wastewaters (RDW) originating from textile industry are highly colored and have high total organic carbon (TOC), turbidity and salinity content. Ultrafiltration (UF) scenario suggested here aims to keep salt in permeate and reuse resulting permeate in dyeing process. For this purpose, RDW samples were treated with 5 kDa PES and 2 kDa Thin Film GE Osmonics UF membranes. After single stage filtrations, two stage “5 kDa+5 kDa”, “5 kDa+2 kDa” and “2 kDa+2 kDa” applications were carried out at 2 bar with a concentration factor of 2.5; and all the applications retained less than 10% salt. The first scenario provided the lowest color retention of 94% while the other two provided over 98% color retention. The “5 kDa+2 kDa” and “2 kDa+2 kDa” applications retained turbidity and TOC at similar levels of 97-98% and 78-83%, respectively. However, permeate flux from the 5 kDa first stage application was three times higher than the 2kDa first stage application. Dyeing tests have shown that the permeate of “5 kDa+2 kDa” was successful in dyeing middle and dark shaded green, and that of “2 kDa+2 kDa” in dyeing light and middle shaded green. In coloring dark red, both permeates achieved good results. There were no significant loss in permeate qualities of both applications when concentration factor was taken to 10. When the filtration pressure was doubled,

filtration fluxes were doubled for both membranes, however the decrease in filtration flux of first stage 5 kDa was more drastic than first stage 2 kDa.

Keywords: Ultrafiltration, reactive dyeing, salt recovery, membrane filtration



ÖZ

REAKTİF BOYAMA ATIKSULARININ ULTRAFİLTRASYON YÖNTEMİYLE ARITIMI VE ARITILMIŞ TUZLU SUYUN YENİDEN KULLANIMI

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Tekstil sanayi kaynaklı reaktif boyama atıksuları (RBA), yüksek renkliliğe, yüksek toplam organik karbon (TOK), bulanıklık ve tuzluluk içeriğine sahiptirler. Burada önerilen ultrafiltrasyon (UF) senaryosu, RBA'nın tuz içeriğini süzüntü içerisinde muhafaza etmeyi ve elde edilen süzüntüyü boyama işleminde tekrar kullanmayı amaçlamaktadır. Bu amaçla, RBA örnekleri 5 kDa PES ve 2 kDa Thin Film GE Osmonics UF membranları kullanılarak arıtılmıştır. İlk aşama filtrasyon uygulamalarından sonra iki aşamalı “5 kDa+5 kDa”, “5 kDa+2 kDa” ve “2 kDa+2 kDa” seri uygulamaları 2 barda ve konsantre etme faktörü 2.5 olacak şekilde gerçekleştirilmiş ve bu aşamaların her birinde tuz giderimi %10 değerinin altında kalmıştır. İlk senaryo %94 ile en düşük renk giderimini sağlarken, diğer iki senaryoda bu değer %98'in üzerindedir. Seri uygulamardan “5 kDa+2 kDa” ve “2 kDa+2 kDa” seçeneklerinde bulanıklık ve TOK giderim değerleri birbirine yakın ve sırasıyla %97-98 ve %78-83 olacak şekilde gözlenmiştir. Ancak 5 kDa ilk aşama uygulamasında ölçülen akı değeri 2 kDa ilk aşama değerinden en az 3 kat fazladır. Boyama testleri sonucu, “5 kDa + 2 kDa” süzüntü suyu orta ve koyu tonlu yeşil boyamada başarılı olurken, “2 kDa + 2 kDa” süzüntü suyu açık ve orta tonlu yeşil boyamada başarılı olmuştur. Her iki süzüntü suyu da koyu kırmızıya boyamada

başarılı sonuçlar vermiştir. Bu seri uygulamalar, konsantre etme faktörü 10 olacak şekilde tekrarlandığında, süzüntü suyu kalitesinde kötüleşme gözlenmemiştir. Filtrasyon basıncı iki katına çıkarıldığında ise, filtrasyon akıları da iki katına çıkmıştır. Ancak ilk aşama 5 kDa ile gözlenen akı düşüşü 2 kDa için gözlenenden daha fazla ve hızlı olmuştur.

Keywords: Ultrafiltrasyon, reaktif boyama, tuz geri kazanımı, membran filtrasyon



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LIST OF ABBREVIATIONS

ARS	Alternative Recycling Scenario
CMF	Concentration Mode Filtration
COD	Chemical Oxygen Demand
CP	Concentration Polarization
J_{cwi}	UPW flux measured before filtration
J_{rw}	Flux measured during filtration with wastewater
J_{cwf}	UPW flux measured after filtration
J_{cwp}	UPW flux measured after physical cleaning
J_{cwc}	UPW flux measured after chemical cleaning
MF	Microfiltration
MFWM	Ministry of Forestry and Water Management
MWCO	Molecular Weight Cut-off
NF	Nanofiltration
NTU	Nephelometric Turbidity Unit
RDW	Reactive Dyeing Wastewater
RO	Reverse Osmosis
R_{mem}	Membrane's intrinsic resistance
R_{tot}	Total resistance
R_{cp}	Resistance due to concentration polarization
R_{ph-irr}	Fouling resistance remaining after physical cleaning
R_{ch-irr}	Fouling resistance remaining after chemical cleaning
SAC	Spectral Absorption Coefficient
TDS	Total Dissolved Solids
TMP	Trans Membrane Pressure
TRMF	Total Recycle Mode Filtration
TOC	Total Organic Carbon
UF	Ultrafiltration
UPW	Ultra-Pure Water
UNIDO	United Nations Industrial Development Organization
VRF	Volume Reduction Factor

CHAPTER 1

INTRODUCTION

Tackling with industrial wastewaters is becoming a more serious problem and a crucial need as effects of inadequate handling accumulate together with the industrial growth. As industrial activities gain new branches or implemented processes evolve, there occur changes in characteristics of wastewaters which reveals, as a result, new problems if proper treatment is not achieved. Thus, the treatment techniques applied for dealing with industrial wastewaters should keep pace with these changes and overcome revealing problems. Here in this study, one of the main problems related to textile industry and solution to this problem is presented. Problem defined is the need for handling of the wastewaters resulting from reactive dyeing process which is realized during coloring of a textile good in textile manufacturing process. As usage of reactive dyestuff become widespread, salinity of resulting wastewater was added to the color removal problem for textile wastewaters. Solution that is suggested to this problem includes membrane filtration technique as a treatment alternative to the conventional methods.

Textile industry in Turkey stands in a critical place among all manufacturing industry sectors. Being the major contributors to the gross domestic product (GDP) of Turkey with food, chemical, automotive and pharmaceutical industries, textile industry is the 5th fastest growing sub-sector with a 18% share in GDP produced by manufacturing industries. Being among the sector leaders in the region, Turkey exports textile goods to many European Countries and also USA and Russia. Turkey's strategy is to preserve its position and increase its total textile export in the upcoming years by achieving more sustainable textile manufacturing models (Ministry of Science Industry and Technology, 2015; *The Manufacturing Industry in Turkey*, 2014). In

order to sustain the successful profile of textile industry, problems related to manufacturing processes should be handled carefully.

Some manufacturing steps taken place in textile industry, employ processes that need usage of huge amounts of water. Dyeing step of the textile good is one of them. Not only great amounts of water but also various chemicals are used during dyeing process (Yperen, 2006; European Commission, 2003). A special method for dyeing, characterized by the dyestuff used in the method, got more common in recent years. This dyeing method employs reactive dyestuff. These dyes form strong bonds with the fiber that is dyed (Kulkarni et al., 1985). The main auxiliary added to dyebath for dyeing is the salts and the amount of salt used may be up to 2 kg per kg of fabric that is to be dyed. Moreover, for bonding between the fiber and the dyestuff to occur, alkaline conditions with high temperatures are needed. (Schonberger & Schafer, 2003). Used auxiliary chemicals along with the dyestuff identify the characteristics of effluent wastewater. Reactive dyeing wastewater (RDW) is known to be heavily colored and to have high salt content. Moreover, high dissolved solids, organic and suspended matter concentrations and high pH are observed in RDW. Depending on the type of reactive dye used, heavy metals may also be present in the effluent (Correia et al., 1994).

Salt usage in textile industry had started with the emergence of direct and reactive dyes. Being the most suitable dye class for cotton dyeing, utilization of reactive dyestuff and therefore the salinity problem in wastewaters increased (Cook, 1994). Considering the size of the textile industry in Turkey, RDW or textile effluent treatment problem is a recognized issue. The salinity and color problem in receiving bodies as a result of textile manufacturing process has drawn greater attention in Turkey with the pollution observed in Ergene River. National news dating back to 2008, increased public awareness about the problem (Cinokur, 2008; Keskinilic, 2011; Ozmen, 2016). There are more than 2000 factories functioning around the river and in the river basin, quarter of which is producing textile and leather goods (Ministry of Forestry and Water Management [MFWM], n.d.). Resulting industrial effluents with municipal wastewater that is discharged to Ergene River caused the

pollution. River flowrate was observed to be the four times greater than it usually is as a result of wastewater discharges. There were certain increases in the temperature and the conductivity content of the river compared to the case three decades ago, when industrialization was not such widespread in the region. (Arslan, 2012). One of the main problems related with the pollution in Ergene River has been observed on the agricultural activities in the basin. River water contains high concentrations of sodium and chloride. This makes the water unsuitable for irrigation and causes accumulation of sodium and chloride in soil. Resulting salinity and alkalinity causes a decrease in the quality of the agricultural products (Kocaman et al., 2011).

Ergene River Basin Case recovery studies has lead to an addition in Water Pollution Control Regulation¹. In 2011, a parameter for color content of textile and leather industry wastewater was added to the regulation (MFWM, n.d). Integrated Pollution Prevention and Control Regulation in Textile Industry² was also published in the same year to minimize the negative effects of the textile industry related activities.

The sustainability need in textile manufacturing industry and the severity of the problem related with the wastewater of this industry makes successful handling of the wastewater a must. Treatment techniques for textile industry effluents vary with the wastewater composition and the effluent quality to be achieved. Receiving body standards or the will to recover the treatment effluent determines the method applied for handling textile effluents (Aouni et al., 2012). Commonly applied techniques for treating these wastewaters are biological treatment, adsorption processes, oxidation processes with ozone and coagulation-flocculation (Naim & El Abd, 2002; Carmen & Daniela, 2010). Dyestuffs observed in textile effluents are not easily biodegradable which may make biological treatment option troublesome. The usage of chemicals during treatment may result in sludge problem. Advanced oxidation processes or the usage of adsorption with activated carbon, on the other hand, are less favorable since they are comparably costly (Lin & Lo, 1997; Crini, 2006; Streat, 1988). One

¹ Water Pollution Control Regulation, Official Gazette, dated 24.04.2011, numbered 27914.

² Integrated Pollution Prevention and Control Regulation, Official Gazette, dated 14.12.2011, numbered 28142

technique alternative to the ones mentioned above is the membrane filtration. This method has gained more attention in handling textile effluents since it is easy to implement and quite efficient in removing dyestuff and other pollutants from dyeing wastewaters. Water recovery can also be achieved with this method which makes it more preferable considering the need for saving water resources.

Membrane filtration methods used in treating textile effluents are mainly the ones that are driven by pressure difference in application, namely, microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) (Hoek, Pendergast, & Tarabara, 2013). In the studies where membrane filtration method is used to treat RDW, the most common succeeded outputs are reported for NF and RO usage (Qin et al., 2007; Yu et al., 2010). These membranes are quite successful in yielding treatment effluents that are purified from dyestuff, salt and other pollutants. The ones with larger pore sizes, MF and UF, are usually suggested to be efficient pre-treatment options (Ciardelli et al., 2001; Ellouze et al., 2012).

The objective in this study is to investigate the efficiency of UF membranes in removing dyestuff, organic and suspended pollutants from wastewater. The inability of these membranes in removing salts are known. Low rejection rates for salts by these membranes are desired for the sake of the treatment objective which also aims obtaining brackish water as a result of UF treatment to recycle salt and water back to the process.

In order to carry out the UF treatment experiments, RDW samples were taken from an industry where dyeing and following rinsing steps are realized. These wastewater samples were subjected direct UF. Two different UF membranes varying in pore sizes were used in experiments. Both single stage and serial applications with these membranes were tried. In order to check the re-usability of permeates resulting from UF experiments, dyeing tests with these permeates were realized. The optimization studies for treatment scenarios lead to test changes in volume reduction factors (VRF) and trans membrane pressure (TMP). With the increase in VRF, 9/10 of the feed wastewater was attained as permeate. Finally, alternative recycling scenario was

presented in order to meet the need of permeate amount that is just enough for dyebath preparation. This way no storage of permeate would be required.





CHAPTER 2

TEXTILE MANUFACTURING: DYEING PROCESS AND REACTIVE DYEING WASTEWATER

2.1. Textile manufacturing processes

The processes that are realized in a textile industry may vary depending on the raw material handled and the end product to be manufactured. Shortly, it starts with preparing fibers synthetically or naturally. Prepared fibers are used for making yarns and these yarns are subjected to further processing steps such as dyeing and finishing. The process ends with the manipulation of the yarns into desired product (United Nations Industrial Development Organization [UNIDO], 2012). Although the steps applied may vary and narrow down for sub-industries, textile manufacturing process may be summarized as in Figure 2.1.

To end up with a garment or any other textile product (used for furnishing, carpeting etc.) may require the usage of various chemicals. Surface agents, detergents, solvents (CFCs, HCFCs) sizings such as polyvinyl alcohol, bleaching agents (hydrogen peroxide, sodium chlorite etc.) and many other countless chemicals can be used depending on the process applied (Yperen, 2006). In addition to employing chemicals, textile manufacturing process is known for spending huge amounts of water. Contrary to dry processes as fiber production, knitting and weaving; wet processes such as fiber preparation, pretreatment including desizing, scouring and mercerizing in production chain requires great amounts of water usage. Dyeing of the fiber, yarn or fabric that is followed by rinsing steps are usually the most water demanding ones (European Commission, 2003).

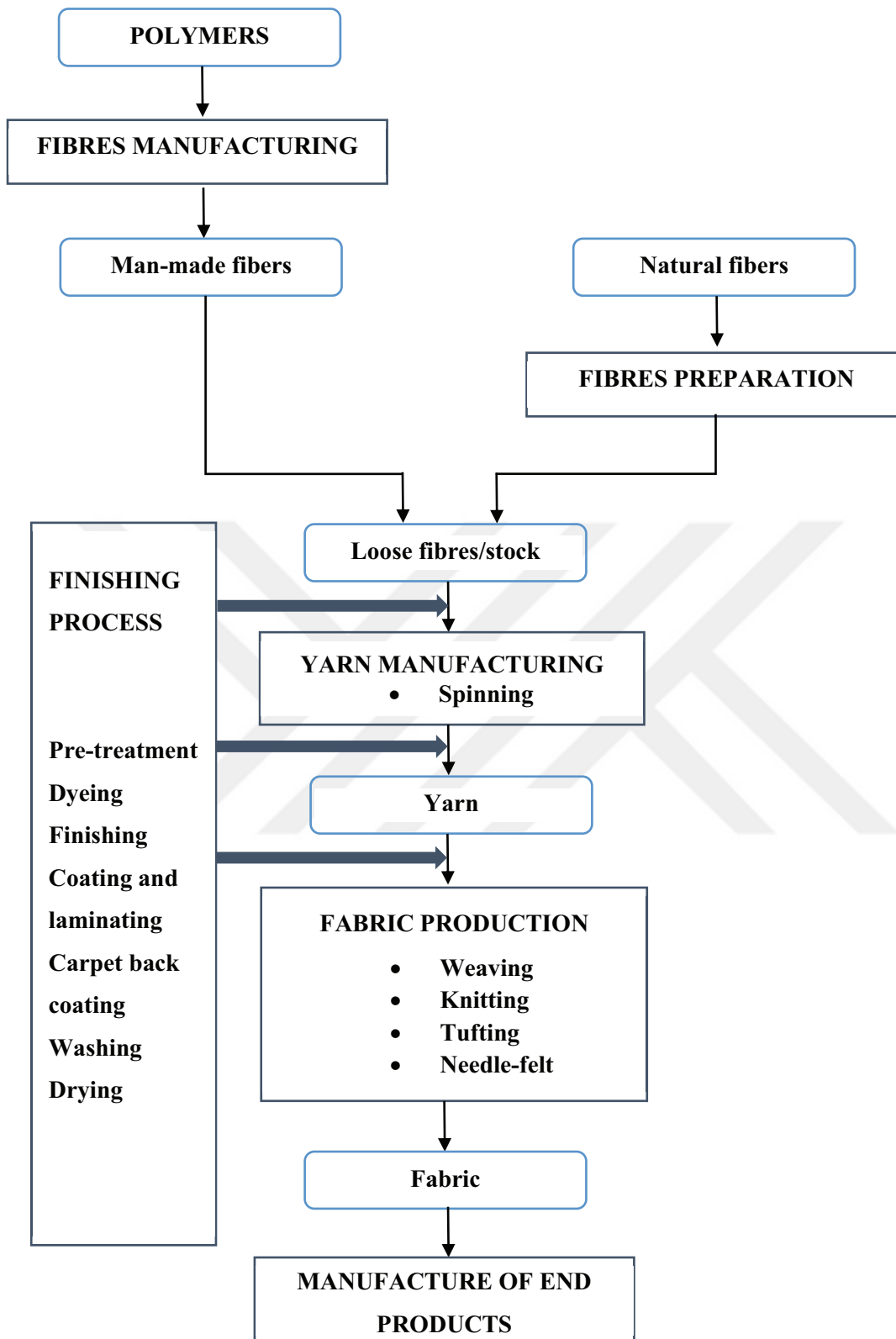


Figure 2.1. Textile manufacturing processes (European Commission, 2003)

2.2. Dyeing of the textiles

From an environmental point of view, coloring textile good has a significant place in textile manufacturing process as it needs huge amounts of input of energy, water and other chemicals (UNIDO, 2012), and generates highly loaded wastewaters. By dyeing textile purpose is to make textile product have the same color shade throughout. Dyestuffs with molecules containing chromophoric group reflect and absorb the light and cause the impression of color. To achieve this, the material to be dyed is faced with aqueous solution containing dyes and dyeing auxiliaries. For the coloration process to be finished, dyes should be adsorbed on and penetrate through the fiber. Coloration can also be achieved by the precipitation of the dye inside the fiber and the reaction of the dyestuff with the material. Once this is completed, diffusion of the dyes back to the solution should be prevented (European Commission, 2003).

Many different types of dyes are used coloring different types fibers. Types of dyes (reactive, acid etc..) used in textile dyeing process depends on the success obtained in fastness (Broadbent, 2001). Fastness is a term used to define the success of the coloring. Colored textiles are subjected to agents (water, light, chemicals etc.) both during manufacturing and use. Good fastness characteristics would mean that dyes are not easily washed away from the textile and not easily fade away (Annis, 2012). There are different ways of classifying the dyes that are used in textile manufacturing. Grouping them in terms of chemical constitution and method of application are the widely used approaches. Some dyes like acid, direct, mordant and reactive dyes have anionic functional groups in common. Vat, azoic and sulfur dyes necessitate chemical reaction before application. Contrary to the first group, basic dyes have cationic functional groups (Needles, 1986).

Table 2.1. Chemical classification of dyes and dyeing application they are used in

Classification according to textile usage	Dyeing application
Acid dyes	Acrylic, wool, nylon, nylon/cotton
Azoic dyes	Cotton, cellulosic fibers
Basic dyes	Cellulosic, protein, nylon, acrylic fibres
Direct dyes	Cotton, cellulosic fibers
Disperse dyes	Polyester, nylon, acetate and triacetate fibres
Mordant dyes	Protein and polyamide fibres
Pigments	Hydrophilic fibres
Reactive dyes	Cellulosics, wool, nylon, silk
Sulphur dyes	Cotton, rayon
Vat dyes (Broadbent, 2001), (Kulkarni et al., 1985)	Cellulosic and synthetic fibers (Needles, 1986)

Acid, direct and reactive dyes are used more than others in textile dyeing. Acid dyes contain sulphonic acid groups, which are usually present as sodium sulphonate salts, and are mainly employed in dyeing acrylic, wool, nylon and cotton. They are applied to the fiber in acidic solutions. Acid dyes have relatively low wet fastness. Direct and reactive dyes are also used dyeing cotton. Electrostatic forces are in function for bonding direct dyes to fiber. Reactive dyes differentiate from other groups with its mechanism of bonding. Covalent bonds between reactive dyestuff and fiber result in strong fastening in reactive dyeing. After their first appearance in the sector in 1956, reactive dyes maintained their increase in dye production until nowadays (Kulkarni et al., 1985).

Reactive dyes are now the most common dye class used to dye cotton textile and this increased their production and application since cotton is one of the highly used raw materials in textile manufacturing. Reactive dyes are known to be anionic and water soluble. Their bonding mechanism makes them have better fastness and substantivity than other dyes. Color shades that are producible with reactive dyes are broad

(Chinta & Vijaykumar, 2013). The characteristics of reactive dyes are presented in more detail in upcoming section since specifications and method of application determines the wastewater characteristics resulting after dyeing process.

2.3. Reactive dyes

Reactive dyes are different from other dyes since they make covalent bonds with the fiber during coloration. Covalent bond that is formed is so strong that dye is thought to become a part of the fiber (Kulkarni et al., 1985). During dyeing, reactive group within the structure of the reactive dye reacts with the reactive group of the fiber. Mechanism which is developed by Ratte and Stephen in 1955 for dyeing cotton with reactive dyes summarizes the reactive dyeing system.



During dyeing, cellulose with the hydroxyl group reacts with the reactive dye with chlorine atom in alkali conditions and dye-fiber covalent bond is formed (Broadbent, 2001) Since reactive dyeing needs reactive group in the fiber to be dyed as well, usage of reactive dyes is mostly suitable for cellulosic, protein and nylon fibers (Needles, 1986).

2.4. Reactive dyeing wastewater

Dyeing wastewater characteristics in textile industry are determined by the dye bath conditions and the chemicals used as dyestuff and dyeing auxiliaries. Not all dyestuff and chemicals used during process remain on the fiber. Unfixed dyes and chemicals after reactions go into the effluent causing deep color, high COD and high dissolved solids. Chemicals that are added are usually identified by the dyeing prescription which is specific for material to be dyed and the used dyestuff. Dyeing process generally follows the steps of preparing the dye and dye bath, interaction of the material with the solution containing dyes and auxiliary chemicals, fixation of the

dye to the material and upcoming washing and drying phases (European Commission, 2003)

Table 2.2. Generally used auxiliary chemicals in dyeing (Correia et al., 1994)

Description	Composition	Function
Salts	Sodium chloride Sodium sulphate Calcium chloride	Neutralize zeta potential of the fiber; Retarder
Acids	Acetic and sulphuric acid	pH control
Bases	Sodium hydroxide Sodium carbonate	pH control
Buffers	Phosphate	pH control
Sequestering agents	EDTA	Complex hardness; Retarder
Dispersing and surface active agents	Anionic, cationic and non-ionic	Disperse dyes; Regulate dye application; Softeners
Oxidising agents	Hydrogen peroxide Sodium nitrite	Insolubilize dyes
Reducing agents	Sodium Hydrosulphite Sodium sulphide	Solubilize dye; Remove unreacted dye
Carriers	Phenyl phenols Chlorinated benzenes	Enhance absorption

In the application of reactive dyes, sodium hydroxide or sodium carbonate is used as alkali in order to create alkaline conditions. Alkaline conditions cause the fiber and the dye to interact. The dyeing bath temperature and the dye bath pH are increased, if the dye is not active enough towards the cellulosic fiber. Reactive groups of dyes do not only tend to bound with cellulosate ion, also hydroxyl ions present in dye bath lead them to make bond with themselves and consequently hydrolysis of the dye takes place. About 20% of the dyes react with water instead of fiber. As a result, unfixed dyes are observed in the effluent and designate the high color content of the wastewater. Another major constituent used in reactive dyeing process is salt. The salt (NaCl or CaCl₂) is added to the dye bath to increase the affinity of dye to fibre, and also to neutralize the negative charge on the surface of the fibre when immersed in solution. Amount of salt required depends upon the affinity of the dye used for the

shade to be produced. Low affinity dyes require more salt addition, whereas high affinity ones need less (European Commission, 2003; Chinta & Vijaykumar, 2013; Broadbent, 2001).

The need for dyestuff and dyeing auxiliaries differs for color shade to be achieved. Dark shades not only require higher usage of dyestuff but also dyeing auxiliaries and salt. In “Best Available Techniques (BAT) Reference Documents (BREF) for Textile Industry”, salt need for dyeing cotton knit fabric with reactive dyestuff is stated to vary between 90 grams per kilogram of textile to 2000 grams, depending on the color tone (Schonberger & Schafer, 2003). Dark shades demand up to 2 kg salt addition for dyeing 1 kg textile. In the same document, RDW characteristics are given for both light and dark shade dyeing (Table 2.3). For these two applications, dye bath is seen as the most polluted one for all parameters tested since that is where the salt, alkali and dyestuff addition takes place.

The other major constituents of the reactive dyeing bath are alkali, urea and soap. Alkali is added to maintain proper pH in dye bath and thus as a dye fixing agent. Urea is added to get required shade of dye. Darker shades require more and lighter shades require less of urea. Soap application is for the removal of the extra colour from fibre surface, and to increase the brightness and stability of dye.

The wastewater, so called “reactive dyeing effluent” resulting from the application of these chemicals, is consequently with high dissolved solids, COD, and color content (Table 2.3). The TSS and BOD content is stated to be intermediate. The wastewater is with a high pH and temperature, since dyeing mostly requires presence of alkaline conditions with hot water. Depending on the structure of the dyestuff molecules, i.e. when metal salts and metallized dyes are used, dyeing wastewater may have heavy metal content. The presence of toxic metals such as cadmium, chromium, copper in fiber dyeing wastewater was reported in earlier studies (Correia et al., 1994).

Table 2.3. Characteristics of RDW both for light shade and dark shade dyeing
(Schonberger & Schafer, 2003)

Exhaust dyeing of cotton knit fabric with reactive dyestuff for <u>light shade</u>							
# of bath	Name of bath	COD (mg O ₂ /L)	pH	Conductivity (mS/cm)	SAC* 436 nm (1/m)	SAC 525 nm (1/m)	SAC 620 nm (1/m)
1	Exhausted dye bath	920	11	72	43	18	6
2	Rinsing bath	180	10.6	10	9	4	2
3	Rinsing bath	33	10	2.8	4	2	1
4	Rinsing bath	23	9	1	2	1	1
5	Rinsing bath	5	8.3	0.8	1	0.5	0.2
Exhaust dyeing of cotton knit fabric with reactive dyestuff for <u>dark shade</u>							
1	Exhausted dye bath	3400	12.1	140	328	315	320
2	Rinsing bath	2980	11.8	55	325	298	308
3	Neutralization bath	2530	4.5	25	309	220	246
4	Rinsing bath	1060	4.7	8.3	316	185	196
5	Rinsing bath	560	5.3	2.1	316	164	154
6	Soaping bath	450	6.7	0.8	321	177	132
7	Rinsing bath	150	7.0	0.5	205	94	61
8	Rinsing bath	76	7.6	0.4	63	27	17
9	Rinsing bath	50	7.6	0.4	29	13	7

* SAC: Spectral Absorption Coefficient

2.5. Treatment alternatives for textile wastewater

Methods used in treating textile effluents vary depending on the desired resulting effluent quality. The receiving body for the treated wastewater or the treatment aim (such as reuse of the water) determines the level of treatment required or the

treatment process to be employed (Aouni et al., 2012). Common treatment techniques applied for textile dyeing effluents include; biological treatment (aerobic or anaerobic), adsorption processes (such as activated carbon adsorption), oxidation processes with ozone, H_2O_2 , etc., coagulation-flocculation processes followed by separation mechanisms and membrane filtration applications (Naim & El Abd, 2002; Carmen & Daniela, 2010)

The type of biological process applicable firstly depends upon the biodegradability of the effluent. Aerobic methods may be suitable for low strength waters, whereas anaerobic conditions are better for high strength ones (Naim & El Abd, 2002). However, dyestuffs used in textile manufacturing are not easily biologically degradable (S. H. Lin & Lo, 1997).

Employing chemicals as in the processes coagulation-flocculation or using oxidizing agents like ozone are effective for color removal. Yet, the problem of sludge handling is the major drawback of coagulation-flocculation process. Moreover, this process alternative does not provide complete COD removal. Another associated drawback is the lower color removal as compared to advanced oxidation techniques or adsorption. Advanced oxidation techniques which employ strong oxidizing agents are effective; but usually with a high cost of treatment (Crini, 2006). Advanced oxidation techniques are more applicable as secondary or tertiary treatment as they require lower suspended solids content.

Another alternative in the treatment of colored textile effluents is the use of activated carbon adsorption. In recent years, the application of carbon adsorption for removing a wide range of contaminants from industrial wastewaters has increased extensively (Dabrowski, 2001). Where biological treatment processes were ineffective and chemical usage was costly, adsorption which is a physical process, has found extensive field of application for color removal and also COD removal. Similar to advanced oxidation processes, adsorption also requires low suspended solids content and also low COD load for an effective treatment, and therefore preferably applied as polishing treatment. Several researchers reported satisfactory removal rates with

activated carbon adsorption for textile effluents (Tanthapanichakoon et al., 2005; Ip et al., 2009). However, the main drawback of activated carbon adsorption process is known to be the cost for supplying and regenerating activated carbon (Streat et al., 1995). The literature on the adsorptive treatment of textile effluents indicate that not only activated carbon but several other adsorbents have been tried in treating RDW. In most of the recent adsorption studies, the efforts have been focused toward finding non-conventional inexpensive adsorbents (Crini, 2006).

As indicated above, each treatment method has its own advantages and disadvantages and range of wastewaters to which it can be applied. Some have drawn more attention in recent years. Methods that promise water recovery and reuse has been studied more recently as a result of growing need for water saving. One of those, membrane filtration applications, are getting more and more widespread in the treatment of textile wastewaters.

CHAPTER 3

MEMBRANE FILTRATION

Membranes are semipermeable interfaces that are used in separating two phases. They have very small pores inside that allow the passage of materials which are smaller than pores and block the ones that are larger (Servos, 2014). Studies related with membrane phenomena first took place in 18th century. It was when osmosis was used to describe transfer of water through diaphragm. Materials used as diaphragms - membranes of first membrane studies- were usually parts of animal digestive systems. After using bladders, guts as membranes, scientists were able to produce nitrocellulose filters of porous structure. First microporous membrane has become commercial after two decades. Microfiltration applications with other polymers emerged by mid 1900s. Membrane filtration technology found its first application for drinking water treatment purposes in World War II as a result of potable water assurance crisis. Following this, one of the breakthroughs in membrane technology history was the improvement of the anisotropic reverse osmosis membranes that make the technology useful for industrial applications (Baker, 2012). Commercial applications of ultrafiltration for drinking water and wastewater treatment increased in line with the studies starting after 1980s (American Water Works Association[AWWA], 2005).

Today, application of membrane technology has diversified further. Some of those may be listed as; NF, UF, MF, electrodialysis, gas separation and pervaporation. Usage options of membranes have recently concentrated in both wastewater treatment and pure water output (for drinking or industrial purposes) and also health sector (Strathmann et al., 2006).

Different membrane processes have varying driving forces in function. Pressure, electrical potential, concentration may be the variable parameter between the feed and permeate sides of the membrane. Pressure-driven processes (MF, UF, NF, RO) employ pressure difference to make particles smaller than pores pass from one side of the membrane to other. Pore sizes within the membranes differ for each 4 processes (Hoek et al., 2013). Among those, microfiltration has the biggest pore size whereas reverse osmosis membranes are dense. Sieving mechanism is in function for transfer between two phases for MF and UF. For RO, membranes are nonporous and transport is described by solution-diffusion model. In this model, permeation of the molecule to the permeate side occurs by diffusing of the molecule to the other side once it is dissolved in membrane. NF membranes have pore sizes between RO and UF. Their transport mechanism is both sieving and solution-diffusion (Baker, 2012).

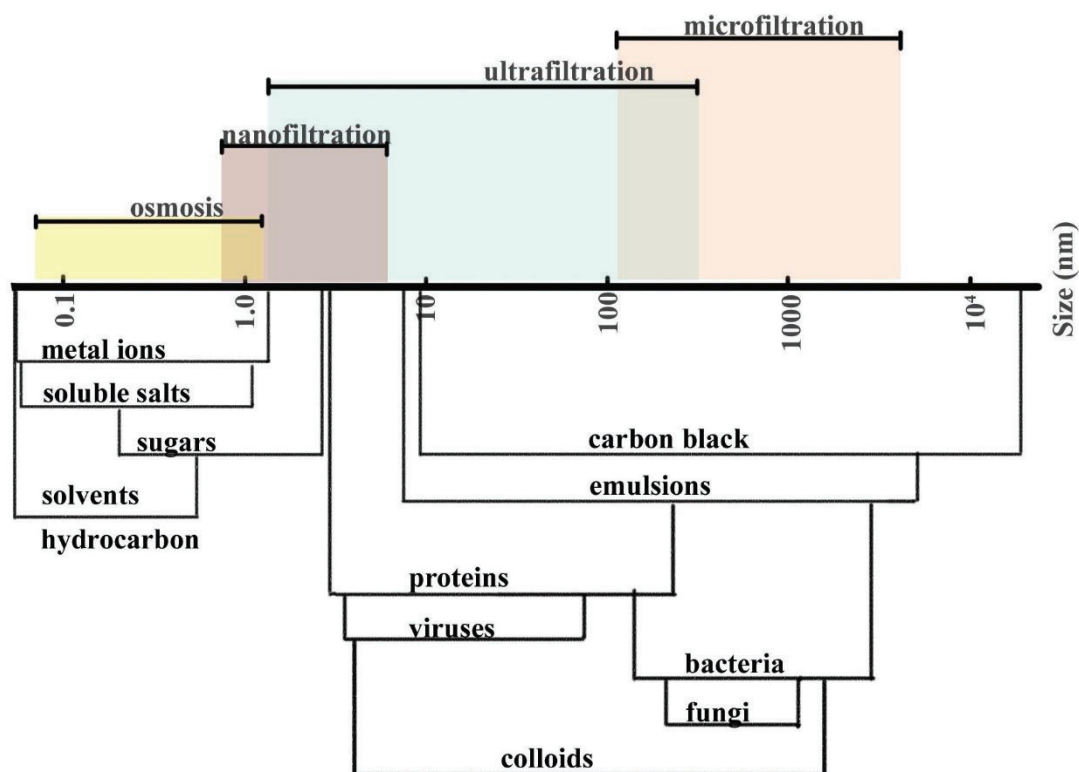


Figure 3.1. Filtration spectrum of RO, NF, UF and MF (Scott & Hughes, 1997)

In the separation of two phases in membrane filtration, feed solution is forced to pass through the membrane by applied pressure. The part of feed passing through the membrane is called permeate. It is formed by particles smaller than pores. Particles rejected by the membrane are kept in retentate. Membrane's ability to differentiate the concentration of a certain solute in permeate and retentate part is defined by the retention of membrane for that given solute. It is defined by the Eqn 1 where C_p stands for the concentration of the solute in permeate and C_f is the concentration in the feed side of the membrane (Hoek et al., 2013).

$$R = 1 - \frac{C_p}{C_f} \quad (\text{Eqn. 1})$$

In addition to retention, permeance is an important parameter to define membrane characteristics. Permeance is the permeation rate of the component passing through the membrane per certain area and applied TMP. Being membrane specific, permeation rate usually increases with the driving force applied (dX/dx), which is the TMP difference between two phases for pressure-driven membrane processes. Flux is the measure of volume passing through the membrane per unit area and time. The flux of the component (J), is defined in the Eqn. 2. Unit of flux is usually $\text{L m}^{-2}\text{hr}^{-1}$ (Mulder, 1996).

$$J = -A \frac{dX}{dx} \quad (\text{Eqn. 2})$$

Pressure-driven membrane processes are easy to operate compared to other treatment alternatives. Efficiency of the pollution removal is satisfactory as well. Main drawback with membrane applications is its cost of procurement and operation. Combination with conventional methods can be done to decrease the cost.

Other disadvantages which studies aim to overcome are concentration polarization (CP) and membrane fouling (Strathmann et al., 2006). In membrane separation, solutes that are not able to pass through membrane form a high concentration boundary layer on the surface. Increasing solute concentration on membrane surface

causes a higher difference between the solute concentrations of the two sides of the membrane. This leads to more resistance to permeation and consequently lower driving force for solvent permeation. As a result, CP causes a decrease in permeate flux (Servos, 2014).

Fouling of membranes may occur in different ways. Particles, microorganisms, organics may adsorb on pore walls. Pores within membranes may be clogged with particles to be removed. Particles can also form a cake layer on membrane surface again resulting in a decrease in permeation rate. CP may be overcome partially by tangential flows. However, to eliminate fouling, cleaning steps in membrane filtration systems are required (Li et al., 2016; Environmental Protection Agency [EPA], 2005)

CP and membrane fouling are both resistances to permeate flow. CP is the main resistance for membranes such as RO and NF that are used for separating small molecules. Pore plugging and formation of a fouling layer are primarily responsible for flux decline for UF and MF (Hoek et al., 2013).

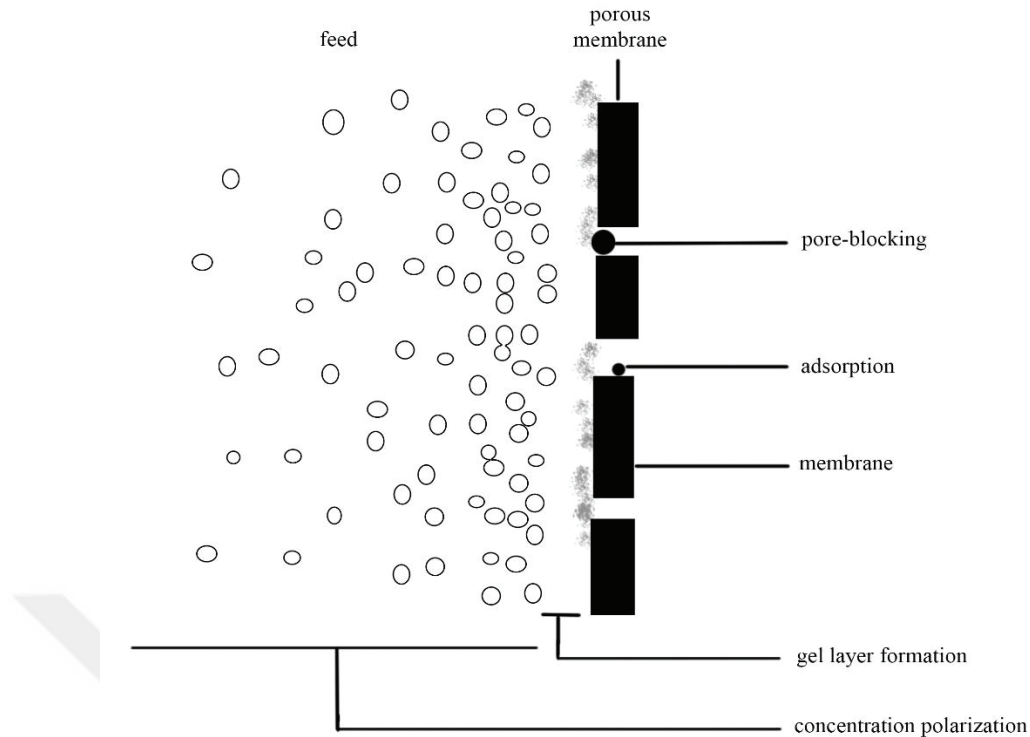


Figure 3.2. Representation of feed and membrane interaction with resulting CP and fouling (Mulder, 1996)

In order to overcome the deterioration in flux and maintain permeate quality, fouling and CP should be prevented. Cleaning options for fouling may necessitate ceasing of the process. Moreover, cleaning chemicals may damage membrane properties eventually. To prevent CP, higher tangential flow options are considered. Briefly, dealing with both CP and membrane fouling means higher cost for membrane applications and are stated to be the main restrictions for membrane processes (Ochando-Pulido et al., 2015).

3.1. Reverse Osmosis

When a semi-permeable membrane is placed between two phases, one formed of water and the other of salt solution, water tends to move to the salt solution side to have osmotic equilibrium. This process is called osmosis. If enough pressure is

applied to overcome osmotic pressure, the process can be reversed. This phenomena is called reverse osmosis (Scott & Hughes, 1997). RO membranes are being used for removing dissolved solids, small molecules such as glucose and ionic substances from a solvent (EPA, 2005). RO membranes have non-porous structure. Solutes passing through them dissolve in membrane polymer and diffuse in the direction that applied pressure determines. Thereby, they follow solution-diffusion model whereas porous membranes (UF and MF) adopt pore flow model (Baker, 2012).

In RO applications, the pressure applied to overcome osmotic pressure may range between 20-100 bars. These membranes are mostly used to obtain potable water from brackish water or seawater. Obtaining ultrapure water for electronics industry or concentrating one stream for food and dairy industries are other fields of application (Mulder, 1996).

3.2. Nanofiltration

Molecular weight cut-off (MWCO) is a parameter used to relate membrane pore size and the size of a macromolecule that is 90% rejected by the membrane, where the MW of this macromolecule is taken as the MWCO for that membrane. It is usually given in Daltons (Baker, 2012). NF membranes are placed between RO and UF membranes in pressure-driven processes based on their MWCO. They are both stated to be non-porous or to have pores of a few nm size. They need less pressure during operation, less energy and yield higher flux compared to RO membranes. Their nanometer-size pores allow them to remove solutes of a few nm size. Multivalent ions and small organics can be removed by NF membranes (Hoek et al., 2013; Lu et al., 2002).

Being able to remove multivalent ions, initially NF applications were used for softening in an attempt to obtain potable water. They were also good at removing organic content from surface waters (Hilal et al., 2004; Van Der Bruggen & Vandecasteele, 2003). Moreover, NF membranes can be used to remove color, DBP

precursors, TDS, and salinity content. Pesticides from agricultural activities and viruses can also be eliminated by this process (AWWA, 2007).

3.3. Ultrafiltration

Introducing asymmetric structure (thin layer on top for high permeability and thick layer below for support) to UF membranes has made this process feasible for industrial applications. Usage of UF technology has spread later on. First UF membranes were made of cellulose acetate. Nowadays, polymers such as polyacrylonitrile (PAN), aromatic polyamides (PA), polysulfone (PS), polyvinylidene difluoride (PVDF) etc. are used to produce these membranes (Porter, 1989). Pores within membrane vary between 0.05 μm to 1 nm in size. Removal of particles depends on the size relation between the solute and the pores and follow sieving mechanism. Particles smaller than pores in top layer of UF membrane are retained. Permeation rate increases with applied pressure. UF processes can take place under 1-10 bar TMP (Mulder, 1996).

Pore size range of UF membranes allows the passage of solvents, salts and low MW compounds enables them to remove turbidity, macromolecules, protozoa and microorganism from aqueous solutions (Scott & Hughes, 1997; AWWA, 2005).

Primary success of UF membranes were on the treatment of water and wastewater by removing particulate matter and macromolecules. Afterwards, it has found substantial amount of industrial application areas. Examples include paint recovery in electrocoating industry, supplying high quality water for electronics and pharmaceutical industries, milk production and cheese whey partitioning in dairy industry. UF treatment is quite good for industrial wastewaters such as pulp and paper, textiles, leather and tanning that are not easily handled by conventional methods (Cheryan, 1998) .

3.4. Microfiltration

MF membranes arose with the studies aiming to supply pathogen-free water in Germany during World War II. Commercialization attempts succeeded after war have revealed one of today's biggest membrane producer, Millipore Corporation (Porter, 1989). MF membranes have biggest pore sizes ranging between 0.1-10 μm among pressure-driven processes (EPA, 2005). Low trans-membrane pressures as 1-3 bars are enough for MF applications since low osmotic pressure occurs as a result of the ionic content preserved in both sides of membrane (Hoek et al., 2013).

MF is used in pharmaceutical industry to obtain particle and bacteria free drug solutions ready for injection. Other fields of application for MF membranes are pre-treatment for RO and NF applications to reduce fouling, bacteria and yeast removal for food industry, last step treatment of readily filtered ultrapure water for electronics industry, drinking water treatment with UF membranes (Baker, 2012).

CHAPTER 4

LITERATURE REVIEW

Treating textile wastewater, especially those containing reactive dyestuff by conventional methods is not easy and effective. Studies to overcome this issue have revealed new implementation examples to be used with colored wastewaters that have high TDS and salinity content. Huge water consumption observed in textile industry is coupled with the need to save water and this favored techniques that promise reclamation of raw materials used in process, especially water (Vandevivere et al., 1998).

Membrane filtration technology had the potential of both meeting the necessary discharge criteria and good effluent quality that has capability to be reused (Wenzel et al., 1996; Marcucci et al., 2001). This need met with the improvements in membrane industry and as a result, huge numbers of studies concerning membrane filtration method for textile effluent treatment has found place in literature.

Commonly used treatment methods such as activated sludge were falling short in producing color-free effluents. Salinity content in the final effluent was also another problem (Jiraratananon et al., 2000). Membrane filtration techniques such as RO and NF were the options to remove the color and salt from treated wastewater (Petrinic et al., 2007; Chakraborty et al., 2003). Membrane filtration can be applied directly to the textile effluent or to the effluent of a pretreatment step. In some studies, the direct application of textile effluents to NF membranes was stated to be problematic due to fouling and CP that result in a decrease in permeate flux (Debik et al., 2010; Zahrim et al., 2011). Concurrent application of membrane filtration with conventional methods were claimed to be advantageous where pretreatment need

was met before membrane filtration treatment (Van der Bruggen et al., 2001). There are also studies employing MF or loose UF membranes as pretreatment to the NF/RO step. In many studies, though, with individual applications of NF, good removal efficiencies for color and organic content are reported (Qin et al., 2007; Yu et al., 2010; Amini et al., 2011). On the other hand, the ability of UF membranes to successfully treat textile effluents is only recently being studied.

In order to recover the wastewater coming from a textile plant, Suksaroj et al. (2005) applied further NF and RO treatment to the effluent of the existing activated sludge wastewater treatment plant. The COD removal by biological treatment was satisfactory with an effluent COD value of below 65 mg/L, but color removal was not sufficient for the reuse of the effluent back in the process. As expected, salinity of the effluent was also high. In order to reclaim the wastewater, NF and RO membranes were tested after applying coagulation-flocculation as pretreatment to decrease fouling. Both NF and RO membranes tested provided full color removal. Salinity removal was lower with NF than with RO, yet both the permeates were of satisfactory quality to be re-used. In this study, physicochemical treatment was found to provide an increase in permeate flux. Effect of applying coagulation-flocculation pretreatment on permeate quality from NF, was also investigated by Riera-Torres et al. (2010). In this study, removal rates for different reactive dyes by direct NF was stated to be between 40-80%. When NF was combined with coagulation-flocculation pre-treatment, the removals increased up to 98%.

In another study, wastewater resulting from dye bath and rinsing processes in textile dyeing industry were collected separately. In order to obtain re-useable water from both channels, rinsing waters were treated by physicochemical and biological steps which are followed by NF treatment. Dye bath wastewater was subjected to sand filtration before RO application. As a result, permeates were reported to have good quality by not only removing high percentages of COD, TDS, sodium and chloride but also having water of low hardness which is essential for textile process waters (Ranganathan et al., 2007).

Membrane filtration applications together with conventional treatment techniques has the advantage of easy implementation since placing NF/RO unit at the end of already existing plants would also mean that pretreatment need is met (Van der Bruggen et al., 2001). Thus, number of examples such as the studies presented above can easily be increased (Zheng et al., 2013; Suksaroj et al., 2005). Treating textile effluents with combination scenarios, which employ bigger to lower pore sized membranes, were also an option. In fact, in their studies Ellouze et al., (2012) noted that pretreatment with MF before NF is better than coagulation-flocculation. In experiments with textile industry effluent, color was removed fully in both alternatives. With MF/NF treatment scheme, COD and salinity removal was enhanced up to 35% and 39.6%, respectively. Permeate flux in the MF pre-treatment case was observed to be two times higher.

In another work, wastewater from finishing and dyeing steps of a textile plant, was treated by 100 kDa UF membrane as pre-treatment to RO. The feed to UF was the effluent from sand filtration of the biologically treated wastewater. After UF and RO sequential treatment, the permeate was reported to have a better quality than the process water used in textile plant with a conductivity of less than 1 mS/cm and no color and COD content (Ciardelli et al., 2001).

One other way to treat these effluents left pre-treatment aside. Effluents passed through coarse screens were subjected to direct NF or RO. In their studies, Sojka-Ledakowicz et al. (2010) treated real textile wastewater by individual NF and RO applications using pilot-scale spiral wound membranes. Color removal rates was close to 100% for both cases. Salt removal with NF treatment was lower (20%) than with RO (80%). As a result, usage of NF permeate in rinsing step and RO permeate in dyebath preparation was suggested. Employing UF membrane as an alternative to the MBR+NF treatment, was also proposed for recycling raw materials used in textile finishing plant (Schoeberl et al., 2005). Wastewater coming from different processes was first treated biologically with MBR and then NF. Final permeate water has good quality to be re-used in any process. More economical UF option was pointed out to treat washing wastewaters which have high surfactant content. After

concentrating wastewater up to 20 factors, not only significant amount of water savings (up to 90%) was achieved but also a considerable amount of surfactant recovery (over 30%) was noted.

Aouni et al. (2012) tried treating rinsing wastewater that is coming from textile dyeing plant by 1 kDa UF and two different NF membranes. Color was removed up to 90% with UF whereas almost total decolorization was achieved with NF. Being able to remove at most 30% of salinity, UF treatment was suggested to be a pre-treatment step for RO or NF treatment to be able to obtain reuse water. In the same study, another UF membrane with a bigger pore size (10 kDa) was used to treat synthetic dye bath wastewaters with three different reactive dyes. Everzol black removal was stated to be worse than 15%. However, Ahmad et al. (2006) shown that the effect of surfactant in the wastewater may change the removal efficiency. In their study, the change in color removal rates with the presence and absence of micellar aggregates was investigated. Reactive dyestuff (reactive black and reactive orange) within the water was removed up to 3% with 10 kDa UF membrane. With surfactant addition this value was observed to be over 97%.

Studies listed above employed NF or RO membranes to produce color and salt free permeates. One other approach in treatment of textile effluents (especially processes where huge amount of salt is used) suggests the recovery of salt along with the water. Doing so may also present a solution for problems mentioned in following studies. In their work Van der Bruggen et al. (2001), have compared different NF membranes for directly treating synthetic dye bath water and for biologically treated wastewater before membrane filtration. Though both options of treatment are said to be applicable, the increase in osmotic pressure as a result of removing salt from wastewater with small pore sized NF is stated to be disadvantageous. The result that is pointed out was when treating textile wastewaters, pore sizes should be small enough to be able to remove dye molecules and also big enough to retain not all the monovalent ions to prevent excessive osmotic pressure increase. In another study 3 different NF membranes were studied to recover water from RDW (Jiraratananon et al., 2000). Two of these membranes were negatively charged and achieved high

removal rates over 95% for color and 85% for salt. Obtained permeate was of good enough quality to be re-used. However, a significant decrease in permeate flux was reported for both membranes as a result of osmotic pressure build-up.

Salt recovery with water may be profitable for closing cycle applications in textile industry. Where monovalent ions are not retained, salinity content does not change much between two sides of the filter and this means less osmotic pressure to work against (Akbari et al., 2006). Moreover, to be able to use membranes that are not necessarily used for removing monovalent ions favors the usage of UF membranes or loose NF membranes for textile effluents. This means higher permeate flux. In two case studies from the BREF document for textile industry (European Commission, 2003), wastewater coming from dyeing and following rinsing steps are treated with two different objectives. Activated carbon technique was used to obtain brine water which is free of color and organic content. The combination of UF/NF/RO treatment was employed to have water where salt is also retained. Membranes can also be utilized to obtain saline water. First example of UF+NF treatment to obtain saline water can be traced back to Koch Membrane's pilot scale application in a fabric dyeing plant (Woerner, 1993). Wastewaters coming from dyeing and first rinsing steps are collected and initially subjected to UF and then NF treatment. This sequential treatment removed dyestuff and other chemicals but let the passage of water and most of the salt. pH of permeate water was adjusted and a little amount of salt was added before the permeates were used in dyeing tests. Results were satisfactory. With the water, 60% of salt was recovered.

In another work, membranes with different pore sizes were both used directly and in combination to treat real dye bath wastewater (Vergili et al., 2012). UF, loose NF, tight NF and RO membranes were employed during experiments. UF and loose NF membranes were found appropriate for pre-treatment yet fouling did not let direct usage of tight NF. Treatment scenarios where RO membranes were on duty had the best permeate quality as expected. However, from an economic point of view, the scenario of UF followed by tight NF was stated to be the best. Because, contrary to RO it enabled recovery of caustic and salt from wastewater. In a similar study, two

NF membranes (SR90 and NF90) were used to obtain brine to be used back in dyeing process. The effect of UF pre-treatment on removal efficiency and fouling tendency was also analyzed (Chollom et al., 2015). NF90 permeate had conductivity values less than 1 mS/cm. A looser NF membrane SF90 achieved less color, COD and conductivity removals but stated to be better if objective was to recover salts as well. Dyeing tests gave satisfactory results with SR90 permeate for dark shade recipes (which necessitates water of less quality than light and middle shades) and NF90 for any shade. Although both scenarios saved salt, more salt addition was needed with NF90 permeate. There are other studies in literature including different NF membranes and examining the effect of color/salt amount in wastewaters on rejections and salt recovery (Tang & Chen, 2002; Koyuncu et al., 2004; De Vreese & Van der Bruggen, 2007). In their study, Lin et al. (2015) used loose NF membranes to obtain aqueous salt solution while rejecting the dyes present in wastewater. Two different commercial NF membranes were used in study and both achieved over 99% dye removal. Meanwhile, salt rejection was reported to be below 33%. Fractionation of salts from textile dyeing wastewaters was also studied with a tight UF membrane (Lin et al., 2016). UF membrane of 4700 Da MWCO was used to remove dye content of synthetic textile wastewaters containing direct and reactive dyes. Dye retention rates up to 98% were reported. Rejection of salts observed in loose NF membranes were close to zero with tight UF membrane. Since low osmotic pressure occurred during filtration, high flux values were reported.

UF membranes offer quite good retention rates for textile wastewater purification. The recovery of the salt, either by further fractionation steps such as forward osmosis (FO) or in a brine solution, is possible. However, more studies examining the performance and benefits of single UF membrane usage in treating RDW are needed. This would also help describing the best modification of membrane treatment process aiming recovery of the raw materials. For this purpose, RDW is tried to be purified by using UF membranes in this study, rejecting dyes while permeating salts for reuse. By obtaining brackish water, objective was to suggest a membrane filtration based process that would prevent salt discharges to receiving body and save salt by using the ones in dyeing bath repeatedly.

CHAPTER 5

MATERIALS AND METHODS

5.1. Wastewater

RDW samples used in the present study were taken from a cotton textile plant located in Denizli. In the plant, reactive dyes are used to dye cotton towel fabric. Cotton towel fabric woven in the mill are dyed in four main steps (Figure 5.1). The first step is dyeing where dyestuff from the dye bath is transferred to the fabric. The bath solution containing dyestuff, salt and other auxiliary chemicals such as caustic (NaOH) and soda (Na_2CO_3) in the amounts as defined on the dyeing recipe is used. Fixation of dyes on the fabric is achieved under alkaline conditions and with hot water. Dye bath is followed by a rinsing step (2nd step) where only hot water (80°C) is used. Third step is the washing of the dyed fabric with soap. Final rinsing step with warm water ends the dyeing process. The four-step dyeing process is implemented batch-wise in a single tank in which the fabric is kept, but the solution is changed. In all the four steps, water level is kept constant. The dyeing recipe used in dyeing process before wastewater sampling is given in Appendix A.

Wastewater samples to be used in the experiments were taken from each of four steps in equal volumes of 20 L. The samples were transferred to the laboratory and stored at 4°C without mixing. Mixing of the samples was done before each experiment. In UF experiments, the mixture of four samples and the mixture of the first two (dyeing bath and first rinsing bath) were used as feed wastewater. Wastewaters were strained by a coarse filter before mixing.

The characteristics of the wastewater samples from each step, the mixture of all four steps and the mixture of the first two steps are given in Table 5.1. As the dyeing bath is the step where dyestuff, salt and other chemicals are added to water, the wastewater from this step is with the highest salinity and dye content. Unfixed dye and also salt characterizes the characteristics of the second step's wastewater. The third step's wastewater is relatively lower in strength with a high surfactant content. The last step; final warm water rinsing generates an effluent with the lowest pollution load.



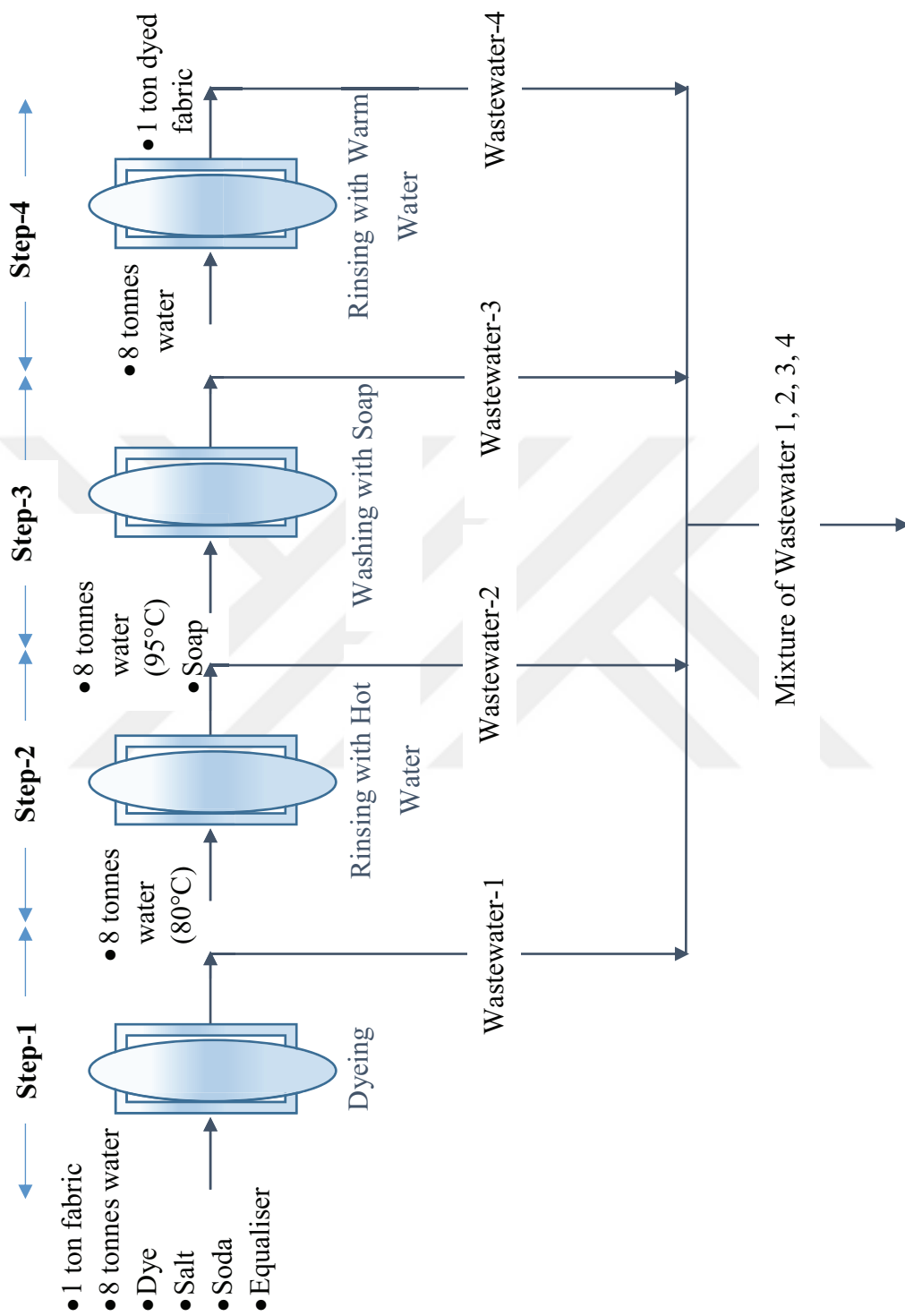


Figure 5.1. Dyeing steps in the factory and sampling points

Table 5.1. Wastewater characteristics for sampling lines and mixture of 1+2+3+4 and 1+2

Wastewater/ Sampling line	TOC (mg/L)	Conductivity (mS/cm)	Turbidity (NTU)	SAC (m ⁻¹)			pH
				436 nm	525 nm	620 nm	
Dyeing bath/ 1	543±8	64.9±0.1	113±1.7	292	429	68	9.5
Rinsing with hot water/ 2	333±7	39±0	65±1.6	196	334	43	9.4
Washing with soap/ 3	80±3	6.6±0	14.8±0.3	29	21	9	7.7
Rinsing with warm water/ 4	44±2	1.7±0	19.3±1	43	77	7	7.7
1+2+3+4	230±1	27.9±0	53.2±0.8	115	195	14	9.4
1+2	392±3	53±0.3	57.7±0.3	216	344	29	9.3

5.2. Experimental methods

5.2.1. UF experiments

Ultrafiltration experiments were achieved by using SEPA Cross-Flow (CF) Membrane Filtration Unit (GE Osmonics) shown in (Figure 5.2). Flat sheet membranes with dimensions appropriate (manufactured accordingly) to be used in this unit were used in UF experiments. Active membrane area defined by the SEPA CF manufacturer is 0.0140 m^2 . Filtration unit were both used in total recycle mode filtration (TRMF) and concentration mode filtration (CMF). In TRMF of experiments, both retentate and permeate line were directed back to the feed tank. In CMF tests, permeate was collected in a separate tank, but the retentate was recycled back to the feed tank.

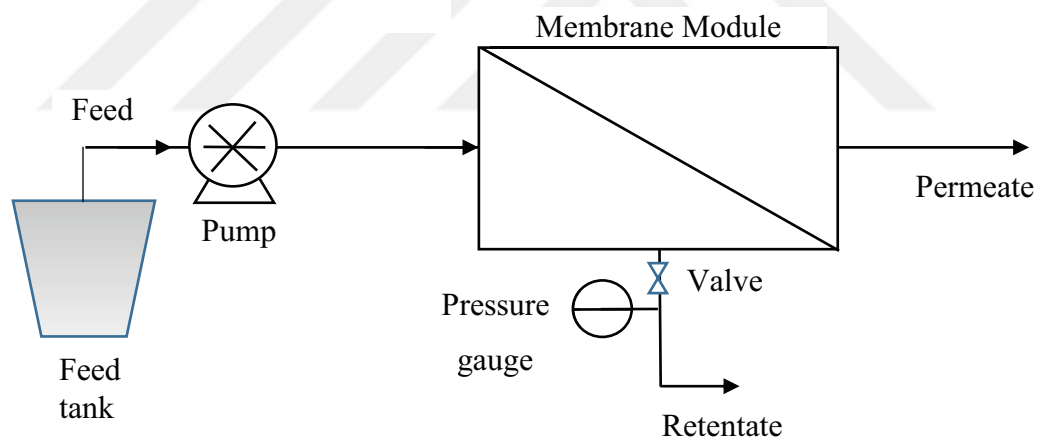


Figure 5.2. Membrane filtration set-up

Steps followed in experiments had started with the compaction of the membranes if it was the first usage of that piece of membrane. Chemical cleaning of the membrane and the ultrapure water (UPW) permeance measurements were done after

compaction. After that, filtration with wastewater samples was done. Physical and chemical cleaning steps followed filtration. UPW permeances before and after cleaning steps were measured.

5.2.1.1 Compaction and chemical cleaning

Compaction is done to observe the decrease in permeation flux (if there would be any) as a result of first pressurized usage before filtration step. Before the usage of each membrane sheet, membranes were put in a 0.25% sodium bisulfite solution a day before the compaction. Wetted membranes were rinsed with water thoroughly and placed in SEPA CF filtration unit. Compaction was achieved at trans-membrane pressures (TMP) which are 1 bar over the filtration pressure. For filtrations to be achieved at 2 bar, compaction pressure is arranged to be 3 bar, and for 4 bar filtration pressure, compaction pressure was fixed at 5 bar. Compaction was realized with UPW in dead-end mode with retentate line fully closed. Water coming from permeate line was discarded. Compaction was done until steady flux is observed (after at least 3 hours) or for 4-5 hours. After compaction, basic and alkaline solutions were passed through the membranes under pressures that filtration would be achieved. Acidic solution was prepared by using 65% HNO_3 and pH value of 3 was arranged. Basic solution was prepared by using NaOH pellets and pH value was fixed at 10. UPW was passed through the membrane between each chemical cleaning step.

After cleaning, pure water flux was measured at different pressures. TMPs where UPW flux measured were 1, 2 and 3 bar for filtrations achieved under 2 bar, and 1, 2, 3, 4 and 5 bar for filtrations under 4 bar. The slope of the graph, flux as a function of pressure, were taken as the permeance ($\text{L/m}^2\text{hbar}$) of the membrane.

Table 5.2. Steps followed during experiments and operational parameters

Steps followed in experiments	Pressure (bar) 1st set/ 2nd set*	Feed water	Cross-flow velocity (m/s)	Time
Compaction	3/5	UPW	-	Until steady state is reached
Chemical cleaning before filtration	2/4	HNO ₃ (pH 3±0.5)	-	30 min
		UPW		20 min
		NaOH (pH 10±0.5)		30 min
		UPW		20 min
UPW permeance measurement	1-2-3/1-2-3-4-5	UPW	-	-
Filtration	2/4	Mixture of #1,2,3,4**	0.035/0.14***	Until steady state is reached or desired VRF
UPW flux measurement before cleaning	2/4	UPW	-	-
Physical cleaning	-	UPW	0.37	30 min

Table 5.2 (Cont'd)

Steps followed in experiments	Pressure (bar) 1st set/ 2nd set*	Feed water	Cross-flow velocity (m/s)	Time
UPW flux measurement after physical cleaning	2/4	UPW	-	-
Chemical cleaning	2/4	HNO ₃ (pH 3±0,5)	-	30 min
		UPW		20 min
		NaOH (pH 10±0,5)		30 min
		UPW		20 min
UPW flux after chemical cleaning	2/4	UPW	-	-
Storage	-	0.025% Sodium bisulfite solution	-	-

* There are experiments with either 2 bar or 4 bar filtration pressures. Compaction and cleaning pressures are determined accordingly.

** Feed wastewater was the mixture of wastewaters 1+2 in some of the experiments

*** First value is for CMF and second for TRMF experiments. Cross-flow velocities are adjusted for each experiment.

5.2.1.2 Filtration

Filtration tests were carried out in either TRMF or CMF. In TRMF experiments, permeate flowrate was measured at 30 min or 1 h time intervals and samples were taken from the permeate line firstly at the beginning of the filtration. More sampling was done after steady flux was observed. In CMF experiments, filtration continued until the desired volume reduction factor (VRF) is realized. VRF is calculated as follows:

$$VRF = \frac{V_{\text{initial}}}{V_{\text{final}}} \quad (\text{Eqn. 3})$$

Where V_{initial} refers to the feed wastewater volume at the beginning, and V_{final} to the retentate volume remaining once the filtration is finished. VRF values ranging between 2-10 were used during experiments.

During experiments, UPW flux before filtration, filtration flux with wastewater, UPW flux after filtration, UPW flux after physical cleaning and UPW flux after chemical cleaning were measured sequentially. By using the measured flux, resistances were found using the relation given below where R stands for resistance and μ for viscosity of water. Sample calculation for resistances are given in Appendix A.

$$R = \frac{TMP}{\mu \times J} \quad (\text{Eqn. 4})$$

Table 5.3. Measured fluxes during and after filtrations

Measured flux*	Definition
J_{cwi}	UPW flux measured before filtration
J_{rw}	Flux measured during filtration with wastewater
J_{cwf}	UPW flux measured after filtration
J_{cwp}	UPW flux measured after physical cleaning
J_{cwc}	UPW flux measured after chemical cleaning
Normalized flux	J_{rw} divided by J_{cwi}

* Flux measurements are achieved in given order.

Table 5.4. Resistances calculated by using measure fluxes

Resistances	Definition
R_{mem}	Membrane's intrinsic resistance. Calculated by using UPW flux
R_{tot}	The summation of R_{mem} , R_f and R_{cp} . Calculated by using J_{rw} .
R_f	Resistance due to fouling. Calculated by using the difference between J_{cwf} and J_{cwi} .
R_{cp}	Resistance due to concentration polarization. Calculated as $R_{cp} = R_{tot} - R_f - R_{mem}$.
R_{ph-irr}	Fouling resistance remaining after physical cleaning. Calculated by using J_{cwp} .
R_{ch-irr}	Fouling resistance remaining after chemical cleaning. Calculated by using J_{cwc} .

Filtration of wastewater was done at low and high cross-flow velocities. Cross-flow rates were measured during experiments and the cross-sectional value stated by Hoek et al. (2002), was used to obtain cross-flow velocities. Cross-sectional area of SEPA CF system was taken as 0.82 cm^2 . Cross-flow rates were obtained in ml/s during experiments. This value was divided by 0.82 cm^2 to obtain cross-flow velocities.

Sampling from feed and permeate line was done during wastewater filtration. Retention rates were calculated using the result of analysis of these samples. Instantaneous retention rates were calculated and given for experiments where sampling from both feed and permeate line was carried out at different VRF values during experiment. Measurements realized for feed and permeate samples at that VRF were used in instantaneous retention calculations. Overall retention rate was

calculated using the analysis of feed sample at the beginning and permeate samples taken from the final permeate collected (cumulative permeate at the end of filtration). Retention rates were calculated by using the formula given below. Note that “value” stands for TOC, turbidity, conductivity or SAC values.

$$\text{Retention \%} = \frac{\text{Value in feed} - \text{Value in permeate}}{\text{Value in feed}} * 100 \quad (\text{Eqn. 5})$$

Filtration fluxes and parameters that are measured are given with bars in figures. These bars demonstrate standard deviations. For repeated experiments, standard deviations are calculated by taking the average of the values from each tests. Filtration fluxes, UPW fluxes and TOC, turbidity, conductivity and SAC values have standard deviations calculated for repeated measurements. Retention rates are also calculated by taking the standard deviations of values into account.

5.2.1.3 Membrane cleaning

After filtration is done, the wastewater is drained from the system. Cross-flow velocity during drainage was not over the filtration cross-flow velocities. UPW was passed through the system to clean the residual wastewater again with very low cross-flow velocities. UPW flux was measured at filtration pressure (J_{cwf}). Two types of cleaning is carried out in order to recover the flux decline which is observed by measuring J_{cwf} . Physical cleaning is achieved first at high cross-flow velocities (0.37 m/s) for 30 minutes. After physical cleaning UPW flux is measured (J_{cwp}). Chemical cleaning is the second cleaning step. Acidic and basic solutions (pH = 3 and pH = 10, respectively) which are used after compaction were used again in cleaning steps after filtration. First acidic solution was passed through the membrane at filtration pressure for 30 minutes. Cleaning was achieved while retentate line was fully closed and permeate was discarded. UPW was passed through the membrane for 20 minutes again at filtration pressure. Same steps were followed with basic solution. After chemical cleaning UPW flux was measured (J_{cwc}).

5.2.1.4 Membrane storage

After the experiments, the membranes were stored wet in containers containing 0.25% aqueous solution of sodium bisulfite to prevent the growth of microorganisms on them. The containers were stored at 4 °C.

5.2.2. Dyeing tests

Dyeing tests are achieved in order to confirm that permeates obtained as a result of filtration experiments are of good quality enough to be re-used back in dyeing process. Tests are done in the laboratory of the textile dyeing plant where wastewater samples were taken from. Datacolor 600 spectrophotometer was used in these tests. Main principle is to compare the piece of cotton which is dyed using tap water with the one that is dyed by using the permeate obtained at the end of the filtrations. Other chemicals that are defined in the recipes are added identically in both dyeing tests except for salt addition in one of the tests. Spectrophotometer takes the first one as reference and gives the difference of the second one from the reference as a reading. The reading is named CMC dE as developed by ``Color Measurement Committee of the Society of Dyers and Colorists`` (Raheel, 2006). Low readings mean that color difference that can be seen by human eye is low, too. The CMC dE value under 1 is labeled as ``Pass`` for that specific test. Readings above 1 are marked as ``Fail``. It was indicated by the laboratory staff that CMC dE criteria value may be different from 1 (usually above) depending on the customer`s will.

5.3. Membrane specifications

The specifications of membranes used in experiments are given in (Table 5.5).

Table 5.5. Specifications of the UF membranes used in the experiments

Membrane	Manufacturer	Material	MWCO (g/mol)	Permeance (L/m ² h psi)	pH range
UF-GH	GE Osmonics	Thin Film Composite	2000	20/150	1-11
UF-PT	GE Osmonics	Polyethersulfone	5000	90/50	1-11

5.4. Analytical methods

Color of wastewater samples was measured as absorbance at the wavelengths of 436 nm, 525 nm and 620 nm by following the method of EN ISO 7887 using a Varian Cary 100 model spectrophotometer. Measurements were done at three different wavelengths because wavelengths between 400-500 nm, 500-600 nm and 600-700 nm give absorbance for yellow and its shades, red and its shades and blue and its shades, respectively. Absorbance of samples were read by using absorption cuvettes of 10 mm spectral band. Feed samples were passed through 0.45 Whatman Glass Fiber filter before readings in order to remove the suspended material that would interfere the absorbance readings. This was not done for permeate samples. Absorbance values were used to obtain spectral absorption coefficient (SAC) values by using the formula given below (Ministry of Environment and Urban Planning, 2013).

$$SAC(\lambda) = \frac{A}{d} \times f$$

Where; A: Absorbance of the sample (cm^{-1})

d : Spectral band (mm)

f: Constant to obtain spectral absorption coefficient in m^{-1} unit

SAC : Spectral Absorption Coefficient (m^{-1})

Total organic carbon (TOC) content of the samples were determined by using a Shimadzu 5000A model TOC analyzer employing “the 680°C combustion catalytic oxidation method”. The 680°C combustion catalytic oxidation method achieves total combustion of samples by heating them to 680°C in an oxygen-rich environment inside TC combustion tubes filled with a platinum catalyst. The CO_2 formed is detected by an infrared gas analyzer. The IC (inorganic carbon) in the sample is then measured by subjecting the oxidized sample to the acid sparging process and converting it to carbon dioxide. The CO_2 is detected using the infrared gas analyzer and IC concentration is obtained. The instrument then calculates the difference between TC and IC to obtain TOC value according to Standard Method No 5310 B (APHA/AWWA/WEF, 1998). TC and IC calibration curves were generated with the standards for 0-200 mg/L range and curves obtained are given in Appendix C.

Turbidity of samples were measured by using HACH model 2100 turbidimeter by using the Standard Method No. 2130B. Conductivity and pH measurements were done with a HACH Sension 378 pH/Conductivity/DO meter. The Standard Method No 2510B and 4500- H^+ were followed during the analyses for conductivity and pH, respectively (APHA/AWWA/WEF, 1998).

CHAPTER 6

RESULTS AND DISCUSSION

In the first series of experiments, two different UF membranes with the specifications given in Table 5.5 were used for the treatment of RDW which is highly colored with a high salinity content. The aim in this UF treatment is to remove color, suspended and organic matter content of the wastewater but to keep its salt for its possible reuse. Thus, the success criteria for the experiments are almost complete retention of color, suspended matter and organic carbon and almost complete permeation of salt through the membrane. To trace these criteria, SAC values of the permeate samples were measured at three different wavelengths for color removal. Turbidity, TOC and conductivity are parameters that are checked for suspended matter, organic matter and salinity removals, respectively. Section 6.1 presents the results of the UF experiments performed using two UF membranes (5 kDa and 2 kDa) in single stage application. These experiments were done at TRMF. Secondly single stage CMF experiments were achieved in order to see performances of these two UF membranes at higher concentration of the wastewater, in order to simulate batch, concentration mode filtration or continuous filtration with a high permeate to feed ratio. Results of these experiments are presented in Section 6.2. Wastewater samples used during these filtration tests were the mixture of the 4 samples that are taken from the 4 stages of the reactive dyeing process applied in the textile factory. Serial applications of these two UF membranes were also tested and the results presented in Section 6.3 were obtained. Treatment scenarios realized are summarized in Figure 6.1.

The reuse of permeates from the UF of RDW was studied performing a series of dyeing tests using permeates from the serial application UF tests. The results from these tests are presented in Section 6.4.

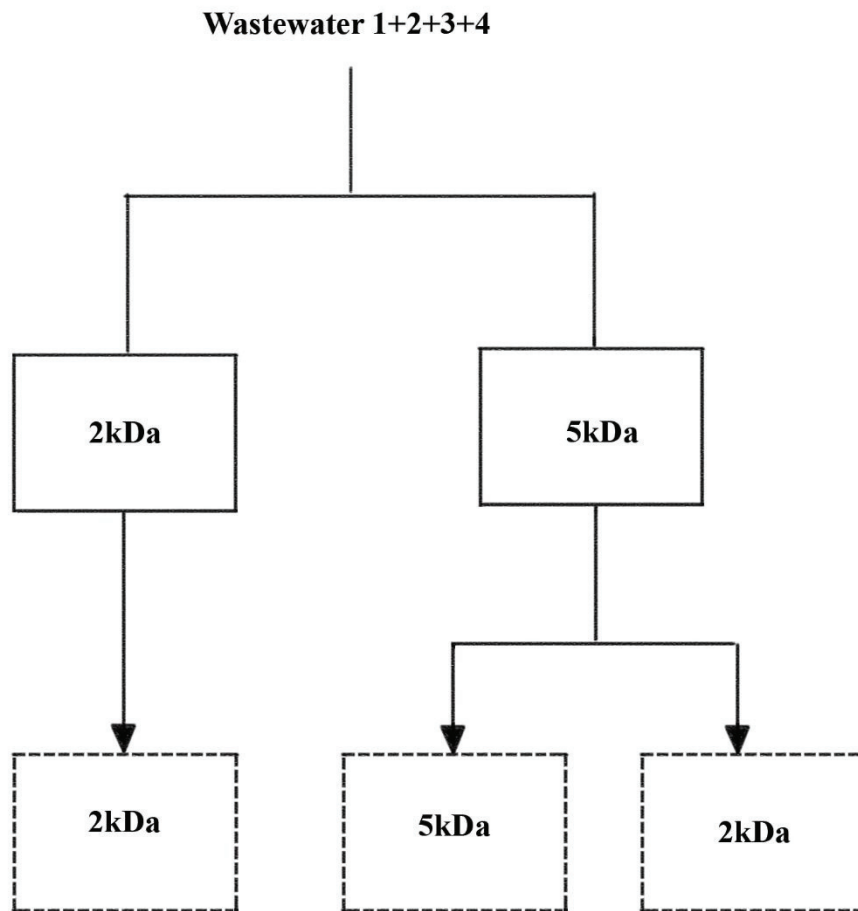


Figure 6.1. Single and two stage filtration tests that are realized during experimental studies

The effects of operational parameters such as TMP and VRF were checked later on. Firstly, VRF value was increased for serial applications and then the TMP value was doubled. Changes in retention rates were traced and results are given in Section 6.5. After observing the performances of serial applications with changing experimental parameters, alternative recycling scenario was suggested. In these scenario, feed wastewater was formed of the mixture of only first two sampling lines. Results of

these scenario are given in Section 6.6. Analysis of the filtrations with respect to fouling resistances is presented in Section 6.7.

6.1. Comparison of different UF membranes in TRMF tests

6.1.1. 5 kDa UF membrane

UF membranes are with pore sizes big enough to let the permeation of salts through the membrane. Between two UF membranes used throughout the study, 5 kDa is the one that has larger pore size. Although both membranes may be classified as tight UF membranes, high salt permeation is expected as ionic size species are not retainable by this size of membranes. On the other hand, the effectiveness of the UF membranes in removing color and dissolved organic matter is less foreseeable since both efficient and inefficient color removals have been reported for different UF membranes (Aouni et al., 2012; Ahmad et al., 2006; Lin et al., 2016).

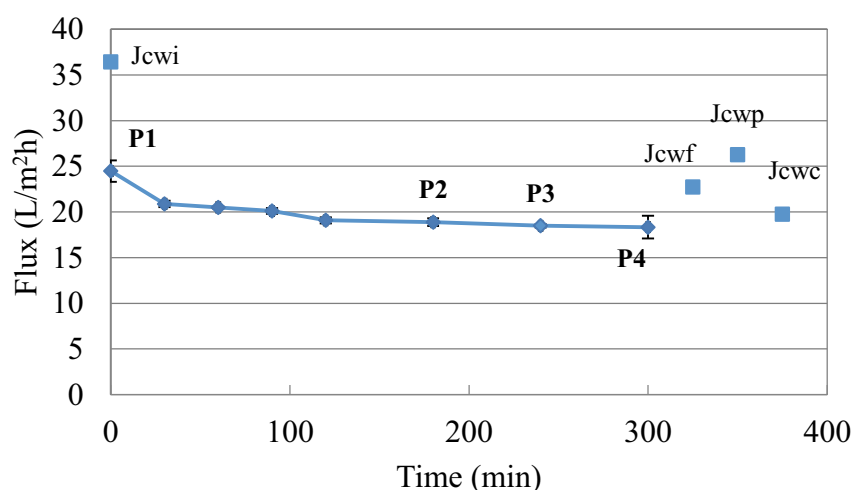


Figure 6.2. The change in filtration flux with time and sampling times (P1, P2, P3, P4) and UPW fluxes for 5 kDa filtration

UF tests with 5 kDa membrane were performed firstly under TRMF conditions and the timely flux variation presented in Figure 6.2 was observed. As seen, there was a decrease in filtration flux with time. This decrease was more drastic during the first 60 min and relatively gradual after that. Decrease in filtration flux was the result of CP and fouling of membrane.

In this 5 kDa test, UPW flux was measured to be about 35 L/m²h. As depicted in Figure 6.2, steady state filtration flux was considerably lower (51%) than the UPW flux, as indicated above due to CP and internal fouling. J_{cwf} , measured after filtration, with no cleaning done, was higher than the filtration flux at the end of the filtration period, implying that part of the flux decline was due to CP. As J_{cwf} was still lower than J_{cwi} , it was concluded that fouling on or in the membrane also played a role in the flux decline. There was a slight increase in UPW flux after physical cleaning. After chemical cleaning, however, UPW flux has decreased. This was not expected and was seen in some of other 5 kDa PES UF membrane experiments, too. (The reason of flux decline after chemical cleaning, was not clear and thus further investigated by a different line of research). UPW flux was taken to 26.3 L/m²h after physical cleaning which corresponds to the total flux recovery of 72% after physical cleaning. Note that UPW fluxes measured before and after filtration are not factors that depend on time or VRF values in flux figures.

During 5 kDa TRMF experiment, sampling was done at the beginning of the filtration (P1), at time = 0 min, and three more times after steady flux was observed (P2, P3, and P4). Average conductivity removal was observed to be less than 8% (Figure 6.3). TOC removal was about 70% for each sample. Feed TOC value of 260±6 mg/L was taken down to 70 mg/L with 5 kDa filtration (Table 6.1). Turbidity removal was observed to be over 98%, which make turbidity no more a problem by taking it under 1 NTU.

Table 6.1. TOC, conductivity, turbidity and SAC values of the feed and permeate samples for 5 kDa filtration

Sample	TOC (mg/L)	Conductivity (mS/cm)	Turbidity (NTU)	SAC (m ⁻¹)		
				436 nm	525 nm	620 nm
Feed	260±6	28.25±0.16	46.37±0.35	118.1	195.4	16.2
P1	81±3	26.69±0.02	0.89±0.05	7.0	16.1	0.8
P2	78±3	26.19±0.01	0.61±0.02	8.3	13.6	0.7
P3	79±3	27.2±0.03	0.66±0.11	8.8	14.0	0.8
P4	78±5	26.25±0.01	0.79±0.06	9.2	14.6	1.0

Color content of wastewater and permeate was evaluated by measuring absorbance values at three different wavelengths; 436 nm, 525 nm and 620 nm. SAC values at each wavelength are measured both for wastewater and permeate samples and these values are given in Table 6.1. Average SAC removal rates were 93±1%, 93±0% and 95±1% for 436, 525 and 620 nm, respectively. The aim mentioned at the beginning of the section was to remove color and organic pollutants and let the passage of salts. It seems to be partially achieved with the TRMF experiments of 5 kDa membrane since permeate conductivity content is kept close to same with feed and significant turbidity and color removal was achieved. However, permeate still had color in it that can easily be seen by bare eye. TOC content is about 80 mg/L. Sufficiency of the treatment is going to be evaluated in upcoming sections.

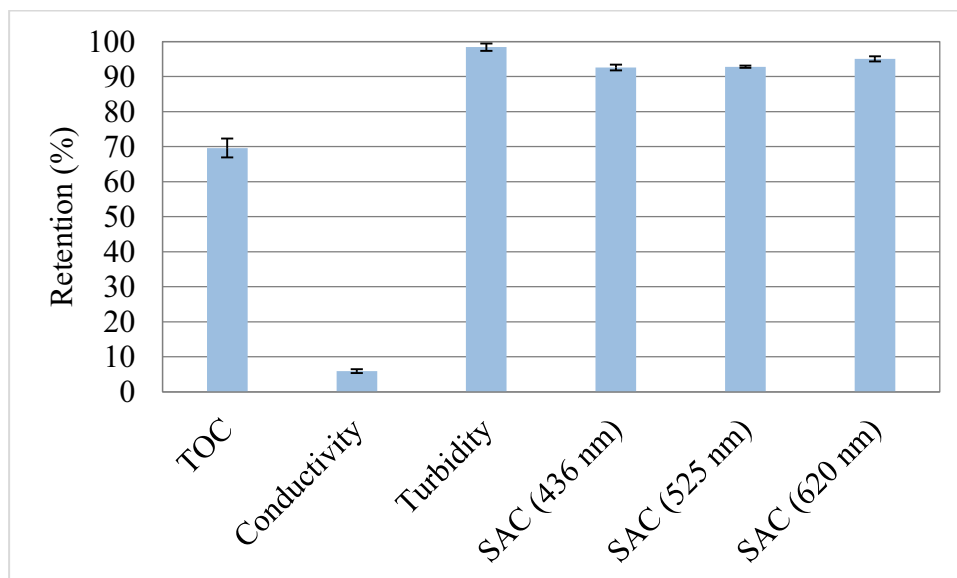


Figure 6.3. Retentions rates for 5 kDa TRMF

6.1.2. 2 kDa UF membrane

After 5 kDa PES UF membrane, a tighter one, 2 kDa Thin Film UF membrane was tested with the same wastewater mixture in a TRMF experiment. As indicated in Section 5.2, wastewater samples taken from 4 different steps of the reactive dyeing process were stored unmixed and feed wastewater samples were prepared mixing equal volumes from each of four steps before each experiment. The characteristics of the feed wastewaters used in this experiment is presented in Table 6.2.

Figure 6.4 presents the change in filtration flux with time observed during the test with 2 kDa UF membrane. As can be seen, filtration flux was measured at the beginning and in 30 minutes increments for a duration of 4 hours. There were no significant change in filtration flux during TRMF and average filtration flux after steady state was measured to be 3.8 ± 0.1 L/m²h.

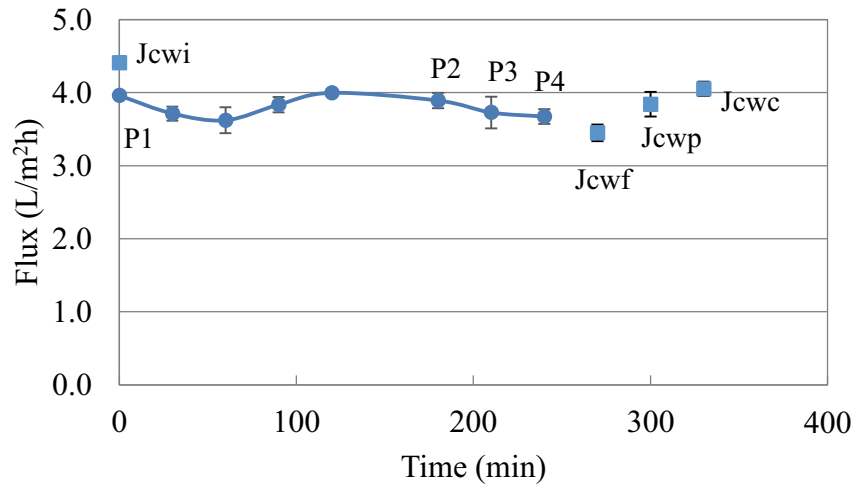


Figure 6.4. The change in filtration flux with time and sampling times (P1, P2, P3, P4) and UPW fluxes for 2 kDa filtration

Figure 6.4 also presents UPW fluxes before and after wastewater filtration, and after cleaning processes. As can be seen, there was not much difference between the UPW flux and the filtration flux with 2 kDa UF membrane implying little CP & fouling. The UPW flux measured after wastewater filtration was slightly lower than the initial UPW flux and almost equal to the wastewater flux, which shows that there was slight fouling on or in the membrane only. Low permeation rate in 2 kDa filtration and high cross-flow velocity used in TRMF tests seems to avoid the formation of CP and a cake layer. A slight recovery in UPW flux with physical cleaning and relatively a little more with chemical cleaning application were achieved. The UPW flux after physical cleaning (3.8 ± 0.2 L/m²h) was about 87% of initial UPW flux (4.4 ± 0.1 L/m²h). Chemical cleaning, however, was able to increase the UPW flux 5% more to the 4.1 ± 0.1 L/m²h which corresponds to total flux recovery level of 92% after all cleaning applications.

The treatment performance of the membrane was evaluated by the analyses of the permeate samples collected with regard to its TOC, color, turbidity, and conductivity. The results presented in Table 6.2. In essence, permeate from this 5 kDa membrane

filtration was sampled for 4 times and the samples named P1 to P4 were taken. P1 is the first sample taken while P2 to P4 are the samples taken after steady-state. As can be depicted from Table 6.2, the permeate quality was almost steady right after the start of the test and there was almost complete removal of turbidity. TOC removal was relatively low (about 70%) with a permeate TOC of 80 mg/L (Figure 6.5). On the other side, as expected; conductivity retention was not over 9%; and the permeate's conductivity was 25 mS/cm that indicates the gathering of about 91% of salt in the permeate.

Table 6.2. TOC, conductivity, turbidity and SAC values of the feed and permeate samples for 2 kDa filtration

Sample	TOC (mg/L)	Conductivity (mS/cm)	Turbidity (NTU)	SAC (m ⁻¹)		
				436 nm	525 nm	620 nm
Feed	261±8	27.45±0.04	53.3±0.3	113.7	191.5	14.6
P1	77±3	24.9±0.07	0.35±0.03	2.4	3.3	0.5
P2	79±5	25.44±0.03	0.2±0.01	3.4	4.1	0.3
P3	82±6	25.32±0.02	0.85±0.02	3.8	4.5	0.5
P4	81±7	25.49±0.03	0.16±0.01	3.7	4.5	0.3

The performance of the 2 kDa membrane was also very good in terms of color removal; SAC removal was observed to be 97±1%, 98±1% and 98±1% at 436, 525 and 620 nm, respectively. Although several of the other researchers indicated UF as inefficient in the removal of reactive dyes from wastewater (Sostar-Turk et al., 2005), in the present case, single UF membrane application was quite successful in removing color from the wastewater and the SAC values of the permeate samples were markedly low (Table 6.2). Similar to the 5 kDa membrane, 2 kDa membrane also gave promising results in meeting the success criteria defined for the study. Conductivity rejection was low, whereas turbidity and color removals were considerably high. However, permeate color level can be considered as unacceptable

when the target end use of the permeate is considered. In this respect, TOC content of the permeate (80 mg/L) can also be considered to be high.

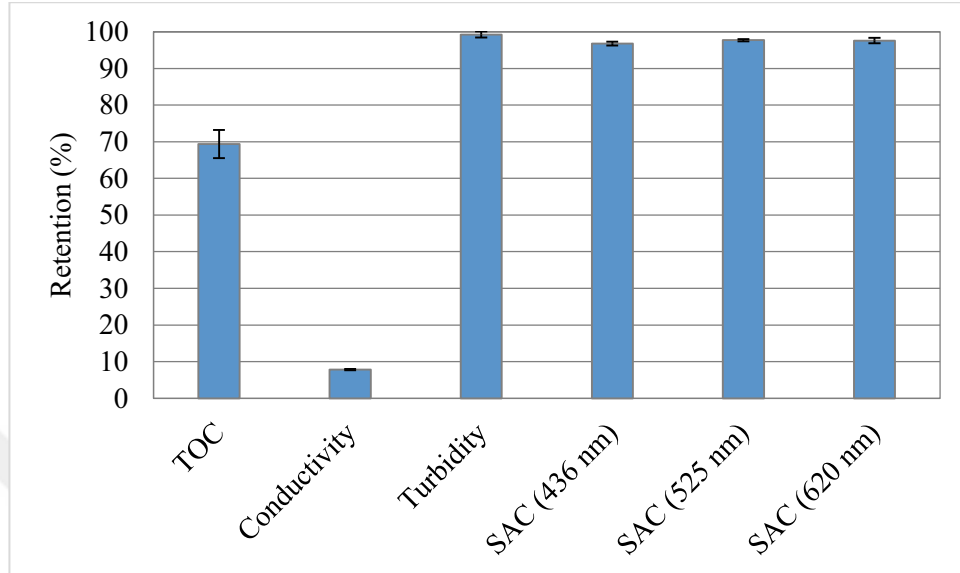


Figure 6.5. Retentions rates for 2 kDa TRMF

6.1.3. Comparison of 5 kDa and 2 kDa membranes

The experimental results presented in the preceding sections for 5 kDa and 2 kDa UF membranes under TRMF conditions, clearly indicate promising results to claim that colored RDW can be treated for the purpose of reuse, by only UF. In both 5 kDa and 2 kDa applications, suspended matter content of the wastewater was almost fully removed. The turbidity of the permeate from 2 kDa was less than 0.5 NTU and that of 5 kDa was about 0.8 NTU. Conductivity retention level, which we desire to keep low, was below 10% for both membranes; with the conductivity values almost equal to that of the feed wastewater, which is a mixture of four wastewater samples taken from the four stages in dyeing process. In both applications, TOC removal was about 70% and the permeates of both 5 kDa and 2 kDa membranes have TOC values close to 80 mg/L. As the textile mill or the relevant literature provides no acceptance

criteria in terms of TOC, the evaluation of the acceptability of this level TOC was achieved by dyeing tests performed with the permeate obtained under CMF (Section 6.3).

The most challenging aspect of UF treatment of RDW is to solve the color problem. Even the tighter 2 kDa UF membrane, having a pore size of 2 kDa MWCO (2000 g/mol) is normally not expected to retain dye molecules which are smaller than 2 kDa (See Appendix A). However, rejection rates for SAC values were significantly high for both applications. At all three wavelengths, over 90% removal achieved for the 5 kDa membrane. The rejection rates were higher with the 2 kDa membrane, with retentions over 97% at three different wavelengths. This unexpectedly high color removal with UF membranes was attributed to possible micelle formation inside feed wastewater due to other constituents or chemicals present in the wastewater as indicated before by Ahmad et al. (2006). Wastewater resulting from the 3rd step of dyeing process has soap in it which might cause the formation of micelles, which may be larger than membrane pores, including dye molecules inside.

6.2. Performances of 5 kDa and 2 kDa membranes in CMF tests

In the previous part of the thesis, two UF membranes were tested at a high cross-flow velocity and rejection of pollutants were monitored in TRMF. In order to shed light on the effect of feed concentration on UF performance and to gain insight into the behavior of the membranes in real RDW filtering operations, CMF tests were carried out for both UF membranes. Cross-flow velocity were kept at lowest level to mimic the actual operation conditions that would be adjusted with the minimum operational cost consideration. Actual operations that are realized at low cross-flow rates would also mean more probable CP and thus, CMF tests are applied to see the worse situations for membrane performance.

In CMF experiments, as distinct from total recycle mode of experiments, permeate collected is not recycled back into feed tank but collected separately. The total

amount of permeate to be collected is determined by the VRF value to be tested. VRF values of 2.5-2.67 are used for first performance assessments. A VRF value of 2.5 means that 40% of feed water is gathered as concentrate and the rest 60% as permeate. Permeate characteristics stand for this cumulative permeate in the given results. Conductivity, turbidity, TOC and SAC values are checked instantaneously as VRF value increases from 1 to final determined amount.

6.2.1. 5 kDa UF membrane

In CMF tests with 5 kDa UF membranes, a new pair of membrane sheets was used and two tests (Test 1 and Test 2) were performed. Although both membranes are from the same batch, they were seen to have different initial UPW fluxes. The UPW flux of the membrane used in Test 2 was 1.5 times higher than that of the membrane used in Test 1. Parallel to this difference in UPW flux, filtration fluxes for RDW were different (Figure 6.6). As can be depicted from Figure 6.6, flux decline curves were similar for Test 1 and Test 2; but, Test 2 has much higher filtration flux at time = 0 than Test 1. The difference in filtration fluxes appeared to get smaller as VRF increases. When UPW fluxes are taken into account for two membranes, normalized fluxes curves of two tests coincide with each other.

A decrease in filtration flux had been observed for 5 kDa membrane even at high cross-flow velocities during TRMF. A sharper decrease has occurred in CMF experiments probably by the effect of low cross-flow velocities (about 0.035 m/s). Moreover, solute concentration increase in feed side has probably decreased the flux with the effect of CP. Cross-flow velocities were adjusted to almost one fourth of TRMF test for Test 1 and Test 2. At the VRF values of 2.67, there revealed a total filtration flux decline of 46% for Test 1 and 56% for Test 2 at the end of filtration. The UPW flux of 5 kDa membrane used in 2nd test was higher than the first one and it appeared to increase after cleaning processes. Both membranes did react similarly to the cleaning steps. Flux recovery as a result of physical cleaning application was about 76-77% and chemical cleaning steps took this value up to 83-85%.

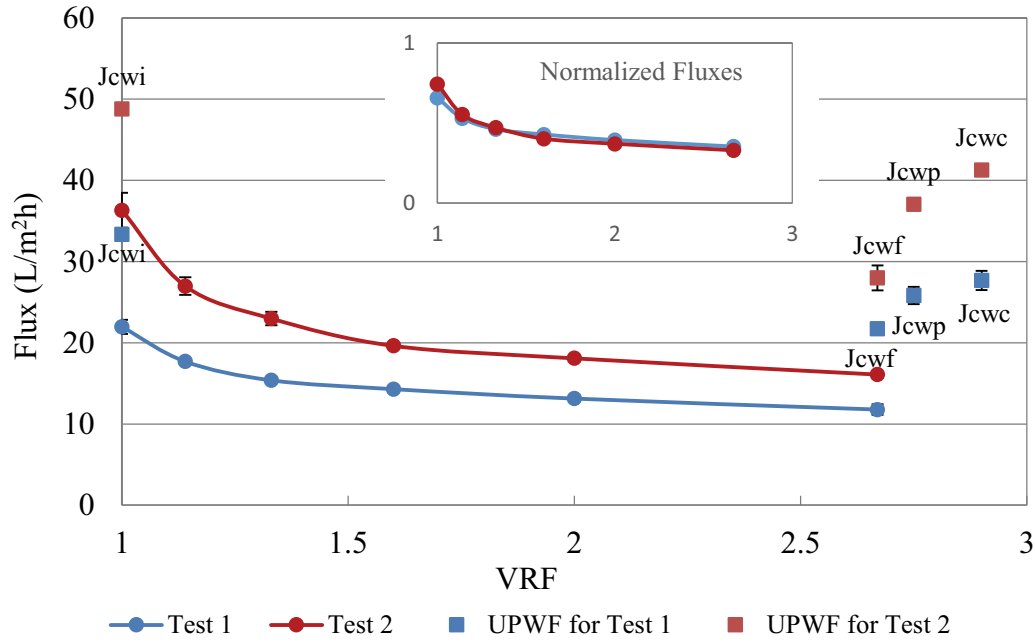


Figure 6.6. Filtration fluxes as a function of VRF for 5 kDa CMF

Samples were taken both from feed and permeate lines during filtration as feed wastewater gets more concentrated. Retention rates for parameters are determined for each sample when sampling for feed line is done too. The overall retention rates, on the other hand, are based on the feed at the beginning and cumulative permeate.

In both tests, it can be seen easily that TOC concentration of feed increases with increasing VRF value (Figure 6.7). Although the feed characteristics worsens significantly, instantaneous permeate characteristics do not change markedly with VRF. To illustrate, feed TOC value at the beginning of filtration (when VRF = 1) was 249 ± 3 mg/L and this value has increased to 410 ± 3 mg/L at VRF value of 2. However, corresponding permeate values were 56 ± 4 and 69 ± 5 mg/L for VRF values of 1 and 2, respectively. The removal rate for TOC increased steadily with increasing VRF, consequently. This was expected considering that removal in UF membranes mostly depends on pore size; and molecules smaller than pore size permeates to the

other side. Thus, final permeate value depends more on the relation between molecule size and pore size and less on feed wastewater concentration.

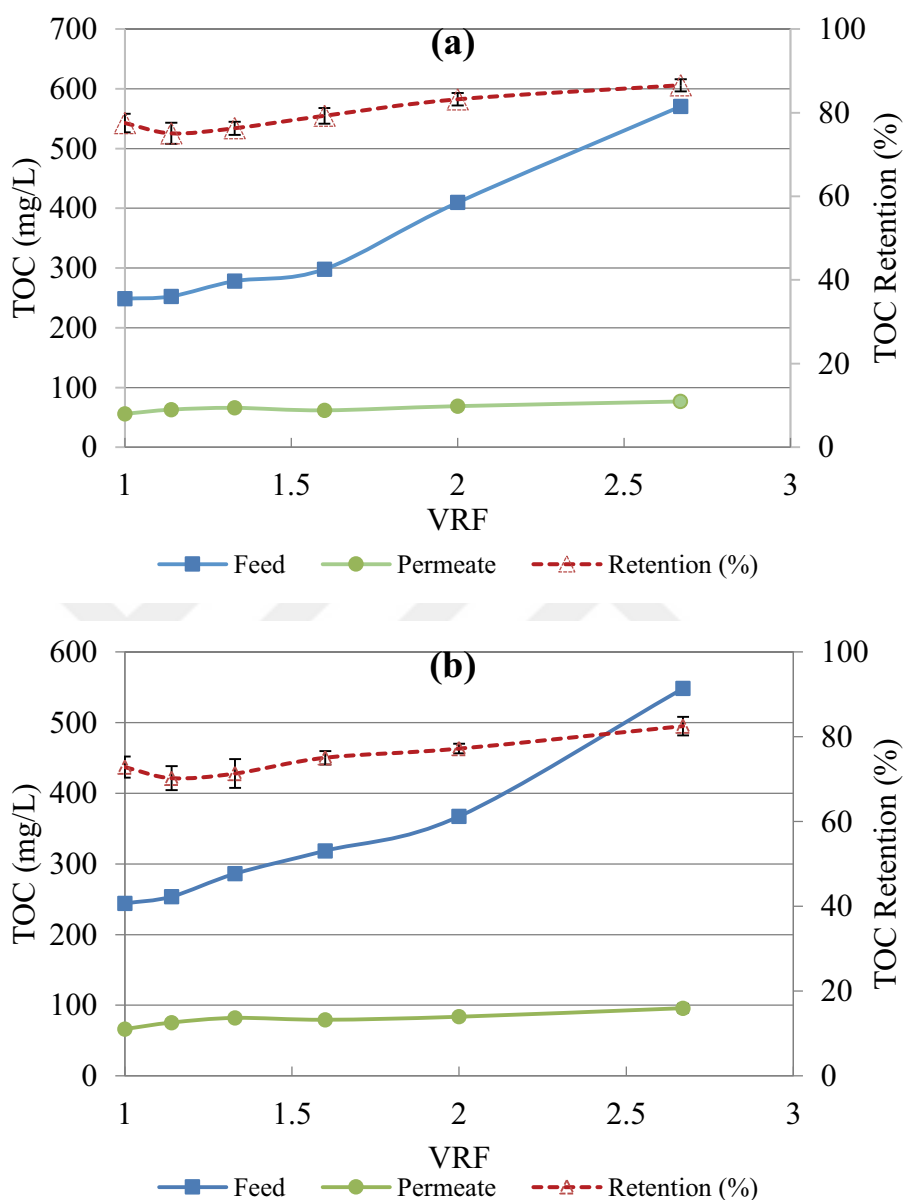


Figure 6.7. TOC values for feed and permeate with retention rates as a function of VRF for a) test 1 b) test 2 for 5 kDa CMF

During Test 1, the highest difference in conductivity values of feed and permeate was for the sample P1 (taken when VRF = 1) and conductivity retention for this sample was less than 4%. Situation was the same for Test 2 except 1st sampling. At the VRF value of 1, conductivity retention was about 7% (Figure 6.8). However, in all the rest of the samplings, this value was less than 3%. The low rejection values for 5 kDa for salinity content seems to be valid for CMF experiments, too.

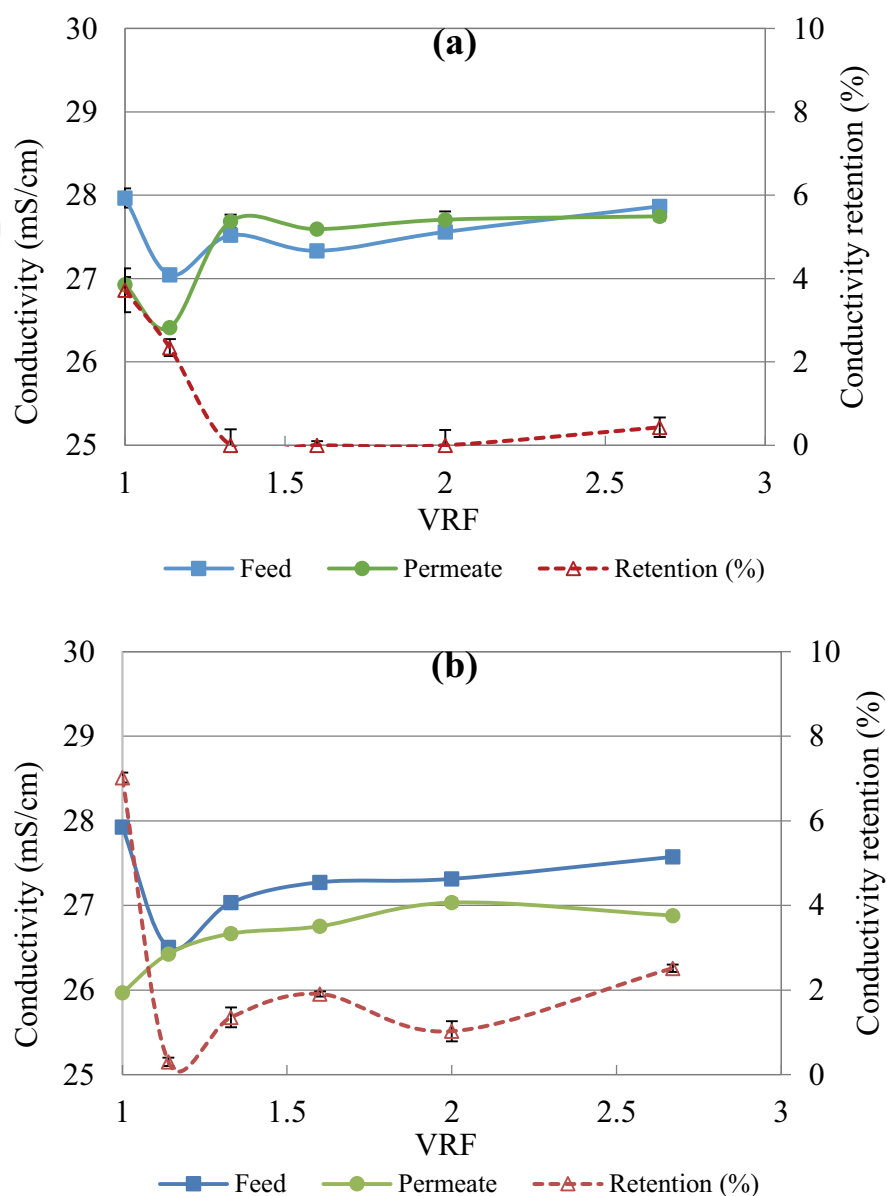


Figure 6.8. Conductivity values for feed and permeate with retention rates as a function of VRF for a) test 1 b) test 2 for 5 kDa CMF

Turbidity content of wastewater had been eliminated by over 98% in TRMF experiments with 5 kDa. This value was different in CMF tests especially in 2nd one. Least removal rates of $95\pm 2\%$ was observed in two sampling times during Test 1 (Figure 6.9). In those points, permeate turbidity value was close to 2 NTU. This rate has increased up to 99% as VRF value increases. The case was similar in 2nd test. Removal rates have changed between $96\pm 1\%$ and $98\pm 2\%$. It could be expected to see a sharp increase in feed turbidity value (as in TOC) as turbidity of the wastewater gets removed and feed wastewater gets more concentrated. However, feed turbidity does not change much until VRF value is over 2. The reason of not seeing the removed suspended matter content in feed wastewater is probably the internal fouling tendency of 5 kDa membrane. Suspended matter content seems to have adsorbed on the inner structure of the membranes.

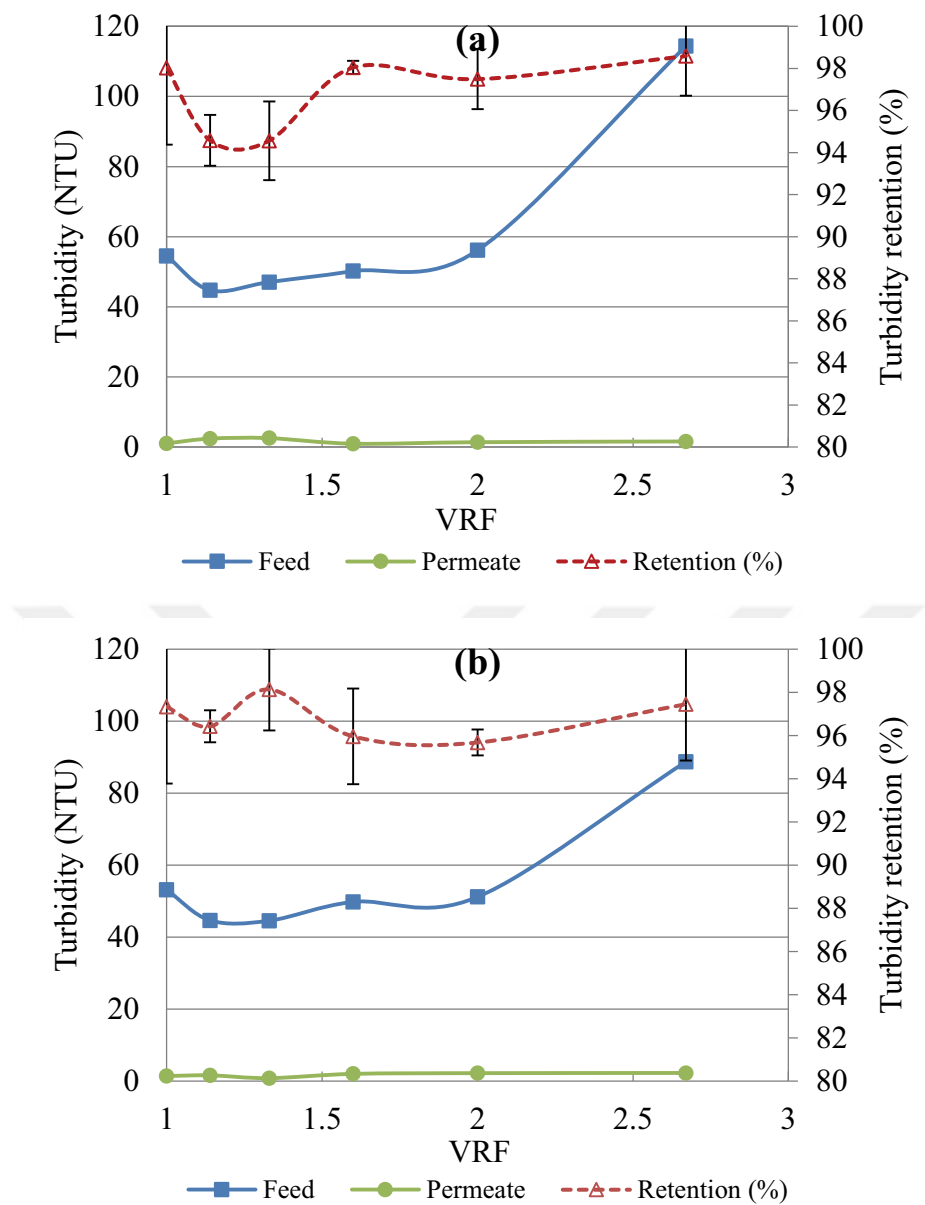


Figure 6.9. Feed and permeate turbidity as a function of VRF for a) Test 1 b) Test 2 for 5 kDa CMF

The color of the wastewater was rejected in amounts of over 93% in all SAC values that are measured in different wavelengths during 5 kDa TRMF test. Here in CMF tests, the SAC values of permeate samples that are taken seems to increase as feed wastewater gets more concentrated (Figure 6.10). P1 is the sample taken at the beginning of the filtration ($VRF = 1$), and trend in SAC values goes up going from P1 to P6. As in the case with permeate TOC values, SAC values for instantaneous permeate sampling seems to increase as feed wastewater gets more concentrated. When retention rates were calculated between cumulative concentrate and final instantaneous permeate samples (P6), it was seen that retention rate has increased up to 96% at all wavelengths. This value is higher than the retention rates observed during TRMF tests (Figure 6.3).

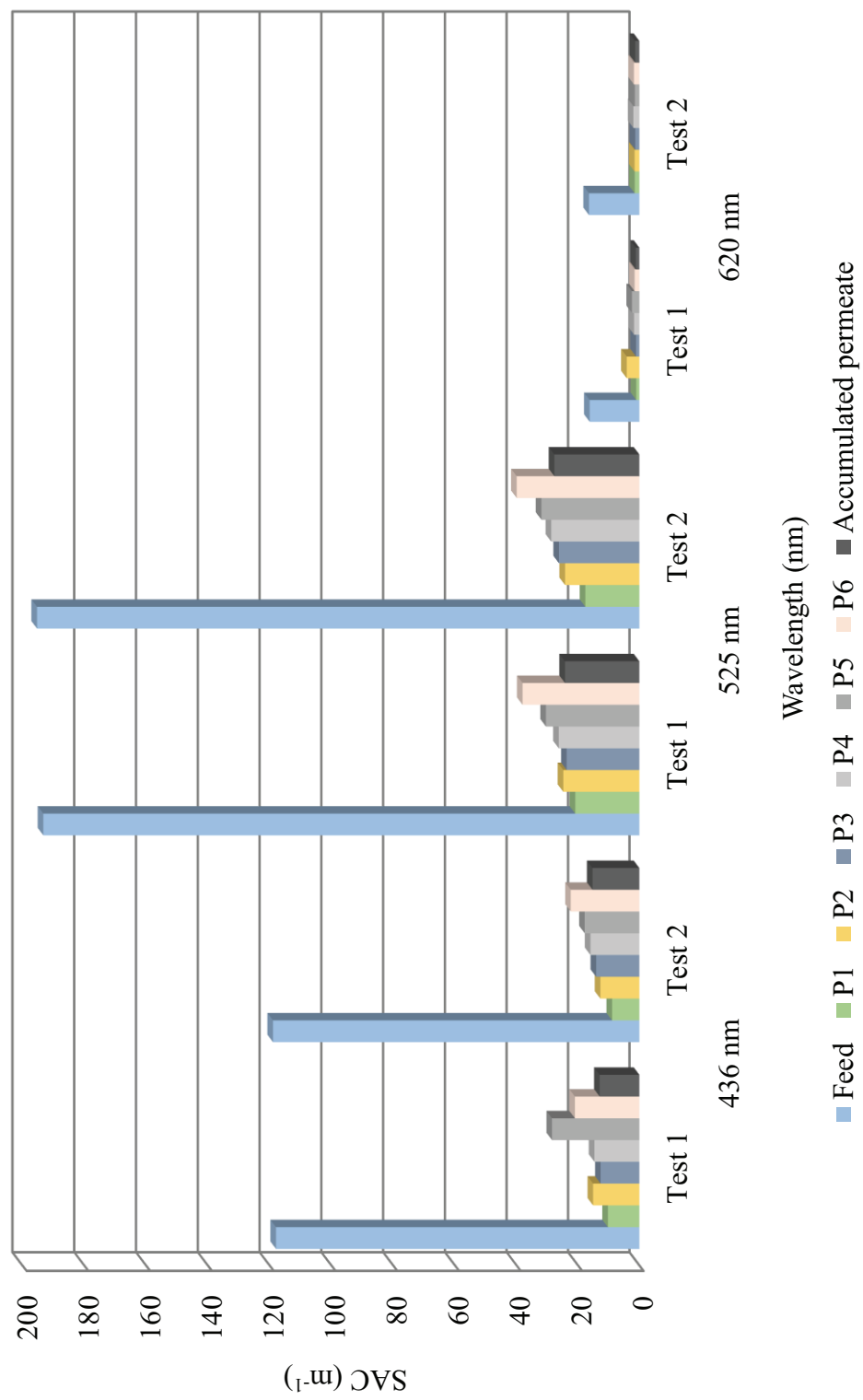


Figure 6.10. SAC values for Test 1 and Test 2 for 5 kDa CMF

Overall removal rates for 5 kDa UF tests are given in Figure 6.11 for TOC, conductivity and turbidity values. Membrane used in Test 1 has shown TOC rejection value of $76\pm3\%$ and permeate had TOC value of 60 ± 6 mg/L (Table 6.3). TOC rejection observed in Test 2 was $68\pm3\%$, and permeate TOC value was 77 ± 3 mg/L. Conductivity removal was quite low as expected with an UF membrane. It can be said that salinity content of permeate is mostly preserved even when 60% of feed obtained as permeate with VRF value of 2.5.

Turbidity removal was a bit lower when mode of filtration was changed to concentration mode. The difference between $94\pm4\%$ and $98\pm1\%$, which are turbidity removal rates for two tests presented here, may be negligible when standard deviations are taken into account. However, final cumulative permeates have a value over 3 NTU for Test 1. The reason of seeing turbidity value of 3 NTU in the permeate of 5 kDa is considered to be the result of agglomeration of particles after filtration. Wastewater has some surfactants in it and these surfactants result in the formation of suspended particles in the permeate. Yet, the lower value in Test 2 may be the indicator of that better permeate turbidity removal rates may be achieved by 5 kDa filtration.

Color retention rates have ranged between 87% and 92% for different wavelengths (Figure 6.11). Highest retention was observed at 620 nm during Test 2 and it was 93%. However, the color removal rates were over 93% in all the tested wavelengths when experiment is done at TRMF. Permeate samples taken during filtration had SAC values about 8-9, 14 and 1 m^{-1} for wavelengths 436, 525 and 620 nm, respectively (Table 6.4). Feed wastewater samples are mixed prior to each experiment and feed SAC values have not changed much in all three experiments. However, cumulative permeate values for Test 1 and Test 2 at CMF experiments were significantly higher than TRMF values. Contrary to TOC, conductivity and turbidity, permeate color characteristics have deteriorated with the change in filtration mode. It was mentioned before that as feed wastewater gets concentrated, SAC retention rate had increased according to the retention rate calculation between

final concentrate and P6. However, the deterioration of color content in instantaneous permeate samples seems to increase the SAC values of cumulative permeate.

Table 6.3. TOC, conductivity and turbidity values of the feed and permeate samples for Test 1 and Test 2 for 5 kDa CMF

	TOC (mg/L)		Conductivity (mS/cm)		Turbidity (NTU)	
	Feed	Permeate	Feed	Permeate	Feed	Permeate
Test 1	249±3	60±6	27.97±0.12	27.17±0.01	54.5±1.42	3.12±0.31
Test 2	244±4	77±3	27.93±0.01	26.08±0.03	53.17±1.35	0.94±0.14

Table 6.4. SAC values as a function of wavelength for Test 1 and Test 2 for 5 kDa CMF

	SAC- 436 nm (m ⁻¹)		SAC- 525 nm (m ⁻¹)		SAC- 620 nm (m ⁻¹)	
	Feed	Permeate	Feed	Permeate	Feed	Permeate
Test 1	117.9	12.9	193.2	24.2	16.2	1.1
Test 2	118.8	15.3	195.2	27.7	16.4	1.3

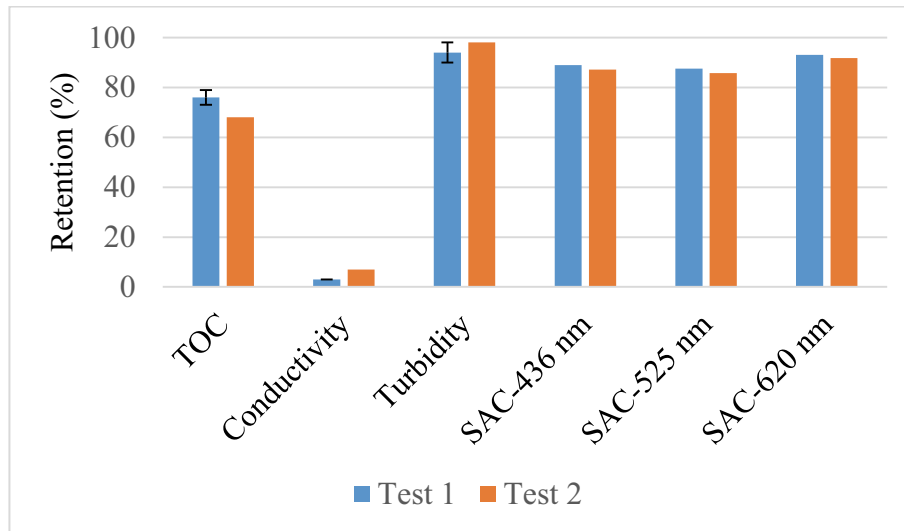


Figure 6.11. Retentions for Test 1 and Test 2 for 5 kDa CMF

6.2.2. 2 kDa UF membrane

Figure 6.12 depicts the evolution of filtration flux of 2 kDa thin film membrane during two parallel CMF experiments (Test 1 and Test 2). As seen, there was no significant change in filtration flux with time that could be attributed to fouling of membranes. In essence, the trend observed in filtration flux is the same that observed in TRMF experiments, and even when the feed was concentrated up to a VRF value of 2.5, the permeate flux was not seriously affected during CMF tests.

The evolution of permeate flux during parallel experiments of Test 1 and Test 2 was similar; and filtration fluxes of both tests at the end of experiments were same. This observation indicated that 2 kDa UF membranes were not prone to clogging by this specific wastewater. Also, due to lower pure water permeability (PWP) of this membrane, at the same TMP the permeate flux was lower than 5 kDa which made CP negligible. Raw water flux was a little lower than UPW flux for both tests. UPW flux of the membranes measured after filtration were very close to the ones measured before filtration. This is expected, since no CP or fouling was observed during

filtration as can be concluded from J_{rw} being close to J_{cwi} and the absence of change in filtration flux with time. UPW flux has almost remained the same (considering the standard deviations) after physical and chemical cleaning applications. Little increase in UPW flux may be due to the swelling in the pores of membranes as result of cleaning applications.

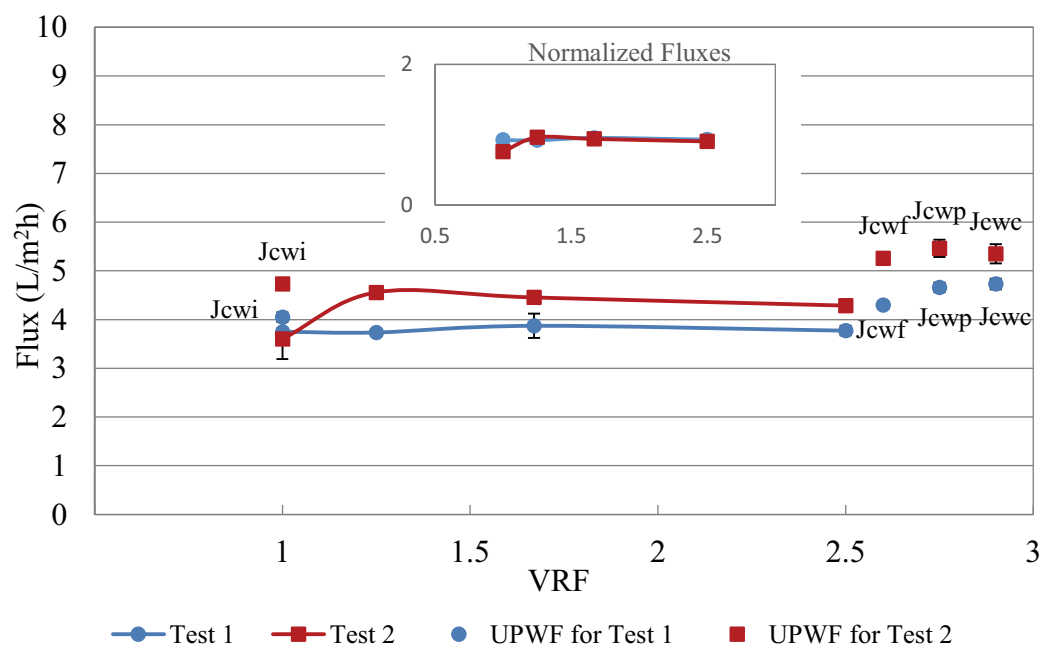


Figure 6.12. Filtration fluxes as a function of VRF for 2 kDa CMF tests

Contrary to the 5 kDa experiments, instantaneous sampling was done for permeate line only in this test. Thus, removal rates presented in Figure 6.13 are based on the initial feed and cumulative permeate concentrations. TOC retention rates were observed to be close to 80% in both 2 kDa UF tests (Figure 6.13). This value is higher than the TOC rejection value achieved in TRMF with 2 kDa. Turbidity removal is higher than 96% in both applications. However, permeate turbidity value of Test 2 was close to 2 NTU. This amount is at least the double of the value observed in TRMF tests of 2 kDa membranes.

Table 6.5. TOC, conductivity and turbidity values of the feed and permeate samples for Test 1 and Test 2 for 2 kDa CMF

	TOC (mg/L)		Conductivity (mS/cm)		Turbidity (NTU)	
	Feed	Permeate	Feed	Permeate	Feed	Permeate
Test 1	228±3	50±3	26.56±0.04	25.46±0.03	56.8±1.3	1.1±0.1
Test 2	244±5	55±5	28.27±0.01	26.98±0	49.5±1.6	1.8±0.3

Table 6.6. SAC values for Test 1 and Test 2 for 2 kDa CMF

	SAC- 436 nm (m ⁻¹)		SAC- 525 nm (m ⁻¹)		SAC- 620 nm (m ⁻¹)	
	Feed	Permeate	Feed	Permeate	Feed	Permeate
Test 1	113.9	4.0	190.3	4.9	14.8	0.4
Test 2	114.8	4.4	193.7	6.0	14.4	0.2

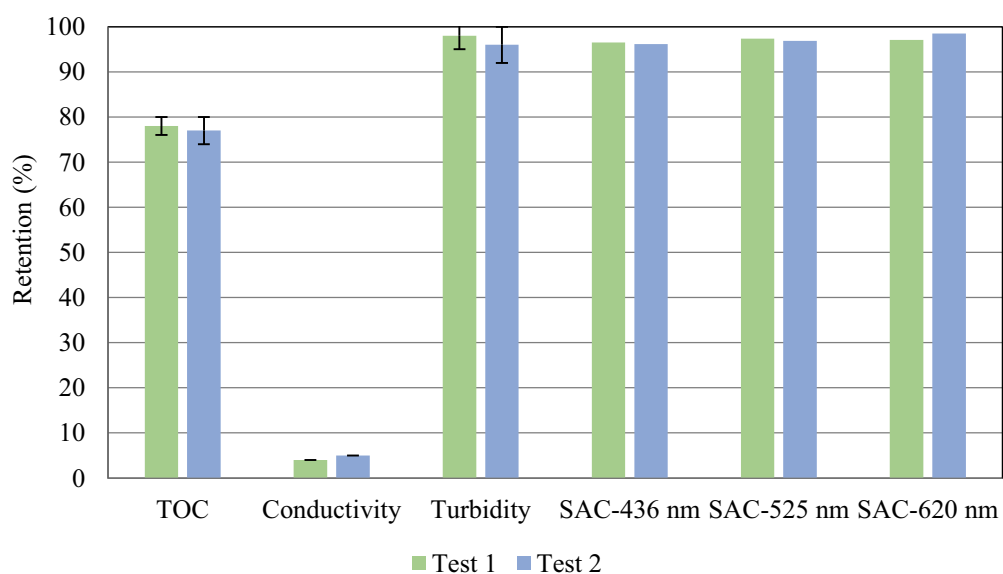


Figure 6.13. Retentions for Test 1 and Test 2 for 2 kDa CMF

The major driving force to suggest UF based treatment to RDW handling is to obtain saline water as permeate. In this respect, 2 kDa membranes were found to perform very well in CMF experiments by rejecting little amount of salinity. Conductivity retention was below 5% in 2 kDa UF performance tests, too.

The color retention by 2 kDa membrane in filtering RDW samples in TRMF tests was previously noted to be at least 97% (Section 6.1.2). This rate have not decreased with the change in filtration mode (Figure 6.13). As can be depicted from Figure 6.13, at all three wavelengths, color removal achieved were similar. Although the feed wastewater is concentrated and conditions were more close to real operations, the color retention remained the same.

Timely variation in permeate TOC values during 2 kDa filtration in CMF tests is presented in Figure 6.14. During both of the Test 1 and Test 2, TOC values of permeates have increased as the feed wastewater TOC increases. However, the deterioration of the permeate TOC level were not much as the increase in the feed wastewater TOC. At the end of the filtration, the concentrated wastewater had a TOC value of 707 ± 8 mg/L. As can be seen on Figure 6.14, the change of TOC values of permeate samples of Test 2 was between 43 ± 4 (at VRF =1) and 70 ± 8 (at VRF = 2). This is significantly less when the change of feed wastewater is considered which was 244 ± 5 at the beginning and 707 ± 8 once the filtration has ended (VRF = 2).

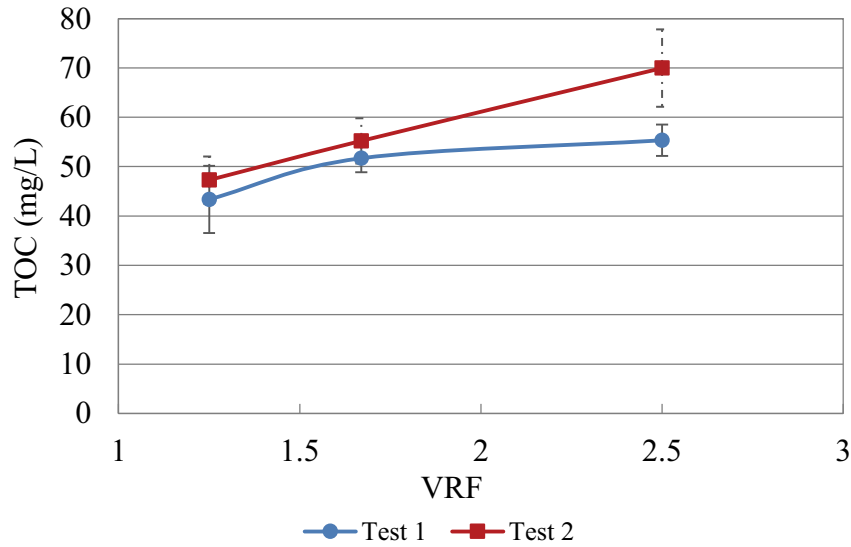


Figure 6.14. Permeate TOC as a function of VRF for Test 1 and Test 2 with 2 kDa CMF

Figure 6.15 presents conductivity values of the permeates from CMF tests with 2 kDa membrane. As shown, conductivity increased slightly for Test 2 as VRF increases. However, it remained the same for Test 1. In general, feed wastewater conductivity does not change much by VRF. Concentrated feed wastewater had a slightly lower conductivity when Test 2 has ended (27.5 ± 0 mS/cm). Since the salt content of feed wastewater has not changed much, permeation of salt through the membrane observed to be close to constant throughout the CMF.

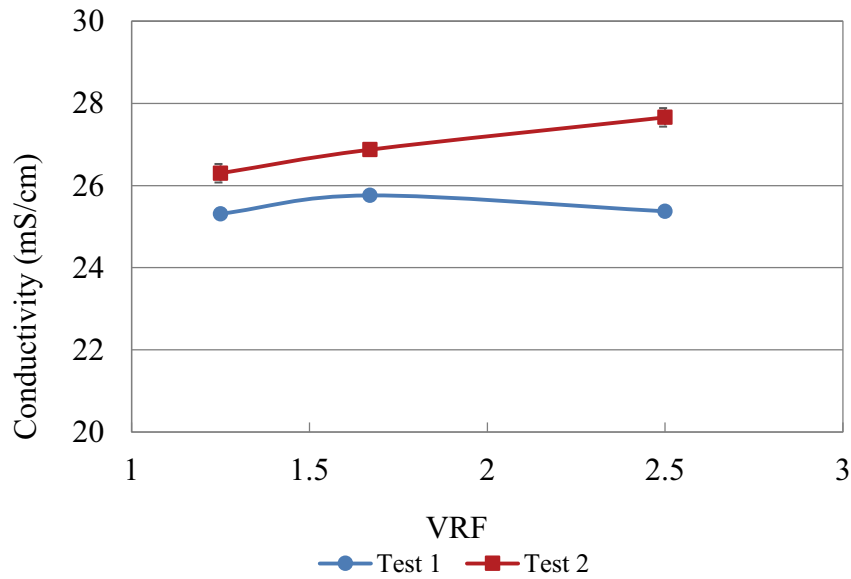


Figure 6.15. Conductivity values for permeate as a function of VRF for Test 1 and Test 2 for 2 kDa CMF

Turbidity values of the permeates obtained with TRMF experiments with 2 kDa membrane were values lower than 1 NTU (Section 6.1.2). Instantaneous permeate sampling had higher turbidity values during 2 kDa CMF test (Figure 6.16). When 2 kDa membrane was tested in CMF, molecules that are removed by 2 kDa are probably not adsorbed in the membrane pores, which was considered to be the case with 5 kDa membrane. The absence of change in filtration flux of 2 kDa supports this suggestion. Contrary to 5 kDa test there observed an increase in the feed turbidity during 2 kDa CMF test. Although the turbidity value to be treated increases, the permeate turbidity value remains the same. This is favorable for the application of 2 kDa since it would make it generic for the treatment of other wastewaters with higher turbidity. However, the permeate turbidity value of 2 NTU which is observed during Test 2 is high considering the TRMF performance of the same membrane. The reason of seeing turbidity value of 2 NTU is again speculated to be (as in the case with 5 kDa CMF) the result of presence of surfactants that are causing agglomeration even after filtration. Better turbidity values of permeates of Test 1, on

the other hand, make 2 kDa filtration still successful for removing suspended matter content of real RDW.

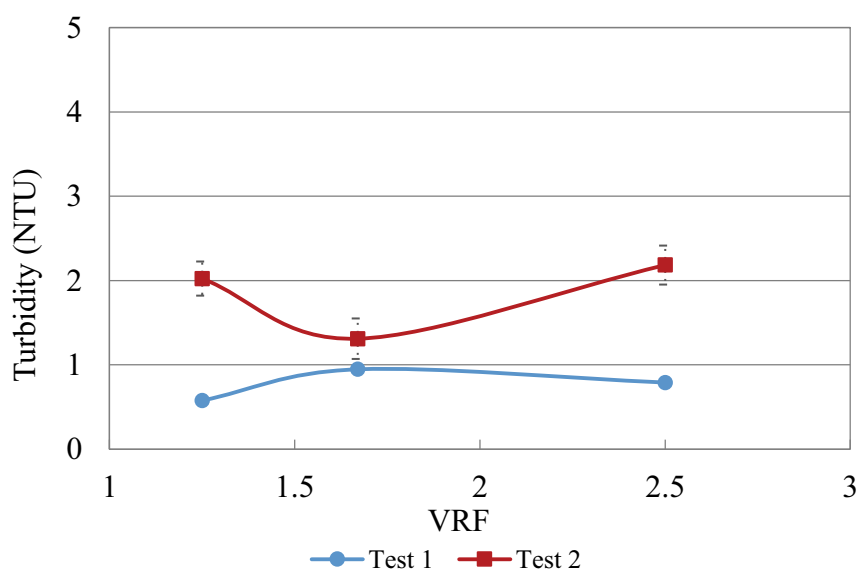


Figure 6.16. Turbidity values for permeate as a function of VRF for Test 1 and Test 2 for 2 kDa CMF

The SAC values of samples during CMF are given in Figure 6.17 together with the cumulative permeate values. As it was mentioned above when commenting on overall retentions, color removal performance was quite similar to that of the TRMF test. Permeate samples had increasing SAC values with increasing VRF values. In other words, permeate was more colored when the feed wastewater was more concentrated and had higher SAC values. The average of the SAC values of TRMF test was 3.3, 4.1 and 0.4 m^{-1} for 436, 525 and 620 nm respectively. The average cumulative permeate SAC values at these wavelengths were 4.2 m^{-1} , 5.4 m^{-1} and 0.30 m^{-1} for two tests done with 2 kDa UF membranes in CMF.

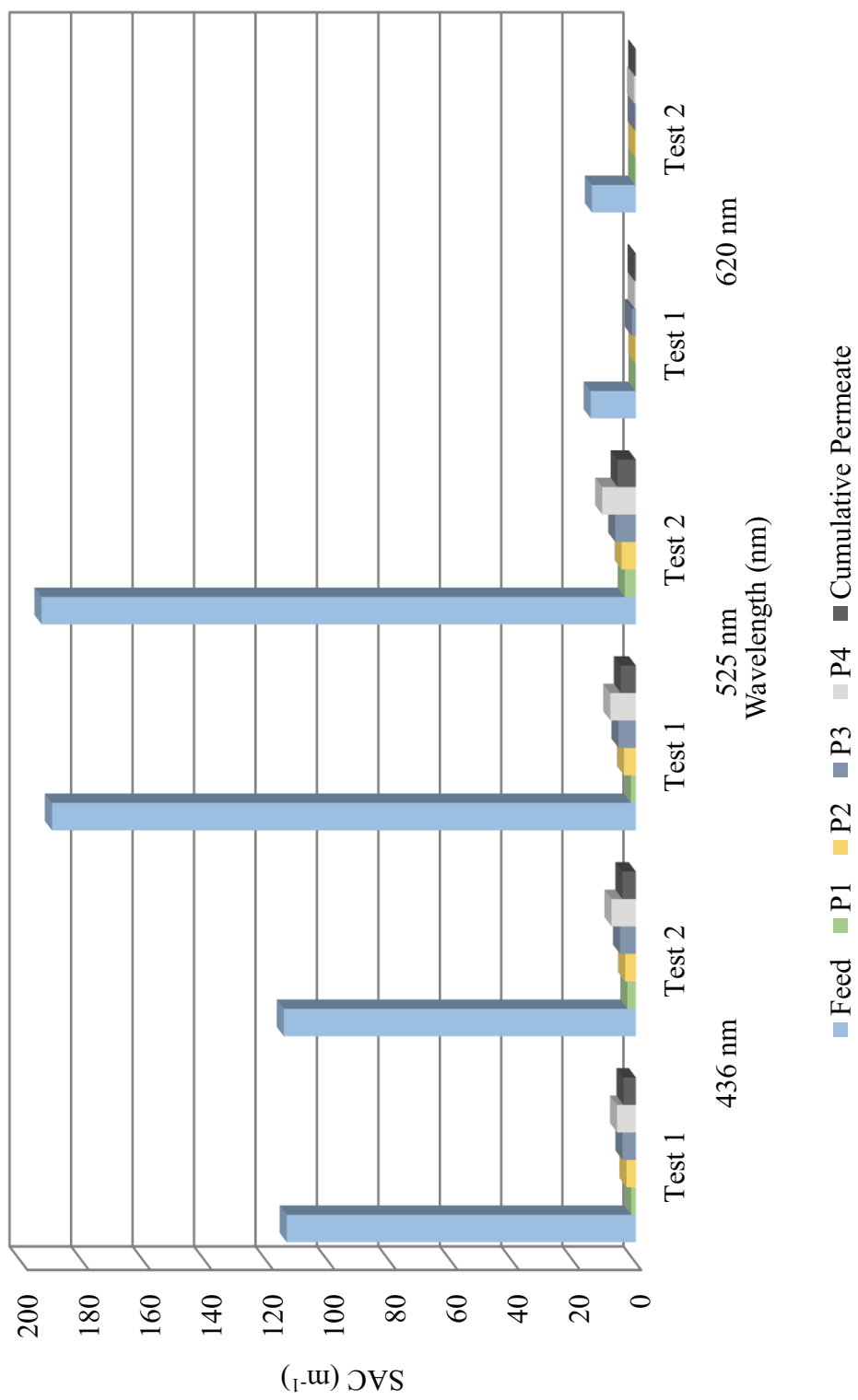


Figure 6.17. SAC values as a function of wavelength for Test 1 and Test 2 for 2 kDa CMF

6.2.3. Comparison of 5 kDa and 2 kDa membranes

As presented above, both UF membranes performed well in TRMF tests, and removed almost all the turbidity and let the passage of almost all the salts in the feed. TOC retention rates were about 70%, and color removal rates over 93% and 97% were observed for 5 kDa and 2 kDa applications, respectively. In order to better compare the performances of these two membranes in treating RDW, CMF experiments were realized and the results presented in Sections 6.2.1 and 6.2.2 were observed. In the present section, the performances of the two UF membranes in treating RDW by CMF tests are compared.

The preliminary observation from CMF tests is that both membranes have achieved TOC removal at the level of TRMF tests or higher. Between these two membranes, 2 kDa had higher TOC removal rate, as expected (Figure 6.18). Both membranes, however, had shown similar conductivity removal. Turbidity removal was less in CMF than that in TRMF. As feed gets concentrated in performance tests, overall turbidity retention rates have decreased for both UF membranes.

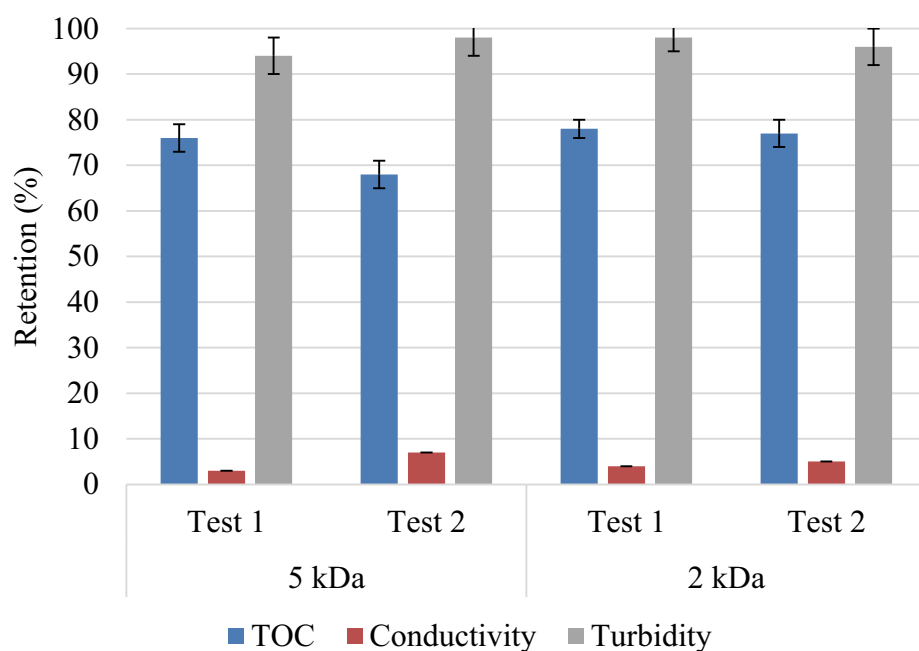


Figure 6.18. Comparison of TOC, conductivity and turbidity retention rates of 5 kDa and 2 kDa CMF tests

When the filtration mode is changed to CMF, color removal rates up to 85% for 525 nm for Test 2 of 5 kDa CMF tests were observed (Figure 6.19). Removal rates were higher for 2 kDa CMF. Tests have shown that 2 kDa membrane has significantly higher color removal rates compared to 5 kDa for CMF experiments, too.

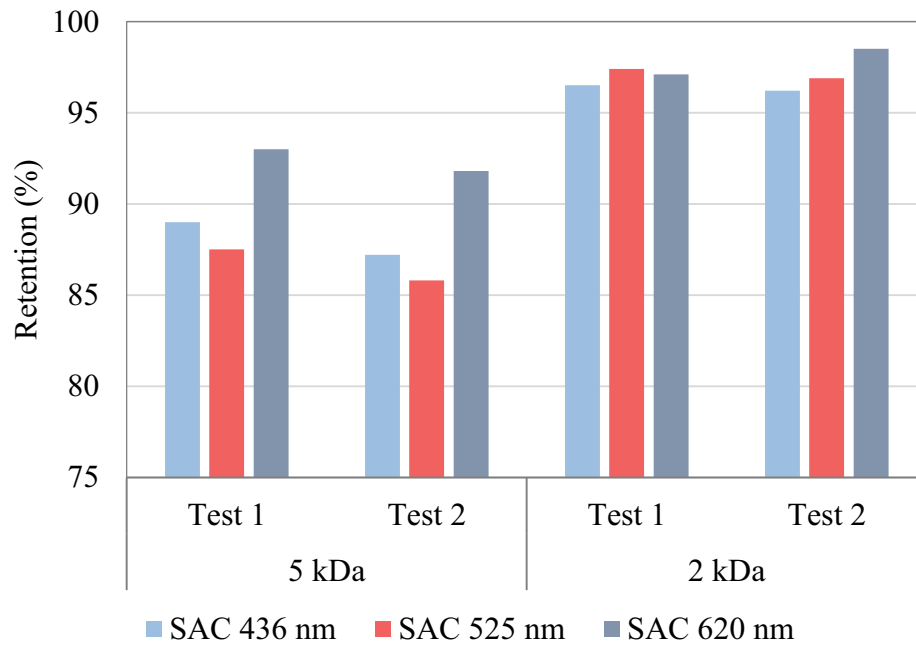


Figure 6.19. Comparison of SAC retention rates of 5 kDa and 2 kDa CMF tests

When the overall treatment efficiency of two UF membranes is compared, it can easily be said that 2 kDa UF has better purification ability considering better TOC and color removal efficiencies. However, 5 kDa was better in terms of flux performance. Filtration flux of 5 kDa was at least 2 to 3 times of the filtration flux of 2 kDa.

The aim in treating RDW by employing UF membranes was to obtain permeate water that is good enough to be used back in dyeing process. The characteristics that are needed for re-use in textile dyeing processes are not completely defined yet (Chollom et al., 2015). However, there are different criteria for different dyeing applications tried in studies. “No color content” in permeate was the common observation in successful dyeing tests as stated by De Vreese & Van der Bruggen (2007). It is clear that permeates of 5 kDa and 2 kDa UF still have suspended matter and dyestuff in the purified waters even though retention rates are considerably high. Among those, color content was at a level that is detectable by naked eye easily. In

order to enhance the quality of the final permeate, serial application of these two UF membranes is proposed. The idea behind this proposal was again not to go to NF application but to stay “UF application” which uses these two UF membranes sequentially.

6.3. Serial application of 5 kDa and 2 kDa membranes

As the treatment of RDW samples with both 5 and 2 kDa UF membranes provided TOC values that would be high for reuse, serial application was considered. Such an application was also thought to further decrease the color of permeates from 5 kDa and 2 kDa membranes.

In order to increase the rejection of TOC and color, and obtain permeate samples with better quality, further UF treatment was applied to the permeates of the single stage applications. Two stage applications tested are; “5 kDa + 5 kDa”, “5 kDa + 2 kDa” and “2 kDa + 2 kDa”. First membrane stands for first stage membrane filtration application, and the latter for second stage application in which feed water to second stage was permeate of first stage.

In the proceeding sections, the results from the three serial UF membrane applications, are presented firstly, and then their comparison is presented.

6.3.1. “5 kDa + 5 kDa” serial application

In two stage “5 kDa + 5 kDa” application, the feed to the 2nd stage 5 kDa UF was the permeate of Test 1 of 5 kDa CMF test. The second stage 5 kDa application was held also in CMF. In the first stage applications, the feed wastewater was the raw wastewater and therefore highly loaded with suspended and organic matter and highly colored compared to the feed of the second stage. By the first stage treatment with 5 kDa, the pollutants in wastewater were removed in significant amounts (Table 6.3, Table 6.4). The suspended matter content that caused fouling at the first stage

application was not present anymore. As a result, a constant filtration flux was observed with the 2nd stage 5 kDa filtration application (Figure 6.20). High filtration flux achieved with 5 kDa membrane is an important advantage of it over 2 kDa even if permeate flux decreased as VRF value increased. The decrease observed in the permeate flux during 1st stage application was not seen during the 2nd stage.

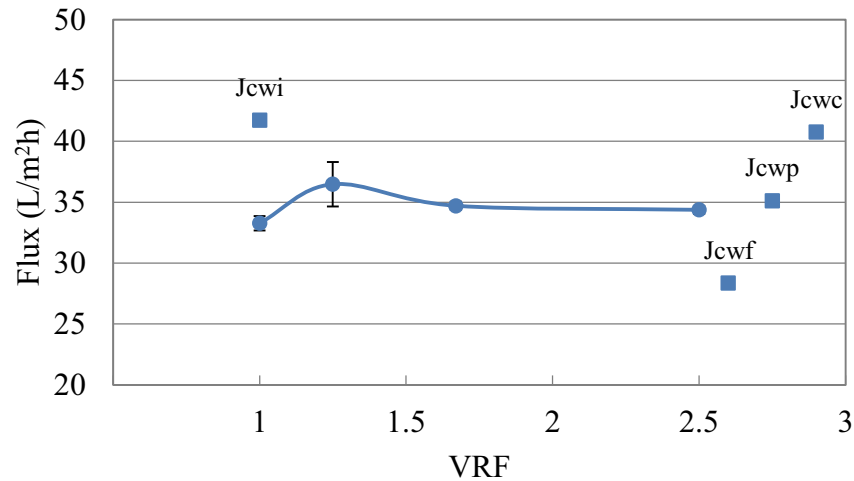


Figure 6.20. Filtration fluxes as a function of VRF and UPW fluxes for 2nd stage 5 kDa CMF

Main problem with the 5 kDa applications related to filtration rate was the UPW flux loss which remains even after physical and chemical cleaning applications. However, in the 2nd stage 5 kDa filtration, final UPW flux after cleaning steps was measured to be close to the initial value (Figure 6.20). The expectation with the clean water flux just after filtration (J_{cwf}) would be to see flux levels close to or higher than raw water flux since CP would be eliminated in flux measurement with UPW. However, the J_{cwf} value measured and given in Figure 6.20 is smaller than J_{rw}.

Serial two stage UF application is expected to provide better permeate quality than single stage application. In parallel to this expectation, TOC removal rates of above

70% achieved with the 1st stage 5 kDa application not measured with second stage 5 kDa application. . Instantaneous sampling from feed and permeate has shown that the percentage TOC removal observed with the second stage 5 kDa treatment was only about 10% at the VRF of 2.5. For a feed TOC value that has changed from 60 to 70 mg/L, the permeate TOC was measured to change between 50 and 60 mg/L as VRF value increases (Figure 6.21). Thus, it was thought that molecules that could be removed with 5 kDa were rejected at the first stage and there were not much molecules in the wastewater to be removed by the second stage application of 5 kDa membrane.

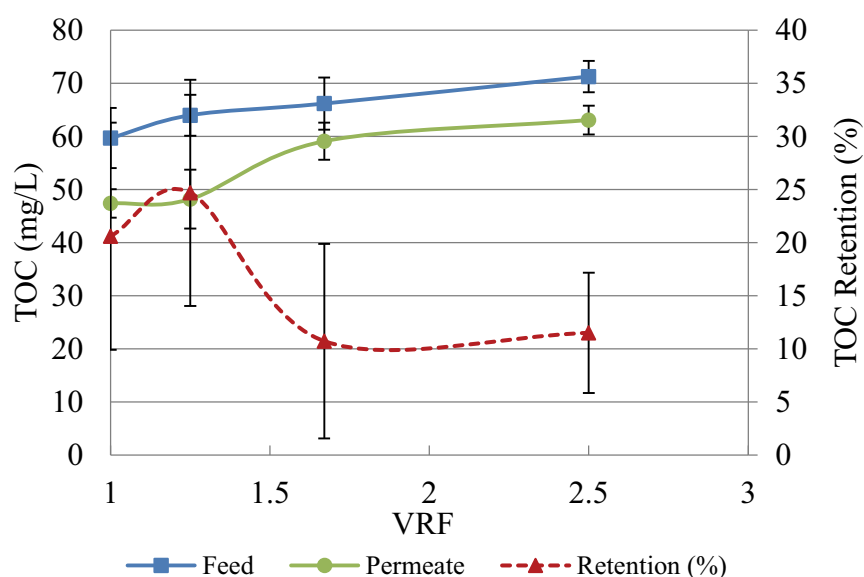


Figure 6.21. Variation of feed and permeate TOC values with VRF for the 2nd stage 5 kDa CMF

As it is desired, conductivity or the salt content of the wastewater was not decreased considerably, with the application of 2nd stage filtration (Figure 6.22). As can be depicted from the figure, the permeate from the 2nd stage application of 5 kDa filtration was measured to have a conductivity level of 25-27.5 mS/cm which is

almost equal to that of the feed (Figure 6.22). So, there was no loss observed in salt content of the permeate at this stage as VRF value increased up to 2.5.

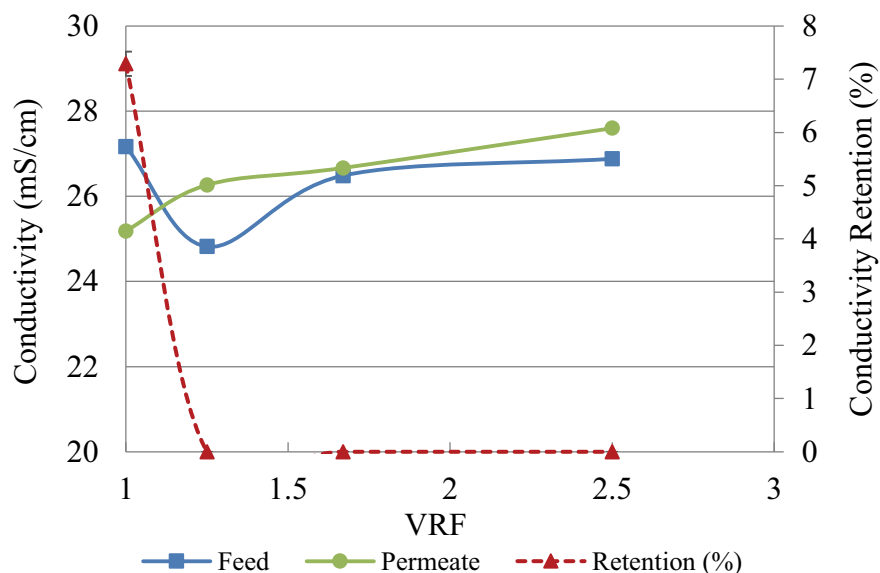


Figure 6.22. Conductivity values for feed and permeate with retention rates as a function of VRF for 2nd stage 5 kDa CMF

As it is clear from Figure 6.23, turbidity was not a problem. Even after the first stage, the permeate was with an acceptable turbidity level and the permeate turbidity characteristics has not changed much with 2nd stage applications. Turbidity values lower than 2 NTU was obtained when VRF value increased from 1 to 2.5.

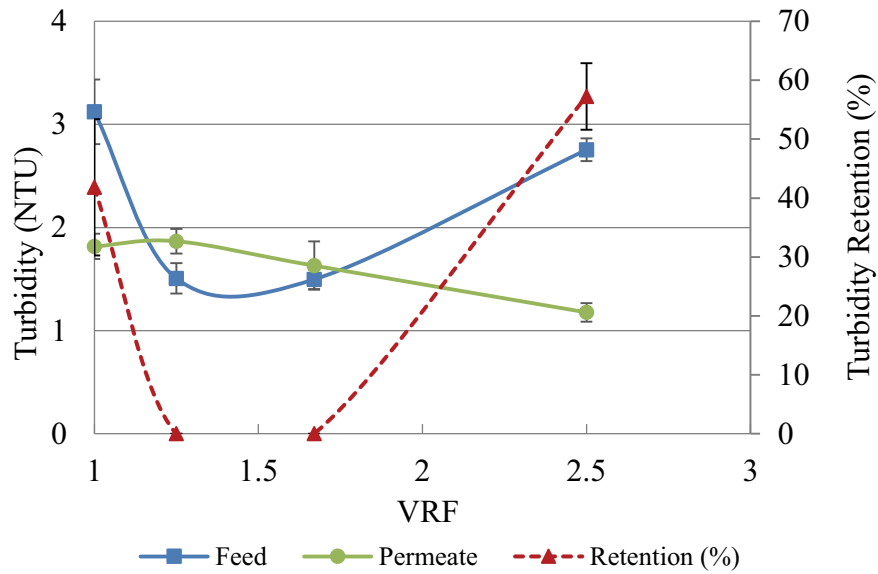


Figure 6.23. Turbidity values for feed and permeate with retention rates as a function of VRF for 2nd stage 5 kDa CMF

SAC values measured for the permeate of “5 kDa + 5 kDa” application had shown that the second stage application of 5 kDa membrane has its most important effect on final SAC values of the permeate. As seen in Figure 6.24, further 5 kDa treatment was found to have no effect on the permeate conductivity, which is good for the sake of the objective, and enhanced the final turbidity and SAC values.

The contribution of 2nd stage 5 kDa can be seen more easily in retention rates in Figure 6.24. Overall retention rates for TOC, conductivity, turbidity and SAC are not much different than the single stage applications. RES removal rates over 40% were observed at 436 and 525 nm wavelengths with the 2nd stage 5 kDa application. However, the retention rates read at the second stage do enhance the final permeate quality. Adequacy of this enhancement is discussed in Section 6.3.4.

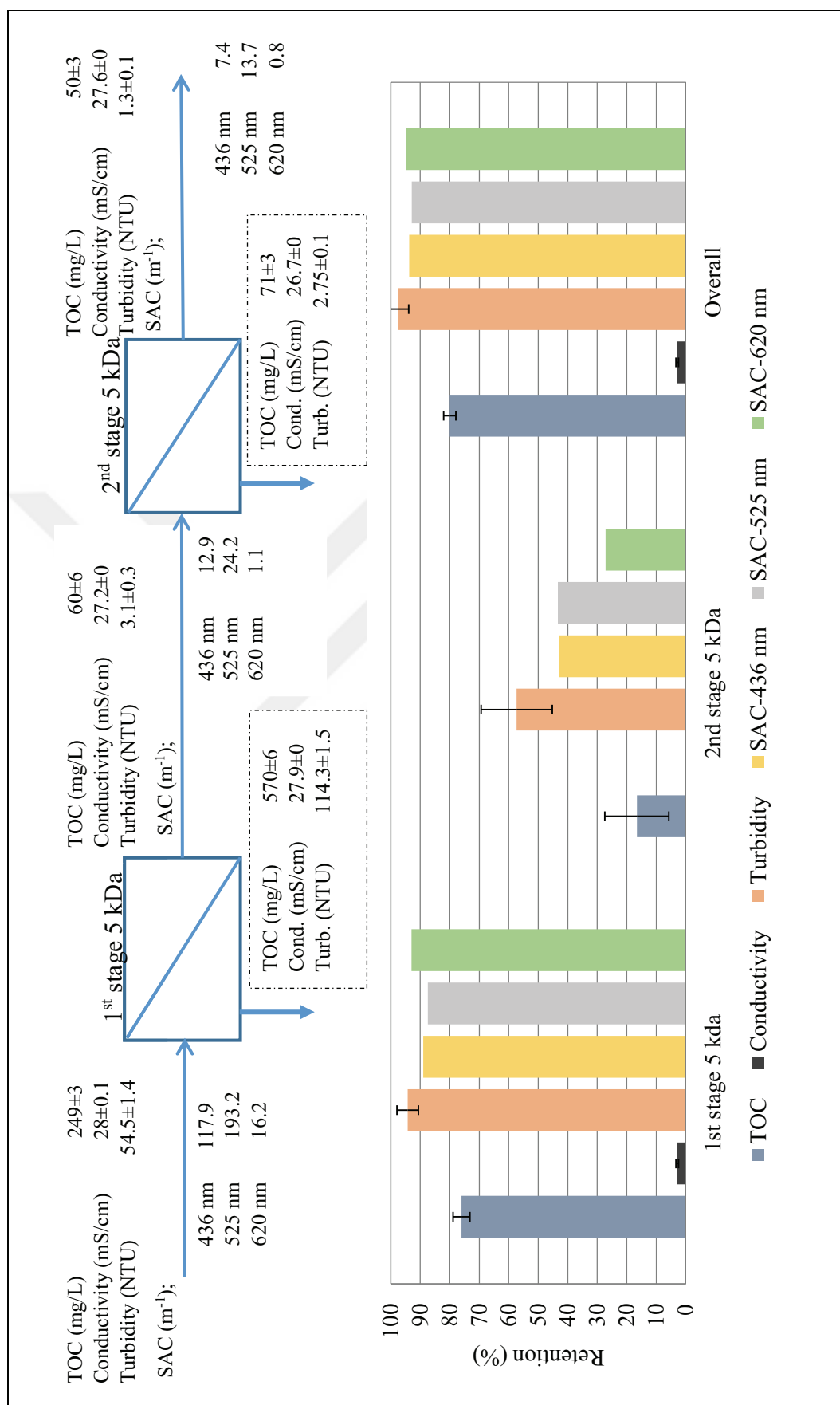


Figure 6.24. Feed and permeate characteristics for “5 kDa + 5 kDa” application with retention rates

6.3.2. “5 kDa + 2 kDa” serial application

The advantage of 5 kDa usage was to have a higher flux as compared to 2 kDa, On the other hand, 2 kDa membrane appeared to provide a better quality permeate. Thus, serial combination of these membranes was expected to provide efficient removal of pollutants under high filtration flux condition. So, the 2nd stage 2 kDa filtration was applied to the permeate of the 5 kDa CMF experiment (Test 2).

Even at the 1st stage applications of 2 kDa, where the feed was highly polluted RDW, there was no change in filtration flux with time in both TRMF and CMF first stage 2 kDa tests. This finding was enough to indicate that 2 kDa membrane do not get fouled at 2 bar up to the VRF of 2.5 (Section 6.1.2 and Section 6.2.2). When this membrane was applied as the second stage after 5 kDa, permeate flux did not change as VRF value was increased; therefore, 2 kDa membrane was not fouled when applied after 5 kDa too (Figure 6.25).

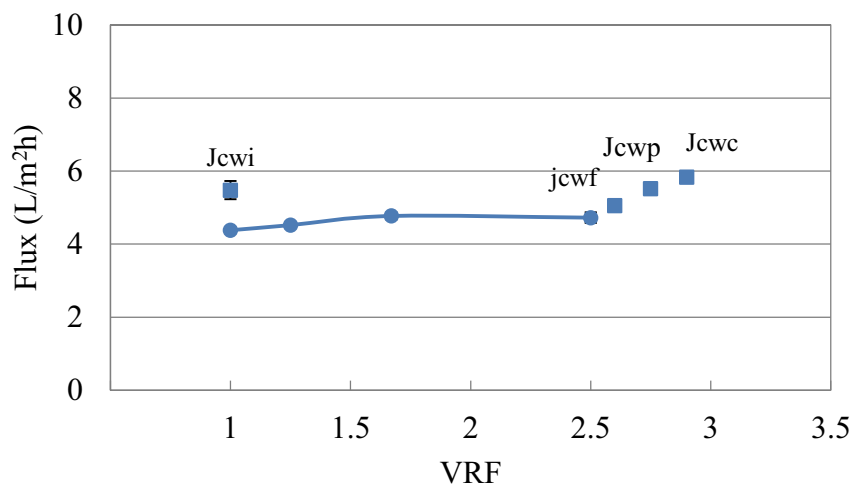


Figure 6.25. Filtration flux as a function of VRF and UPW fluxes for the 2nd stage 2 kDa CMF test

On the other side, average raw water flux of the 2nd stage 2 kDa application was a little lower than the UPW flux as similar to its 1st stage application. The UPW flux just after filtration was measured as very close to its initial value (when standard deviations are considered). This is the result of observing slight fouling and CP as a result of low permeation rate of 2 kDa. Fouling at second stage application is also less probable since feed is less polluted than first stage application. After cleaning applications, there remained no flux loss and resistance due to irreversible fouling.

When TOC removal with this serial application is considered, it is seen that the second stage UF application with 2 kDa after the first stage 5 kDa, provides a TOC reduction from 77 ± 3 mg/L to 48 ± 1 mg/L at the VRF of 1; and there occurs a steady slight increase in permeate TOC with an increase in VRF (Figure 6.26). At the VRF of 2.5, the permeate TOC increases to 66 ± 5 mg/L. The increasing trend observed in permeate TOC with increasing VRF was similar to the trend observed for the 1st stage applications of both 5 kDa and 2 kDa, and the percentage TOC reduction was changing between 30% and 45% as the feed gets more concentrated.

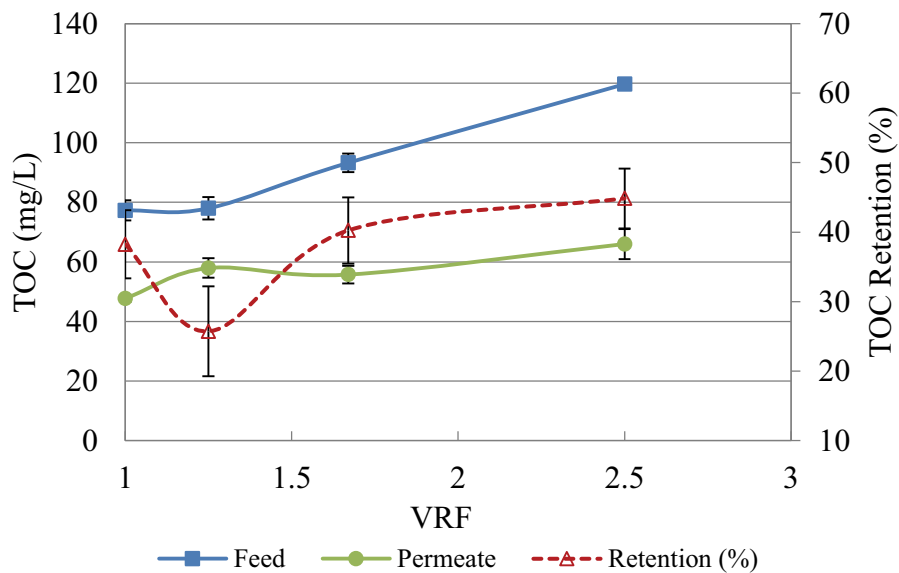


Figure 6.26. Change in feed and permeate TOC values with VRF during the 2nd stage 2 kDa CMF Test

As can be seen from Figure 6.27, conductivity content was not compromised by the second stage 2 kDa application, since there was no further conductivity removal.. Feed and conductivity values was read quite close to each other which made removal rates lower than 3%. The situation was the same for the 2nd stage 5 kDa application.

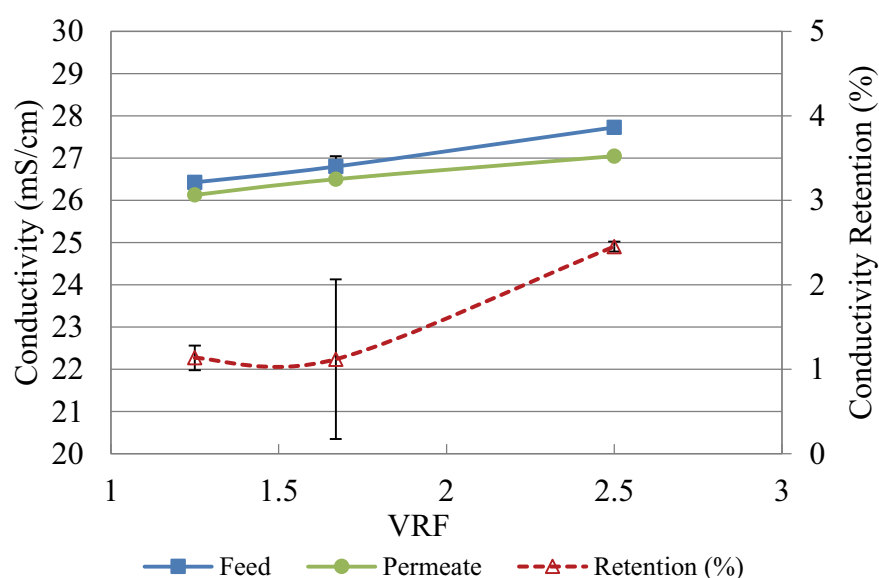


Figure 6.27. Change in feed and permeate conductivity values with VRF during the 2nd stage 2 kDa CMF Test

As stated in Section 6.2.3, permeate turbidity from the first stage applications was sufficiently low. This was attributed to 2 kDa filtration tests and one of 5 kDa filtration tests (Test 1)(Section 6.2.1). Other test, permeate of which is used as the feed in this test, had turbidity value over 4 NTU. By applying 2nd stage 2 kDa UF, turbidity of the feed, 4 NTU, has increased up to 8 NTU when VRF value was 2.5 (Figure 6.28). However, permeate turbidity was about 1 NTU. Consequently, an enhancement in the suspended matter removal can also be reported for 2nd stage 2 kDa application.

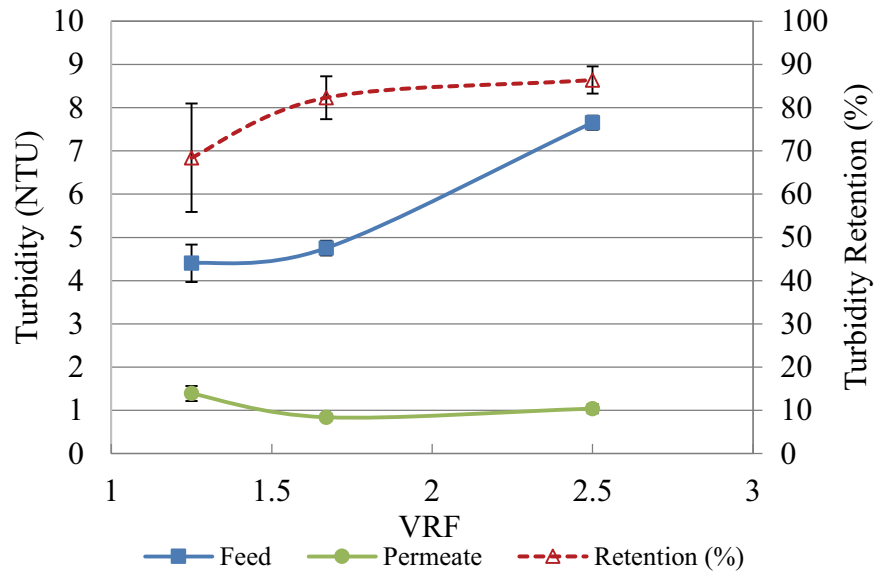


Figure 6.28. Turbidity values for feed and permeate with retention rates as a function of VRF for 2nd stage 2 kDa CMF

Serial “5 kDa + 2 kDa” application was tested 3 more times using a new pair of membrane to confirm the results achieved in the first application. Filtration flux curve obtained in the first trial with 5 kDa membrane (Figure 6.6) was confirmed in the next three tests done under the same conditions (Figure 6.29). Significant decreases in flux values were observed in all the tests, which are done with RDW as the feed to 5 kDa 1st stage application. As VRF increased, filtration flux decreased.

The filtration flux trend obtained in the 2nd stage 2 kDa application, was also reproducible with repeated tests. Filtration flux remained constant in all the experiments with increasing VRF value.

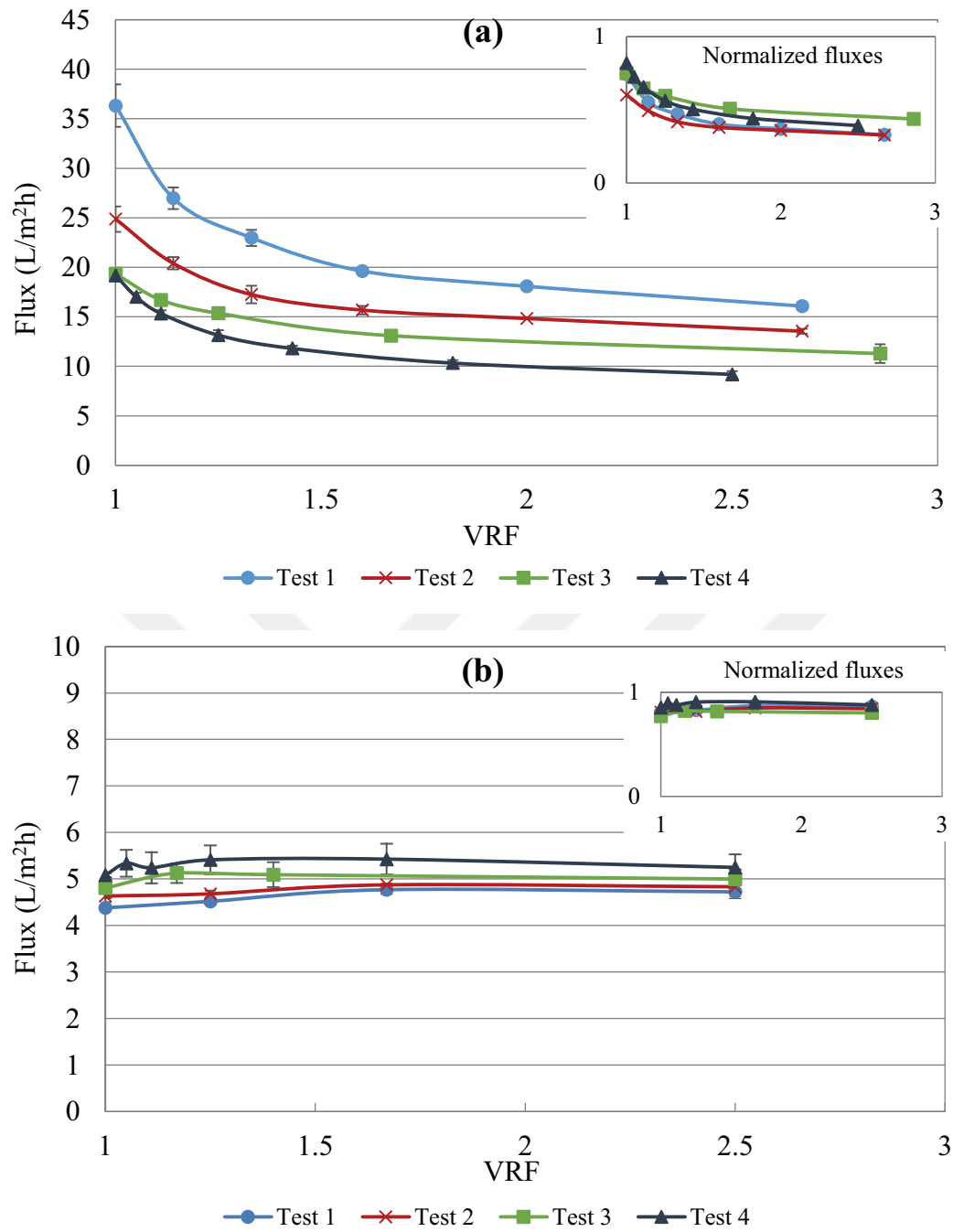


Figure 6.29. Filtration fluxes as a function of VRF and UPW fluxes for Test 1, Test 2, Test 3 and Test 4 for a) 1st stage 5 kDa b) 2nd stage 2 kDa

Figure 6.30 presents TOC, conductivity, turbidity and SAC values of the feed wastewater, 1st stage permeate and 2nd stage permeate for the “5 kDa + 2 kDa” tests. The values are the averages of the results from 4 parallel tests. The TOC value of the RDW (240 ± 9 mg/L), was decreased down to 53 ± 8 mg/L when two stage “5 kDa + 2 kDa” filtration was applied. Final permeate’s conductivity was, however, not much different than that of the feed. Permeate’s turbidity was close to 1 NTU after 2nd stage 2 kDa application. Final permeate SAC values were at most the 3% (at 525 nm) of the entrance value. Even though the color content that can be seen with bare eye after 1st stage has decreased after 2nd stage, the final permeate was still a bit colored.

TOC, conductivity and turbidity retention rates have not changed the final permeate quality much. There were considerably low retentions at 2nd stage when compared to 1st stage. The color retention, on the other hand, was quite high when further 2 kDa filtration is applied, too. The usage of additional 2 kDa filtration seems to have its most favorable effect on color retention.

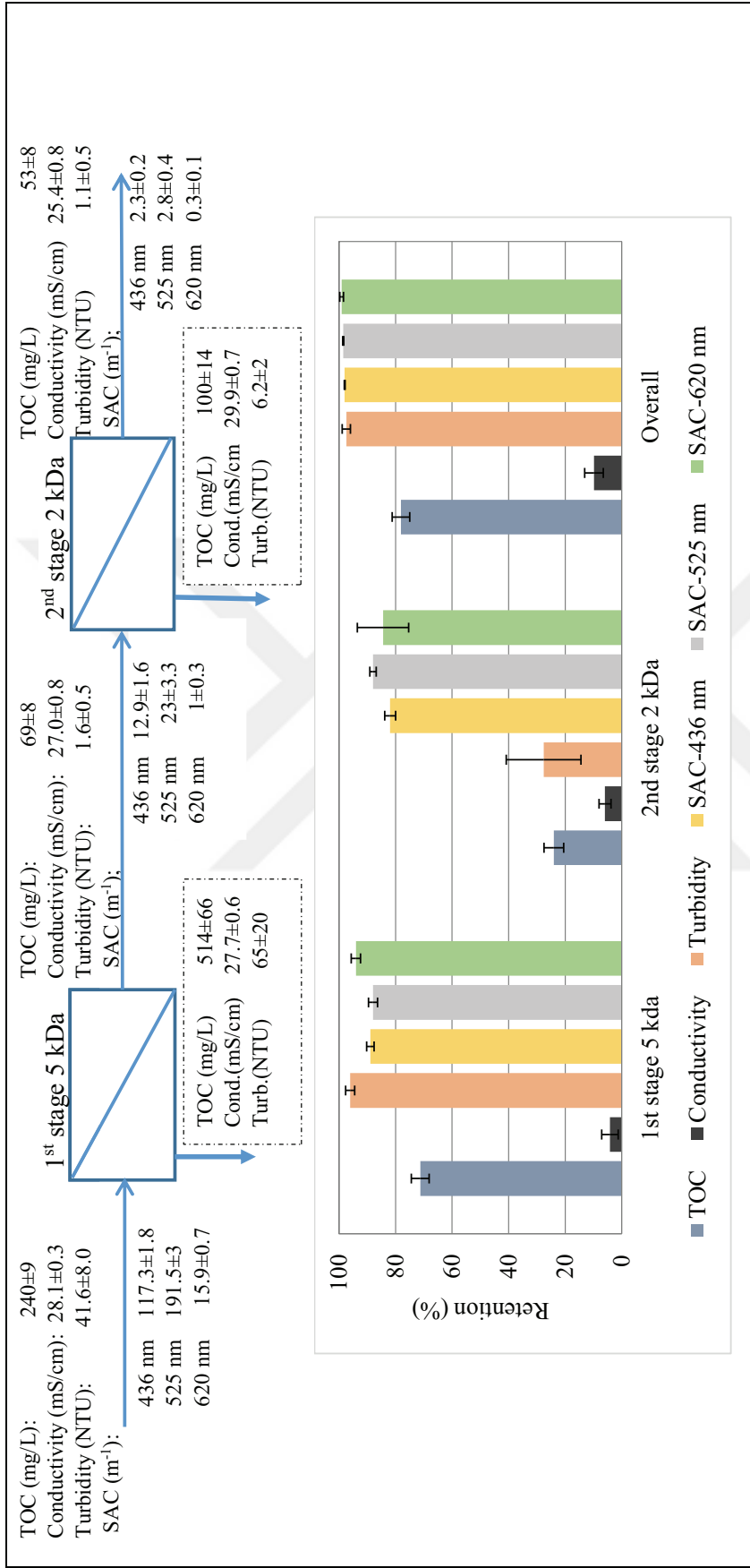


Figure 6.30. Feed and permeate characteristics for “5 kDa + 2 kDa” application with retention rates

PW fluxes measured after filtration are given in Figure 6.31 both for 1st and 2nd stages. As mentioned above, the tests for “5 kDa + 2 kDa” serial application were realized with different pairs of membranes for Test 1 and Test 2-3-4 for both stages. Membrane used in the 1st test in the 1st stage seems to have a lower intrinsic resistance and consequently a higher initial UPW flux compared to others. Other UPW fluxes were also relatively higher for this membrane. Membranes in 1st stage have shown similar reactions to physical and chemical cleanings. It is noted for all tests that flux recovery was not enough to see the initial UPW flux values for 5 kDa membranes during 1st stage filtration.

Contrary to 1st stage 5 kDa application, 2nd stage 2 kDa filtration has not shown a significant decrease in permeation flux during filtration. With UPW flux measurements after filtration, the difference of J_{cwi} from J_{cwf} and J_{rw} from J_{cwf} proves that a little decrease observed in filtration flux was due to both CP and fouling. With cleaning applications initial UPW flux values were achieved yielding full flux recovery.

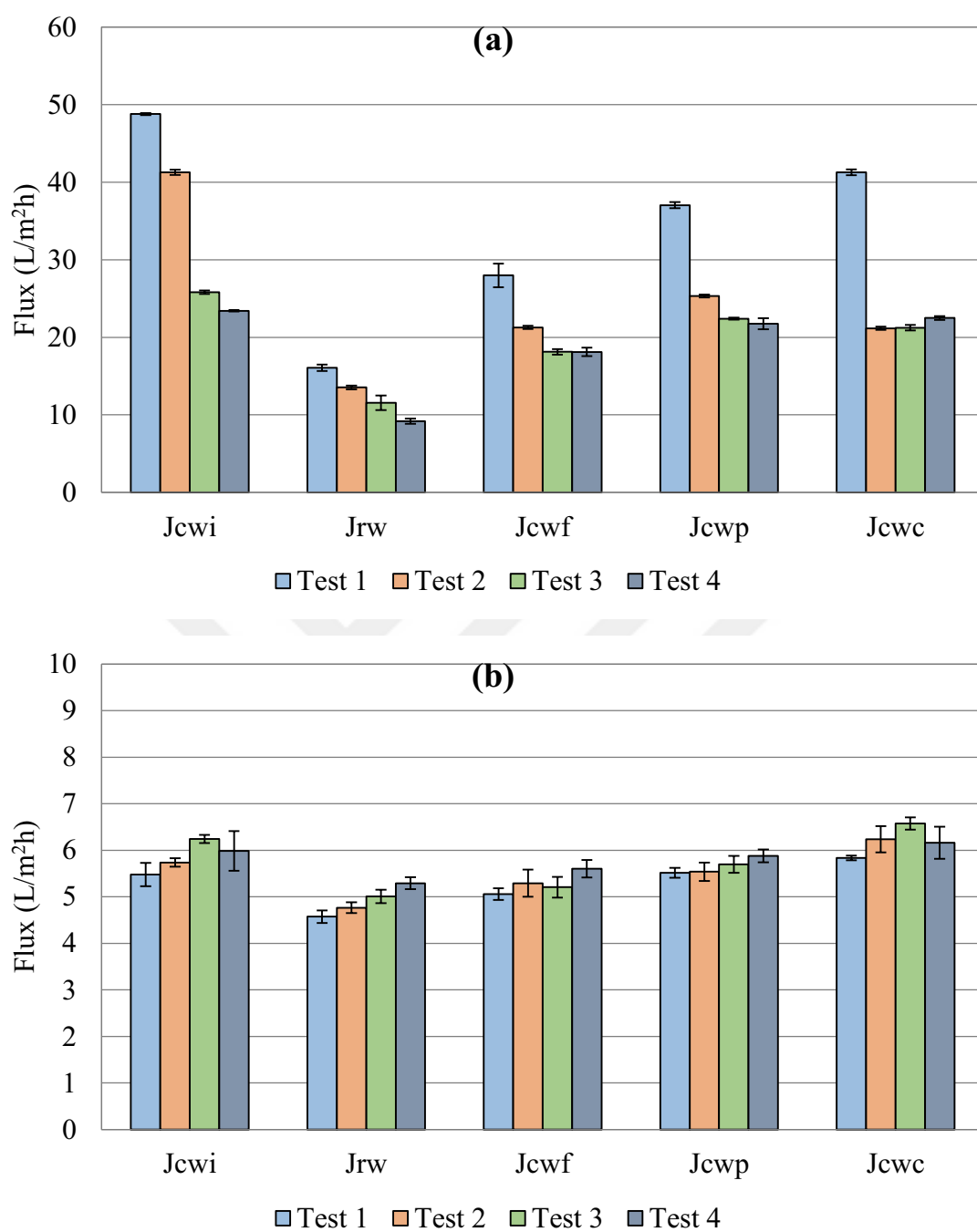


Figure 6.31. UPW fluxes for Test 1, Test 2, Test 3 and Test 4 for a) 1st stage 5 kDa
b) 2nd stage 2 kDa CMF

6.3.3. “2 kDa + 2 kDa” serial application

In this scenario, two 2 kDa membranes were used in series. The treatment efficiency had not increased much with 2nd stage application in “5 kDa + 5 kDa” scenario, where two membranes of same characteristics are used. What amount of enhancement would be observed was the question with 2nd stage 2 kDa application to permeate of 2 kDa filtration.

In the 1st trial of “2 kDa + 2 kDa” scenario, permeates obtained as a result of CMF experiments with 2 kDa, Test 1 and Test 2, are mixed and used as feed in 2nd step. Filtration flux had not changed during the first step filtration. Flux values close to constant profile was expected for 2nd stage 2 kDa application, too, where condition were the same as 2 bar, and VRF = 2.5. Both filtration flux value and profile were very similar to 1st stage and it started at 4 L/m²h and ended close to this value when concentration factor was 2.5 (Figure 6.32).

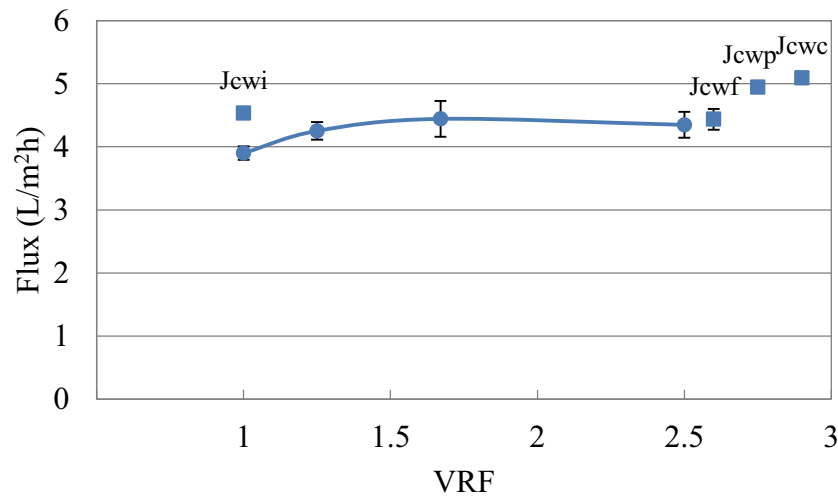


Figure 6.32. Filtration fluxes as a function of VRF and UPW fluxes for 2nd stage 2 kDa CMF after 1st stage 2 kDa filtration

The flux profile of 2 kDa membranes during second stage filtration flux measurements was as expected. This was foreseeable considering that the pollutants that had the potential to decrease the flux were removed in 1st stage. So the flux is determined mostly by membrane's ability to let the permeation of purified water. UPW flux measured before filtration was about the same with the flux measured just after filtration and cleaning applications. The J_{cwc} value was a bit higher than the initial UPW flux. This may be due to the swelling of the membranes as a result of chemical cleaning applications.

TOC of the mixture of the first 2 kDa applications was 50 ± 6 mg/L. This starting value has increased with increasing VRF (Figure 6.33). Feed TOC and permeate TOC profiles were very similar to the ones obtained in the 1st stage application. Permeate TOC value was about 40 mg/L during all the VRF values. So, a further retention of about 30% was the average for instantaneous sampling.

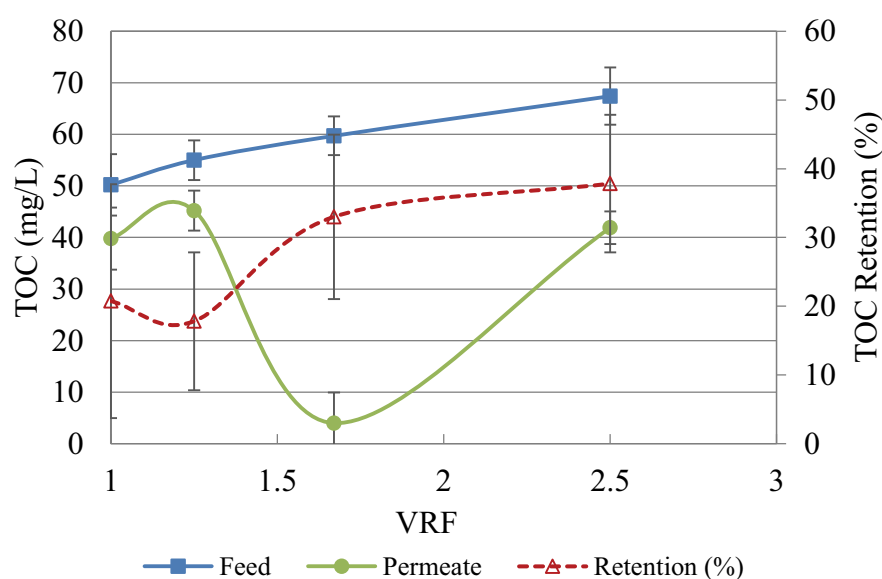


Figure 6.33. TOC values for feed and permeate with retention rates as a function of VRF for 2nd stage 2 kDa CMF after 1st stage 2 kDa filtration

On the other side, further 2 kDa treatment did not decrease the conductivity content of water further that is planned to be reused in dyeing process with less salt addition (Figure 6.34). Feed and permeate conductivity values were read close to each other at different VRF values. The conductivity retention by the 2nd stage was below 1.5% at most.

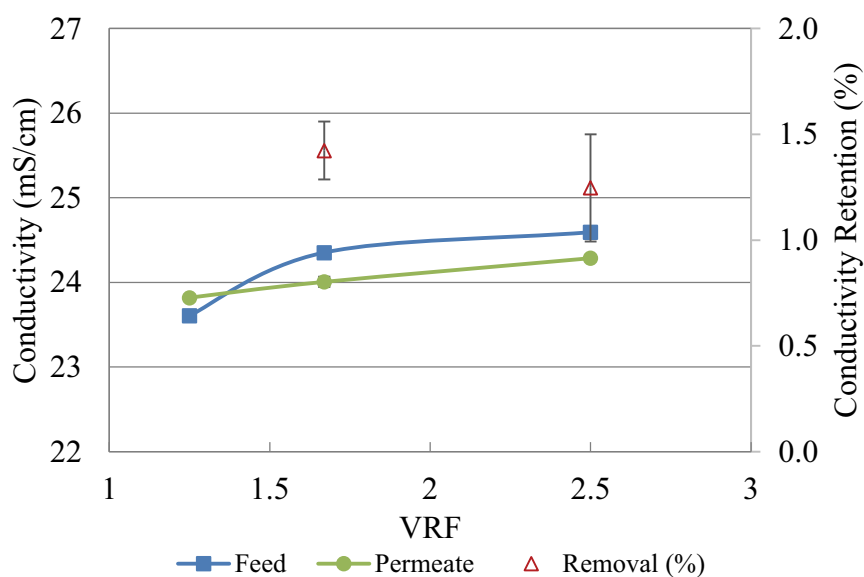


Figure 6.34. Conductivity values for feed and permeate with retention rates as a function of VRF for 2nd stage 2 kDa CMF after 1st stage 2 kDa filtration

After 1st stage CMF experiments done with RDW, it was noted that turbidity was no longer a problem for both 5 kDa and 2 kDa applications. Turbidity values of 1 NTU were read in these filtrations. With 2nd stage application, permeate turbidity value has decreased only about 15% more at the beginning of the filtration (Figure 6.35). However, as the feed water gets concentrated, permeate turbidity value was constant and mostly lower than 1 NTU.

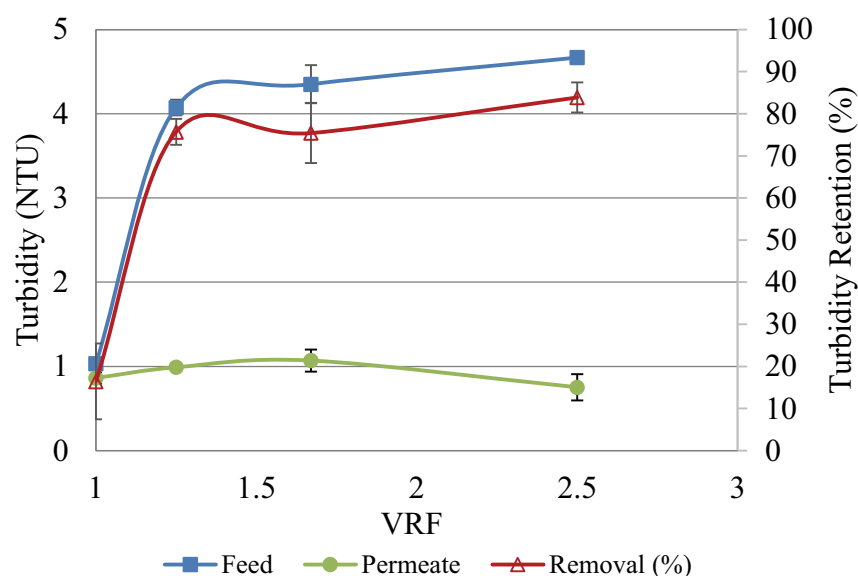


Figure 6.35. Turbidity values for feed and permeate with retention rates as a function of VRF for 2nd stage 2 kDa CMF after 1st stage 2 kDa filtration

Similar to “5 kDa + 2 kDa” serial application, “2 kDa + 2 kDa” application was also tested 3 more times. Figure 6.36 presents filtration flux profiles for the 1st and 2nd stage 2 kDa applications. In these tests, membranes used in 1st test and in the rest of the tests were different pieces. The pieces used in 2nd stages are also different for Test 1 and Test 2-3-4. The difference between permeate flux of Test 1 and those of other tests, may be explained by usage of different pieces. A little higher filtration flux values were observed with membrane used in the last 3 tests. This has also occurred in the 2nd stage applications where totally different and new pieces of membranes are used. The difference in flux may be attributed to the manufacturing phases of the membranes, which determines the intrinsic membrane resistances and initial UPW fluxes.

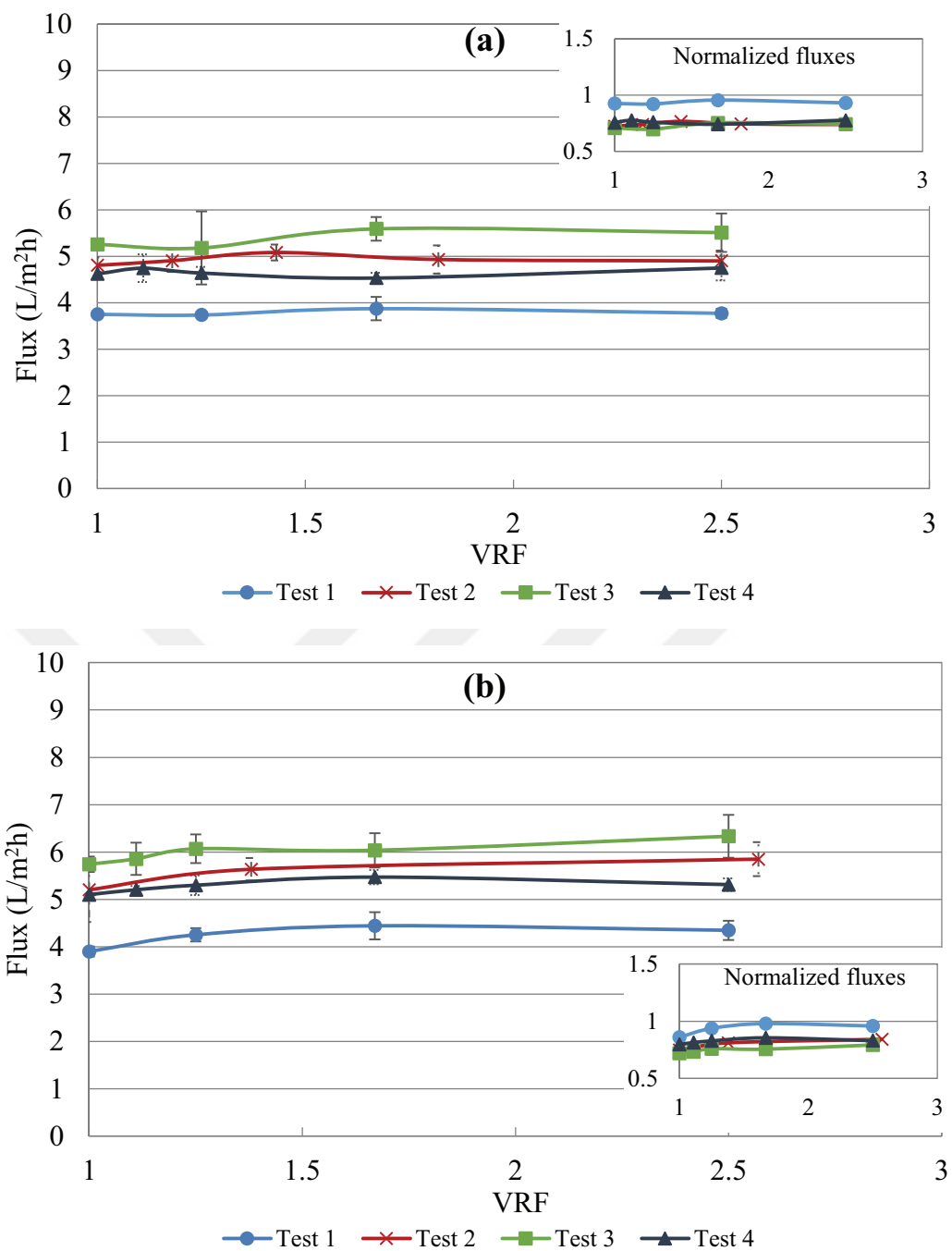


Figure 6.36. Filtration fluxes as a function of VRF and UPW fluxes for Test 1, Test 2, Test 3 and Test 4 for a) 1st stage 2 kDa b) 2nd stage 2 kDa

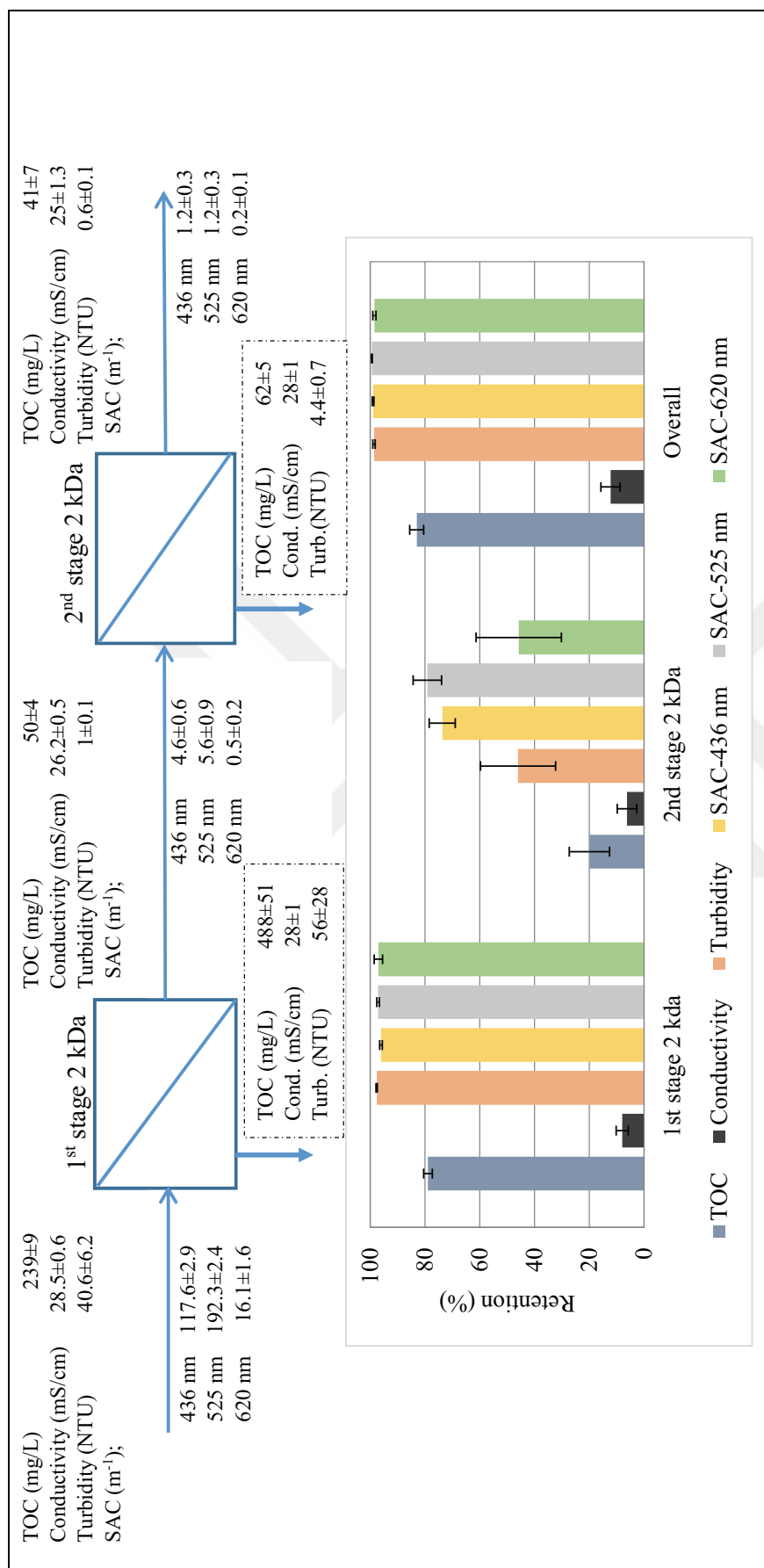


Figure 6.37. Feed and permeate characteristics “2 kDa + 2 kDa” application with retention rates

Figure 6.37 shows the average feed, 1st stage permeate and 2nd stage permeate characteristics for 4 parallel tests. As seen, with two stage serial 2 kDa application, permeate TOC value was taken down to 40 mg/L. The repetitive usage of 2 kDa membranes had the possibility of rejecting more of the salts. However, the change in salinity content was low and permeates still had conductivity values greater than 25 mS/cm. Further turbidity reduction may seem not very useful because it was seen both with 5 kDa and 2 kDa CMF tests that turbidity was no longer a problem. However, this enhancement in suspended matter reduction may show its benefits when these permeates are used in dyeing tests. In water reuse criteria stated by British Textile Technology Group, turbidity value lower than 5 NTU was said to be enough for dyeing cotton fabric whereas turbidity value lower than 1 NTU was claimed to be a must when dyed material is knitted cotton. Thus, as suspended matter content of permeate decreases, the potential for reusability in dyeing different types of textile goods increases (BTTG, 1999, cited in Capar, 2005).

As can be depicted from Figure 6.37, TOC reduction of 80% was increased by only 2 to 3% with the 2nd stage 2 kDa application. This has led to a 10 mg/L of decrease in permeate TOC content. Conductivity retention by the 2nd stage 2 kDa membrane, was lower than that by the first stage. Further turbidity reduction was close to 50% by the 2nd stage. The benefit of applying 2 kDa filtration again has shown its efficiency in color removal. Although the treatment by only single stage 5 kDa and single stage 2 kDa filtration resulted in significant TOC and turbidity removals, permeates were still colored. Color retention of up to 80% was obtained during the 2nd stage 2 kDa membrane as SAC at 525 nm which is indicative of red color and its tones.

Figure 6.38 presents UPW flux profiles obtained in the repeated “2 kDa + 2 kDa” application. During both 1st and 2nd stages, 2 kDa UF membrane exhibited a slight decrease in permeation flux when RDW was filtered. UPW flux after filtration revealed the fouling of membranes (in greater amounts for the 1st stage) and membranes reacted positively to both cleaning steps and good flux recovery was observed both after physical and chemical cleaning.

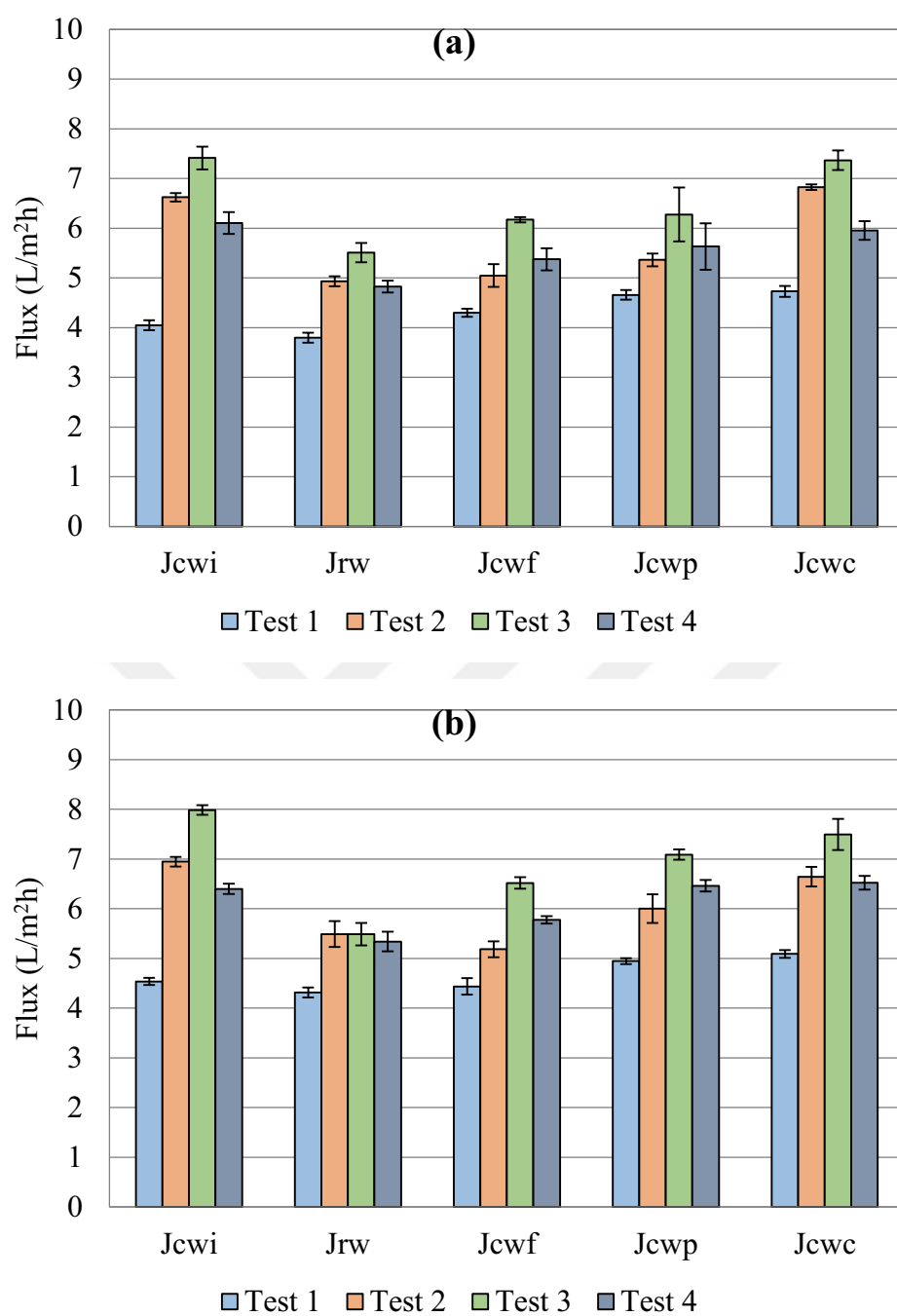


Figure 6.38. UPW fluxes for Test 1, Test 2, Test 3 and Test 4 for a) 1st stage 2 kDa b) 2nd stage 2 kDa CMF

6.3.4. Comparison of serial applications

As presented in Sections 6.2.1 and 6.2.2, with the single stage applications of 5 kDa and 2 kDa membranes, colored permeates having TOC values over 50 mg/L were obtained. With the addition of a second stage UF membrane application, the permeate quality tried to be improved. To achieve this, the permeates of both 5 kDa and 2 kDa filtration tests were subjected to both 5 kDa and 2 kDa 2nd stage treatment. There were three scenarios tested which are formed of possible treatment process combinations of these membranes.

Among serial application scenarios, “2 kDa + 2 kDa” option had the highest TOC removal efficiency (Figure 6.39). This was expected since tighter UF membrane option was employed in both stages. Turbidity removal efficiency has shown no distinguishable difference for three treatment scenarios. Overall conductivity removal rate was lowest for “5 kDa + 5 kDa” scenario and highest for “2 kDa + 2 kDa” scenario. This makes sense since it is hard for 5 kDa membranes to remove monovalent ions but more possible for 2 kDa to reject some. However, this is a drawback for “2 kDa + 2 kDa” application since salt is intended to be kept in permeate.

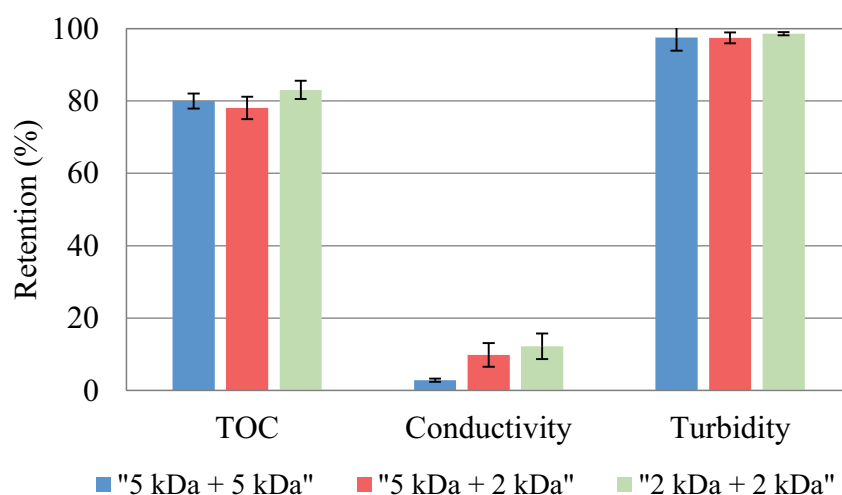


Figure 6.39. Comparison TOC, conductivity and turbidity retention rates of two stage applications

In three scenarios compared here, it is obvious that “5 kDa + 5 kDa” option falls short of removing color in contrast to others (Figure 6.40). Color removal efficiency increases in scenarios where 2 kDa membrane is employed. Best color retention rates were achieved in “2 kDa + 2 kDa” serial application in terms of SAC at 436 and 525 nm.

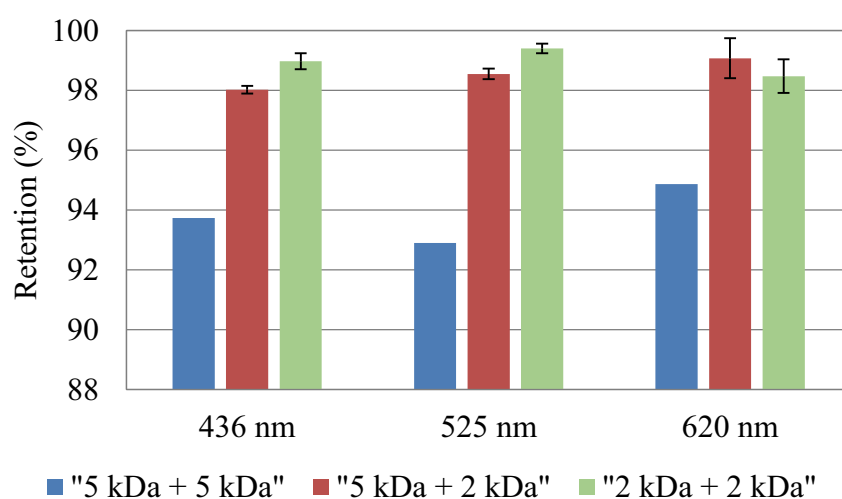


Figure 6.40. Comparison of SAC retention rates of two stage applications

As the feed wastewaters used at the beginning of each scenario are of similar characteristics, it was possible to compare three options by their retention rates. In Table 6.7 , final permeate characteristics are given. As shown, least TOC and turbidity values are for permeate from “2 kDa + 2 kDa” application. On the other side, the lowest color removal is with “5 kDa + 5 kDa” application that provided the lowest turbidity and conductivity retentions. The third sequential UF application of “5 kDa + 2 kDa” was better in overall performance than “5 kDa + 5 kDa”, due to the improvement in performance by the presence of 2 kDa membrane. When comparing 5 kDa and 2 kDa CMF tests, it was noted that 5 kDa membrane has the potential of providing a higher flux than 2 kDa membrane. Although the permeate flux achieved with 5 kDa membrane was advantageous, its purification capacity was lower with a less removal of color and TOC.

Table 6.7. Final permeate characteristics of two stage UF applications

Application scenario	TOC (mg/L)	Conductivity (mS/cm)	Turbidity (NTU)	SAC (m ⁻¹)		
				436 nm	525 nm	620 nm
"5 kDa + 5 kDa"	50±3	27.6±0	1.3±0.1	7.4±0	13.7±0	0.8±0
"5 kDa + 2 kDa"	53±8	25.4±0.8	1.1±0.5	2.3±0.2	2.8±0.4	0.3±0.1
"2 kDa + 2 kDa"	41±7	25.0±1.3	0.6±0.1	1.2±0.3	1.2±0.3	0.2±0.1

To sum up, 5 kDa had the flux yield advantage when applied at both stages, whereas 2 kDa was better in removing pollutants. So the combination of these two, “5 kDa + 2 kDa” was judged as reasonable to be used where high flux yield at 1st stage of 5 kDa was thought to be combined with better removal efficiency at the 2nd stage of 2 kDa. The slightly better final permeate quality of the “2 kDa + 2 kDa” application seems to be advantages when its possible success in reuse tests is taken into account. Although the lowest conductivity retention by “5 kDa + 5 kDa” application makes its usage attractive, its inability in removing color makes it inappropriate for brackish water recovery. So this option was left aside for the rest of the study. Both of the

scenarios left were planned to be examined in further studies. In these studies, the possibility of usage of permeates in reactive dyeing process is tried in dyeing tests. Permeates of both applications had still certain amount of TOC, and color that could make them inappropriate for reuse. However, De Vreese & Van der Bruggen (2007) have claimed in their studies that, salt amount in treated waters is more important than organic pollutants and color. They note that TOC content and color of water do not necessarily disable the recovery option but lack of electrolyte in dyeing solution does.

6.4. Dyeing tests

Dyeing tests were realized in order to determine whether or not permeate samples were appropriate for reuse. The idea in dyeing was to use permeates that are obtained as a result of “5 kDa + 2 kDa” and “2 kDa + 2 kDa” applications instead of tap water in dyeing baths. Permeates had more salt than tap water. Sufficiency of the salt amount in permeates for the successful dye-fiber bonding was investigated. More salt was added to permeates in order to close down the difference between dyeing bath salinity and permeate salinity.

Permeates of the mentioned scenarios are used in 2 different dyeing tests. These tests are done for 3 different recipes which give 3 different color for textile piece that is dyed. Fabrics were dyed to obtain light shaded, middle shaded and dark shaded green. These colors were chosen based on the suggestions of the laboratory staff since it would show the defects in dyeing clearly. This color choice is stated to be “hardest to dye” by the staff. Additional trials were done with a dark red color recipe during dyeing test which is stated to be “comparably easier to dye”.

6.4.1. Dyeing Test 1

In first dyeing test, the mixture of first three tests for each scenario is used as permeate. Characteristics of this mixture is given in Table 6.8 for both combinations of UF treatment. This permeate was used to prepare dyeing bath liquor by the addition of dyestuff and auxiliary chemicals. Caustic, soda and softener were added also for pH and hardness arrangements. Addition of these chemicals was done in amounts that are determined in the dyeing recipe. Different approaches were tried at the first dyeing test. In order to check the sufficiency of the salt amounts of permeate, dyeing of the fabric was done without adding salt to the dyeing bath. In the other trial, salt was added to the dye baths in the amounts that is defined in the recipes.

Table 6.8. Characteristics of permeates used in dyeing bath in 1st dyeing test

Parameter		“5 kDa + 2 kDa” Permeate	“2 kDa + 2 kDa” Permeate
TOC (mg/L)		57±2	44±3
Turbidity (NTU)		1.41±0.05	0.6±0.02
Conductivity (mS/cm)		26.03±0.03	26.36±0.04
pH		9.17	9.14
SAC	436 nm	3.79	1.45
	525 nm	3.86	1.33
	620 nm	1.14	0.2

6.4.1.1 Dyeing Test 1 with permeate of “5 kDa + 2 kDa” serial application

Dyeing tests that have employed “5 kDa + 2 kDa” permeate has given the results in Table 6.9 with and without the addition of salt. Note that other chemicals were added as in the case of dyeing was done using tap water. CMC dE values read for all the trials for 3 different color shades failed the tests. This failure decision is given if success criteria is specified to be CMC dE values lower than 1. Different maximum

CMC dE value may be defined when labeling the tests as passed. To illustrate, this value was 1.5 for a textile mill dyeing plant in a study where there was the same dyeing test. (Buscio et al., 2015). In all of the color recipes dyeing with extra salt addition gave better results. CMC dE values were lower than 2 for these tests.

Table 6.9. Results of 1st dyeing test for 3 different recipes with “5 kDa + 2 kDa” permeate

Recipee	Water used in dyeing bath	CMC dE value	Decision
Light Shaded Green	“5 kDa + 2 kDa” permeate	1.73	Fail
	“5 kDa + 2 kDa” permeate with salt addition	1.65	Fail
Middle Shaded Green	“5 kDa + 2 kDa” permeate	2.16	Fail
	“5 kDa + 2 kDa” permeate with salt addition	1.45	Fail
Dark Shaded Green	“5 kDa + 2 kDa” permeate	5.41	Fail
	“5 kDa + 2 kDa” permeate with salt addition	1.46	Fail

One of the reasons of failing the tests was speculated to be related to the pH of the water. Addition of the caustic and soda was done according to the recipe which was prepared for tap water applications. This caustic and soda addition could have caused higher pH value for permeate than what is needed. So, another trial with these permeates were done without adding caustic and salt contrary to previous test where there was caustic addition for all samples. However, worse CMC dE values were read (Table 6.10). This was probably due to the insufficiency of the electrolytes that would favor the dyeing process.

Table 6.10. Results of 1st dyeing test for 3 different recipes without caustic and soda addition for “5 kDa + 2 kDa” permeate

Recipe	Water used in dyeing bath	CMC dE value	Decision
Light Shaded Green	“5 kDa + 2 kDa” permeate	2.11	Fail
Middle Shaded Green	“5 kDa + 2 kDa” permeate	3.85	Fail
Dark Shaded Green	“5 kDa + 2 kDa” permeate	3.94	Fail

6.4.1.2 Dyeing Test 1 with permeate of “2 kDa + 2 kDa” serial application

The permeate of “2kDa + 2 kDa” had slightly better characteristics with lower TOC and color. With the dyeing tests of this permeate, only one decision was labeled as “pass” (Table 6.11). Successful reading was for dyeing light shaded green by adding extra salt to the dye bath. As in the previous tests, the CMC dE values where extra salt added were lower than the cases where no salt addition was done.

Table 6.11. Results of 1st dyeing test for 3 different recipes with “2 kDa + 2 kDa” permeate

Recipe	Water used in dyeing bath	CMC dE value	Decision
Light Shaded Green	“2 kDa + 2 kDa” permeate	2.00	Fail
	“2 kDa + 2 kDa” permeate with salt addition	0.69	Pass
Middle Shaded Green	“2 kDa + 2 kDa” permeate	2.03	Fail
	“2 kDa + 2 kDa” permeate with salt addition	1.48	Fail
Dark Shaded Green	“2 kDa + 2 kDa” permeate	3.01	Fail
	“2 kDa + 2 kDa” permeate with salt addition	2.78	Fail

Attempts without adding caustic and salt was done simultaneously for the tests where “2 kDa + 2 kDa” permeate was used. Again the CMC dE values were worse than the previous trial in which caustic was added, too (Table 6.12).

Table 6.12. Results of 1st dyeing test for 3 different recipes without caustic and soda addition for “5 kDa + 2 kDa” permeate

Recipe	Water used in dyeing bath	CMC dE value	Decision
Light Shaded Green	“2 kDa + 2 kDa” permeate	2.11	Fail
Middle Shaded Green	“2 kDa + 2 kDa” permeate	3.85	Fail
Dark Shaded Green	“2 kDa + 2 kDa” permeate	3.94	Fail

6.4.2. Dyeing test 2

The wastewater subjected to the UF treatment was the mixture of 4 sampling lines and therefore with a salt content lower than that in dyeing bath due to dilution at rinsing steps. Due to this fact, it was necessary to add salt to the reclaimed wastewater samples. However, it was a difficult to adjust the salt content applied in the real dyeing process. Thus, the trials in first dyeing tests either lacked salt or had more salt than necessary. Similarly, caustic and soda addition were done according to the recipe that is for tap water. Here in this 2nd dyeing test, conductivity and the pH of permeates were fixed at the desired values. To do this, salt (NaCl) is added to tap water in the amounts that are defined for each recipe. Conductivity values of these samples are measured. Then, conductivity of permeates was taken up to this rate by adding less salt than standard. Same adjustments were done for the pH of permeates. pH of dyeing bath was reported to be 10.8 by the laboratory staff. The pH value of permeates was fixed at 10.8 by NaOH addition. This adjustment was done at the Environmental Engineering laboratory of METU and these samples prepared were labeled with (1) in the tables. Another trial was made in which pH value of 10.8 was fixed in the laboratory where the dyeing test occurs. Salt was added to these permeates as in the amounts defined in the recipe. These samples are labeled with (2) in the tables. Characteristics of permeates for 4th test of each scenario are given in Table 6.13. It is noticeable that TOC values are little less than permeates that are used in 1st dyeing test.

Table 6.13. Characteristics of permeates used in dyeing bath in 2nd dyeing test

Parameter	“5 kDa + 2 kDa” Permeate	“2 kDa + 2 kDa” Permeate
TOC (mg/L)	44±2	31±5
Turbidity (NTU)	0.96±0.09	0.53±0.08
Conductivity (mS/cm)	26.54±0.07	25.48±0.07
pH	9.22	9.15
SAC	436 nm	2.35
	525 nm	2.93
	620 nm	0.46

6.4.2.1 Dyeing Test 2 with permeate of “5 kDa + 2 kDa” serial application

In dyeing tests where “5 kDa + 2 kDa” permeate was used, two successful readings were observed (Table 6.14). Dyeing done for middle shaded green by permeate (1) has given CMC dE value of 1 which also is counted as “Pass”. A piece of textile colored by using permeate (1) of this scenario in dyeing bath was not different much from the standard and it gave CMC dE value of 0.72. It is noticeable that light shaded green dyeing with permeate (2) was close to success criteria. It is noted that both of successful readings were done with permeates that are adjusted for salinity and pH in METU laboratory (“permeate (1)”).

Table 6.14. Results of 2nd dyeing test for 3 different recipes with “5 kDa + 2 kDa” permeate

Recipee	Water used in dyeing bath	CMC dE value	Decision
Light Shaded Green	“5 kDa + 2 kDa” permeate (1)	2.44	Fail
	“5 kDa + 2 kDa” permeate (2)	1.17	Fail
Middle Shaded Green	“5 kDa + 2 kDa” permeate (1)	1.00	Warn
	“5 kDa + 2 kDa” permeate (2)	1.92	Fail
Dark Shaded Green	“5 kDa + 2 kDa” permeate (1)	0.72	Pass
	“5 kDa + 2 kDa” permeate (2)	4.95	Fail

Color recipes that are used in dyeing tests, were hard to dye or showed dyeing errors easily. Dyeing tests with comparably “easy to die” recipe was also done with permeates. pH and conductivity of the permeate were adjusted in the laboratory of METU and dyeing test for claret red was successful (Table 6.15).

Table 6.15. Results of 2nd dyeing test for claret red recipe with “5 kDa + 2 kDa” permeate

Recipee	Water used in dyeing bath	CMC dE value	Decision
Claret red	“5 kDa + 2 kDa” permeate (1)	0.99	Warn

6.4.2.2 Dyeing Test 2 with permeate of “2 kDa + 2 kDa” serial application

There were only 1 successful reading in 1st dyeing test and it was with the “2 kDa + 2 kDa” permeate. There were 2 CMC dE readings lower than 1 this time with permeate

of this scenario (Table 6.16). These values were for dyeing light shaded green with permeate (2) and middle shaded green with permeate (2). So, in 2nd dyeing test passing readings were for permeates adjusted in the laboratory where dyeing tests are accomplished.

Table 6.16. Results of 2nd dyeing test for 3 different recipes with “2 kDa + 2 kDa” permeate

Recipee	Water used in dyeing bath	CMC dE value	Decision
Light Shaded Green	“2 kDa + 2 kDa” permeate (1)	1.58	Fail
	“2 kDa + 2 kDa” permeate (2)	0.60	Pass
Middle Shaded Green	“2 kDa + 2 kDa” permeate (1)	6.10	Fail
	“2 kDa + 2 kDa” permeate (2)	0.29	Pass
Dark Shaded Green	“2 kDa + 2 kDa” permeate (1)	1.84	Fail
	“2 kDa + 2 kDa” permeate (2)	2.58	Fail

As in the case with “5 kDa + 2 kDa” permeate, “2 kDa + 2 kDa” permeate also gave CMC dE value lower than 1 with an “easier to dye” recipe (Table 6.17). It seems that both permeates can be used to dye textile to claret red.

Table 6.17. Results of 2nd dyeing test for claret red recipe with “2 kDa + 2 kDa” permeate

Recipee	Water used in dyeing bath	CMC dE value	Decision
Claret red	“2 kDa + 2 kDa” permeate (1)	0.97	Warn

6.4.3. Evaluation of dyeing tests

In dyeing tests, successful readings were observed for the permeates of both treatment scenarios. Dyeing tests without salt addition has shown that, salt deficit of permeate should be compensated for successful dyeing. Similarly, if pH of permeate was not fixed at the value that is defined in the recipe, it is probable to have failures in dyeing.

Among the two treatment alternatives, “5 kDa + 2 kDa” has given good readings for middle and dark shades of green in dyeing tests when conductivity and pH of permeate was adjusted. Other scenario has succeeded in coloring light and middle shades of green. However, there were more salt addition than needed in this case. When permeates are used in dyeing tests according to claret red recipe, both permeates have passed the test. No extra salt addition was done in this trial. To conclude, dyeing tests have proven that permeates of UF treatment of RDW have the potential to be re-used back in dyeing process.

Further studies were to check the probability of attaining permeates with the similar characteristics that have succeeded in dyeing tests by changing operational parameters. Parameters that are changed were TMP and VRF value.

6.5. Effect of VRF and TMP on serial application performances

In this part of the thesis, effect of TMP and VRF on the performances of the serial UF applications of “5 kDa + 2 kDa” and “2 kDa + 2 kDa” were investigated to better assess the practical applicability and also to optimize the operational conditions. To this end, tests were performed with the above-mentioned serial applications at the TMP values of 2 and 4 bars while increasing the VRF up to 10.

6.5.1. TMP = 2 bar, VRF = 10 experiments

Treatment scenarios for RDW with two UF membranes were conducted under 2 bar. The concentration factor reached in experiments was 2.5. This would correspond to 60% permeate recovery. In order to check how much the final concentrate could be lowered without compromising from permeate quality, VRF values of 10 were tested for two scenarios. Other experimental conditions were kept constant.

6.5.1.1 “5 kDa + 2 kDa” serial application

In these tests, where effects of VRF and TMP change were investigated, filtration experiments were carried out just for 1st stage of “5 kDa + 2 kDa” serial application. In other scenario, both 1st stage 2 kDa and 2nd stage 2 kDa wastewater filtrations were achieved with changes in VRF and TMP. This was done so because 5 kDa application had higher flux advantage during 1st stage among serial applications and not much difference was observed between characteristics of 1st stage permeates both for 5 kDa and 2 kDa. So, 1st stage 5 kDa tests were thought to be sufficient to assess the effects of changing parameters.

Among serial application scenarios, “5 kDa + 2 kDa” had a higher flux advantage. Filtration flux observed with 1st stage 5 kDa filtration was significantly higher than that observed with 2 kDa filtration. Decrease in filtration flux at 1st stage 5 kDa applications is given in Figure 6.29 for lower VRF values. Here in this test, a decrease observed in filtration flux was similar to the lower VRF value (2.5) case. Moreover, decline in filtration flux has continued with increasing VRF value. As can be seen in Figure 6.41, UPW flux measured after filtration (J_{cwp}) was considerably lower than the initial UPW flux. This is due to CP and internal fouling of 5 kDa UF membrane. Almost full UPW flux recovery were achieved after physical cleaning and chemical cleaning has not contributed much as in previous 5 kDa filtration tests.

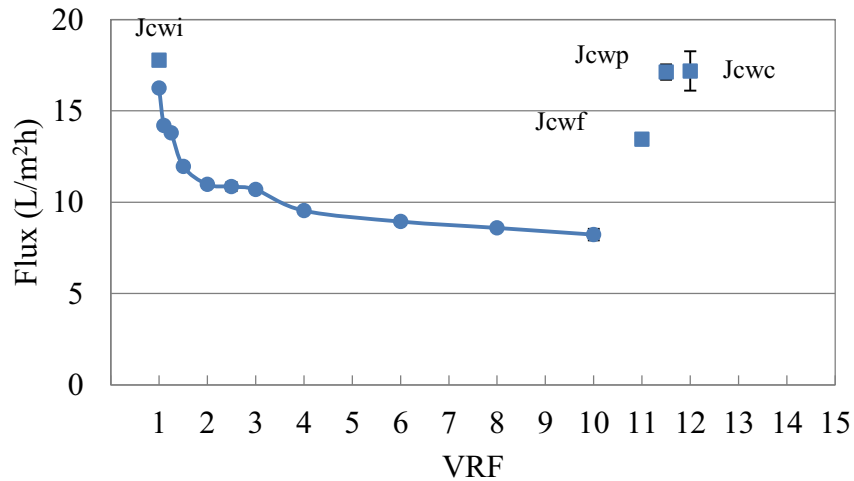


Figure 6.41. Filtration fluxes as a function of VRF and UPW fluxes for 1st stage 5 kDa CMF at 2 bar, VRF = 10

Instantaneous sampling was done in these tests to see the changes in retention rates for TOC and SAC at different VRF values. It can be easily seen in Figure 6.42 that as feed wastewater get concentrated, permeate characteristics worsened comparably much less. This shows that increasing VRF value up to 10 does not mean a considerable decrease in permeate quality. Retention rate has reached over 95% at VRF value of 10.

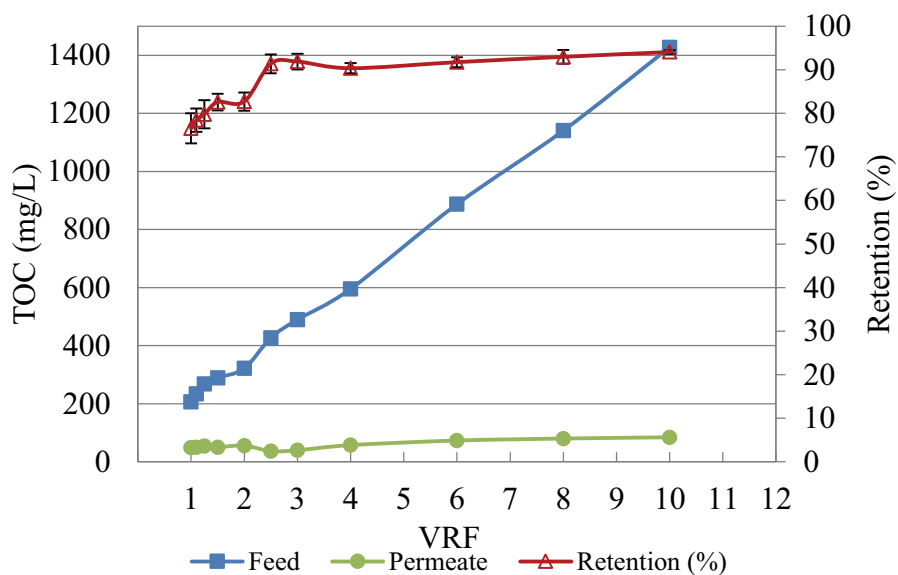


Figure 6.42. TOC values for feed and permeate with retention rates as a function of VRF for 1st stage 5 kDa CMF at 2 bar, VRF = 10

Feed wastewater used in the experiment became darker in color as VRF value increases. Contrary to TOC, SAC values of permeate samples taken at different VRF values have increased considerably. Permeate SAC value at 436 nm was about 10 m^{-1} at about VRF value of 2.5 and it was over 30 m^{-1} when VRF value was 10. The decline in permeate sample quality was worse at 525 nm measurements. SAC value was about 20 m^{-1} and was over 60 m^{-1} at last sampling when VRF was 10.

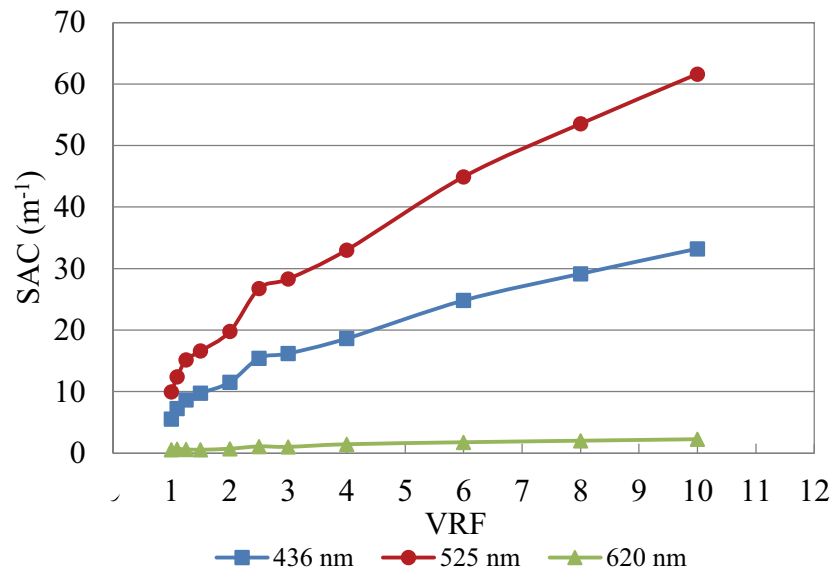


Figure 6.43. Permeate SAC values as a function of VRF for 1st stage 5 kDa CMF at 2 bar, VRF = 10

Instantaneous sampling showed that permeate quality has worsened a little with respect to TOC content and much more with color as VRF value increases. The difference in profiles of TOC and color is speculated to be due to the pollutants other than dyes that cause TOC. Dyes are not the only source of TOC in RDW. The effect of the SAC profiles observed during instantaneous sampling in permeate quality can be read from final permeate quality of 1st stage 5 kDa wastewater filtration which is given in Table 6.18. Final permeate qualities for 1st stage wastewater filtration with 5 kDa at VRF values of about 2.5 were given in Table 6.3 and Table 6.4. It seems that final permeate characteristics have not changed much since it was 60 ± 6 mg/L, 27.17 ± 0.01 mS/cm, and 3.12 ± 0.31 NTU for TOC, conductivity and turbidity, respectively, in one of these tests. This same test realized at lower VRF value had SAC values which were 12.9 m^{-1} , 24.2 m^{-1} and 1.1 m^{-1} , for 436 nm, 525 nm, and 620 nm, respectively. Table 6.18 has SAC values for test realized at VRF value of 10 and it is quite close to the values for lower VRF case.

Table 6.18. TOC, conductivity, turbidity and SAC values of the feed and permeate with removal rates for 5 kDa filtration at 2 bar, VRF = 10

		Feed	1st Stage 5 kDa Permeate	Retention (%)
TOC (mg/L)		207±2	59±3	71±2
Conductivity (mS/cm)		27.89±0.01	27.39±0.01	2±0
Turbidity (NTU)		26.17±0.58	1.24±0.16	95±3
SAC (m ⁻¹)	436 nm	121.1±0.1	13.2±0	89±0
	525 nm	195.5±0	22.9±0	88±0
	620 nm	16.2±0	0.9±0	94±0

6.5.1.2 “2 kDa + 2 kDa” serial application

Between two UF membranes, 2 kDa is the one that has smaller pore sizes. It was seen in the earlier studies that 5 kDa was more prone to fouling and thus flux declines were observed during filtration tests. In contrast, there were totally no reduction in the flux of 2 kDa. These results were obtained when final VRF value was 2.5. The membrane that is used in Test 4 of “2 kDa + 2 kDa” applications were used in studies where VRF value was taken up to 10. The change in VRF has not led to changes in the filtration flux profiles of 2 kDa membranes both during 1st and 2nd stages (Figure 6.44). Permeation of purified water was constant as feed wastewater gets concentrated.

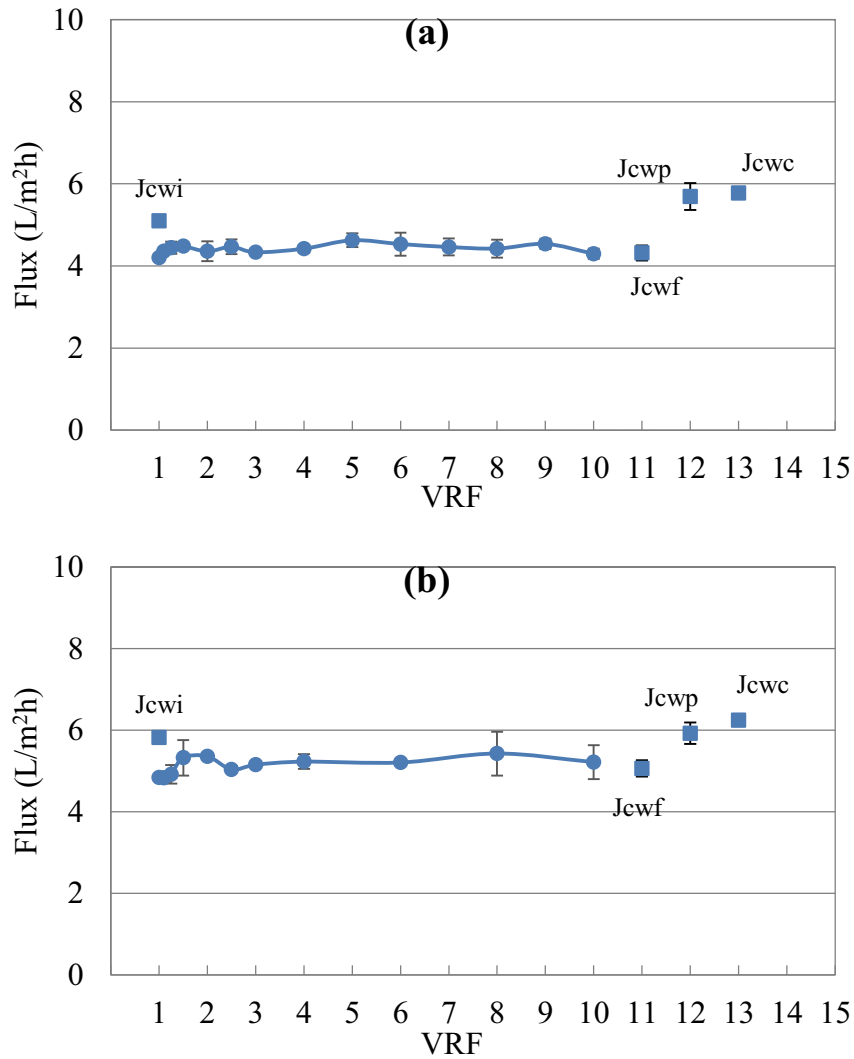


Figure 6.44. Filtration fluxes as a function of VRF and UPW fluxes for a) 1st stage 2 kDa b) 2nd stage 2 kDa CMF at 2 bar, VRF = 10

The changes in flux profiles and removal efficiencies were the parameters to be checked when VRF value increases. Since feed wastewater gets much more concentrated as VRF increases, flux decline and membrane fouling could be expected. When feed wastewater was concentrated 10 times, there was no change in filtration flux (Figure 6.44). Similarly, UPW fluxes for 1st and 2nd stages were also similar to VRF = 2.5 case. Full flux recovery was achieved with physical and chemical cleaning applications, as indicated in Figure 6.44.

TOC values of the feed was found to increase as VRF increases (Figure 6.45). This was expected since rejected organic matter remains in retentate. Similar to earlier CMF studies, permeate TOC did not changed even though the treated TOC value increased significantly. This was valid both for 1st and 2nd stage applications. Instantaneous sampling has shown that TOC retention ability of 2 kDa membrane has increased up to 95% in 1st stage.



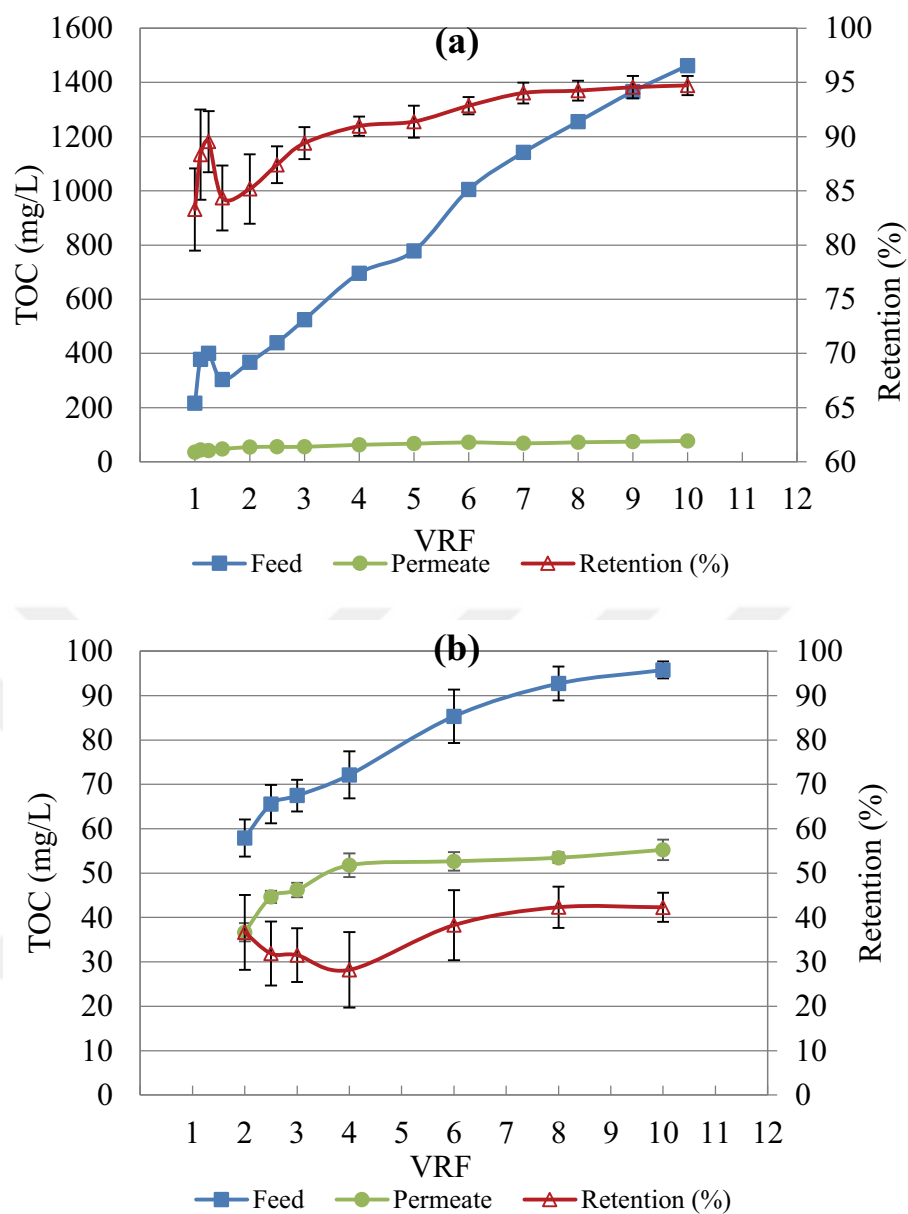


Figure 6.45. TOC values for feed and permeate with retention rates as a function of VRF for a) 1st stage 2 kDa b) 2nd stage 2 kDa CMF at 2 bar, VRF = 10

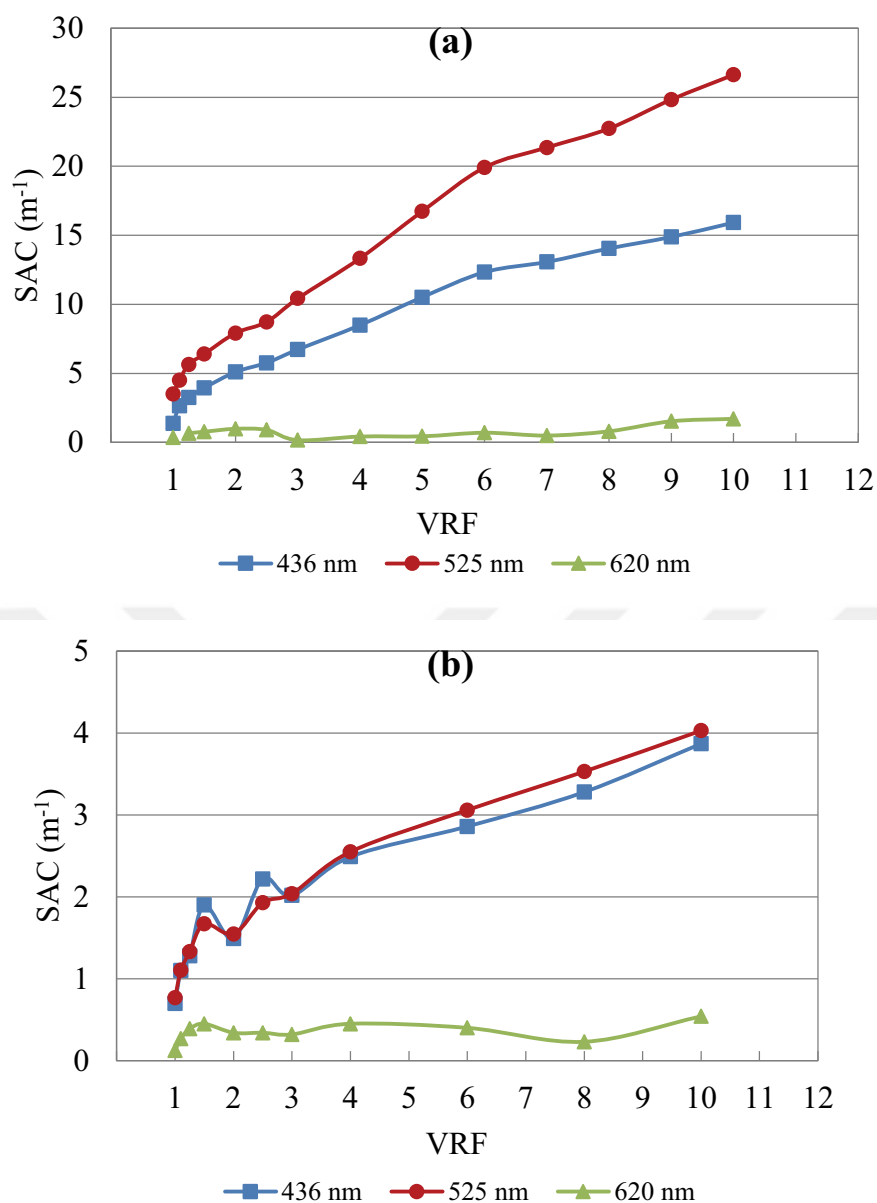


Figure 6.46. SAC values for feed and permeate with retention rates as a function of VRF for a)1st stage 2 kDa b)2nd stage 2 kDa CMF at 2 bar, VRF = 10

When samples taken instantaneously are examined, permeate TOC values had shown similar characteristics with a little bit increase as VRF value increases (Figure 6.45). The situation is not the same with SAC values. As VRF value increases, i.e. as feed wastewater gets more polluted with color, permeate samples had worse SAC

characteristics (Figure 6.46). It seems that final cumulative permeate characteristics will get worse with the increasing contribution of permeates obtained at high VRFs. It can also be speculated that the increase in TOC values of permeates taken at different VRFs may be the result of the increase observed in SAC values in instantaneous permeate samples. Color content is one of the aspects that cause TOC in the wastewater.

Final permeate characteristics and removal rates (Figure 6.47) have shown that treatment efficiency does not change for “2 kDa + 2 kDa” application when permeate recovery ratio increases. Cumulative permeate values were very similar to ones obtained when $VRF = 2.5$ where final TOC, conductivity and turbidity values were 41 ± 7 mg/L, 25 ± 1.3 mS/cm and 0.6 ± 0.1 NTU, respectively. Moreover, there seems to be a decrease in conductivity removal rate. It was about 12% in $VRF = 2.5$ experiments. Now with an increase in VRF it is measured as 5%.

Although deterioration in SAC values were significant with instantaneous sampling, it seems to have comparably low effect on cumulative permeate. Final SAC values of permeate for “2 kDa + 2 kDa” ($VRF = 2.5$) experiment were 1.2 ± 0.3 , 1.2 ± 0.3 and 0.2 ± 0.1 for 436, 525 and 620 nm, respectively. These values are 2.1 ± 0 , 2 ± 0 and 0.6 ± 0 for 436, 525 and 620 nm, respectively for $VRF = 10$ case. When retention rates between SAC values of feed wastewater and cumulative permeate were checked, values over 98% were measured for overall two stage treatment at $VRF = 10$. The treatment done in 2nd stage has contributed much to these values by achieving over 60% and 75% removal rates for 436 nm and 525 nm, respectively

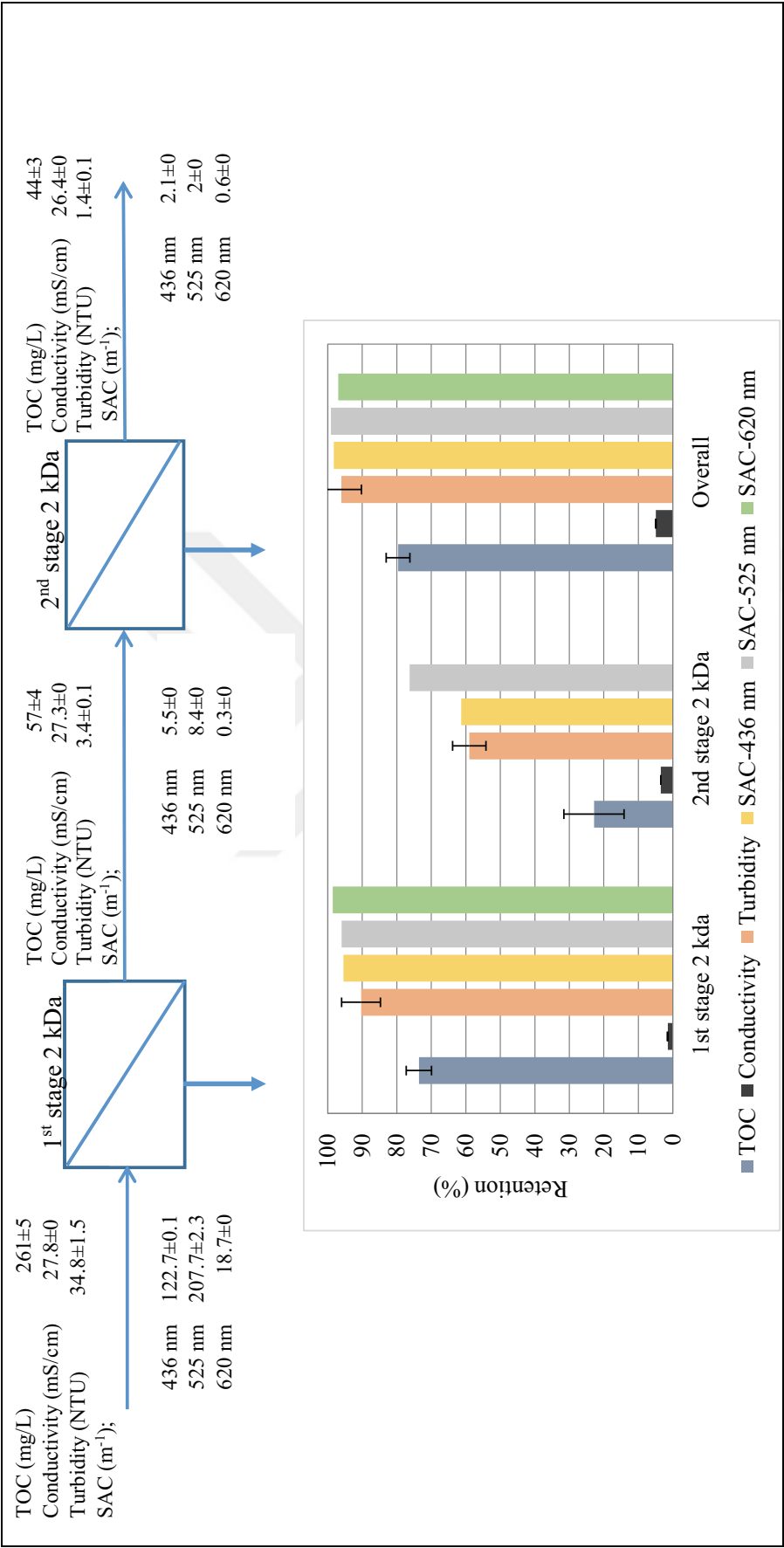


Figure 6.47. Feed and permeate characteristics for “2 kDa + 2 kDa” application at 2 bar, VRF = 10 with retention rates

6.5.2. TMP = 4 bar, VRF = 10 experiments

In order to increase the permeate recovery ratio, tests to obtain 9/10 of the feed wastewater as permeate, that corresponds to a VRF of 10, was conducted. It was seen that increasing VRF value to 10, had no remarkable effect on final permeate quality (Section 6.5.1). Another parameter that had the potential to enhance the feasibility of UF treatment was the filtration TMP. A series of CMF tests were conducted under 4 bar TMP for both stages of all the scenarios, and the changes in both removal efficiency and flux profiles with an increase in TMP was investigated. Other parameters were kept same as the previous tests.

6.5.2.1 “5 kDa + 2 kDa” serial application

The membrane piece used in this experiment was different than the membrane pieces used in other 1st stage 5 kDa wastewater filtration tests. When flux performances of these different pieces are compared, initial filtration flux seems to have at least twice higher a value in Figure 6.48 than in Figure 6.6 and Figure 6.41. Doubling the TMP has doubled the initial fluxes. However, the decrease in filtration flux was observed to be sharper in this test. As VRF value increases, filtration flux decreases almost down to 10 L/m²h, which is almost the value observed with 2 kDa membrane. This decrease was mostly due to CP as J_{cwf} indicates and fouling was eliminated by physical cleaning.

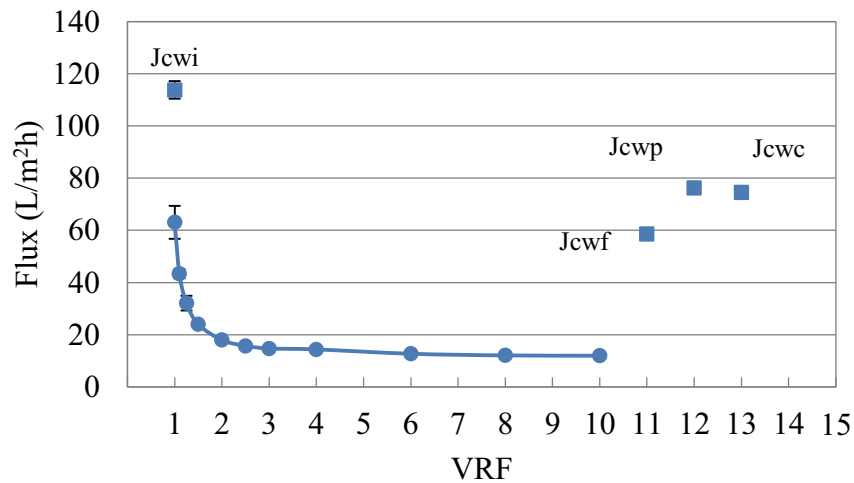


Figure 6.48. Filtration fluxes as a function of VRF and UPW fluxes for 1st stage 5 kDa CMF at 4 bar, VRF = 10

The change in VRF value has increased the feed wastewater TOC concentration as expected. As in the case with other tests both with 5 kDa and 2 kDa, permeate TOC concentration almost remained the same as can be seen in Figure 6.49. Doubling the TMP has not changed the instantaneous permeate quality in TOC content.

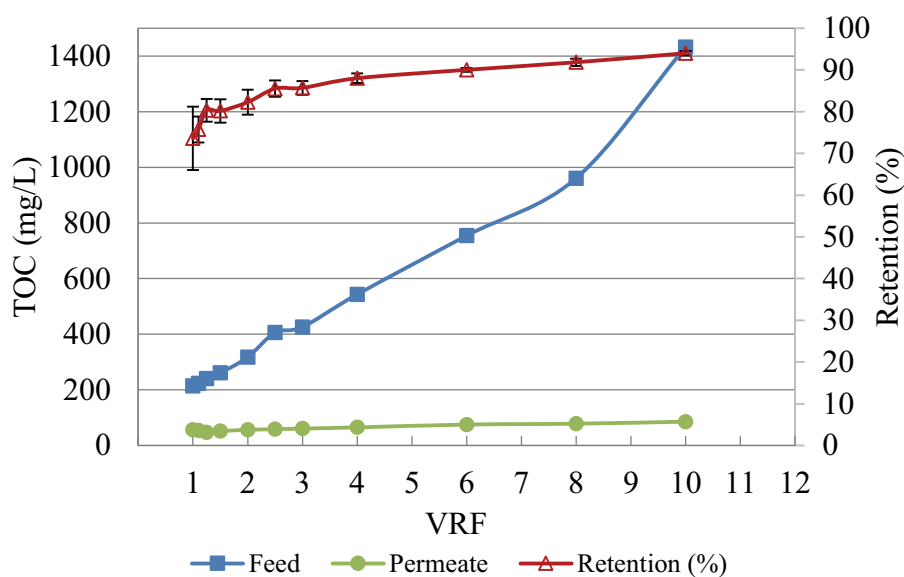


Figure 6.49. TOC values for feed and permeate with retention rates as a function of VRF for 1st stage 5 kDa CMF at 4 bar, VRF = 10

Instantaneous permeate sampling done at different VRF values has shown in Figure 6.50 that the permeate SAC values have increased with increasing VRF as in the case with lower TMP. Especially, the measurements at the wavelengths of 436 nm and 525 nm, are seen to have profiles increasing similar to the ones obtained in Figure 6.43.

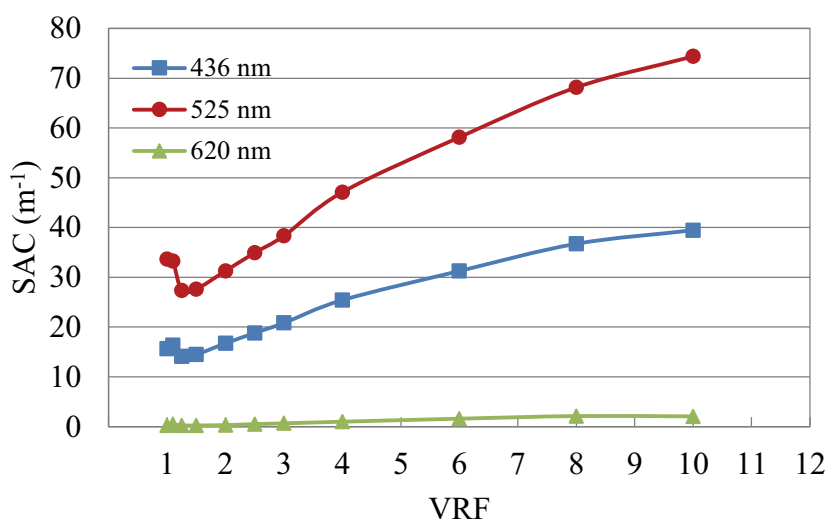


Figure 6.50. SAC values as a function of VRF for 1st stage 5 kDa CMF at 4 bar, VRF = 10

The change in TMP has shown no difference in TOC and SAC profiles (with respect to lower pressure case) as samples obtained at different VRF indicates. The change in permeate characteristics is the main thing to be checked by changing parameters. Final permeate had TOC, conductivity and turbidity values which were 59 ± 3 mg/L, 27.39 ± 0.01 mS/cm, and 1.24 ± 0.16 NTU, respectively, in the previous test where VRF was 10 and TMP was 2 bar. As can be seen in Table 6.19, these parameters have not changed much by doubling TMP. TOC content seems to be a bit higher than the previous case. SAC values seems to have a higher difference. In previous case, these values were 13.2 m^{-1} , 22.9 m^{-1} and 0.9 m^{-1} for 436 nm, 525 nm and 620 nm, respectively. There seems to be an increase for SAC values at 436 nm and 525 nm.

Table 6.19. TOC, conductivity, turbidity and SAC values of the feed and permeate with removal rates for 5 kDa filtration at 4 bar, VRF = 10

		Feed	1st Stage 5 kDa Permeate	Retention (%)
	TOC (mg/L)	213±12	72±7	72±7
	Conductivity (mS/cm)	28.26±0.02	27.76±0.04	2±0
	Turbidity (NTU)	37.43±1.1	1.07±0.06	97±4
SAC (m ⁻¹)	436 nm	119.1±0.1	18.7±0	85±0
	525 nm	199.1±0	35.8±0	82±0
	620 nm	13.9±0	0.5±0	96±0

6.5.2.2 “2 kDa + 2 kDa” serial application

Filtration of RDW with 2 kDa and filtration of permeates of 1st stage 5 kDa and 2 kDa with 2 kDa had not caused any decline in filtration fluxes that are measured at different VRF values. Here in 4 bar TMP applications, 2 kDa membranes have experienced a decrease in flux (Figure 6.51). As TMP increases, permeation rate and consequently CP increases and fouling starts on the membrane. There was a decrease in filtration flux from VRF values 1 to 4 and it remained steady until the end of the filtration. During 2nd stage 2 kDa filtration, a constant flux profile was observed. Solutes concentration was less for the feed of 2nd stage since these molecules were removed in 1st stage, and less permeation of solutes had occurred. This meant less CP when compared to 1st stage.

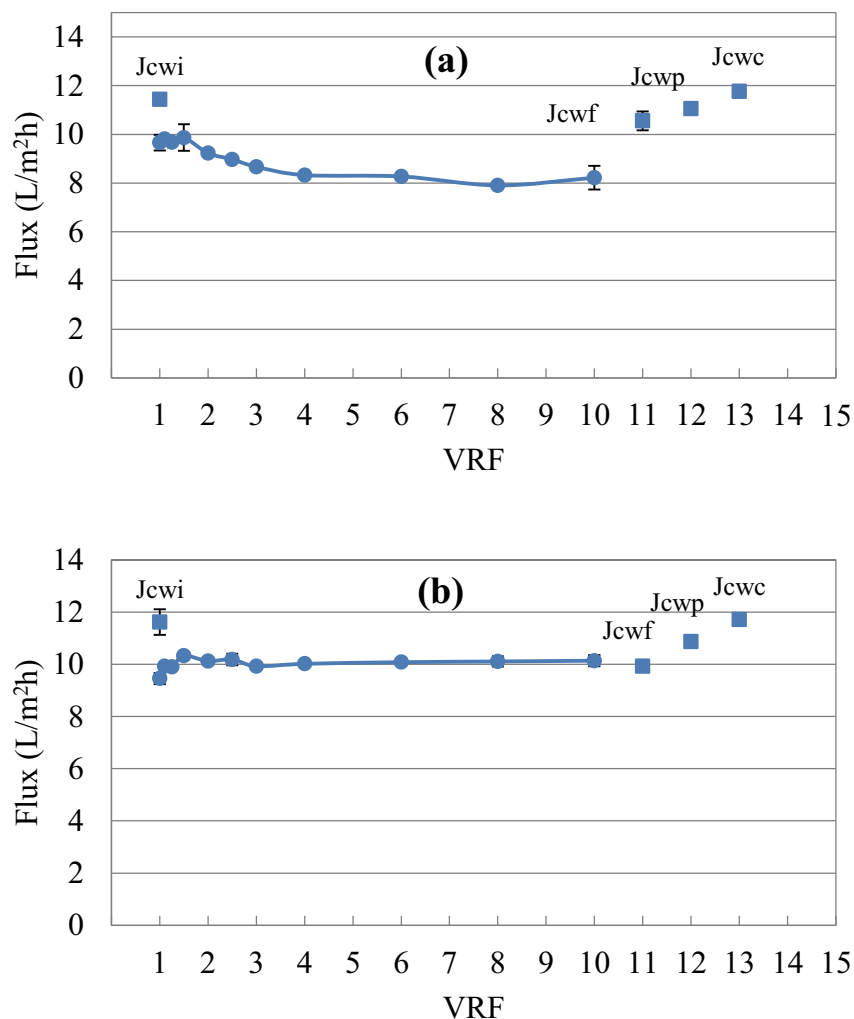


Figure 6.51. Filtration fluxes as a function of VRF and UPW fluxes for a) 1st stage 2 kDa b) 2nd stage 2 kDa CMF at 4 bar, VRF = 10

By doubling TMP values, filtration flux was also doubled for both stages. Yet, there were 20% decrease in the flux for 1st stage application. Initial UPW flux was reached for 1st and 2nd stage after chemical and physical cleaning applications. There was no irreversible losses in UPW fluxes.

TOC profiles were very similar to ones observed in 2 bar, VRF = 10 case. Instantaneous TOC retention rates were up to 95% here in this application, too

(Figure 6.52). Permeate TOC value has not changed significantly as the feed wastewater TOC goes over 1000 mg/L.

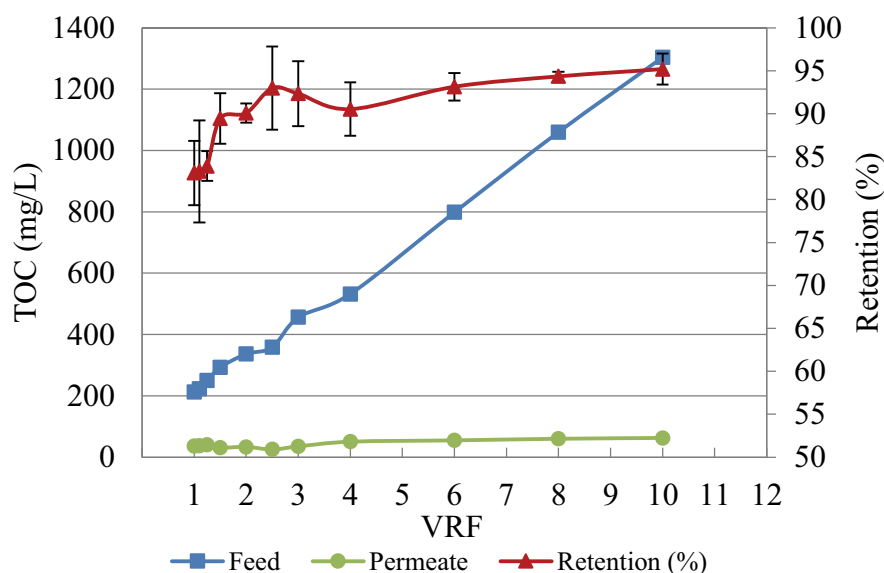


Figure 6.52. TOC values for feed and permeate with retention rates as a function of VRF for 1st stage 2 kDa CMF at 4 bar, VRF = 10

Instantaneous measurements done for color of permeate were also similar to the profile in the previous case for “2 kDa + 2 kDa”. Permeate SAC values were about 2-3 m⁻¹ for 436 nm and 525 nm at the beginning of the filtration for the 1st stage and it was over 15 m⁻¹ and 25 m⁻¹ at the end of filtration for 436 nm and 525 nm, respectively (Figure 6.53). Profiles were the same with the lower pressure case for the 2nd stage color retention. It has changed between 1 and 4 m⁻¹ with increasing VRF value.

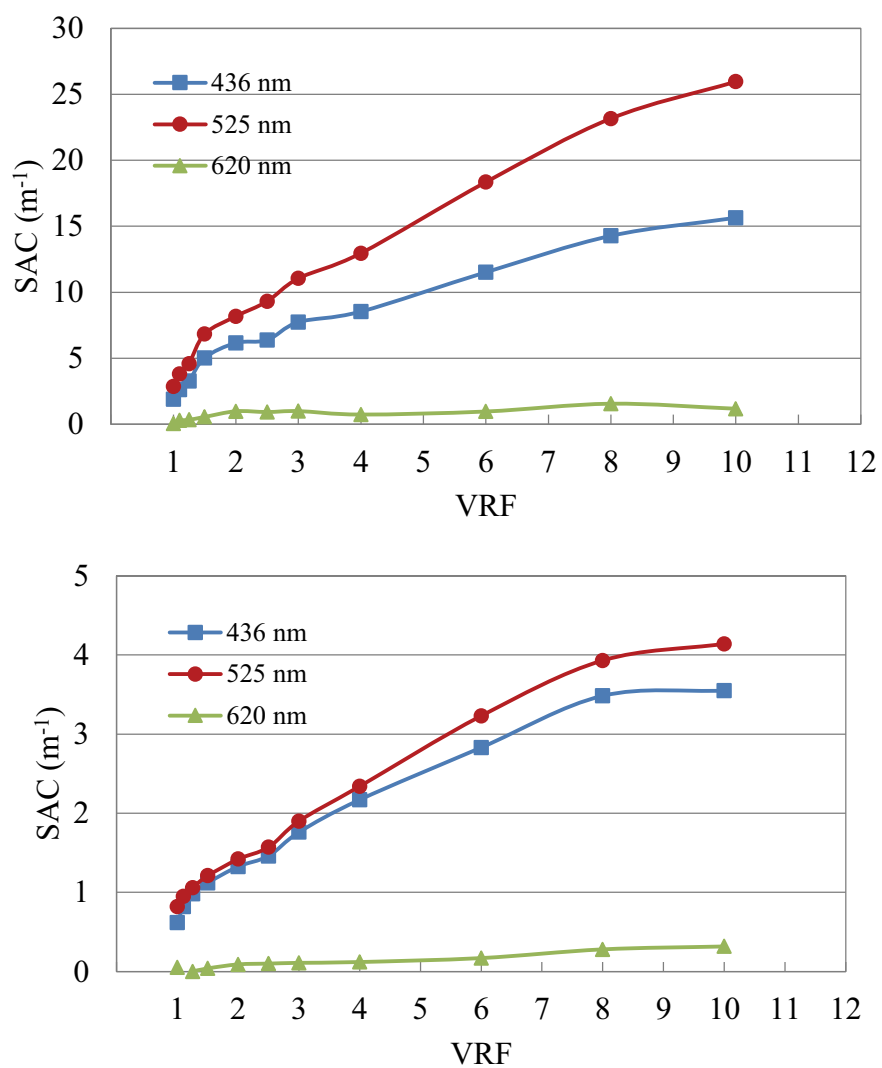


Figure 6.53. SAC values for feed and permeate with retention rates as a function of VRF for a) 1st stage 2 kDa b) 2nd stage 2 kDa CMF at 4 bar, VRF = 10

Overall removal efficiencies did not change in this scenario when VRF value was increased to 10. When concentration value was kept the same, and pressure was doubled, it seems that both removal efficiencies and final permeate quality got better (Figure 6.54). Overall TOC retention rates were over 85% and SAC removals were about 99% for all wavelengths. Final permeate values were better than the previous case (where TMP was 2 bar VRF was 10) for all parameters that are checked. When the applied pressure is doubled, solutes to be removed are forced onto the membrane surface more than the lower pressure case. With the increasing pressure, the possibility of particles to block or fill the pores of 2 kDa membrane increases. Once the pores are blocked with particles, there remains less area for pollutants to pass. The decrease in pore size may positively affect purification ability of the membrane. Thus the increase in rejection rate and permeate quality is speculated to be the result of the pore blocking at 4 bar filtration test.

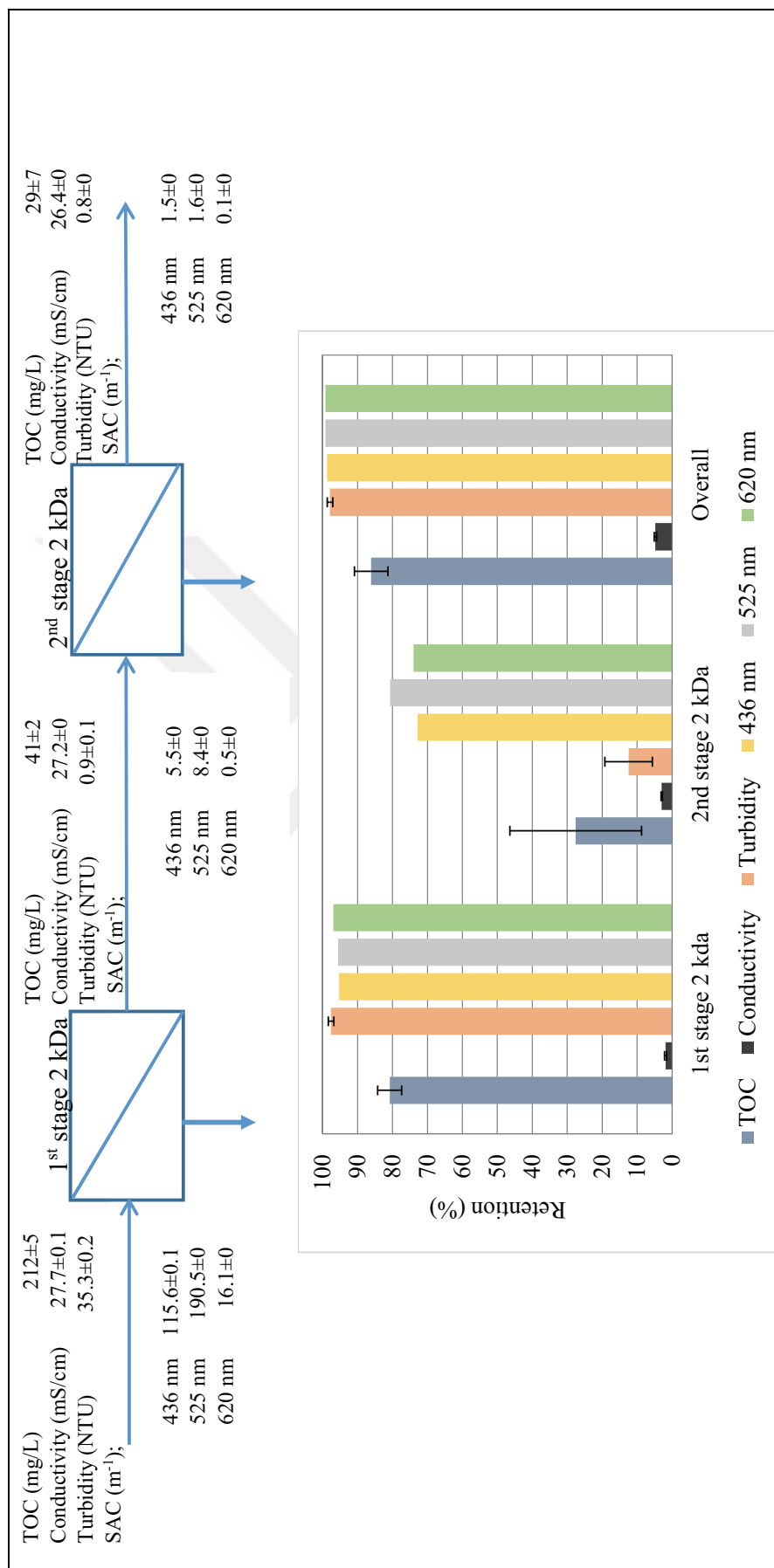


Figure 6.54. Feed and permeate characteristics for “2 kDa + 2 kDa” application at 4 bar, VRF = 10 with retention rates

6.5.3. Comparison of serial applications after changes in experimental parameters

When serial application scenarios are compared in Section 6.3.4, it was noted that “5 kDa + 2 kDa” application was favorable since it had higher flux yields at 1st stage and “2 kDa + 2 kDa” application was more successful in removing TOC and color content. Optimization of these two stage applications were aimed by changing the parameters such as VRF and TMP. Permeates obtained by these applications had successful readings during dyeing tests. For the optimization studies to be successful, there should be not much deterioration in permeate qualities as a result of changes in operational parameters. It was commented before that increasing VRF value up to 10 has caused no remarkable change in final permeate quality for both scenarios. So it was possible to obtain 90% of feed wastewater as permeate without compromising permeate characteristics. Likewise, doubling TMP value has not caused distinguishable deterioration in final permeate qualities except for the increase in SAC values for the 1st stage 5 kDa filtration at 4 bar. The retention rates achieved in these optimization tests was quite close to the ones obtained at lower pressure and VRF values. A little deterioration observed in SAC and TOC values especially for 5 kDa filtration seems tolerable considering the benefits of attaining permeate at high flux.

6.6. Alternative recycling scenario

The objective of the experimental studies was to recover brackish water by UF treatment. As with the last results given above, permeate with characteristics that could be used in dyeing baths was obtained for “2 kDa + 2 kDa” scenario in which recovery rate was 90% and TMP was 4 bar. To illustrate, 90 m³ of 100 m³ wastewater that comes from 4 different lines was purified enough to be used in dyeing baths. The amount of permeate obtained is higher than the amount that can directly be used in dyeing bath and permeates obtained need salt addition for reuse. This need can be met by using the salt content of permeate; however, this would require further

applications to concentrate the salt. Another treatment scenario was suggested instead, to obtain brackish water with a higher salt concentration.

In order to present treatment process that is appropriate for the aim defined above, alternative recycling scenario was suggested. In this scenario, only 50% of the wastewater which is to be collected just from first two lines were intended to be recovered as permeate. This scenario would require less salt make-up, since the wastewater from the first two stage will have a high salinity content.

Since the first two wastewater lines form the two most polluted ones, their mixture used in experiments was high in suspended matter and organic matter content. Dyeing bath water was less diluted than the initial wastewater. Thus wastewater had almost the double salinity and was more colored. Experiments were done under 4 bar and at a VRF value of 2. There were over 20% decrease in flux decline at the first stage when the filtration was ended (Figure 6.55). This is same with the amount observed during 4 bar, VRF = 10 tests. So, wastewater and experimental conditions led to flux decline for 2 kDa even at low VRF values with the contribution of more polluted wastewater this time. There was no decline in the 2nd stage application of 2 kDa as in the previous studies.

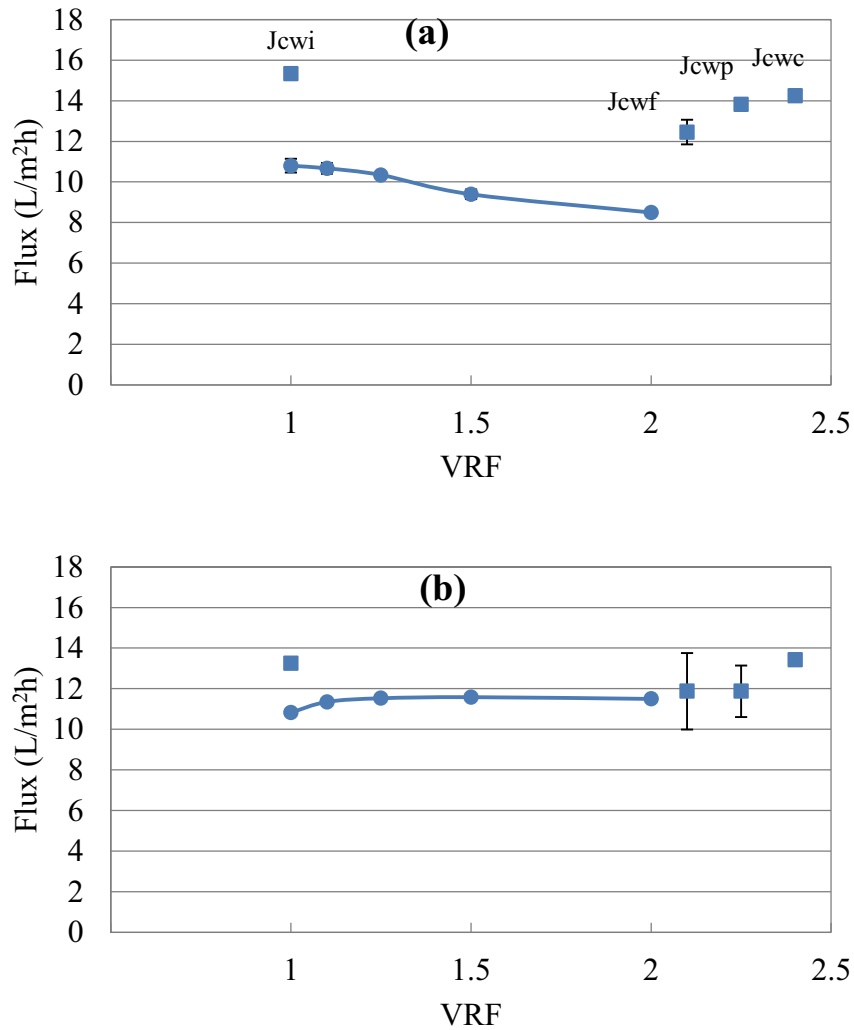


Figure 6.55. Filtration fluxes as a function of VRF and UPW fluxes for a) 1st stage 2 kDa b) 2nd stage 2 kDa CMF with wastewaters #1+2 as feed to 1st stage

The loss observed in UPW flux after filtration at 1st stage seems to be recovered partially by physical cleaning. Chemical cleaning also takes this value up, and makes total flux recovery 93%. On the other hand, full flux recovery was observed in 2nd stage after cleaning applications.

Instantaneous sampling has shown quite similar characteristics with the applications where less loaded wastewater was used as feed. The SAC values has changed between 5 m⁻¹ and 23 m⁻¹ for 436 and 525 nm measurements (Figure 6.56). These

values were lower than 3 m^{-1} for permeate of 2nd stage yet it is deteriorated as feed water gets concentrated.

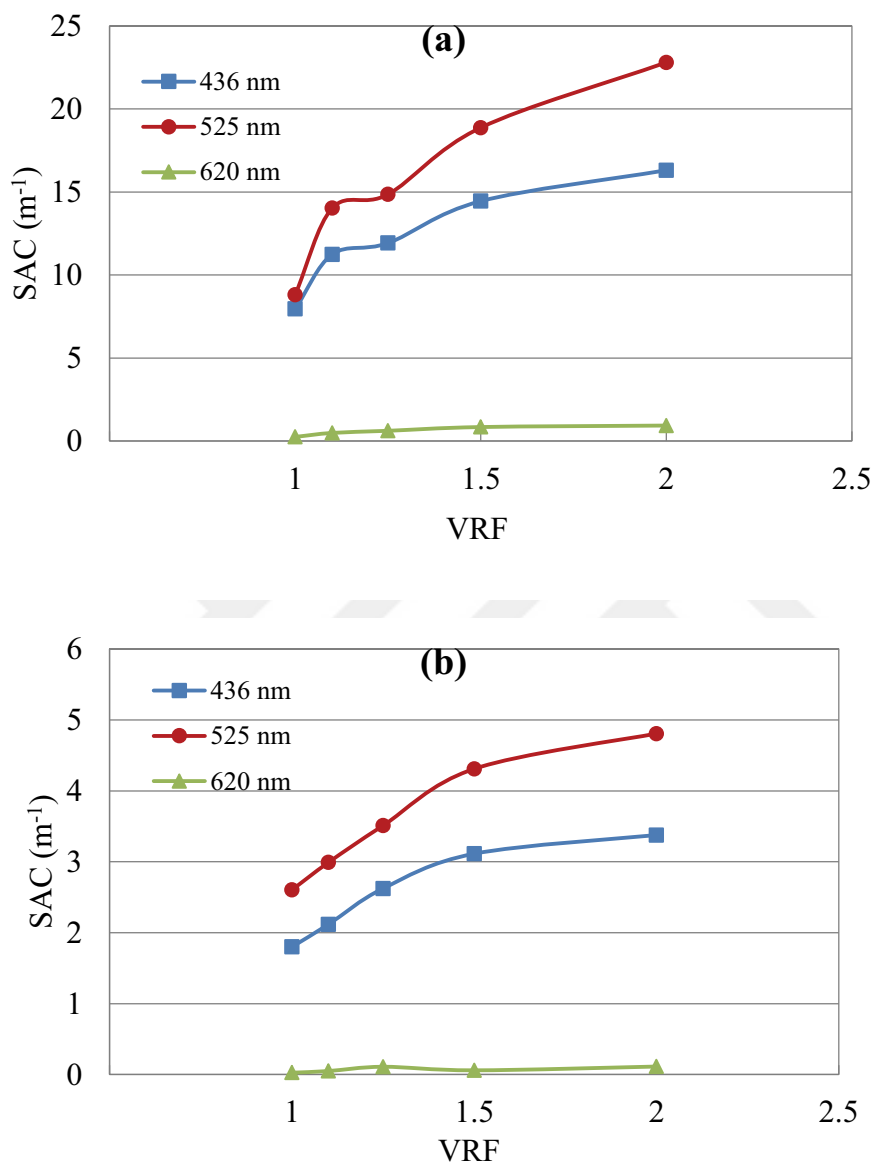


Figure 6.56. SAC values for feed and permeate with retention rates as a function of VRF for a) 1st stage 2 kDa b) 2nd stage 2 kDa CMF with wastewaters #1+2 as feed to 1st stage

TOC value of the feed wastewater was much higher than the wastewater used in initial studies. By 1st stage 2 kDa application, TOC of cumulative permeate was taken below 100 mg/L (Figure 6.57). TOC rejection by 2nd stage 2 kDa application was more than 50% and final permeate had TOC value of 41 ± 2 mg/L. This value is close to the value obtained by previous “2 kDa + 2 kDa” scenarios. It was 41 ± 7 when experiment was done with initial wastewater (mixture of #1,2,3,4) at 2 bar and VRF value was 2.5. Conductivity of the wastewater was removed only by 8% as a result of two stage 2 kDa application. Considering the final conductivity value, this scenario has its strongest side with its salinity content. This would mean less salt addition to permeate when it is re-used in dyeing bath. Turbidity was removed over 98% with this scenario. So there was almost no turbidity that would cause problems in reusability. Final SAC values of permeate of “5 kDa + 2 kDa” application used in 2nd dyeing tests were 2.35, 2.93 and 0.46 m^{-1} for 436 nm, 525 nm and 620 nm, respectively. Successful dyeing tests results were reported for this permeate and permeate of alternating recycling scenario has similar SAC values. Overall color removal was about 99% for all wavelengths. When all the parameters that are checked for permeate of alternating recycling scenario, it can be stated that it also has the potential to be reused in dyeing bath.

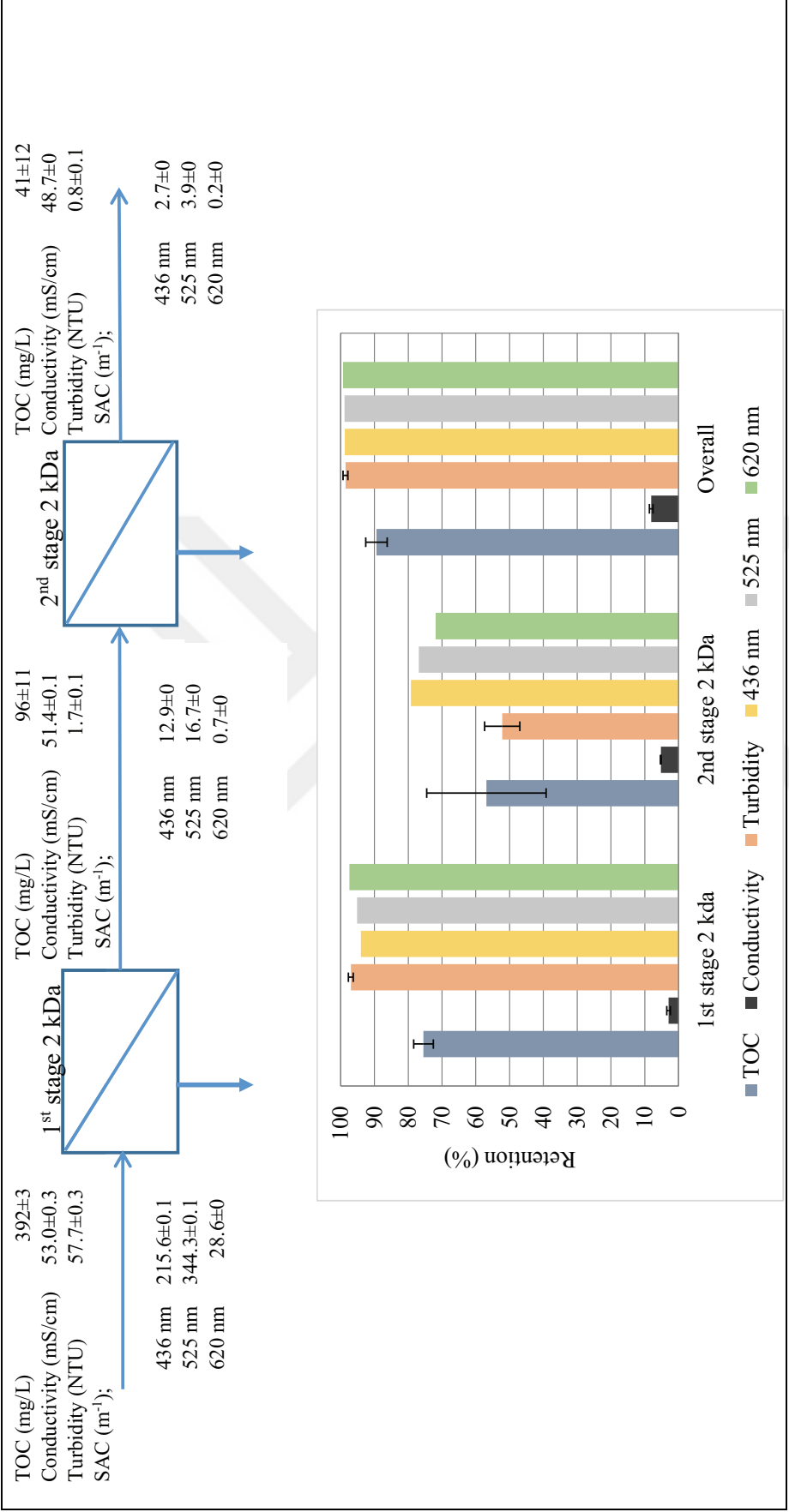


Figure 6.57. Feed and permeate characteristics for “2 kDa + 2 kDa” alternative recycling scenario, at 2 bar, VRF = 10 with retention rates

6.7. Analysis of fouling resistances

Membranes used in studies have reacted differently to RDW filtration and different filtration fluxes were observed. UPW fluxes measured after filtrations also differed for different membranes and applications realized under different experimental conditions. Fouling tendencies of membranes and reaction of membranes to cleaning applications are investigated with analysis of fouling resistances.

6.7.1. Fouling resistances for serial applications

Serial application of UF was formed of 1st stage filtrations of RDW and 2nd stage filtrations applied to permeates of 1st stage tests in order to increase the final permeate quality. When 1st stage applications are compared for 5 kDa and 2 kDa, R_{cp} values are higher for 5 kDa filtrations (Figure 6.58). Permeation rates in 5 kDa applications are higher than 2 kDa filtration and this means more solutes flow through the membrane and, makes CP higher for 5 kDa. Resistances due to fouling are similar for two membranes during 1st stage and physical cleaning seems efficient in removing them. Chemical cleaning was also efficient for 2 kDa membranes but this was not the case for 5 kDa. Resistance due to fouling was not eliminated with chemical cleaning for 5 kDa.

Wastewaters fed to the membranes were significantly purified from suspended and organic matter during 1st stage filtrations. So, fouling observed in 1st stages was less probable to occur during 2nd stages. In 2nd stage application of “5 kDa + 5 kDa”, there was no R_{cp} observed. Resistance due to fouling was removed by physical and chemical cleaning applications. When 2nd stage 2 kDa filtration applied to permeate of 5 kDa, there was CP and fouling related resistances. Physical and chemical cleaning applications were both effective for 2nd stage 5 kDa and 2 kDa for these scenarios. During 2nd stage applications of 2 kDa membrane, application to permeate of 5 kDa has shown similar R_{cp} values to that of application to permeate of 2 kDa.. In

both applications of 2 kDa membranes during 2nd stage, resistance due to fouling was mostly removed by physical and chemical cleaning applications.

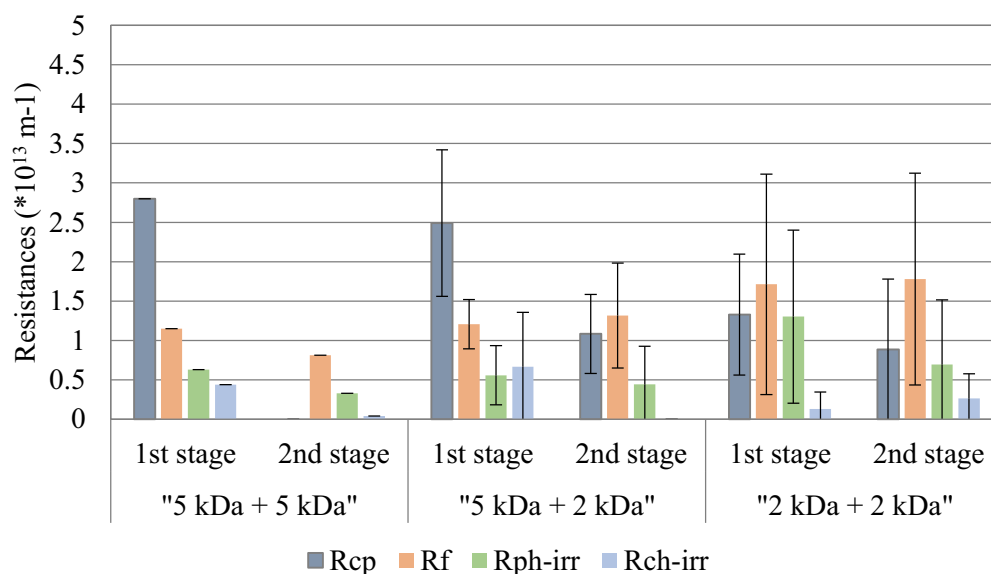


Figure 6.58. Resistances for serial applications

6.7.2. Fouling resistances for serial applications at different TMP and VRF and for alternative recycling scenario

Serial applications were also tried for higher VRF values first and then at higher filtration pressure. The limits of membranes with concentrated wastewaters were checked both in efficiency of purification and flux decline and fouling analysis. When VRF value was increased to 10 at 2 bar, filtration flux of 5 kDa membrane had shown a sharper decrease. When TMP was doubled, the decrease in filtration flux had got even sharper. As depicted in Figure 6.59, resistance to filtration was mostly the result of CP in this lower pressure case. Physical cleaning application was beneficial in recovering flux whereas chemical cleaning had no contribution. When same experiment was done at 4 bar, resistance due CP for 1st stage 5 kDa filtration was much higher. When TMP value doubled, flux also doubled and the increase in permeation rate has caused higher CP. R_f values were similar to each other for both

cases and physical cleaning was efficient in removing those for both cases but chemical cleaning was not efficient for $\text{TMP} = 4$ bar, $\text{VRF} = 10$ case. During $\text{VRF} = 10$, 2 bar experiments, 1st stage filtration with 2 kDa membranes had resistance due to fouling all of which was removed with single physical cleaning application and there was no resistance due to CP. When TMP value was doubled, the flux has increased and there occurred resistance due to CP during 1st stage 2 kDa filtration at $\text{TMP} = 4$ bar, $\text{VRF} = 10$. R_f was eliminated by cleaning steps for this case, too. When the resistance data for 2nd stage filtration with 2 kDa at different TMPs is evaluated, it is seen that there was no resistance due to CP for both cases. There was no irreversible fouling remaining after cleaning steps for both applications.

When alternative recycling scenarios for different wastewaters are considered, the mixture of the wastewater from the first two stage of reactive dyeing process was used as the feed. This test was also done at 4 bar and VRF value of 10. During 1st stage 2 kDa filtration, resistance due to CP was a bit higher than the test realized under same conditions but with different wastewater (Figure 6.59). This was the result of more loaded wastewater usage as feed. Resistance due to fouling was removed mostly by cleaning applications but there still remained unrecovered UPW permeation flux as a result of chemically irreversible resistance. Complete flux recovery was achieved with the test with wastewater that is the mixture of all four lines. On the other hand, since permeate of 1st stage is used as feed, there were significantly less R_{cp} than 1st stage during alternative recycling scenario experiment. There was no R_{cp} during 2nd stage filtration with initial wastewater. R_{cp} value observed during 2nd stage application with wastewater, that is formed of first two lines, is probably due to more concentrated characteristics of feed wastewater. Fouling resistance was removed with chemical cleaning for both applications realized with different wastewaters.

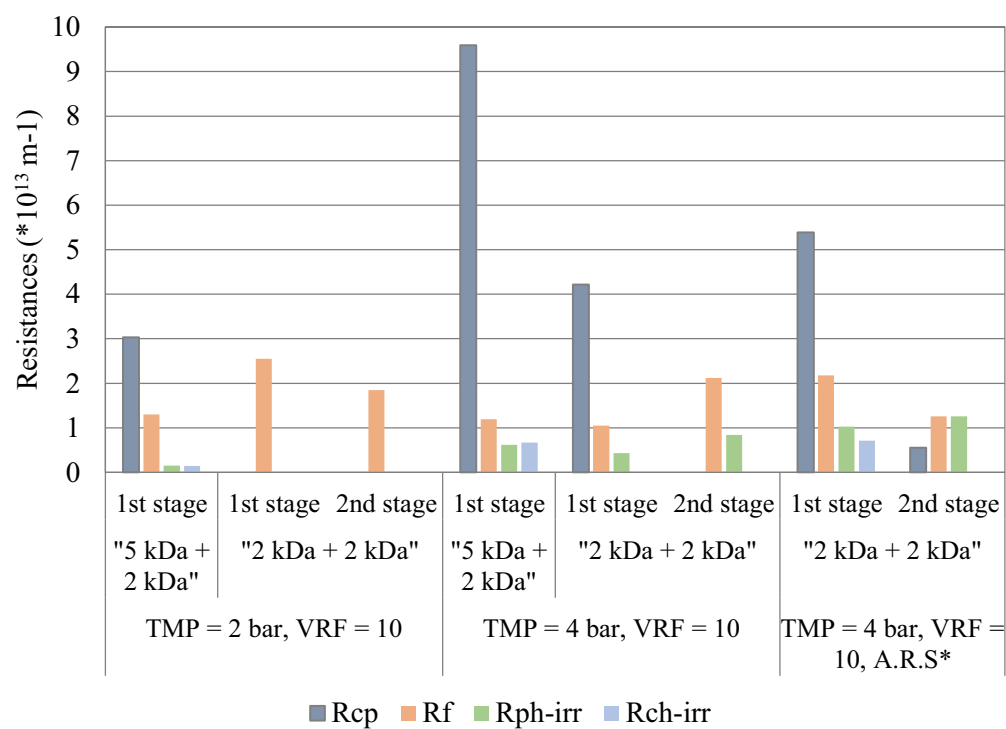


Figure 6.59. Resistances for serial applications when TMP = 2 bar, VRF =10 and
TMP = 4 bar, VRF =10 with alternative recycling scenario

CHAPTER 7

CONCLUSION

Reactive dyeing of textiles is a quite widespread method used in textile industry. This method requires the usage of huge amounts of salts together with other auxiliary chemicals for successful colorization. As a result, resulting RDW is not only highly colored but also do have high salinity content. High TOC and turbidity values are also common for RDW.

Here in this study, RDW originating from textile industry was planned to be treated by UF and obtained brackish water was aimed to be used back in dyeing process. RDW samples were taken from dyeing and following rinsing steps of a textile industry in which cotton is dyed with reactive dyes. RDW samples were first strained and then subjected to direct UF treatment. Two different UF membranes, 5 kDa PES and 2 kDa Thin Film GE Osmonics membranes, with different MWCO were used in filtration studies carried out at 2 bar TMP and VRF of 2.5. Firstly, single stage TRMF experiments were realized with both membranes. With these applications, both membranes could remove suspended matter of wastewater up to 98% and conductivity was retained less than 10%. TOC retentions were over 70% for both applications and color removal were over 90% for 5 kDa and 97 % for 2 kDa single stage applications. These tests were also done at CMF in order to assess the effect of feed wastewater strength on the performances of membranes. Turbidity and TOC retention over 98% and 75% were reported, respectively, for both membranes. Color retention was measured to reach over 87% for 5 kDa and 97% for 2 kDa at 525 nm. Hence, 2 kDa membrane was slightly better in performance; but both the membranes were not sufficient in performance as the reclaimed wastewater was still with an unacceptable TOC.

After single stage UF tests, two stage applications, in which the permeate of first stage 5 kDa or 2 kDa was used as feed, were realized. The objective in the two stage applications was to improve the permeate quality. Three different scenarios under same conditions were tested which were “5 kDa + 5 kDa”, “5 kDa + 2 kDa” and “2 kDa + 2 kDa” two stage applications. Among those, “5 kDa + 5 kDa” achieved color retention up to 93% at 525 nm. Overall TOC rejection after second stage 5 kDa was 80% and 95% of conductivity was kept in permeate. In other two scenarios, “5 kDa + 2 kDa” and “2 kDa + 2 kDa”, color retentions were over 98%. TOC and turbidity rejections calculated to be more than 78% and 97% for “5 kDa + 2 kDa”, and these values were 83% and 98% for “2 kDa + 2 kDa” scenario. Conductivity retention was less than 10% with both applications. Filtration fluxes observed with first stage 2 kDa filtrations were about 4-4.5 L/m²h whereas they were at least three times higher with first stage 5 kDa filtration.

Among two stage application scenarios, the one using 5 kDa membrane at both stages provided the lowest color retention. Remaining two have shown similar rejection values for TOC, color and turbidity, but only the one employing 2 kDa at both stages achieved slightly better color and TOC removal. Scenario having first stage 5 kDa filtration, on the other hand, had the advantage of a higher filtration flux at the first stage.

In order to test the adequacy of the permeates for reuse, permeates obtained as a result of these two scenarios were used in dyeing tests. This test has shown that the permeate obtained from two stage “5 kDa + 2 kDa” application was successful in coloring cotton with middle and dark shaded green. The permeate of the other scenario was successful in dyeing light and middle shaded green. When both permeates were used in another recipe, which was thought to be easier to dye, they both succeeded coloring the cotton in dark red.

Further studies included the changes in experimental parameters. Filtration tests before dyeing tests had been realized at 2 bar and VRF of 2.5. During these final studies, both serial applications were tested at a VRF of 10 which would mean to

obtain 90% of wastewater as permeate. After increasing VRF to 10, it was noted that, both applications has achieved close to the lower VRF cases in terms of color, TOC and turbidity retentions and there were no significant changes in permeate characteristics. Moreover, there were no changes in filtration fluxes in both first and second stage 2 kDa filtrations. However, the decrease in first stage 5 kDa filtration flux, for first stage of “5 kDa + 2 kDa” application, was more than the case where VRF was 2.5. After changing the VRF, TMP was changed to 4 bar to see the effect of TMP on membrane selectivity and filtration flux. Doubling TMP had no effect on permeate characteristics of “5 kDa + 2 kDa” application. On the other hand, both removal efficiencies and final permeate quality got better for “2 kDa + 2kDa” application than the lower TMP case. Doubling TMP has doubled the filtration flux for both scenarios. However, filtration flux of the first stage 5 kDa application had shown even sharper decrease than the lower TMP case and final raw wastewater flux was close to the 2 kDa filtration flux. First stage 2 kDa application has shown 20% flux decline whereas second stage had constant flux profile.

An alternative brackish water recycling scenario was suggested when finalizing the experimental studies. VRF values of 2.5 and 10 were tested in former studies and wastewater used was the mixture of dyeing bath and three rinsing and washing steps. In the scenario mentioned here, VRF of 2 and wastewater formed by mixing just dyeing bath and first rinsing bath was used. This wastewater had much higher salt content (since dyeing bath is less diluted) and VRF of 2 would supply permeate with higher salt content without needing further treatment steps. This scenario employed 2 kDa membranes at both stages of serial application. Permeate characteristics of this two stage application were close to the former “2 kDa + 2 kDa” application in terms of TOC, color and turbidity. Conductivity, on the other hand, was about twice as much than the previous cases which would mean less addition of salt when permeate is used in dyeing bath.

This study shows that, RDW can be treated by treatment scenarios which only employs UF membranes. As a result of serial applications of UF membranes, wastewater can mostly be purified from organic pollution and color content and

resulting brackish water can be used in dyeing bath instead of tap water. Keeping salt in permeate not only suggests a solution for salinity problem of RDW both also means saving from salt usage.



CHAPTER 8

RECOMMENDATIONS

In this study, real wastewater samples taken from a textile dyeing plant were treated with serial applications of UF membranes and permeates that are usable in dyeing process were obtained. Wastewater samples were the result of one recipe used in the textile dyeing plant. For future studies, it is recommended that wastewater samples that are the result of different dyeing recipes be used and tested with serial UF application to generalize the treatment scenarios. Effluents that do not only differ in terms of used recipe but also dyeing process (provided that they contain reactive dyestuff usage) may also be tested.



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APPENDICES

A

Dyeing recipe used before wastewater sampling was done

Table A.1. Dyeing recipe used before wastewater sampling

Dyestuff Used	Amount	Molecular Weight (g/mol)
Everzol Yellow BDF	0.6%	-
Everzol Red ED 3B	2%	788 (Aouni et al., 2012)
Everzol Blue ED	0.1%	628.56 (Bazin et al., 2012)



B

Use the formula given below to calculate resistances.

$$R = \frac{\text{TMP}}{\mu \cdot J}$$

μ : Dynamic viscosity of permeate. Taken as $1 \cdot 10^{-3}$ Pa s for all calculations.

Note that viscosity of water at 20 °C is $1.002 \cdot 10^{-3}$ Pa s.

TMP : Filtration pressure. It was either 2 bar or 4 bar for all experiments.

Note that 1 bar = 10^5 Pa

J : Permeate flux given in L/m²h

To calculate R_{mem} use J_{cwi} . Data set given for 5 kDa TRMF (See Section 6.1.1) experiment is used for sample calculations.

$$R_{\text{mem}} = \frac{20000 \text{ Pa}}{0.001 \text{ Pa.s} \cdot 36.4 \text{ L/m}^2\text{h}} = 1.98 \cdot 10^{13} \text{ m}^{-1}$$

Do the same calculation to find;

- R_{tot} by using J_{rw}
- $R_{\text{mem}} + R_{\text{f}}$ by using J_{cwf}
- $R_{\text{mem}} + R_{\text{ph-irr}}$ by using J_{cwp}
- $R_{\text{mem}} + R_{\text{ch-irr}}$ by using J_{cwc}

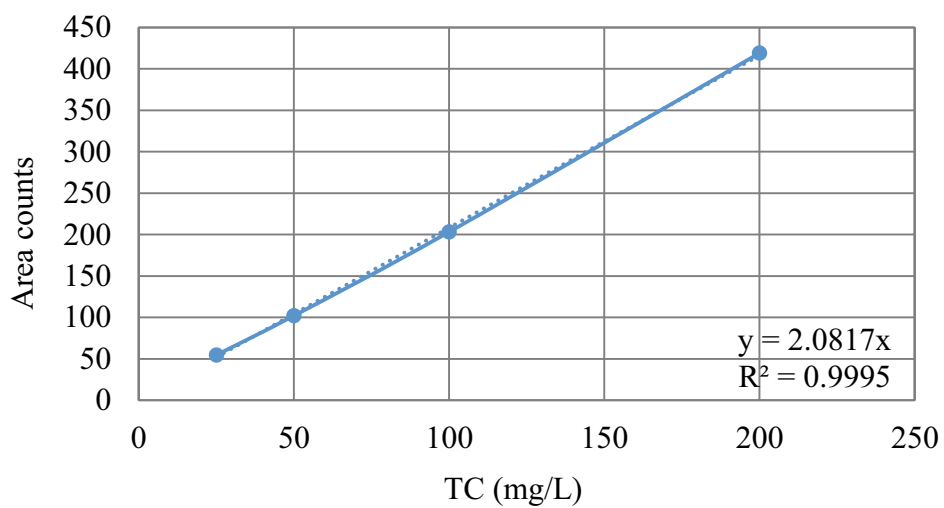
Then calculate R_{f} , R_{cp} , $R_{\text{ph-irr}}$ and $R_{\text{ch-irr}}$ by using the following relations:

- $R_{\text{f}} = (R_{\text{mem}} + R_{\text{f}}) - R_{\text{mem}}$
- $R_{\text{cp}} = R_{\text{tot}} - R_{\text{mem}} - R_{\text{f}}$
- $R_{\text{ph-irr}} = (R_{\text{mem}} + R_{\text{ph-irr}}) - R_{\text{mem}}$
- $R_{\text{ch-irr}} = (R_{\text{mem}} + R_{\text{ch-irr}}) - R_{\text{mem}}$



C

(a)



(b)

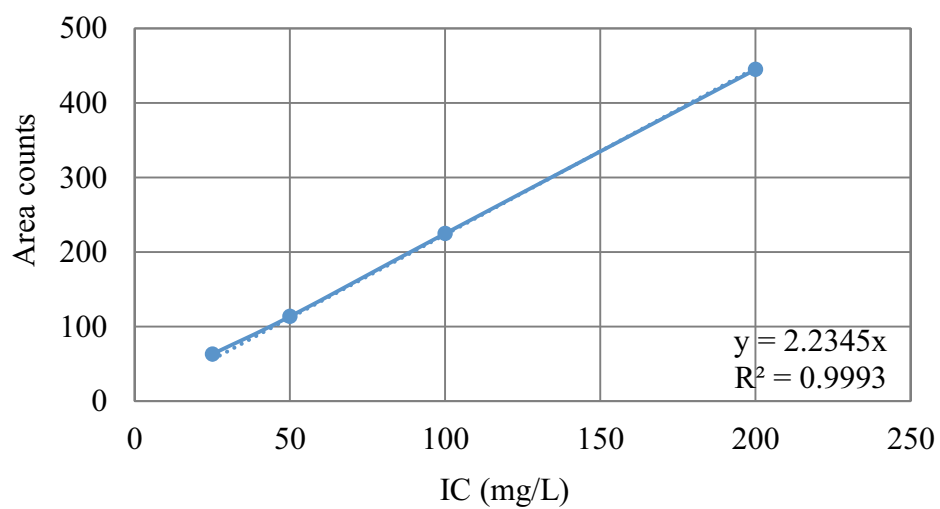


Figure C.1. Calibration curve for a) TC b) IC