ADDIS ABABA UNIVERSITY
SCHOOL OF GRADUATE STUDIES
ADDIS ABABA INSITUTE OF TECHNOLOGY
SCHOOL OF CHEMICAL AND BIO-ENGINEERING

Reuse of Textile Dye house Wastewater by Removal of Reactive Dye Using Nano Membrane

A Thesis Submitted to the Research and Graduate School of Addis Ababa University, Addis Ababa Institute of Technology, School of Chemical and Bio-Engineering in Partial Fulfillment of the Requirements for the Attainment of the Degree of Masters of Science in Chemical Engineering under Environmental Engineering Stream.

By: Daniel Aberra

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Addis Ababa, Ethiopia

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ABBREVIATIONS

EPA: Environmental protection agency

BOD: Biological oxygen demand

COD: Chemical oxygen demand

RO: Reverse osmosis

NF: Nano filtration

UF: Ultra-filtration

MF: Micro-filtration

MWCO: Molecular weight cut-off

TFC: Thin film composite

PVC: Poly vinyl chloride

TS: Total solid

TOC: Total organic carbon

MW: Molecular weight

NTU: Nephelometric Turbidity Units

FTU: Formazin Turbidity Units

Cp: solute concentration in the permeate

Cf: solute concentration in the feed

Au: absorbance unit

ANOVA: analysis of variance

TSS: total suspended solid

HU: Hazen Units

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ABSTRACT

This study was devoted to provide good understanding of the operating characteristics and their effects on NF membranes system, to utilize in the treatment of wastewater containing synthetic reactive dyes which are common in Ethiopia. The effectiveness of NF systems in rejection of reactive dyes was evaluated under different operating conditions, such as working pressure, feed flow rate and dye concentration keeping feed temperature and pH constant. All experiments were conducted on RO/NF pilot scale plant including facility of feeding and product tank, on line measurement of flow rate and pressure.

Wastewater containing reactive Dye was brought from Yirgalem Textile factory and its characteristics were analyzed. The result shows that dye-house wastewaters, containing reactive dyes, are hazardous to the environment since their COD, BOD, TS and pH values are higher than the free discharge limit values and also they are highly colored.

It is found that all the three parameters affect the permeate flow and dye removal significantly. The increase of both inlet flow rate and working pressure has positive effect on the permeate flow rate. But increase in dye concentration generally shows negative impact. On the other hand, the increase of inlet flow rate, dye concentration and working pressure increases percent of dye removal. In this investigation, greater than 99% dye removal and maximum permeate flow rate within the minimum fouling rate was obtained at feed flow rate of 0.86m^3/h, working pressure of 20 bars, and dye concentration 146.1mg/L.

Keywords: *Membrane separation, Synthetic dyes, Nano filtration, Wastewater reuse*

1. INTRODUCTION

1.1 Back ground

Textile industry is among the biggest industries in the world producing a wide variety of products. It ranges from producing fibers and yarns (spinning) up to finishing and processing of cloths (including knitting and garment production). Within this range usually a wide variety of independent factories, which produce different product, exist. The industry plays an important role in the world economy as well as in our daily life. It exists almost in all countries and the number of industries in the sector is being increased. The global consumption of textile products is currently around 30 million tones with expected growth at 3% per annum, the coloration of which needs approximately 8×10^5 tons of dyes [2].

Besides its great economic contribution, the industry is known by the consumption of large quantity of water and generation of huge amount of wastewater. The textile finishing sector, especially the dyeing unit, is the major source of polluting wastewaters in the industry [3]. To dye 1kg of cotton, which represents half of the world fiber consumption [3], 70- 150 liters of water will be consumed and almost similar amount of wastewater will be generated after the process. The wastewater, especially that from spent cotton reactive dye baths, contains high salt, dyes that are hard to biodegrade, since the currently being used dyes are synthetic complex organic dyes, and high alkalinity[3]. In fact textile industry is considered among the most polluting industries based on the volume and composition of wastewater it releases [3].

In Ethiopia textile industry is among the largest manufacturing industries, which the government has given special attention. Following the promotion and incentive given to the textile sector by the government, significant number of textile factories are currently operating in the country. Most of them are engaged in processing natural fibers, especially cotton. There are more than fourteen major state-owned and private textile and garment factories [7, 8]. But most of them lack effluent treatment plants. Instead, they directly discharge untreated colored and toxic effluent into the nearby canals, rivers, lakes, and streams [7]. All organic and inorganic chemicals in wastewater are much higher than allowable limits and extremely harmful to aquatic flora and fauna and can reach human beings through food chains. This wastewater has serious negative impact not only on underground, surface water bodies and land in the surrounding area but also on the aquatic ecological system [7]. Besides the waste contains a large amount of water, useful chemicals and heat which are economically attractive. So it is crucial to find treatment technology which could bring the water to re-usable quality. The stringent environmental discharge regulations on the one hand and the economical attractiveness of the resources in the wastewater, such as the huge amount of water and salt, on the other hand, leads to the search of highly effective wastewater treatment technology that can bring the resources to their reusable quality. Water reuse can take a number of forms; such as recycling within the process itself on segregated process streams, and end of pipe treatment of mixed effluent streams. The appropriate wastewater treatment and recycling breaks the negative impact of human activities on the environment as well [9]. There are different treatment mechanisms for textile dye house wastewater. But the conventional wastewater treatment technologies such as biological waste water treatments, adsorption on activated sludge process etc, cannot be efficient due to the high resistive nature of the dyes to biological degradation and voluminous of the wastewater [5, 6]. But the recently emerged membrane technology is found to be effective enough to treat the large amount of wastewater continuously in small area and to bring the resources to their reusable quality. Membrane separation processes have the ability to clarify, concentrate and most importantly, separate dye continuously from dye house wastewater.

1.2 Statement of the Problem

Textile industry is one of the sectors to which the government of Ethiopia currently gives a great attention. Hence, many textile factories are emerging in the country. Most textile industries are water intensive and are also known by generating tremendous amount of wastewater. It is becoming difficult for the government to facilitate all the water need of the growing industry sector and public use. Due to the limited supply capacity, the public pressure on water supplied by the government is getting higher and higher. Therefore industries have to think on efficient water consumption and conservation strategy. Among the alternative options; reusing wastewater after treating it to the reusable quality has a paramount importance. Especially, highly wastewater generating industries, like textile industries, will benefit more from this option. On the other hand, Most of reactive dyes are toxic to some organisms and may cause direct destruction of aquatic life. Moreover, colorant may interfere with light penetration and oxygen in water bodies. The dyes comprise likewise an aesthetic problem and color restricts which lead to conflict between upstream discharger and downstream water user.

The increasing cost of water and its wasteful consumption necessitate a treatment process which is integrated with in-plant water circuits rather than as a subsequent treatment. From this standpoint, membrane filtration offers potential applications. Processes using membranes provide very interesting possibilities of separating hydrolyzed dyestuffs and dyeing auxiliaries, thus simultaneously reducing coloration and the BOD/COD of the wastewater [11].

From reviewing the articles found membrane technology is used by many process in industries for product purification and wastewater treatment to reduce water usage by recycling wastewater treated into the Plant. To treat textile dye house wastewater membrane separation technology is the best candidate because of its technical feasibility and ability to bring the water to reusable quality. From the different membrane types nano membrane is found to be the best among other membranes by giving a rejection value of more than 99.5% (deliver colorless permeate) and delivering a better permeate flow rate value from those that pass the quality test [14].Therefore, in this study nano filtration membrane treatment of actual day house wastewater with lab scale membrane module and machine will be conducted and the effect of operating conditions will be determined.

1.3 Objective

1.3.1 General objective

- To Show the possibility of recycling water from dye-house wastewater using membrane separation technology by removal of reactive dye.

1.3.2 Specific objectives

- To characterize reactive dye house wastewater sample.
- To pre filter the representative dye house wastewater using appropriate filtering mechanism
- To study effect of the individual and the best combination of operating parameters (working pressure, inlet flow rate, dye concentration) on Nano-membrane operation.
- To characterize the dye house wastewater membrane permeates and compare it with the environmental discharge limits.

1.4 Significance of the Study

Successful completion of this research will play an invaluable role by providing substantial baseline information for treatment and reuse of textile dye house wastewater for Ethiopia textile industries.

1.5 Scope of the Study

In this study membrane separation technology, which is technically best fit for close-loop type recycle system, will be analyzed using actual dye house wastewater. This will be done starting from analyzing characteristics of representative dye-house wastewater, pre filtration and then will continue by treating with nano membrane for a specific actual textile wastewater and finally it will end up with determination of effect of operating conditions, which leads to high quality permeate with high flux and with relatively lower fouling rate. Moreover, membrane cleaning effectiveness will be checked.

1.6 Limitations

- Most textile industries were not willing to give their waste water.
- The effect of temperature and salt concentration on the permeate flux and dye removal cannot be analyzed due to the absence of reliable measuring instrument and the incapability of the existing membrane separation unit to control the temperature.

2. LITERATURE REVIEW

2.1 Dyes used in textile manufacturing industries

There are more than 100,000 commercially available dyes with over $7*10^5$ tons of dyestuff produced annually. Due to their chemical structure, dyes are resistant to fading on exposure to light, water, and many chemicals also many dyes are difficult to be decolorized and decomposed biologically. There are many structure varieties such as acidic, basic, disperse, azo, diazo, anthroquinone based, and metal complex dyes. These dyes are very stable and can be decomposed only at temperatures higher than 200℃. For this reason, synthetic dyes often receive considerable attention from researchers in textile wastewater treatment [21], [10].

There are several different classes of dyes used in textile dyeing and printing operations. The most commonly used dyes are reactive and direct dyes for dyeing cotton and disperse dyes for dyeing polyester [13]. Reactive dyes react with the fiber to form chemical bonds with the fiber essentially becoming part of the fiber. Direct dyes can be added to fibers “directly” without the aid of affixing agents. While reactive and direct dyes are water soluble, the low water solubility of disperse dyes requires them to be applied as a dispersion of finely ground powders in a dye bath. Disperse dyes require either heat and high pressures or dye carriers to penetrate synthetic fibers. In addition to polyester, disperse dyes are used on other synthetic fibers, such as nylon, rayon and acrylic. Other dye classes include acid dyes for wool and nylon, basic dyes for synthetics, sulfur and vat dyes for cotton and other cellulosic fibers, and pigments. Pigments, unlike dyes, require binders to attach to fibers, remain insoluble during application and are typically used during printing operations. Table 2-1 shows the different classes of dyes and their application.

Table 2-1: Dye classification [17]

Dye Class	**Description**	**Fibers Typically Applied to**	**Typical Fixation (%)**	**Typical Pollutants Associated with Various Dyes**
Acid	water-soluble anionic compounds	wool, nylon	80-93	Color, organic acids, unfixed dyes
Basic	water-soluble, applied in weakly acidic dye baths; very bright dyes	acrylic, some polyesters	97-98	N/A
Direct	water-soluble, anionic compounds; can be applied directly to cellulosic without mordant's (or metals like chromium and copper)	cotton, rayon, other cellulosic	70-95	Color, salt, unfixed dye, cationic fixing agents; surfactant, defoamer, leveling and retarding agents, finish, diluents
Disperse	not water-soluble	polyester, acetate, other synthetics	80-92	Color, organic acids, carriers, leveling agents, phosphates, defoamers, lubricants, dispersants, delustrants, diluents
Reactive	water-soluble, anionic compounds; largest dye class	cotton, other cellulosic, wool	60-90	Color, salt, alkali, unfixed dye; surfactants; defoamer, diluents, finish
Sulfur	organic compounds containing sulfur or sodium sulfide	cotton, other cellulosic	60-70	Color, alkali, oxidizing agent, reducing agent, unfixed dye
Vat	oldest dyes; more chemically complex; water-insoluble	cotton, other cellulosic	80-95	Color, alkali, oxidizing agents, reducing agents

Reactive dyes are popular in textile manufacturing industries due to their good wet fastness properties [17]. These dyes react with the substrate to form a covalent dye-substrate bond which will not be affected by washing. They gained popularity over time and in the year 2000 represented 20-30% of the total dye market, with usage estimated to reach 50% at the end of 2004 [18]. The main problem of these dyes is their incomplete exhaustion on to the fiber. Due to their incomplete exhaustion, significant amount of the dyes will be lost through the drain and also there will be residual color in the wastewater, which need exhaustive treatment. In current dyeing processes, as much as 50% of the dye is lost in the wastewater. This can lead to acute effects on exposed organisms due to the toxicity of the dyes, abnormal coloration and reduction in photosynthesis because of the absorbance of light that enters the water. Reactive dyes and their hydrolyzed residuals have molecular masses ranging from 500 to 3000 Daltons [6].

2.2 Textile Dye House Operations

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

For a dye house to turn grey goods into a finished product, several sequential steps must occur, including fabric preparation, scouring, bleaching and finishing (dyeing, printing etc…) Of all the fabric finishing unit processes; scouring, bleaching, dyeing and finishing are the most water-intensive and are therefore key targets for the use of tertiary-treated recycled water. While many of these steps are performed at specialized fabric preparation or finishing facilities, some of these operations are employed by dye houses in most industries [18].

2.2.1 Fabric Preparation

Fabric preparation is a series of treatment steps to remove impurities that may interfere with the subsequent dyeing, printing and finishing processes. The preparation treatments usually include desizing, scouring and bleaching, but may also include singeing (a dry process) and mercerizing [18]. The four wet processes are discussed here.

- **Desizing**: Sizing agents are added to fibers in order to improve their strength and bending behavior during the weaving process. Water-soluble sizes are used for synthetic fabrics and water-insoluble starches are used for natural fibers. Once the fibers are woven, the sizing agents need to be removed from the fabric in a process called desizing. It involves a hot water wash for synthetic fibers or an enzyme wash for natural fibers [18]. It is important to remove sizing agents from natural fibers because the starches can react and cause color changes when exposed to sodium hydroxide during the scouring process [18].
- **Scouring**: is performed to remove any impurities present in the fabric. The impurities (i.e. lubricants, dirt, surfactants, residual tints) are removed using an alkaline solution, typically sodium hydroxide, at high temperatures to breakdown or emulsify and suspend impurities. The specific scouring procedures vary with the type of fiber or cloth construction [18]. Because soaps and detergents used during scouring may precipitate in hard water, process water is usually softened prior to the start of the scouring process [18].
- **Bleaching:** is the removal of unwanted color from the textile fibers and typically involves the use of one of three main bleaching agents: hydrogen peroxide, sodium hypochlorite or sodium chlorite [18]. Hydrogen peroxide bleaching is performed under alkaline conditions and, as a result, may be combined with the scouring process [18]. The bleaching process includes three main steps:

  (1) Saturating the fabric with the bleaching agent and other necessary chemicals;

  (2) Raising the temperature to the recommended level for the particular textile and maintaining that temperature for a set period of time; and

  (3) Thoroughly washing and drying the fabric [18].

2.2.2 Dyeing: is adding color to fabrics through the use of several chemicals and dyestuffs, depending on the fabric and processes used. It can be performed either in continuous or batch modes.

Commonly dyeing involves introducing cotton in yarn or fabric form, having been scoured and bleached, in a dye bath at a temperature below the dye bath exhaustion temperature. Dye, electrolyte (sodium chloride or sodium sulphate) and ethylene diamine tetra-acetic acid (EDTA) are added to the Dye bath to increase the exhaustion rate of the dye. The concentration of the electrolyte is dependent on the quantity of dye used and is usually 20 to 100 g/L of NaCl or 15 to 80 g/L Na_2S0_4. The pH is adjusted to a value of 7.0 if necessary. A short time (10 to 20 minutes) is allowed for mixing, during which time the dye liquor is circulated and brought into contact with the cotton fiber. The dye bath is then heated to the dyeing temperature, which ranges from 40 to 95°C depending on the dye class used. This stage is known as the exhaustion phase and lasts from 20 to 40 minutes. Longer exhaustion time is required for darker shades. Alkali fixation is the last stage during which the dye - fiber bond is formed. A reactive dye can either react with hydroxyl groups on the cellulose fiber or with hydroxyl ions in solution. The second reaction, dye hydrolysis, constitutes between 10% and 20% of the dye usage. Sodium carbonate (10 to 20 normal) is added to raise the dye liquor pH to between 10.5 and 11.5. Sodium hydroxide (1normal) is added to raise the pH to between 12.0 and 12.5 after 30 to 60 minutes. After cooling down its temperature to about 70^oC, the dye bath will then be drained. Both the pretreatments and the dyeing are wet processes and are usually done at elevated temperatures. The water consumption and the operating conditions of the process are shown in the form of flow chart on Figure 2-1.

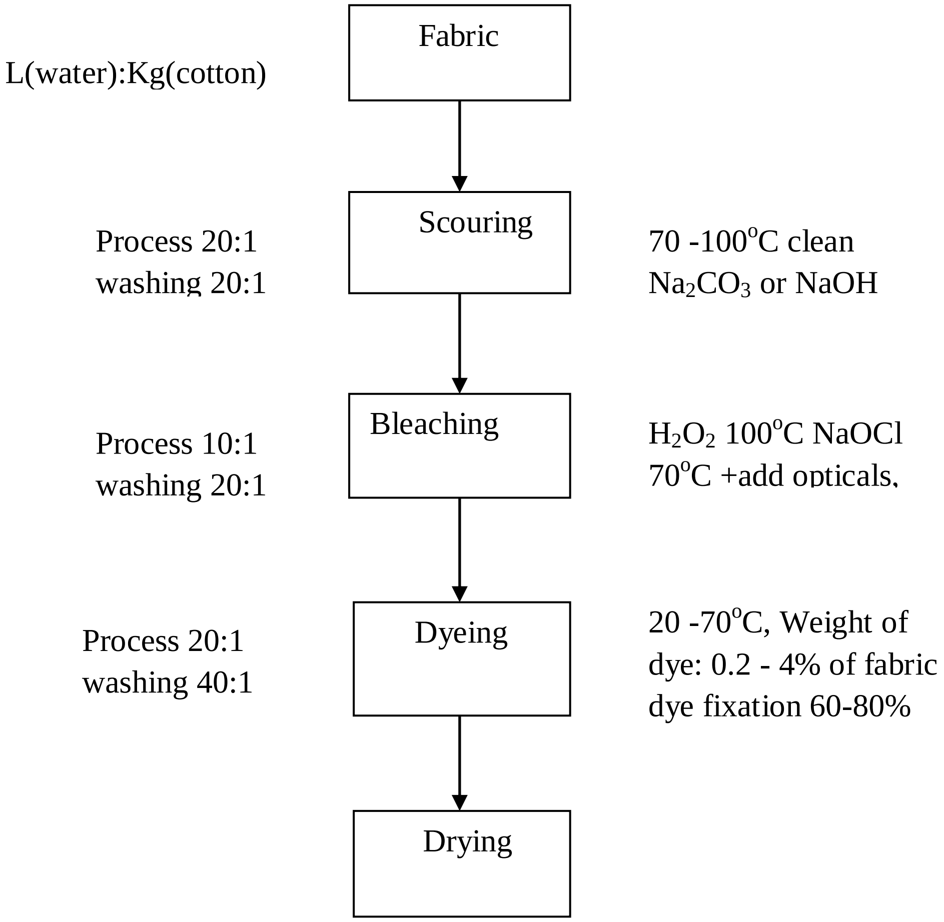


Figure 2-1 Flow chart of wet process in dye house [19]

2.3 Textile Wastewaters

The wastewaters originating from dyeing processes are generally characterized by the high content of color caused by the dyestuffs; salts; chemical oxygen demand (COD) deriving from additives such as acetic acid, detergents and complexing agents; suspended solids including fibers; high temperature and broadly fluctuating PH. [22].

The highest and lowest fixation rates belong to basic dyes (97-98%) and sulfur dyes (60-70%), respectively. In general, approximately 20-40% of the input dye remains in the wastewater. Their concentrations in dye-baths range from 10 to 1000 mg/L. The inefficiency of the conventional biological treatment methods for decolorizing the textile effluents leads to the discharge of highly colored wastewaters into the receiving environment. [22].There are many subcategories of the textile industry, where different types and concentrations of dyes and chemicals are used in a number of processes for the production of a wide variety of fabrics. The diversity of the textile production schemes leads to the generation of wastewaters of highly varying concentrations;

such that, 50-5000 mg/L of COD, 50-500 mg/L of suspended solids, and a highly variable range of color [22]. This fact makes the treatment of textile wastewaters a difficult task, and necessitates the examination of each factory individually for the determination of the best treatment method.

Table 2-2 Source of water Pollution at various stages of textile operations [27].

Process	Possible Pollutants	Nature of Effluent
Desizing	Starch, glucose, PVA, resins, fats and waxes do not exert a high BOD.	Very small volume, high BOD (30-50% of total), PVA.
Bleaching	Hypochlorite,chlorine, caustic soda,hydrogen peroxide, acids.	Small volume, strongly alkaline, low BOD (5% of total)
Mercerizing	Caustic soda	Small volume, strongly alkaline,low BOD (Less than 1% of total)
Dyeing	Dye stuff, mordant and reducing agents like sulphides, acetic acids and soap	Large volume, strongly coloured, fairly high BOD (6% of total)
Printing	Dye, starch, gum oil, china clay, mordants, acids and metallic salts	Very small volume, oily Appearances, fairly high BOD.
Finishing	Traces of starch, tallow, salts, special finishes, etc.	Very small volume, less alkaline, low BOD

2.3.1 Textile wastewater Environmental problems and polluting effects

The characteristics of textile effluents vary and depend on the type of textile manufactured and the chemicals used. The textile wastewater effluent contains high amounts of agents causing damage to the environment and human health including suspended and dissolved solids, biological oxygen demand (BOD), chemical oxygen demand (COD), chemicals, odour and colour. Most of the BOD/COD ratios are found to be around 1:4, indicating the presence of non-biodegradable substances [27]. Dyes in water give out a bad colour and can cause diseases like haemorrhage, ulceration of skin, nausea, severe irritation of skin and dermatitis [25]. They can block the penetration of sunlight from water surface preventing photosynthesis [26]. Dyes also increase the biochemical oxygen demand of the receiving water and in turn reduce the re-oxygenation process and hence hamper the growth of photoautotrophic organisms. The level of toxicity or harmfulness of the textile effluents varies among industries [28]. In the textile dyeing process, there is always a portion of unfixed dye which gets washed away along with water. The textile wastewater is found to be high in the concentration of these unfixed dyes. The dye concentration in a dye house range from 0.01g/L to 0.25g/L depending on the type of the dye and the process carried out [29-31].

Textile dyestuffs are found to contain a large amount of organic substances which are difficult to degrade and are resistant to aerobic process [25]. The suspended solid concentrations in the effluents play an important role in affecting the environment as they combine with oily scum and interfere with oxygen transfer mechanism in the air-water interface [26].

Inorganic substances in the textile effluents make the water unsuitable for use due to the presence of excess concentration of soluble salts. These substances even in a lower quantity are found to be toxic to aquatic life [37]. Some of the inorganic chemicals like hydrochloric acid, sodium hypochlorite, sodium hydroxide, sodium sulphide and reactive dyes are poisonous to marine life [37, 38]. The organic components are found to undergo chemical and biological changes that result in the removal of oxygen from water [37]. The seriousness of water pollution depends on the quantity of water and chemicals used in the wet process degradation. They are also found to be reduced into carcinogenic agents under anaerobic conditions [33]. Some of the carcinogenic compounds produced due to the degradation of azo dyes.

Human exposures to textile dye have resulted in lung and skin irritations, headaches, congenital malformations and nausea [34]. [35], reported evidence of kidney, liver and urinary bladder cancers on workers after prolonged exposure to textile dyes. It was found that dermatitis, asthma, nasal problems and rhinitis were acquired by workers after prolonged exposure to reactive dyes [38].

2.3.2 Characteristics of dye house wastewaters

Wastewater from dye-house is typically alkaline and has high BOD_5 (700 to 2,000 milligrams per liter (mg/L)) and chemical oxygen demand (COD) (approximately 2 to 5 times the biochemical oxygen demand (BOD) level), solids, oil and possibly toxic organics, including phenols (from dyeing and finishing) and halogenated organics (from processes such as bleaching). Dye wastewaters are frequently highly colored and may contain heavy metals such as copper and chromium [20].waste water in the dyeing unit may contain Metals, salt, surfactants, organic processing assistants, cationic materials, colour, BOD, COD, sulphide, acidity/alkalinity, spent solvents.

Table 2-3: Characteristics of wastewaters from different dye house operations [19, 53]

Process	Unit(U)	Waste volume (m^3/U)	BOD$_5$(kg /U)	TSS(kg/ U)	Characteristics of typical untreated textile wastewater
Yarn sizing	Metric ton of cotton	4.2	2.8	-	PH 6-10 Temperature (°C) 35-45 Total dissolved solids (mg/L) 8,000-12,000 BOD (mg/L) 80-6,000 COD (mg/L) 150-12,000 Total suspended solids (mg/L) 15-8,000 Total Dissolved Solids (mg/L) 2,900-3,100 Chlorine (mg/L) 1,000-6,000 Sodium (mg/L) 70% Trace elements (Fe, Cu, Zn, Mn, Ni) (mg/L) <10
Desizing	Metric ton of cotton	22	58	30	
Kiering	Metric ton of cotton	100	53	22	
Bleaching	Metric ton of cotton	100	8	5	
Mercerizing	Metric ton of cotton	35	8	2.5	
Dyeing	Metric ton of cotton	50	60	25	
Printing	Metric ton of cotton	14	54	12	

2.3.3 Water Reuse Requirements

It is quite difficult to define a general standard for water reuse in textile industry because of the different requirements of each fiber (wool, silk, cotton, polyester, etc.) and because of the different quality required for the final fabric. Low hardness water is usually needed for scouring, dyeing and for preparing printing pastes but softening is not necessary for all the washing cycles. A high salt content may interfere with the dyeing process and with the detergent action of the surfactants used in washing the dyed fabric. Chemical reduction of the chromophores in the dye molecules by ammonia, nitrite and sulphide may alter the color and therefore spoil the dyeing process. Organic substances, and particularly surfactants and traces of dyes, may interfere with bleaching, dyeing and printing by causing differences in hues and tones [22]. The recovery and reuse of textile wastewaters have been studied extensively by membrane researchers [22]. Wide variations in the quality of the recovered waters have been reported and their adequacy differs from one process to another.

Tables 2-4 Water Reuse Criteria Set by the British Textile Technology Group [22].

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

* AU: Absorbance units in 10 mm cell

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

Therefore it seems that each textile manufacturing factory needs to establish its own reuse criteria. However, there are a few basic conditions such as the water turbidity, which should be comparable to the groundwater that is used as freshwater, and the water hardness, which should be in the normal range for relatively soft groundwater (not higher than 40 mg/L Ca). Of course, all color should be removed before reuse [22].

2.4 Textile Dye house wastewater treatment technologies

Owing to their high BOD/COD, their coloration and their salt load, the wastewaters resulting from dyeing cotton with reactive dyes are highly polluted [9]. Discharging this wastewater untreated will have dramatic impact on the receiving water body [10]. It is difficult for such wastewater to meet the discharge standards shown in Table 2-1. Besides the parameters and values mentioned in the table, many discharge standards doesn’t allow visible color in the wastewater at all [9]. So treating the wastewater before discharge is becoming mandatory.

Table 2-5 Limit values for discharge to in land water [11]

Parameter	**Limit values**
Temperature	40^oC
pH	6-9
BOD_5 at 20^oC	50mg/l
Total nitrogen (as N)	40mg/l
COD (mg O_2/l)	150 mg/l
Total phosphorous (as P)	10mg/l
Suspended solids	30mg/l
Total ammonia (as N)	20mg/l
Oil, fats and grease	1mg/l

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

2.4.1 Biological methods

Biological treatment technique is adapted from naturally occurring phenomenon which is self purification of streams. Self purification comprises the whole process by which an aquatic environment achieves the re-establishment of its original quality after pollution. Biological treatments differ according to the presence or absences of oxygen, especially the traditional activated sludge process have been widely used for the treatment of textile wastewaters due to their low operational costs [22]. These systems offer high efficiencies in COD removal, but cannot provide a complete color removal because most textile dyes have complex aromatic molecular structures that resist degradation. Moreover, biological systems need constant attention to maintain the correct operational conditions like pH, temperature, oxygen and nutrient concentrations. The bacteria are extremely intolerant to toxicity of the waste, and the problem of sludge bulking is often observed [22].

2.4.2 Physico-chemical treatment

This method has the advantage of being flexible and tolerant to the wide variations in wastewater quality provided that the chemical dosages are adjusted accordingly. Alum, ferric sulfate or ferric chloride is used as coagulant, together with lime or sulfuric acid for pH control. The efficiency of the coagulation and flocculation processes vary with the changing properties of the wastewaters and the color removal may not be sufficient for each case. Therefore, the drawbacks of the chemical methods are generally the excess chemical usage, increased sludge production, and often unsatisfactory dye removal [22].

2.4.3 Adsorption on powdered activated carbon

Activated carbon is a very good adsorbent for removing dissolved organic material from water, especially solvents and low levels of dyestuff or toxic products. However, the degree of color removal is dye-specific and the adsorption capacity can be as low as 20%. In addition, regeneration results in a performance reduction up to 70-80% of that of the virgin carbon and the efficiency becomes dependent on high carbon dosages [22].

2.4.4 The oxidation methods: are usually successful in treating the dyes that are resistant to biodegradation. In oxidative processes it is aimed to break the dye molecule and destroy the chromophore, or convert it into a readily biodegradable form. Ozonation can achieve high color removal, reduce the level of organic compounds, improve biodegradability, destroy phenols, and insure disinfection. One of the drawbacks of ozonation is the cost [22]. Moreover, even high doses of ozone do not completely convert the organics to carbon dioxide and water, particularly for dye wastes containing surfactants and suspended matter. Problems in oxidative treatment can be the formation of toxic intermediates like aromatic amines or elevated heavy metal concentrations in the case of metal-complex azo dyes. If ozonated effluent is reused in the dyeing process, degradation products are likely to accumulate in the recycled liquor and interfere in the dyeing process [22].

2.4.5 Electrochemical processes:

It is a chemical wastewater treatment method. The dye house wastewater is circulated in an electrolytic cell containing iron electrodes. Even though this process is advantageous of being capable for adaptation to different volumes and pollution loads, its use is limited due to the formation of iron hydroxide sludge [12].

All these treatment methods mentioned above are basically applied as end-of-pipe processes to comply with the limits imposed by legislation for discharge. However, the recalcitrance and biotoxicity of most of the compounds together with their fluctuating concentrations and flow rates makes the conventional processes quite insufficient for the treatment of textile wastewaters, especially for color [22]. As a feasible alternative to the conventional methods there is the membrane separation technology, a quite promising process-integrated method allowing not only advanced treatment but also recovery of valuable materials like water, dyes and chemicals [22].

The need for the minimization of water consumption due to the potential shortage of earth's water supplies and the increased rates paid by the manufacturers for fresh water has lead to a growing interest in water reuse. Textile factories are large consumers of groundwater for quality reasons and therefore, water reclamation has become a key topic in the textile industry. There have been an extensively growing number of studies performed on the purification of the complex textile wastewaters using membrane separation processes in the last decade [22]. Almost all the researchers have obtained high removal efficiencies for color and organic matter (80-100%) and also achieved high rates of water recovery (70-100%).

There have been several approaches consisting of two or more step processes for textile wastewater reclamation, where more conventional methods like coagulation, flocculation and clarification are used as well as microfiltration (MF) and ultra filtration (UF) in the pre-treatment stages. After passing through one or more of these stages, the wastewater is further purified in other pressure-driven membrane processes, i.e., nano filtration (NF) or reverse osmosis (RO) to the degree of reuse quality. There has been a shift in trend to MF in the pre-treatment stage as it is economically more attractive as compared to conventional methods [22]. Depending on the requirement of the final permeate quality, the process combinations vary, making the best treatment scheme quite specific to the particular effluent. Therefore, each particular textile effluent needs to be handled individually. In addition, the requirement of more than one unit in the process train points out the disadvantage of increased treatment costs. To this end, production of the final permeates having adequate quality for reuse via the most simple and energy efficient membrane process combinations is of great value. Although most of the textile subcategories use groundwater for dyeing processes, wide variations in the acceptable quality of the recovered process waters have been reported in literature [22]. Therefore it seems that each textile manufacturing subcategory needs to establish its own reuse criteria.

Summary of the available waste water treatment techniques and their pros and cons are stated in Table 2-6. As can be seen from the table nano-filtration is relatively better for our purpose than the others.

Table 2-6 possible treatments for cotton textile wastes and their associated advantages and disadvantages [9]

Processes	**Advantages**	**Disadvantages**
Biodegradation	Rates of elimination by oxidizable substances about 90%	Low biodegradability of Dyes
Coagulation– flocculation	Elimination of insoluble dyes	Production of sludge blocking filter
Adsorption on activated carbon	Suspended solids and organic substances well reduced	Cost of activated carbon
Ozone treatment	Good decolorization	No reduction of the COD
Electrochemical processes	Capacity of adaptation to different volumes and pollution loads	Iron hydroxide sludge
Reverse-osmosis	Removal of all mineral salts, hydrolyzes reactive dyes and chemical auxiliaries	High pressure
Nano-filtration	Separation of organic compounds of low molecular weight and divalent ions from monovalent salts. Treatment of high concentrations	NA
Ultra-filtration–micro-filtration	Low pressure	Insufficient quality of the treated wastewater

2.5 Membrane separation processes

The first membranes produced in Germany in 1920 were used for the filtration of bacteria at laboratory scale. Later in 1960s, the development of the synthetic asymmetric membrane at the University of California, Los Angeles, by Loeb and Sourirajan (1962) for the separation of salt from seawater has lead to a significant development of the membrane technology. Since then, the application areas have been widely spread in many industries, among which beverage, food, pharmaceutical, electronics, paper and textile are only a few. In addition to being used in several industrial production stages, membranes have been widely used in the treatment of wastes and the recovery of valuable materials like dyes, metals, and water. Drinking water treatment is another area where membrane separation processes have recently been introduced [22]. The popularity of the membrane technology in environmental applications has emerged due to the potential scarcity of fresh water supplies and the stringent environmental regulations. Meanwhile, the rapid development of the membrane material science over the recent years has also helped the widespread use of membrane technology due to the availability of membranes from a wide range of materials of different structures, including synthetic polymers, cellulose-based natural products and others like inorganic, ceramic and metals [22].

2.5.1 Definitions and Basic Principles

A membrane can be defined as an inter phase that separates components according to their structure. Some components can be transported more readily than others due to the differences in physical and chemical properties between the membrane and the permeating components. Another definition states that a membrane is a permeable or semi-permeable barrier through which fluids and solutes are selectively transported when a driving force is applied across it. The driving force can be a gradient of concentration, temperature, pressure or electrical potential. It can be inferred from these definitions that the application of conventional filtration of solids and particles from liquid or gaseous streams is further extended by the membrane filtration to include the separation of dissolved solutes in liquid streams and the separation of gas mixtures. The membrane discussion in this chapter is limited to the pressure-driven membranes since this study is based on their performances for textile wastewater treatment and recovery [22].

Although membrane separation process is an extension of the conventional filtration in a way, there are some differences that make the membrane separation one of the most promising new technologies today. The basic difference that distinguishes the membrane separation process from conventional filtration is the flow pattern. In conventional filtration, particles are simply collected on a filter media under an applied pressure, where the liquid flowing perpendicular to the filter media causes the accumulation of the retained particles, leading to the formation of a cake layer at the surface. This is called the *dead-end* filtration. The thickness of the cake increases with filtration time and causes an increase in the pressure drop or a decrease in the filtration rate. When the pressure drop becomes too high, or the filtration rate becomes too low, the cake is removed and the filter media is cleaned. However, in most practical cases, the filter media is simply replaced. Dead-end filtration is generally suitable for concentrated suspensions, and not appropriate for the filtration of very fine and dilute suspensions or production of very pure filtrates [22]. Where dead-end filtration is not appropriate, *cross-flow* filtration is an alternative technique, especially in cases of high purity filtrate requirement. In cross-flow filtration the feed water is recycled under an applied pressure, where the feed flow is parallel to the filter media. The purpose of this flow is to control the thickness of the cake. As the speed of the flow enables the suspended solids to be carried away, the retained particles accumulate on the surface to a low extent, providing longer service lives for the filter media before cleaning or replacing.

Cross-flow filtration and membrane filtration has become synonymous, although they are not, in principle, as the term “membrane filtration” implies nothing about the flow pattern and the term “cross-flow” does not mean anything for the filter media. However, in practice, cross-flow filtration overlaps membrane filtration almost completely. In other words, membrane filtration is almost always carried out by cross-flow, as dead-end filtration through a membrane would end very rapidly due to total clogging [22].

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

The performance of a membrane is defined in terms of two factors, *flux* and *selectivity* [22]. The term *flux* describes the amount of fluid passing through the membrane, i.e., the volumetric flow rate of permeate, which is usually given in terms of volume per unit membrane area per unit time as follows:

$$\mathrm{J} = \frac{1\mathrm{dv}}{\mathrm{Adt}} \qquad (1)$$

Where:
J: flux ($L/m^2/h$)
dV/dt : permeate flow rate (m^3/h)
A: effective membrane area (m^2)

The flux of a membrane basically defines its productivity and the *selectivity* of the membrane defines whether it will be useful or not as it is an indication of how pure the product stream is and how much of it is recovered at the desired purity. Selectivity is generally expressed by one of the two parameters: *retention* or *separation factor.* For dilute aqueous mixtures, consisting of a solvent (mostly water) and a solute, it is more convenient to express the selectivity in terms of retention towards the solute [22]. The solute is partly retained while the solvent (water) molecules pass freely through the membrane.

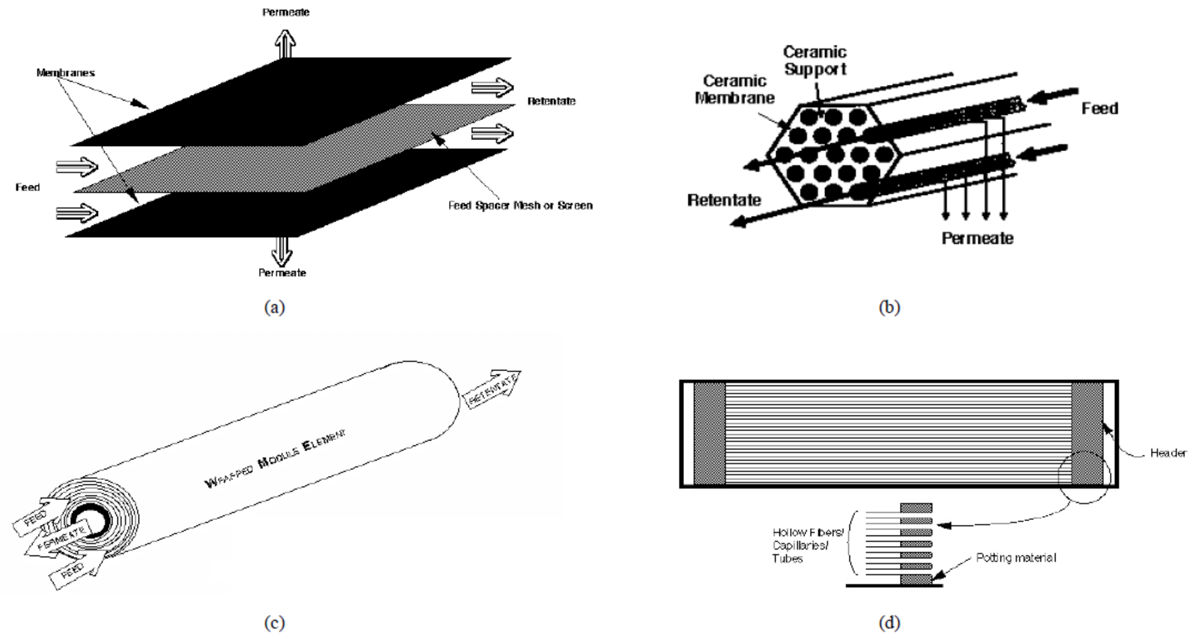
2.5.2 Membrane Materials

Most MF, UF, RO, and NF membranes are synthetic organic polymers. MF and UF membranes are often made from the same materials, but they are prepared under different membrane formation conditions so that different pore sizes are produced [50]. Typical MF and UF polymers include poly (vinylidene fluoride), poly sulfone, poly (acrylonitrile) and poly (acrylonitrile)-poly (vinyl chloride) copolymers, poly (ether sulfone) is also commonly used for UF membranes MF membranes also include cellulose acetate-cellulose nitrate blends, nylons, and poly (tetrafluoroethylene) and RO membranes are typically either cellulose acetate or polysulfone coated with aromatic polyamides [39]. NF membranes are made from cellulose acetate blends or polyamide composites like the RO membranes, or they could be modified forms of UF membranes such as sulfonated polysulfone. Membranes can also be prepared from inorganic materials such as ceramics or metals. Ceramic membranes are micro porous, thermally stable, chemically resistant, and often used for microfiltration [39]. However, disadvantages such as high cost and mechanical fragility have hindered their wide-spread use. Metallic membranes are often made of stainless steel and can be very finely porous. Their main application is in gas separations, but they can also be used for water filtration at high temperatures or as a membrane support [21].

2.5.3 Membrane Modules

There are four main types of modules: plate-and-frame, tubular, spiral wound, and hollow fiber (Figure 2.4) [39]. The plate-and-frame module is the simplest configuration, consisting of two end plates, the flat sheet membrane, and spacers. In tubular modules, the membrane is often on the inside of a tube, and the feed solution is pumped through the tube.

Figure 2.2 types of membrane modules



2.5.4 Pressure-Driven Membrane Separation Processes

Membranes are generally classified in broad categories by their ability to remove particles, ions and other substances in certain size ranges [22]. The type of the driving force applied across the membrane leads to a basic classification of membrane separation processes, as shown in Table 2.7, there are four commonly accepted pressure-driven membrane separation processes, defined based on the size of the material they will remove from the solvent. Ranking from the largest to the smallest pore size, these are microfiltration (MF), ultra filtration (UF), nano filtration (NF) and reverse osmosis (RO). As the pore size gets smaller, the hydrodynamic resistance of the membranes increases, which necessitates the application of higher pressures across the membranes. MF is well understood as the fine end of the particle filtration, with pore sizes ranging from 0.05 to 10 µm, which are visible under a microscope. UF, NF and RO membranes do not have holes as such, but rely on higher pressures to defuse a liquid or gas through the molecular structure of the medium. The molecular spacing can be controlled during manufacturing to permit the creation of membranes having any desired molecular weight cut-off (MWCO) level, which is a means of determining the size of the largest molecule able to permeate a UF, NF or RO membrane [24]. Table 3.2 shows the ranges of material sizes retained, the pressures required, the typical fluxes obtained and the separation mechanisms used by each membrane separation process.

Table 2-7: Typical operating parameters and membrane materials used for pressure driven process [24]

Process	Membrane		Typical operating ranges	
	Material	Structure	Pressure	Recovery
Microfiltration	Polymers Ceramics metals	Porous	0.5-2 bar	90 - 99.9
Ultra filtration	Polymers Ceramics	Asymmetric	1-10 bar	80 – 98
Nano filtration	Polymers	Asymmetric	10-40 bar	50 – 95
Reverse Osmosis	polymers	Asymmetric composite	30 – 70 bar	30 – 90

Table 2-8: characteristics of separation process [24]

Process	Separation principles	Pore size range (nm)	MWCO	Retention characteristics
Microfiltration	Size	50 - 1000	Absolute, Nominal	Absolute, Nominal
Ultra filtration	Size, charge	1 - 50	>1000	MWCO
Nano filtration	Size, charge, affinity	0.6 - 1	200 – 1000	Rejection, MWCO
Reverse Osmosis	Size, charge, affinity, diffusion	<0.6	<200	Rejection

2.5.5 Nano filtration System

NF, which is a relatively recent type of membranes, possesses properties in between those of ultra filtration (UF) and reverse osmosis (RO). This promising technique has attracted increasing attention over recent years due to the development of new applications in the several areas such as textile industry (removal of dye from waste rinse water), paper, plating industry (limiting of consumption of clean water by recycling waste water as far as the discharge waters don't contain too high amounts of mono valent ions), drinking water production and etc. [22].

In general NF has two distinct properties: the first property is the pore size of the membrane which corresponds to a molecular weight cut off value of approximately 200-1000 g/mole. Therefore, the separation of components with these molecular weights from higher molecular weight components can be accomplished. The second property is that NF membranes have a slightly charged surface, because the dimensions of the pores are less than one order of magnitude larger than the size of ions. Charge interaction plays a dominant role. This effect can be used to separate ions with different valences [22].

2.5.5.1 Mechanism of Transport

Separation by NF membranes occurs primarily due to size exclusion and electrostatic interactions [47]. In NF, the distribution of a non-charged solute at the boundary layer/ membrane interface is considered to be determined by a steric exclusion mechanism (sieving). Steric exclusion is not typical for nano filtration and can also be applied to ultra filtration and microfiltration too. Due to its size, a solute only has access to a fraction of the total surface area of a pore; this causes a geometrical exclusion of the solute from the membrane.

Membrane manufacturers use specifications set by a nominal molecular cut-off (MWCO) for their products for use in process design [23, 24].

MWCO is defined as the molar mass that is 90% rejected by the membrane. The MWCO values of the membrane are used in absolute term. For instance, if the membrane is gauged to be 25,000 MWCO, it means that more than 90% of the solutes with molar mass larger than 25,000g/mol are rejected [23,24].

2.5.5.2 Nano membrane Applications

Industry	***Application***
Food	Demineralization of whey, Demineralization of sugar solutions, Recycle of nutrients in fermentation processes ,Separation of sunflower oil from solvent, Recovery of regeneration liquid from discoloring resins in sugar industry
Textile	Effluent treatment, Removal of dyes from waste water , Recovery of water and salts from waste water
Food	Boiler feed water, Raisin rinse water, Sugar recovery, Evaporator condensate, Water recovery
Land fill	Removal of phosphate, sulphate, nitrate and fluoride
Agriculture	Removal of algal toxins, Purification of landfill leachate, Removal of selenium from drainage water
Water production	Removal of degreasing agents from water, Removal of precursors of disinfection byproducts, Hardness removal, Removal of natural organic matter (colour), Removal of pesticides, Removal of heavy metals (As, Pb), Fe, Cu, Zn and silica, Treatment of brackish water
Chemical	Sulfate removal preceding chlorine and NaOH production, CO_2^- removal from process gasses, Preparation of bromide, $CaSO_4$ precipitation, Recovery of caustic solutions in cellulose and viscose production

Table 2-9: Overview of Possible Applications of NF in Various Industries ***[21]***.

2.5.6 Operational Characteristics of Membrane

There are parameters like inlet flow rate, pressure, concentration, temperature etc. which must be measured and/or controlled if optimum operating results are to be realized from membrane system. Some of operational characteristics are discussed below.

2.5.6.1 Pressure*:* The operating pressure affects solvent flux and affects rejection, respectively. Because operating pressure directly affects the driving force for solvent across the membrane, higher pressure will result in higher flux. However, because more solvent has passed through the membrane at higher pressure, the absolute feed concentration in permeate is lower, so it appears as if the feed passage decreases and the feed rejection increases as pressure increases.

2.5.6.2 Concentration

Osmotic pressure is a function of the type and concentration of salts or organics contained in feed water. As (salt, organic) concentration increases, so does osmotic pressure. The amount of feed water driving pressure necessary to reverse the natural direction of osmotic flow is, therefore, largely determined by the level of salts in the feed water.

2.5.6.3 PH: affects the stability of both polyamide composite and cellulose acetate membranes. Cellulose acetate membranes are stable over pH range of 4 to 6, due to hydrolysis at higher and lower pH. (Hydrolysis is a chemical reaction where a compound is broken down by reaction with water). Polyamide composite membranes also react with water, but the pH range of nominal application is much broader, ranging from as low as 2 to as high as 11, depending on the specific membrane and manufacturer. Acceptable operating pH is a function of temperature, with higher temperatures requiring narrower pH ranges of operation [44].

2.5.6.4 Temperature: The temperature influences the system flux and rejection performance. Water flux is linearly proportional to the water temperature. For every 1°C change in temperature, there is a 3% change in water flux. This occurs because the lower viscosity of warmer water allows the water to flow more readily through the membranes. At temperatures greater than 45℃, the structure of the membrane itself changes. The membrane anneals, meaning it gets denser. As a result, it becomes more difficult to force water through the membrane. At temperatures greater than 45℃, flux goes down and rejection goes up, assuming constant driving pressure [41].

2.5.7 Membrane performance losses and Cleaning

The major problem with the application of membrane technology is the flux decline, which is defined as the reduction in the volume of the fluid passing through the membrane per unit time and area. Flux decline is a natural consequence of filtration since the concentration of the retained materials accumulating reversibly and/or irreversibly at the membrane surface, increase with time. Flux decline occurs as a result of two phenomena; concentration polarization and fouling. Concentration polarization is totally reversible and diminishes by the release of the driving force, whereas fouling can either be reversible or irreversible due to adsorption, precipitation, and pore blocking and cake formation. The two phenomena are not completely independent of each other since fouling can also result from concentration polarization. The extent of fouling is strongly dependent on the type of the membrane processes involved and the feed employed. The flux decline is most severe in MF and UF membranes. There are many factors affecting membrane fouling. Fouling depends on the membrane material, bulk concentration, solution conditions (pH, ionic strength), and operating parameters (Trans membrane pressure, cross-flow velocity, temperature, inlet flow rate) [22, 24]. The fouling causing components of the feed solutions are the soluble inorganic compounds, colloidal or particulate matter, dissolved organics, chemical reactants and microorganisms. When fouling occurs, the membrane requires cleaning to restore the membrane properties. The degree of membrane fouling determines the frequency of cleaning, lifetime of the membrane, and the membrane area needed, and this will have a significant effect on the cost, design and operation of membrane plants [24]. Reduction in flux means decreased productivity, therefore a proper pre-treatment stage is often necessary in order to minimize it. Choosing a suitable membrane and the correct module type as well as the optimized operational conditions is also important for achieving the most efficient membrane operation. Reduced fluxes can be restored by cleaning, however cleaning procedures are generally more effective in removing foulants accumulated on the membrane surface rather than within its pores, which may lead to the occurrence of an irreversible fraction of fouling [22]. The following measures can be taken to reduce fouling for the most economical membrane operation:

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

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

2.5.7.1 Causes of membrane performance losses

- **Membrane Fouling**

Fouling is a phenomenon in which the membrane adsorbs or interacts in some manner with solutes in the feed stream, resulting in a decrease in membrane performance, i.e., lowering of the flux and/or increase in rejection of solutes by time. Fouling is usually irreversible, by which it is distinguished from concentration polarization. While concentration polarization is affected by operating parameters such as velocity, pressure, temperature and feed concentration, fouling is primarily time-dependent and also partially concentration-dependent. Fouling effects can only be overcome by shutting down the system and cleaning the membrane by chemical means [22].

Membrane fouling involves the deposition of suspended solids; including bacteria, long chain polymers, and particles on the membrane or components within the membrane module. These foulants form a layer on the surface of the membrane that become an additional barrier for water to flow through to the permeate side of the membrane. Flux decline can be originated by fouling, which is a usual consequence of concentration polarization (CP) [24]. Hence, if the feed pressure is held constant, the permeate flux will decrease. In general, operators focus on observed permeate flux and adjust operating variables to deliver the required permeate flux. Thus, if the permeate flux is decreasing due to fouling, the operating pressure is usually increasing to overcome the additional barrier to transport and to maintain a constant observed permeate flow [21].Membrane fouling can be seen in figure(2.6) [21]. Some of the fouling mechanisms are discussed below.

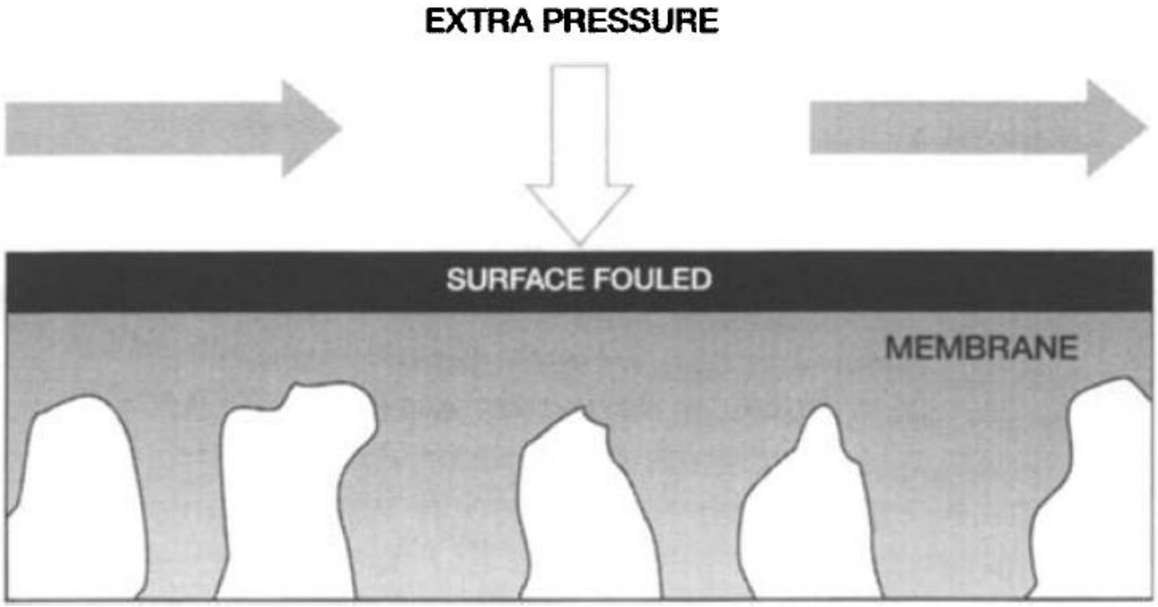


Figure 2.3 membrane fouling

- **Membrane Compaction**

Membrane compaction involves the compressing of the membrane itself that, in essence, makes the membrane "denser" or thicker and reduces the flow and salt passage through it. Compaction can occur under higher feed pressure, and water hammer. (Water hammer occurs when the RO high-pressure feed pump is started and there is air trapped in the membrane modules. On the other hand, Compaction is function of pressure, temperature and environment [48].

- ***Membrane Scaling*** involves the deposition of saturated salts on the surface of the membrane. Scale forms a layer on the surface of the membrane that becomes an additional barrier for water to flow through to the permeate side of the membrane. Typically, the operating pressure will increase to adjust itself for the loss in observed permeate flow due to scaling. Hence, observed permeate flow is not a good indicator of membrane scaling.

❖ Concentration Polarization

Concentration polarization is the build-up of solutes close to or on the membrane surface. Solute is brought to the membrane surface by convective transport; solutes larger than the MWCO of the membrane are retained by the membrane, while solutes smaller than the pores will freely or partially permeate through the membrane. Solutes not passing through the membrane will accumulate on the membrane surface, causing either an increased resistance to solvent transport or an increase in local osmotic pressure, either of which may decrease flux, and possibly a change in the sieving characteristics of the membrane [22]. In other words, Concentration polarization is the term used to describe the accumulation of rejected solute at the surface of a membrane so that the solute concentration at the membrane wall is much higher than that of the bulk feed solution. As water passes through the membrane, the convective flow of solute to the membrane surface is much larger than the diffusion of the solute back to the bulk feed solution; as a result, the concentration of the solute at the membrane wall increases. This is shown schematically in Figure (2.4). Possible negative effects of concentration polarization include

1. A decreases in water flux due to increased osmotic pressure at the membrane wall;

2. An increase in solute flux through the membrane because of increased concentration gradient across the membrane;

3. the precipitation of the solute if surface concentration exceeds its solubility limit, leading to scaling or particle fouling of the membrane and reducing water flux;

4. Changes in membrane separation properties; and enhance fouling by particulate or colloidal materials in the feed which block the membrane surface and reduce water flux [21].

If the concentration of a species is higher at the membrane surface, as is the case with concentration polarization, the amount of solute passing into permeate will be higher than the expected amount of solute based on the bulk concentration of that solute [21].

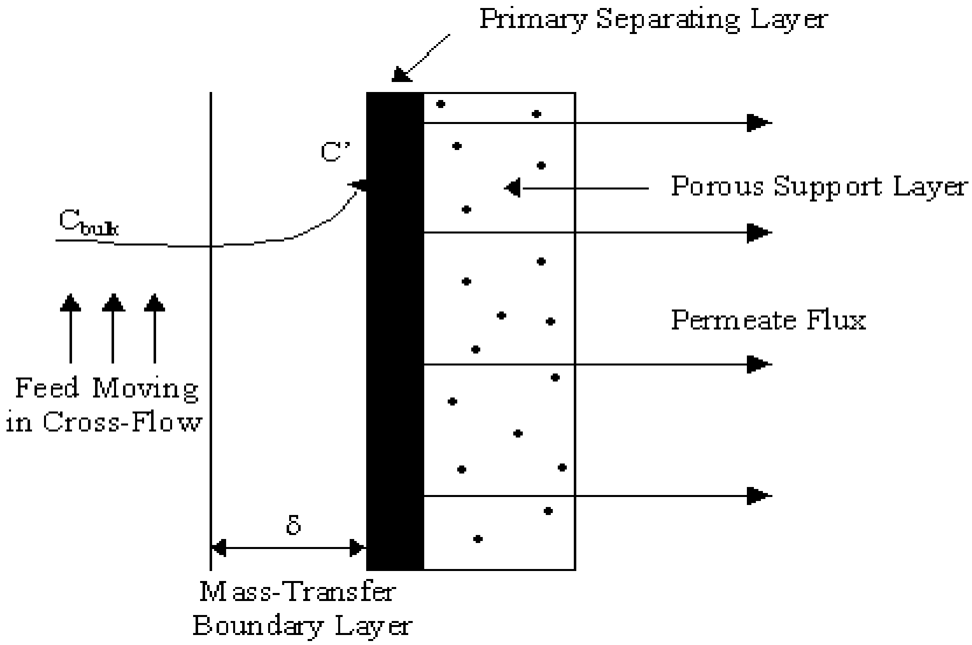


Figure 2.4 Concentration Polarizations [46].

2.5.7.2 Membrane cleaning

Membranes should be cleaned when the normalized permeate flow drops by 10% - 15% from initial stabilized performance or when the differential pressure increases by 10% - 15% [21]. Waiting too long to clean can result in irreversible fouling and/or scaling of the membrane. Membranes with good pretreatment are expected to be cleaned about 4 times per year or even less.

3. MATERIAL AND METHODS

3.1 Materials

3.1.1 Dye House waste water Sample

For this research textile wastewater was brought from dyeing unit of Yirgalem Addis Textile Factory. One wastewater samples from one dyeing unit, which was dyeing cotton fabric with heavy (dark) shade was taken. To prevent the contamination of the dye-house waste with wastes of scoring, bleaching and other operations, the samples were taken at the discharge end of the dyeing machine. The recipe of the dyeing unit wastewater is shown in Table 3-1 below.

Table 3-1 Type and recipes of dye house wastewater sample taken from Yirgalem Addis textile factory P.L.C

Color	Red
Shade depth	Dark(deep)
Recipe	Reactive red 3BS, 4.4% (5.5 g/L)
	Salt ,80g/L
	Soda ash, 6.25 g/L
	Caustic, 2.5 g/L

3.1.2 Membrane modules and machines

All experiments were conducted on a pilot plant scale membrane unit .A test unit is arranged as shown schematically in Figure (3.1) and, photographically in Figure (3.2).

Arm field lab scale UF/RO membrane separation unit has a tubular module which can accommodate six one meter and 20centimeters membranes in series. Out Of the six tubes, only two of them were used for this research.

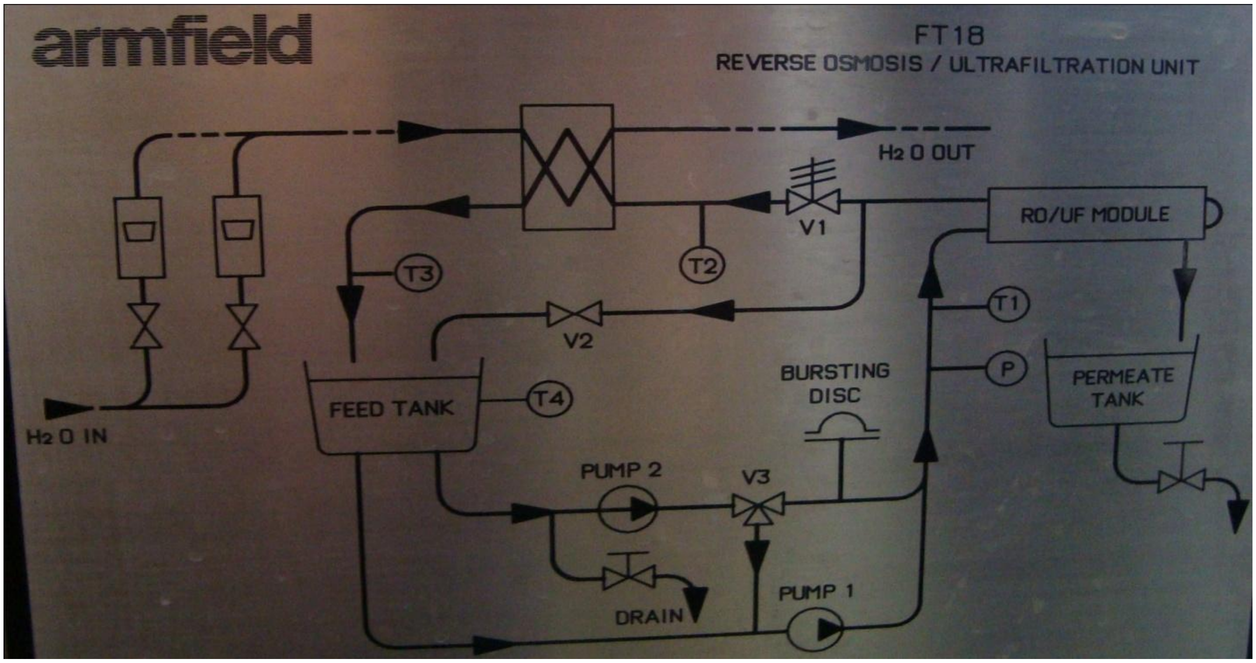


Figure 3-1 Flow diagram for Arm field lab scale UF/RO membrane module

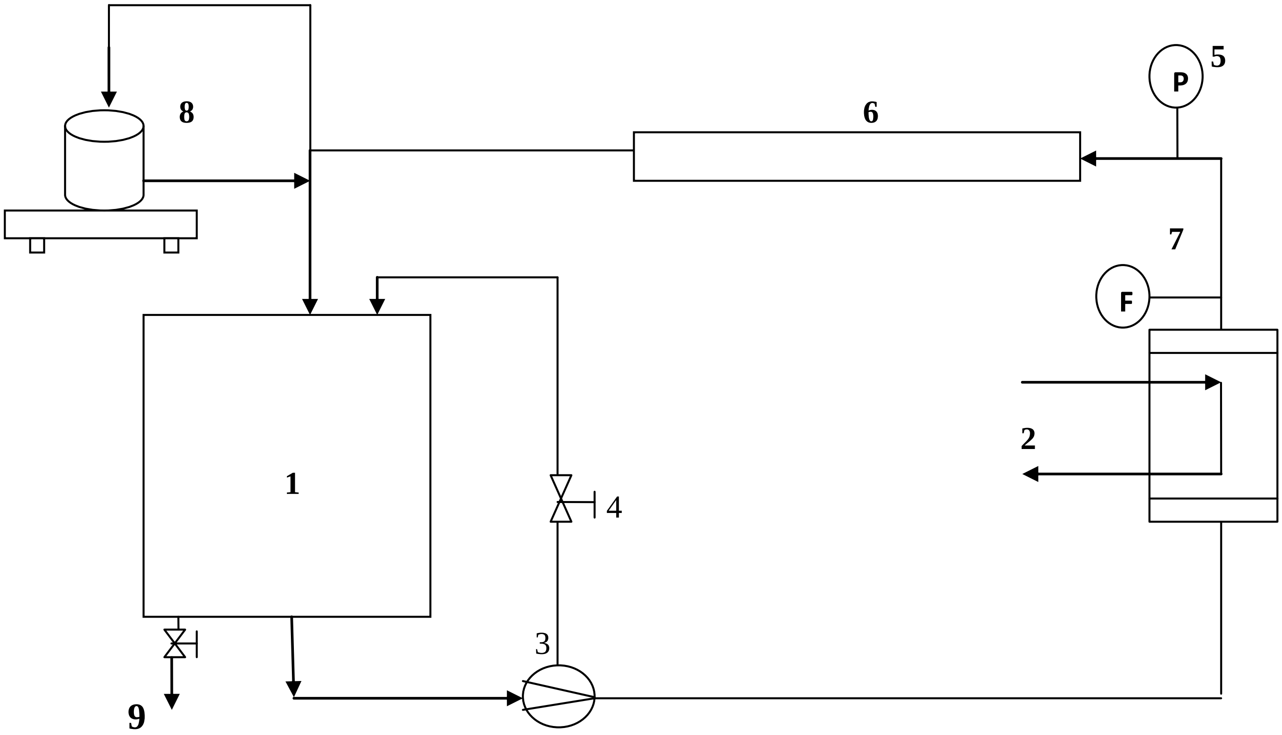


Figure 3-2 UF/RO experimental unit. (1) Feed tank, (2) heat exchanger, (3)pump, (4)by-pass control valve, (5)pressure gauge, (6)membrane module, (7)flow meter, (8) balance and (9) discharge valve.

3.1.3 Membranes

The pressure driven membranes are the heart of the pilot plant. In the present work one type of membrane (NF) AFC 30 membranes (10 in numbers) in two series were used. Each membrane was mounted in turn into stainless steel housing. The characteristics of NF membranes are shown in Table 3.1 below.

Table 3.2 Characteristics and specifications of AFC 30 NF Membranes

Membrane type	**working pressure(bar)**	**Construction materials**	**Internal diameter(mm)**	**Length (m)**	**Effective length(m)**
AFC 30	Max.- 40	polyamide	12.8	1.20	1.10

3.1.4 Filter press and BECO depth filter sheets

There have been several approaches for pre filtration of textile wastewater including conventional methods like coagulation, filtration, as well as microfiltration (MF) and ultra-filtration (UF). There has been a shift in trend to MF in the pre-treatment stage as it is economically more attractive as compared to conventional methods [22].However, in this investigation,

Filter press with Beco steril 40 filter sheets (retention rate 0.4µm and thickness 3.8mm) was used to serve as pre filter for the textile waste water to get rid of suspended solids (available and suitable filtering mechanism in school of chemical and bio engineering lab). (Shown in figure 3.3 below)

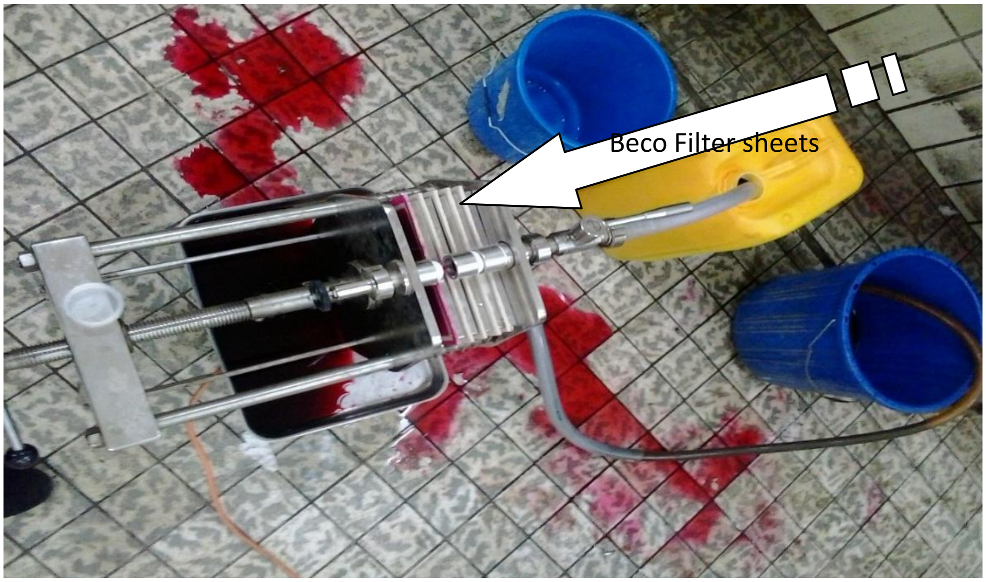


Figure 3-3: Filter press set up

3.1.5Chemicals

3.1.5.1 Dye stuff

Reactive red 3BS was used to do the calibration curves for the spectrophotometer measurements. Reactive read 3BS has the following molecular formula and weight.

Molecular Formula: $C_{31}H_{19}ClN_7Na_5O_{19}S_6$ **[**55**].**

Molecular mass: 1239.77 g/mol [55].

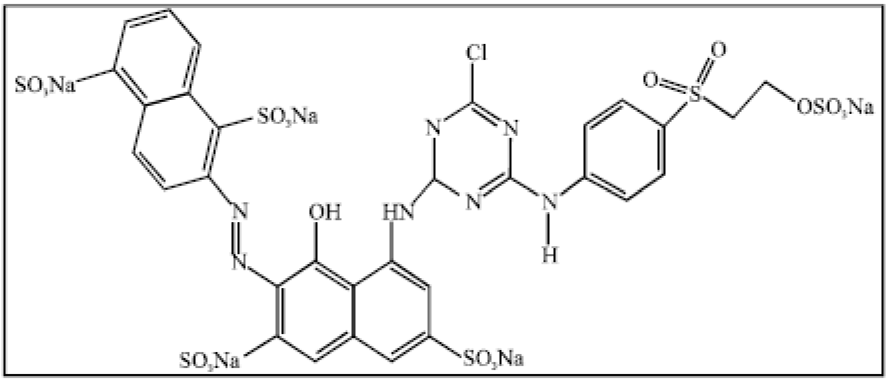


Figure 3-4 chemical structure of reactive red [54]

3.1.5.2 Auxiliary Chemicals

Chemicals	importance
Caustic	To adjust PH for BOD measurement
Phosphoric	For membrane cleaning
Hydrogen per oxide	For membrane sanitation

Table 3.3: auxiliary chemicals

3.1.6 Analytical instruments

UV/Visible spectrophotometer was used to detect the color of the wastewater; digital P^H meter was used for PH measurement. Oxi-Direct BOD measuring instrument and some reagents were used to measure BOD of the wastewater samples and permeate of the real wastewater. HANNA COD reactor, nano color spectrophotometer, and reagents were used for COD measurement. To measure total solids (TS) crucible, oven, desiccators and weighing balance were used. Turbidity was measured using HACH 2100N turbid meter.

3.2 Methods

3.2.1 Experimental procedures

The experiments were carried out in the following steps:

1. The characteristics of the dye house wastewaters (i.e. their BOD, COD, TS, turbidity, pH and color) were determined using the analytical instruments so as to know the degree which the dye-house wastewater is far from the reusable quality and even from the standard discharge limits.
2. New tubular membrane was first cleaned with hydrogen peroxide (0.05%v/v) based on the plant total volume at ambient temperature for 50 minutes (based on manufacturer recommendation)
3. Stabilization of membrane and initial water flux at different pressures.(see Appendix 4)
4. Pre -filtration of the textile dye house wastewater using press filter Beco filter sheets to remove suspended particles.
5. Real Dye wastewater in deep shade was brought from yirgalem textile. It was difficult to find the wastewater in the form of dark, medium and light shade. Thus, sample was

prepared by diluting the wastewater in 1/3, 1/2, 1(no dilution) by volume of tank (6.5L), In order to study the effect of dye concentration on permeate flux and dye removal of the membrane. The dilution was performed by mixing of the waste water with distilled water. The preparation was done in the feed tank.

6. In order to study the performance of the nano filtration of the textile wastewater solution, AFC 30 membrane was used. The process was run under complete recycling mode (constant concentration mode), i.e the feed concentration is constant throughout the run. Because the solution and permeate were recycled in the feed tank. The flux measurements were made at fixed time interval until steady state was reached. The experiments were carried out at different pressures 10, 20 and 30 bars. Therefore, for each individual concentration of the dye, three different pressures were applied in turn. In addition three different feed flow rates (0.38, 0.62 and 0.86m^3/h) were investigated with the above concentrations. The feed pH was left constant with the pH of the real waste water. Temperature was uncontrollable parameter so the experiment was carried out in constant temperature.
7. Cleaning of the membrane, after each run (10, 20 and 30 bars), Membrane chemical washing was done based on the manufacturer's recommendation. Fresh wastewater feed was used after each cleaning. During cleaning Phosphoric acid was used at normal temperature re-circulated for 30 minutes at 20 bars and 0.62m^3/h feed flow rate (average pressure and average flow rate). The procedure were:
    - Flushing with water
    - Flushing with water
    - Phosphoric acid and finally flushing with water.

3.2.3 Sample Analysis

Samples of permeate, concentration and raw wastewater were collected during experiments and were analyzed using the above analytical instruments. In addition, permeate of the membrane were collected and measured using weight balance after each run. All the experiments were carried out based on Standard Method. See (Appendix 2).

The color which is a function of concentration was determined at a dominate wave length of reactive red dye (540nm) by spectrophotometric method. Dye concentration detection, for all cases was done using samples of known Dye concentration calibration curves. (Appendix 1) From the curves using the equation found and depending on the sample, the unknown concentrations were obtained by inserting known values of absorbance in the equation found in appendix 1.

- The dye removal of the membrane was determined is calculated as [22];

$$\mathrm{R} = 1 - \frac{\mathrm{Cp}}{\mathrm{Cf}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(2)}$$

Where, R: retention

Cp: solute concentration in the permeate

Cf: solute concentration in the feed

The value of R varies between 1 and 0, which means complete retention of the solute; means the solute and the solvent pass through the membrane freely.

- The permeate flux (Jw) of the membrane is defined as:

  Jw = $\boldsymbol{Qp/A}$……………………………… ………………………………… (3)

Where: $Qp$is the permeate flow rate and A is the membrane area.

3.2.3 Experimental Design

In this experiment, factorial design method was used for planning the experiments because of its reliability in finding out the effects and interactions between the controlled variables of the operating system. According to the method:

- The total number of experiments should be defined.
- The number of controlled variables (i.e. factors) should be defined as shown.

The number of levels of each factor according to the following relation:

N = L^F……………………………………………………….. (4)

Where N = no. of experiments, L = levels and F = no. of factors

The factors were working pressure, inlet flow rate of the wastewater and concentration of the dye in the wastewater. Each with its respective levels is shown in table 3-4 below.

To show the effects of factors (i.e. working pressure, inlet flow rate and concentration) on permeate flux and dye removal, full factorial method of experimental design with three levels was done. The levels for pressure are the minimum working pressure (10bar), the average working pressure (20bar) and the maximum working pressure (30bar) of the membrane, were taken. The levels for inlet flow rate are the minimum flow rate of the machine (0.38m^3/h), the maximum technically feasible flow rate of the machine (0.86m^3/h) and an intermediate value between them (0.62m^3/h). And the levels for dye concentration were the concentrations of the dye as stated earlier designated as light shade, medium shade, and dark shade of real dye house wastewater.

Table 3-4 Factors for experimental design and their levels

Factors	Level 1(-1)	Level 2(0)	Level 3(1)
Working pressure(bar)	10.00	20.00	30.00
Inlet flow rate(m3/h)	0.38	0.62	0.86
Concentration (mg/L)	82.67	146.1	269.13

The Response variables were permeate flux and percent of dye removal

The combination of three factors, each with three levels gives twenty seven different combinations of factors as shown in Table 3-5.

Table 3-5 different combination of factors for experimental design

Experiment No	Working pressure	Inlet flow rate	Concentration
1	-1	-1	-1
2	-1	-1	0
3	-1	-1	1
4	-1	0	-1
5	-1	0	0
6	-1	0	1
7	-1	1	-1
8	-1	1	0
9	-1	1	1
10	0	-1	-1
11	0	-1	0
12	0	-1	1
13	0	0	-1
14	0	0	0
15	0	0	1
16	0	1	-1
17	0	1	0
18	0	1	1
19	1	-1	-1
20	1	-1	0
21	1	-1	1
22	1	0	-1
23	1	0	0
24	1	0	1
25	1	1	-1
26	1	1	0
27	1	1	1

3.2.4 Statistical Analysis

Each experiment was done two times to insure the reproducibility of the data. The results obtained are plotted graphically using Microsoft Excel to make the result of the experiment easily understandable and to show the relationship between dependent and independent variable clearly. Moreover, ANOVA was run by means of Design-Expert® 7.1 software and a confidence interval of 95% was used. All statistical analysis were compared and treated as being significantly different, if the *P*-value was less than 0.05. The entire collected ANOVA results for each response are presented in Appendix 3.2 and 3.3.

4. RESULT AND DISCUSSION

In this section, we discussed on the findings obtained from removal of reactive dye from textile wastewater .different experimental parameters were investigated to see their effects on the response variables (permeate flux and dye removal). Below, the experiments executed and their results are presented, analyzed and discussed. All flux, pressure and concentration data are reported in L/m^{2}h, bar and mg/L, respectively. Raw data of the experiments and the response average result

4.1 Characterizing of the textile waste water

The real dye house wastewater after it has been analyzed using the analytical instruments shows the following characteristics.

Table 4-1 Characteristics of dye house wastewater sample

Sample type	pH	COD(mg/L)	BOD(mg/L)	TS(mg/L)	Turbidity (NTU)	Color concentration (mg/L)
Red	10.2±0.05	8490±0.75	863±1.94	9440±1.02	30.3±0.12	269.13

The values in Table 4-1 shows that the dye house wastewaters are highly alkaline (a pH value more than 10) which can be hazardous to if it is disposed directly to the environment without treatment. The COD values are also much higher and are very far from the free discharge limit shown in Table 2-5. Though the BOD values are relatively low as compared to other wastewater types, they are still above the free discharge limit. Turbidity and color of the wastewater are extremely higher than the free discharge limit. Especially the color, even the low concentration wastewater is highly colored but the discharge regulation states wastewater to be discharged should be colorless. Generally the result of the characterization shows that dye house wastewaters should be treated before discharge.

4.2 Pre filtration of the textile wastewater sample

After pre filtration using lab scale filter press (Beco filter) the total solid of the textile wastewater was reduced from 9440mg/L (before) to 4080mg/L (After).

4.3 Effect of operating parameters on membrane operations

To discuss the individual and interaction effect of the operating parameters on membrane operations, assume A stands for working pressure, B stands for feed flow rate and C stands for dye concentration.

4.3.1 Effect of operating parameters on permeate flow rate

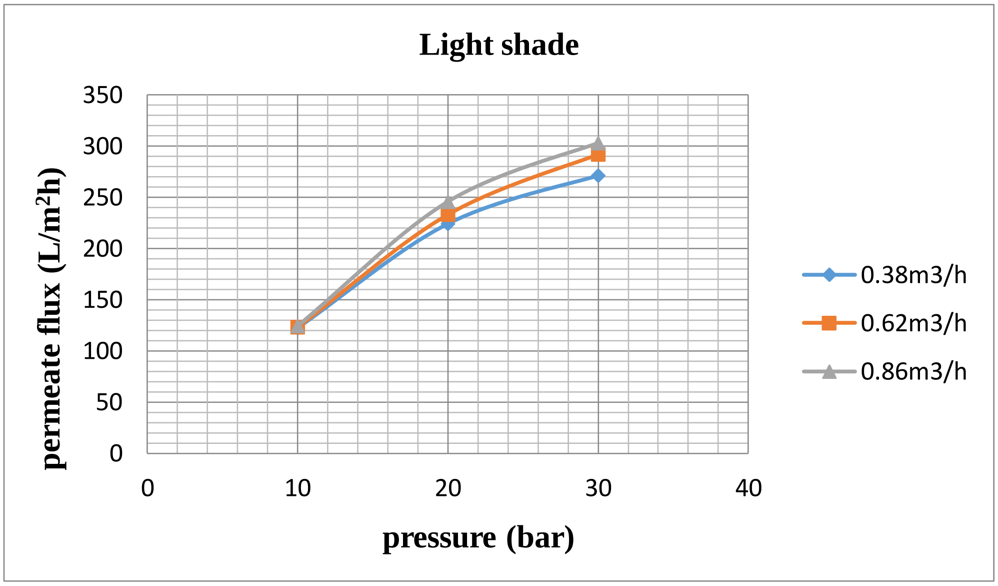
The permeate flux values were significantly affected by A (working pressure), B (feed flow rate), C (dye concentration) and the interaction AC (interaction of pressure and concentration), where $P \leq 0.05$ (Appendix 3.3).

Their individual and interaction effects on permeate flow rate are discussed separately in the following sections.

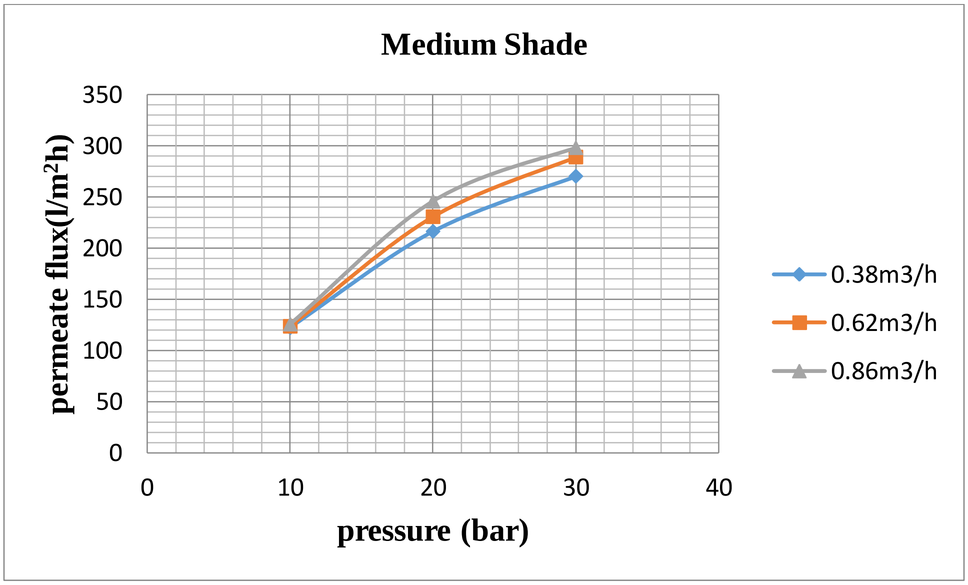
4.3.1.1 Effect of feed flow rate on permeate flux

The following three graphs show the dependence of permeate flux on the feed flow rate at different working pressures (10bar, 20bar and 30bar respectively). On each graph three different curves, representing three different concentrations, are presented)

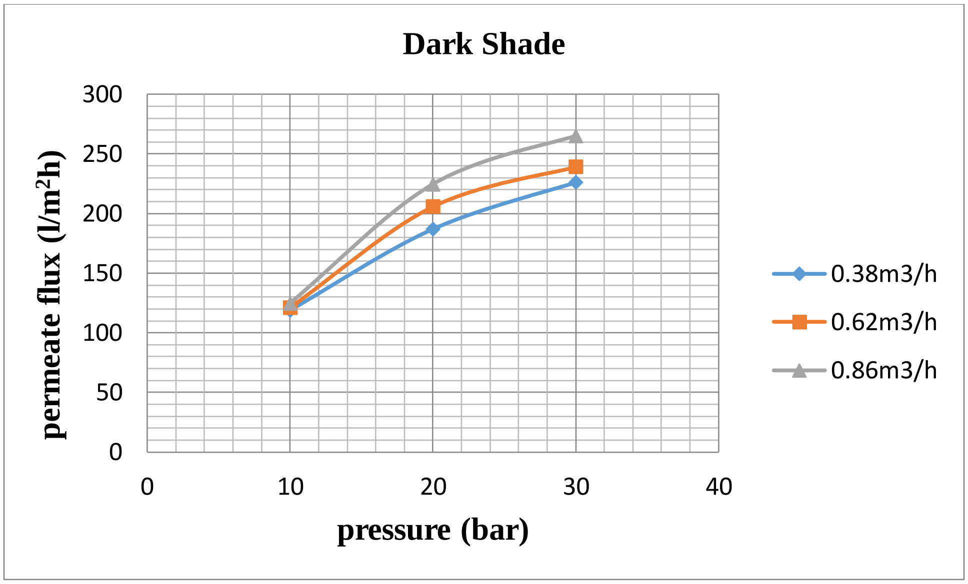
As can be seen from the graphs (figure a, b and c) below, the permeate flux proportionally increases with inlet flow rate for all the three cases and for all the different concentrations. Higher fluxes were observed for higher values of the feed flow rate ($0.86m^3/h$) at each concentration and working pressure as illustrated in the figures below. The reasons for permeate flux increase with inlet flow rate could be due to the increase in shear force exerted on the wall of the tubular membrane, which is proportional to the flow velocity and has a positive impact on permeate flow rate, and also the reduction of concentration polarization effect by the high velocity flow (usually flow at high velocity has turbulent nature). Increasing the velocity (turbulence) of the flowing stream helps to reduce concentration polarization. By increasing the cross flow one can reduce concentration polarization. This is because of an increase in the shearing stress at/near the membrane surface that redistributes the solute at the membrane surface [23]. The effects result observed in this research are the same as the findings of Abeer and Goksen [21] and [22].



(a)



(b)



(c)

Figure 4-1 Effect of feed flow rate on permeate flux at (a) light dye concentration, (b) medium dye concentration and (c) dark shade dye concentration

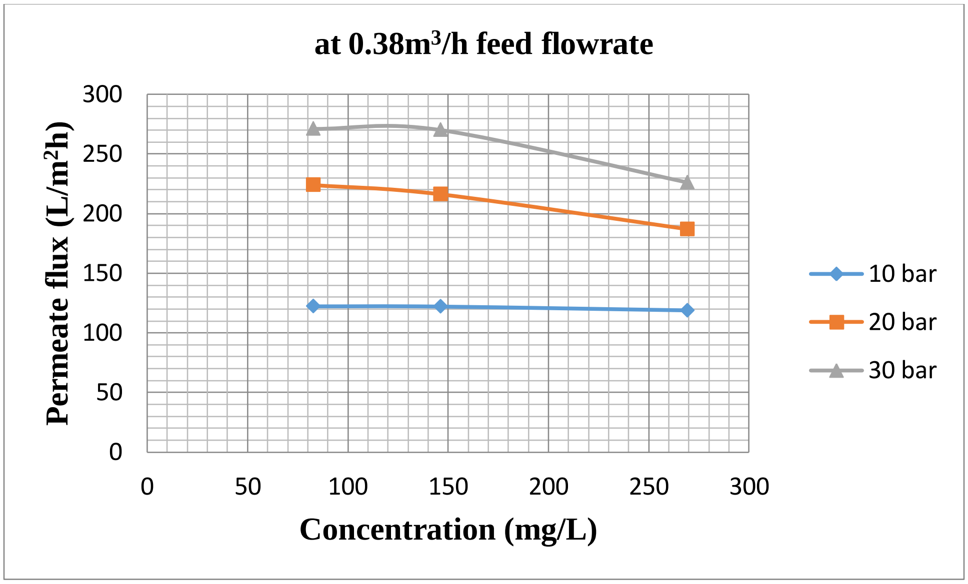
4.3.1.2 Effect of pressure and dye concentration on permeate flow rate

Figure 4.3 (a, b, and c) present the effect of both the operating pressure and dye concentration on permeate flux. It can be seen from these figures that the operating pressure has a positive impact on the permeate flux while the dye concentration has an adverse effect.

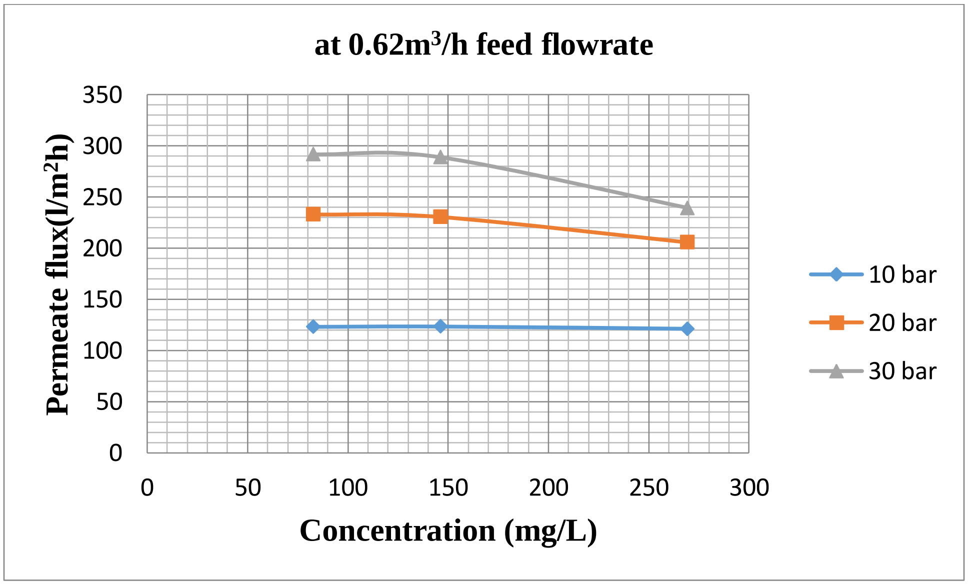
As can be seen from the graphs the higher is the feed concentration, the lower is the permeate flux; this may be attributed to increasing the concentration polarization on the membrane surface and consequently increasing the osmotic pressure. Theoretically, an increase in membrane osmotic pressure results in a decline in permeates flux. The outcome of the experiment was the same as results of Abeer Mushen,Goksen Capar and Berhanu Assefa [21],[22] and [23].

As illustrated below on the graphs, in this investigation increasing the pressure from 10 to 30 bars leads to an increase in the permeate flux. Higher flux values were obtained at 30 bars, since the increase in feed pressure will increase the driving force, overcoming membrane resistance [21].

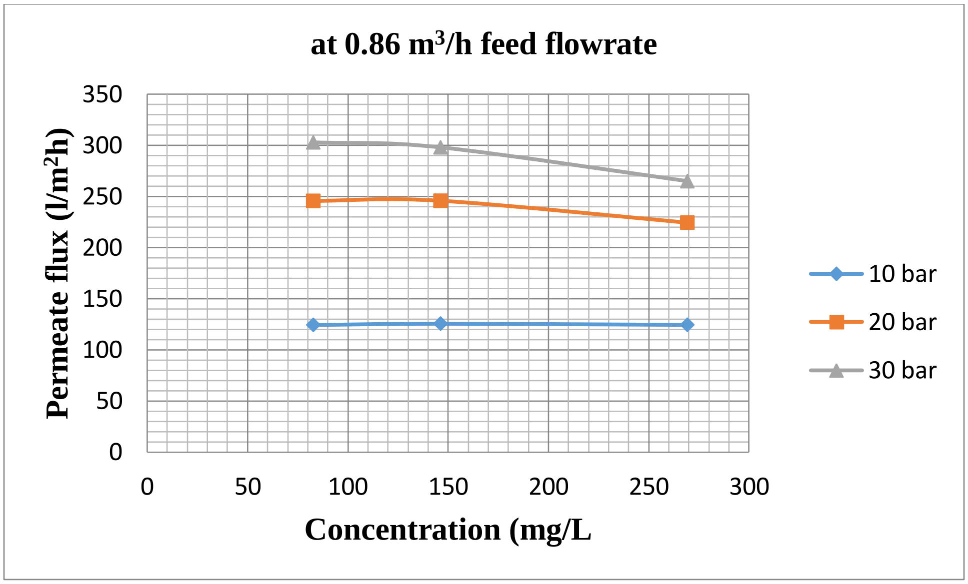
On the other hand, as can be observed from figures a, b, and c, The interaction effect on permeate flux between pressure and concentration (AC) is that as concentration increases from light shade to dark shade (82.67-269.13 mg/L) permeate flux decreases from 303.04 to 265.03m^3/h, respectively and as pressure increases from 10 to 30 bar, permeate flux in general increases. Hence, this two parameters have negative and positive interaction effect on permeate flux and requires optimization for the better permeate flow rate.



(a)



(b)



(c)

Figure 4-2 Effect of pressure and dye concentration on permeate flow rate (a) at 0.38m^3/h inlet flow rate, (b) at 0.62 m^3/h inlet flow rate and (c) at 0.86m^3/h inlet flow rate

Results of permeate flow at any point of the operating parameters can be calculated in Terms of Coded Factors as folows.(Anova results)

Permeat flux = +205.00+73.70 * A+11.27 * B-13.31 * C+7.32* A * B -11.44 * A * C+ 2.29 * B * C+0.59* A * B * C………………………………………………… (5)

4.3.2 Effect of operating parameters on dye removal

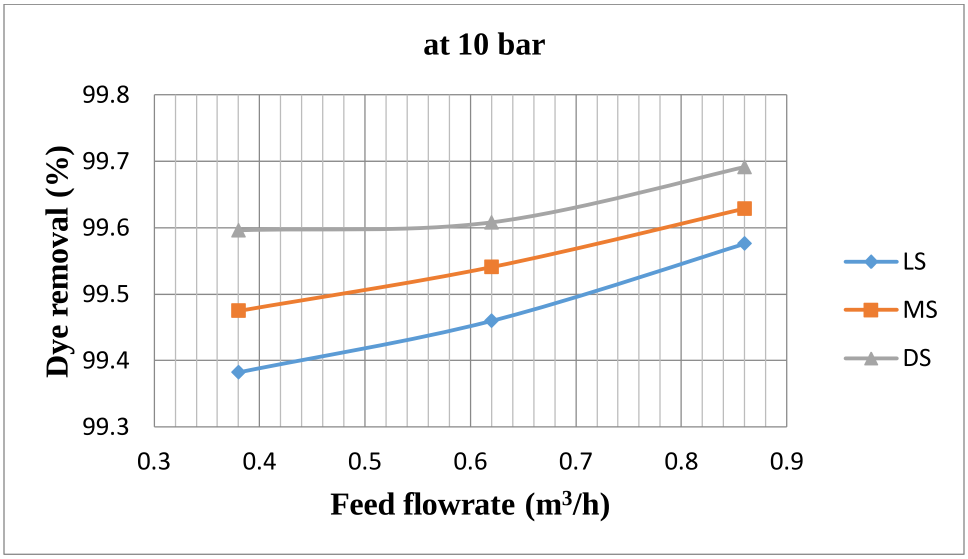
The dye removal of the textile wastewater was significantly affected by A (working pressure), B (feed flow rate), C (dye concentration) and the interaction BC (feed flow rate and concentration), where $P \leq 0.05$ (Appendix 3.2).

The three parameters individual and interaction effects are discussed below separately.

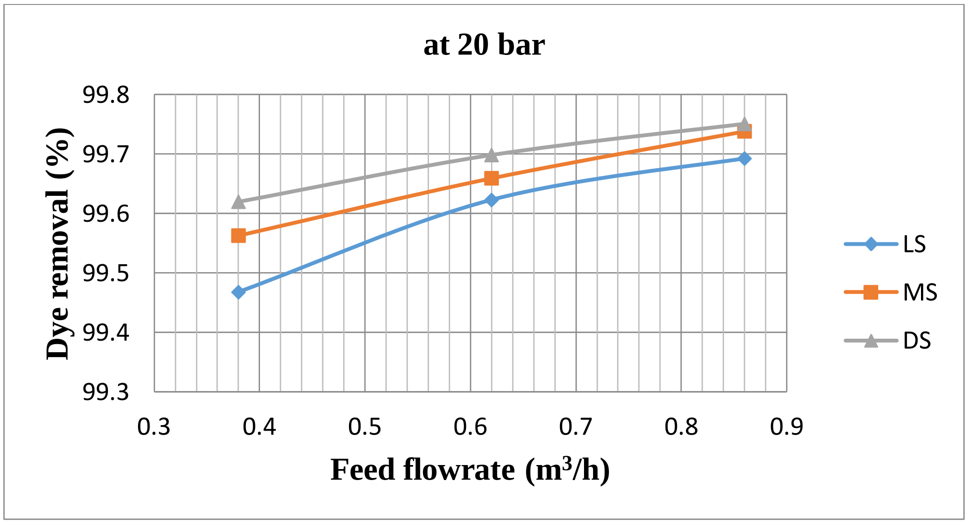
4.3.2.1 Effect of inlet flow rate on dye removal

The following three graph (figure a, b, and c) results show the effect of feed flow rate at different working pressures (10bar, 20bar and 30bar respectively). On each graph three different curves, representing three different concentrations, are presented.

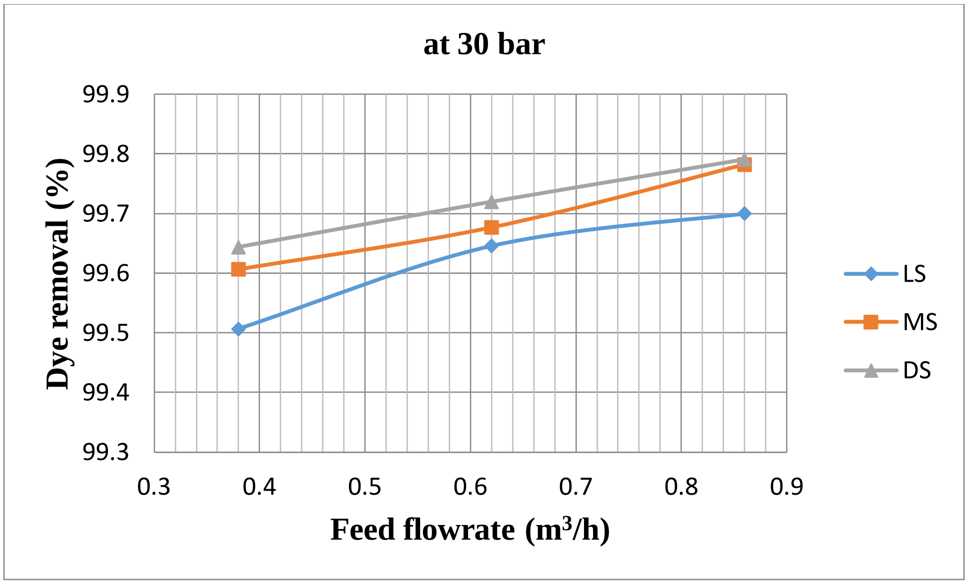
It can be observed from the graphs that as feed flow rate increases dye removal also increases. Higher percentage of dye removal was found at higher pressure and flow rates (0.86m^3/h and 30bar).This might be due to an increase in feed flow rate. Hence, when the feed flow rate or cross flow velocity is increased, the concentration polarization (the concentration gradient across the membrane) is reduced and the flux is increased. As a result, the reduction in concentration polarization may improve dye removal (dye retention).because if there is no concentration polarization more solution can pass through the semi permeable membrane and more solutes could be retained. The same effect was observed in the works of Berhanu [23].



(a)



(b)



(c)

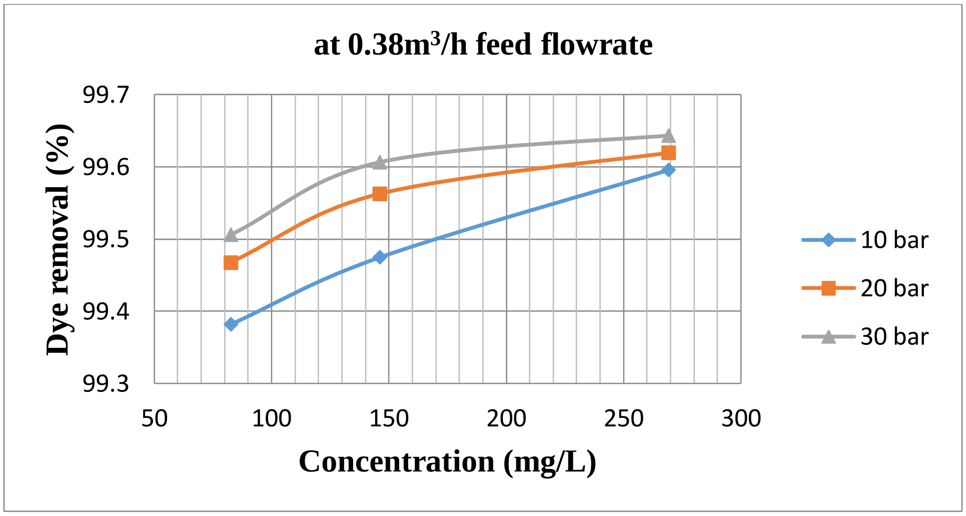
Figure 4-3 Effect of feed flow rate on dye removal for different dye concentration (a) at 10bar, (b) at 20bar and (c) at 30bar

4.3.2.2 Effect of pressure and concentration on dye removal

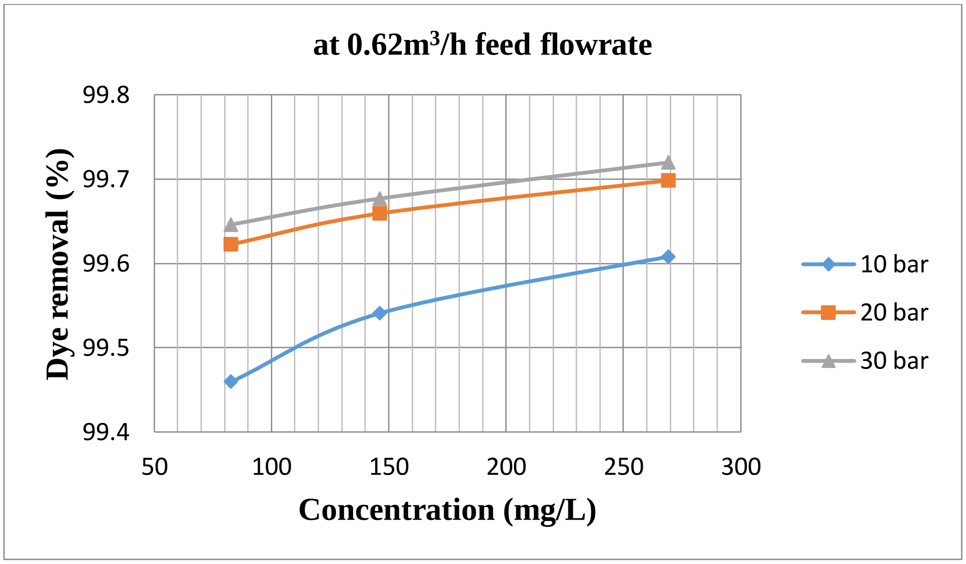
As can be seen in figures a, b, and c below, the dye removal increases in accordance with the increase in pressure. Better dye removal was obtained at 30 bar working pressure and 0.86m^3/h feed flow rate. The increase in dye removal is mainly due to; at higher pressure more water has passed through the membrane so it appears as if the dye passage decreases the dye removal increases as pressure increase. Also the membrane compaction participates to some extent in increase dye removal at higher pressure. As the membrane becomes denser due to compaction, the passage of dye through the membrane is reduced [41]. This leads to the increase in dye rejection. In addition, the deposition of dye on the membrane forms a layer on the surface of membrane that becomes an additional barrier for the flow through to the permeate side of the membrane. The operating pressure is usually increased to overcome the additional barrier to transport. These results are in agreement with the findings of earlier researchers (Ismail and Abeer) [10] and [21].

Moreover, this investigation shows, the higher the applied pressure and feed concentration the higher was the percentage of dye removal (99.7%) [21]. this might be due tighter membrane pores and deposition of particles on the pores of the membrane. Normally, a greater concentration of solutes leads to a greater polarization by concentration which, during the filtration, may lead to a higher degree of membrane clogging, which results in a greater rejection of solutes [54].

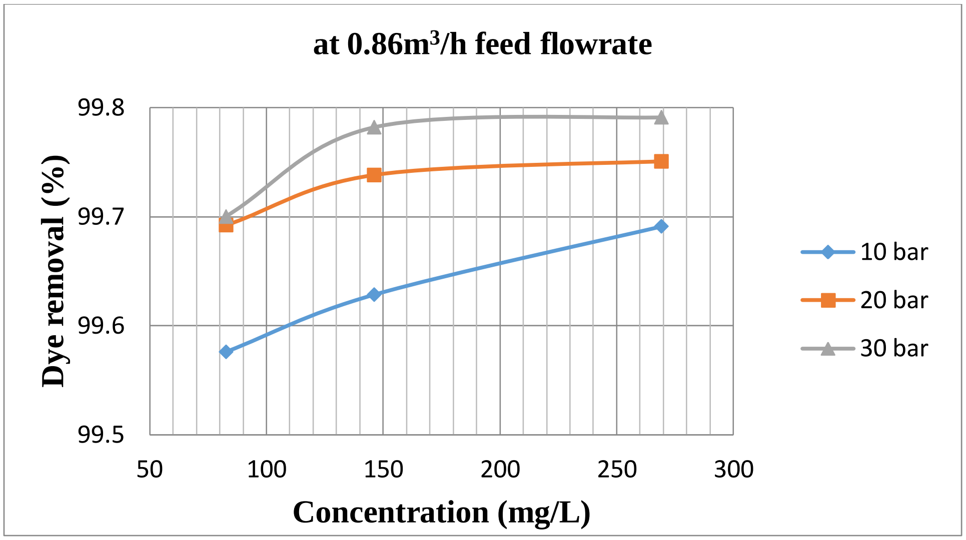
The interaction effect between feed flow rate and concentration (BC) on percentage of dye removal increases when both increases. According to figure (a, b and c) when concentration increases to the right from 82.67 to 269.13mg/L and feed flow rate increases from 0.38 to 0.86m^3/h the percent of dye removal also shows an increment from 99.64 to 99.79%.



(a)



(b)



(c)

Figure 4-4 Effect of pressure and dye concentration on dye removal for at (a) 0.38m^3/h inlet flow rate, (b) 0.62 m^3/h inlet flow rate and (c) 0.86m^3/h inlet flow rate

Textile dye percentage removal at any point of the operating parameters can be calculated in Terms of Coded Factors using the following formula.(Anova results**).**

$$\text{Dye removal} = +99.63+0.060*A+0.081*B+0.056*C+6.881E-003*A*B-0.015*A*C-0.019*B*C+6.444E-003*A*B*C \qquad (6)$$

4.4 Cleaning and performance of used membrane

In order to check the effectiveness of the cleaning procedure and to re - use the membranes, test runs of new and cleaned membrane were done at 20 bar average working pressure and 0.62m^3/h average feed flow rate (shown in the table below). New and used membranes were treated as prescribed in section 3.2.1.

For light and medium shade the cleaned membrane was used for the two runs (20 and 30 bar at 0.38, 0.62 and 0.86m3/h) and 88%, 79% and 86%, 76%, recovery was obtained respectively. This is due to the fact that the dye was diluted and less concentrated compared to the original sample. For concentrated solution three different membranes were used for the three runs. (10, 20 and 30 bar at 0.38, 0.62 and 0.86m3/h) and 74, 72.62 and 71% recovery was achieved in this investigation.

Tables 4.2 permeate flux of new and cleaned membrane at 20 bar, 0.62m^3/h feed flow rate and at normal temperature.

Type	New membrane flux(L/m^{2}h)	First cleaning (L/m^{2}h)	Second cleaning (L/m^{2}h)	Third cleaning (L/m^{2}h)	Number of cleaning
Light shade	286.66 ±0.75	271.3 ±1.64	252.68±2.5	225.96±1.04	6
Medium shade	288.94±1.34	265.75±0.88	245.81±0.67	216.80±0.84	6
Dark shade	289.53±1.25	214.19±2.2	-	-	6
		210.23±3.45	-	-	
		207.99±2.76	-	-	

4.5 Characteristics of the permeate from the reactive dye house wastewater

At the end of the experiment to see its compatibility with the environmental discharge limits, other than the dye removal and permeate flux; the real dye house wastewater permeate was treated using 0.86m^3/h feed flow rate and 20 bar working pressure.

Table 4-3 Characteristics of permeate from real dye house waste water and its comparison with the free discharge limit values

Parameter	Permeate	Dye-house Wastewater	Discharge limit	Retention (%)
BOD_5(mg/L)	51.98±0.8	672±1.72	50	92.26±0.35
COD(mg/L)	170±0.64	8348±0.75	150	97.9±0.5
TS(mg/L)	1220±0.02	4080±1.02	-	70.48±0.012
Turbidity(NTU)	7. 5	30.3±0.12	-	83.49±0.16
pH	8.2	10.2±0.05	6-9	-
Color	Slightly colored	Concentrated color(269.13mg/L)	Colorless	99±0.7

As illustrated in the table above, retention values in the last column of the table, including the BOD_5, COD, and Turbidity were significantly increased in permeate of the waste water. Color removal observed from permeate of the wastewater was excellent compared to the original one. The discharge limit states that any textile wastewater discharged to the environment must be free of any color. However, the result of this investigation shows, the waste water permeate has a very slight color when observed with naked eye. This might show the importance of using micro filtration to serve as pre filters to get rid of suspended solids that passed through the press filter which may alter the proper functioning of the membrane.

The TS in the permeate result was reduced relatively to a lesser extent this was because the salt rejection by the membrane is not significant thus the presence of significant amount of salt in the permeate increases the TS value of permeate. This will help to use the salt again with the treated wastewater [19].

On the other hand when we compare permeate results of the wastewater and the discharge limits ,some values in permeate of wastewater were less and some values were closed to their corresponding discharge limit values, this implies that membrane not only reject the color but also it brings all the parameters close to their discharge limit.

5. CONCLUSION AND RECOMMENDATION

5.1 Conclusion

This study was conducted to investigate the effect of operating parameters (operating pressure, dye concentration and feed flow rate) on membrane operations (permeate flux and dye removal) at different conditions.

In this study AFC 30 membrane was used to study the possibility of recycling textile dye house wastewater. To reuse the huge amount of water that comes from the dye house wastewaters, membrane separation technology is best candidate, since it will bring the dye house wastewater to reusable quality[14],[19].

Working pressure, inlet flow rate of and concentration of dye wastewater are influential operating parameters which have impact on permeate flow and dye removal.

Concentration of dye has negative influence on the permeate flow rate and positive effect to dye removal. Pressure and inlet flow rate, on the other hand, has positive influence on the permeate flow rate and dye removal.

In this investigation, greater than 99% dye removal and maximum permeate flow rate within the minimum fouling rate was obtained at Feed flow rate $0.86m^3/h$, working pressure at 20 bar, and dye concentration at medium concentration.

During cleaning, more than 80% and 70% recovery of membrane for diluted and concentrated waste water was found respectively. Moreover, Membrane Waste water permeates were close to the discharge limits.

5.2 Recommendation

The nano filtration process can be carried out in one, two or three steps, depending on the type of effluent which can be easily determined by its color intensity. After each experiment, washing with water and chemicals allows recovery of permeability of the membrane close to its initial status for less concentrated textile dye house wastewater. It is necessary to make further study in the following areas:

- Studying of an improved pretreatment to extend the membrane service life
- Studying of individual and combined effect of the other parameters (pH, temperature and salt) on permeate flux and permeate quality.
- For concentrated dye textile waste water bringing membrane permeability to its initial permeate was difficult. It could be the textile auxiliaries in the real textile waste water in very small concentration contribute considerably to membrane fouling. As a result, more research towards membrane fouling is necessary.

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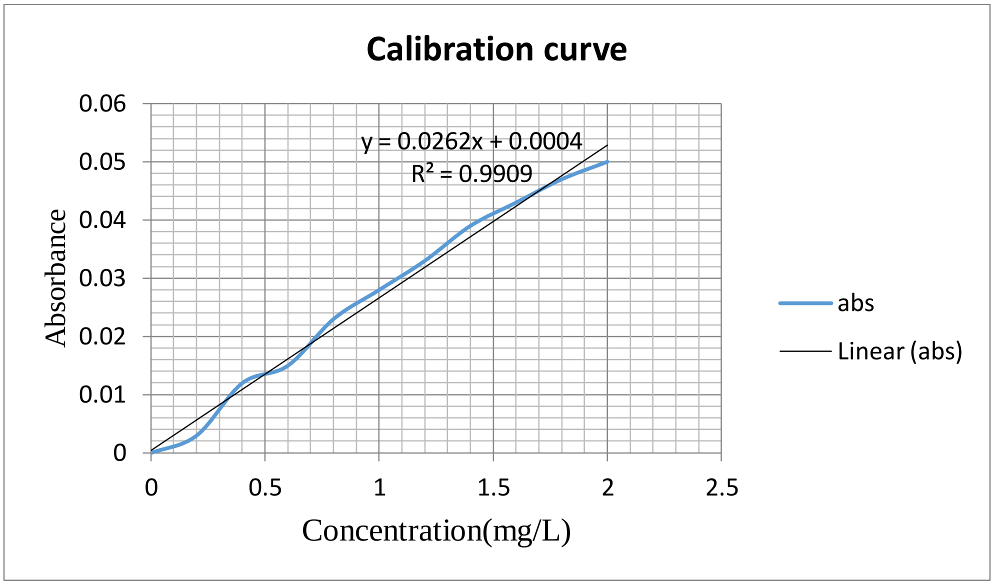
APPENDIX

Appendix 1: Calibration curve for reactive red 3BS (wave length at 540nm)



Appendix 2: procedures to characterize waste water and permeate of the membrane

BOD determination: First the pH of the solution will be adjusted to a neutral value. Then based on the BOD range of the wastewater sample 400ml (for lower range), 157ml (for medium rang) or 27ml (higher range) sample will be taken using overflow measuring flask. The samples will be introduced in to the bottles of BOD measuring unit with the help of funnel, in which magnetic stirrer is put. Then we will add some drops of nitrification inhibitor based on the sample type. The bottle then first be sealed with a rubber seal gasket in which three or four drops of KOH is added to react with the CO_2 evolved during the process; and then screwed with a cover which consists of pressure sensor and can be fit to electronic system ready for the measurement. Finally the bottle will be placed in the bottle rack and then the entire unit will be kept in a thermostat under constant temperature of 105^oC. The data will be recorded every 24 hours automatically. The value obtained at the fifth day is called BOD_5, which is mostly referred.

COD determination: the COD range of the sample should be determined first. Then for lower and medium range 2ml, and for higher range 0.2ml sample is added to the respective reagent vial then inverting each vial up and down a couple of times, the reagent will be mixed with the sample. A blank will also be prepared based on our COD range by mixing equal amount of distilled water with the respective reagent. In the meantime the HANNA reactor will be warmed up until it reaches up to 150^{o}C. Then the sample and the blank will be fed in to the reactor and stayed there for two hours at that temperature. After two hours the reactor will be off and waiting for some time, until the system cools down to reasonable temperature, the sample and the blank will be taken out and put in to a rack until it cools down to room temperature. Finally a bench photo meter will be calibrated using the blank and after that the sample will be inserted in the photo meter for reading.

TS determination: a dry crucible, after being inserted in a desiccator for a recorded amount of time, will be weighed and the result will be recorded. Then the crucible with 50ml well mixed sample will be weighed and the result will be recorded. The crucible with the sample will then be put into an oven at 150^{o}C for 24 hours after that it will be weighed, after being in a desiccator for the same amount of time as the previous. The difference between the two weights will be the amount of TS per 50ml of sample.

Turbidity determination: first the turbid meter will be calibrated using the standards. Then the sample will be introduced and the reading will be obtained.

PH determination: first make sure that the digital pH meter is calibrated by introducing the meter in to distilled water and checking whether the reading is 7 or not. If it is calibrated, insert the pH meter in sample and read the value.

Appendix 3

Appendix 3.1: Raw data of the experiments and the response average result for the full factorial 3 by 3 experimental design.

run	Factor 1 A:pressure(bar)	Factor 2 B:feed flowtare (m^3/h)	Factor 3 C:concentration(mg/L)	Response 1 dye removal (%)	Response 2 permeate flux(l/m^2h)
1	10.00	0.38	82.67	99.38±0.13	122.33±3.59
2	20.00	0.38	82.67	99.47±0.14	224.15±1.02
3	30.00	0.38	82.67	99.50±0.09	271.27±0.84
4	10.00	0.62	82.67	99.46±0.13	123.23±1.43
5	20.00	0.62	82.67	99.62±0.13	233.18±1.78
6	30.00	0.62	82.67	99.66±0.11	291.96±1.92
7	10.00	0.86	82.67	99.58±0.07	124.4±1.34
8	20.00	0.86	82.67	99.69±0.24	245.75±3.8
9	30.00	0.86	82.67	99.70±0.12	303.04±0.34
10	10.00	0.38	146.11	99.47±0.13	122.12±2.24
11	20.00	0.38	146.11	99.56±0.076	216.35±1.09
12	30.00	0.38	146.11	99.61	270.30±1.79
13	10.00	0.62	146.11	99.54±0.07	123.57±0.98
14	20.00	0.62	146.11	99.66±0.069	230.69±1.14
15	30.00	0.62	146.11	99.68±0.066	289.04±2.6
16	10.00	0.86	146.11	99.63±0.14	125.69±0.65
17	20.00	0.86	146.11	99.74±0.13	245.87±3.73
18	30.00	0.86	146.11	99.78±0.076	298.17±4.99

19	10.00	0.38	269.13	99.59±0.04	118.74±3.4
20	20.00	0.38	269.13	99.62±0.04	186.95±2.21
21	30.00	0.38	269.13	99.64±0.07	226.18±1.48
22	10.00	0.62	269.13	99.61±0.04	121.06±1.0
23	20.00	0.62	269.13	99.69±0.05	205.90±2.3
24	30.00	0.62	269.13	99.72±0.06	239.22±1.5
25	10.00	0.86	269.13	99.69±0.04	124.50±2.5
26	20.00	0.86	269.13	99.75±0.04	224.47±2.48
27	30.00	0.86	269.13	99.79±0.06	265.03±0.86

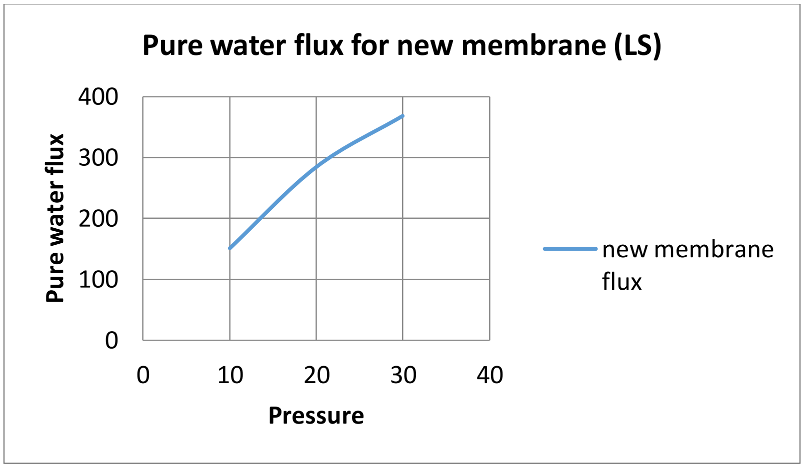
Appendix 3.2: Anova rseult for the response dye removal

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob> F**	**Remark**
Model	0.26	7	0.037	41.37	< 0.0001	significant
A-pressure	0.064	1	0.064	71.75	< 0.0001	
B-feed flowtare	0.12	1	0.12	128.68	< 0.0001	
C-concentration	0.059	1	0.059	65.69	< 0.0001	
AB	5.590E-004	1	5.590E-004	0.62	0.4398	
AC	2.922E-003	1	2.922E-003	3.25	0.0871	
BC	4.681E-003	1	4.681E-003	5.21	0.0341	
ABC	3.435E-004	1	3.435E-004	0.38	0.5435	
Residual	0.017	19	8.977E-004			

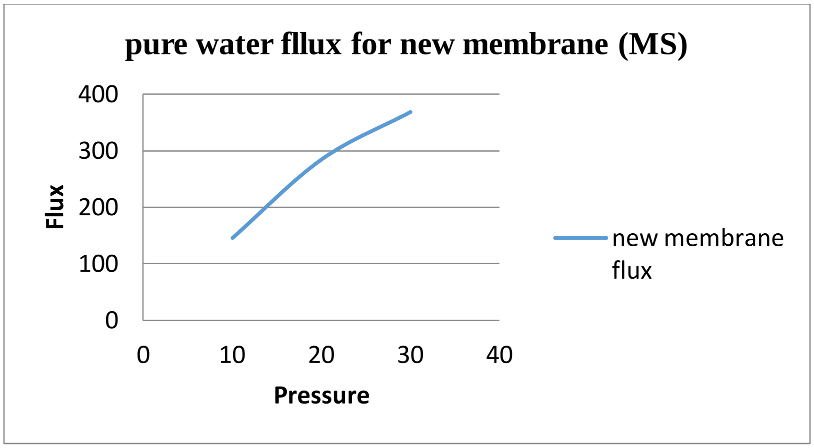
Appendix 3.3: Anova rseult for the response of permeate flux

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	**Remark**
Model	1.088E+005	7	15549.52	63.43	< 0.0001	significant
A-pressure	*96196.11*	*1*	*96196.11*	*392.39*	*< 0.0001*	
B-feed flowtare	*2250.48*	*1*	*2250.48*	*9.18*	*0.0069*	
C-concentration	*3296.95*	*1*	*3296.95*	*13.45*	*0.0016*	
AB	*632.76*	*1*	*632.76*	*2.58*	*0.1246*	
AC	*1622.54*	*1*	*1622.54*	*6.62*	*0.0186*	
BC	*64.80*	*1*	*64.80*	*0.26*	*0.6131*	
ABC	*2.92*	*1*	*2.92*	*0.012*	*0.9143*	
Residual	4657.95	19	245.16			
Cor Total	1.135E+005	26				

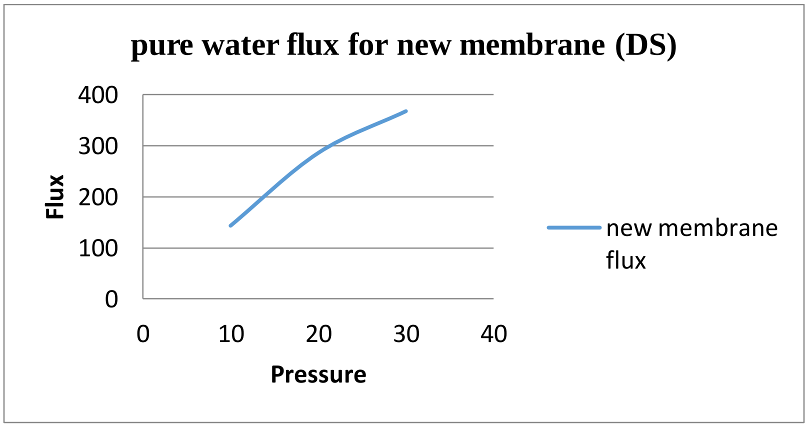
Appendix 4 Average new membrane flux used for (a) light shade, (b) medium shade and (c) dark shade



(a)


pure water fllux for new membrane (MS)
Flux
400
300
200
100
0
0
10
20
30
40
Pressure
new membrane flux

(b)


pure water flux for new membrane (DS)
Flux
400
300
200
100
0
0
10
20
30
40
Pressure
new membrane flux

(c)