RECONCENTRATION AND REUSE OF TEXTILE DYEBATH EFFLUENT USING SURFACTANT DRIVEN FORWARD OSMOSIS TO ACHIEVE MINIMUM LIQUID AND HAZARDOUS CHEMICALS DISCHARGE

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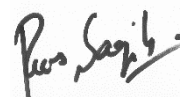
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DEDICATION

*This research is dedicated to my beloved parents **Mr. & Mrs. Raja Ishtiaq Hussain** for their endless love and support to make my dream of having this degree a reality. Words cannot adequately express my deep gratitude to them.*

Acknowledgements

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LIST OF ABBREVIATIONS

AFM   Atomic Forced Spectroscopy

AL-FS   Active layer Feed Side

CFV   Cross Flow Velocity

CMC   Critical Micelle Concentration

COD   Chemical Oxygen Demand

DS   Draw solution

ECP   External concentration polarization

FO   Forward Osmosis

FS   Feed Solution

FTIR   Fourier Transform Infrared

gMH   Grams per meter square per hour

HRT   Hydraulic Retention Time

^{1}HNMR   Proton Nuclear Magnetic Resonance

ICP   Internal Concentration Polarization

LMH   Liters per meter square per hour

MBR   Membrane Bioreactor

MD   Membrane distillation

MF   Micro Filtration

MLD   Minimum Liquid Discharge

NAOH   Sodium Hydroxide

NF   Nano-Filtration

NUST   National University of Science and Technology

OMBR   Osmotic Membrane Bioreactor

RO   Reverse Osmosis

RSF   Reverse Solute Flux

SDS   Sodium Dodecyl Sulphate

SDFO   Surfactant Driven Forward Osmosis

SEM   Scanning Electron Microscopy

TEAB   Tetra Ethyl Ammonium Bromide

TFC   Thin Film Composite

UF   Ultra Filtration

ZDHC   Zero Discharge of Hazardous Chemicals

ABSTRACT

This experimental study explores the feasibility of reconcentration and reuse of denim and polyester dyebath effluents using a forward osmosis (FO) system to achieve zero liquid and hazardous material discharge. The maximum flux achieved using sodium dodecyl sulphate (SDS) as DS was 6.3 LMH with RSF of 0.035 gMH while tetra ethyl ammonium bromide (TEAB) generated 18 LMH of flux and 0.4 gMH RSF with 100% dye rejection. This flux stability comes from the property of surfactants to form micelles and exert a stable osmotic pressure above their critical micelle concentration. The low RSF is due to the greater micelle size. A colored fouling layer was formed on the membrane active layer (AL), which was easily removed using Sodium Hydroxide and Citric Acid. According to fourier transform infrared spectra and atomic forces microscopy images of the AL, the interaction between foulants and membrane active groups did not significantly affect the physiochemical properties of the membrane. The stacked 1D HNMR (Proton Nuclear Magnetic Resonance) spectra of both original and recovered disperse dyes showed >90% similarity, which validates the concept that the recovered dyes maintained their integrity during reconcentration and can be reused in the next batch dyeing process. Importantly, the diluted DS concentration can be directly reused within the same textile industry in scouring and/or finishing processes. The processes of reconcentration and reuse developed in this study do not produce any waste or hazardous by-products and are suitable for scale-up and onsite industrial applications.

INTRODUCTION

1.1 Background

Global demand for freshwater has increased mainly due to rapid population growth, so protecting available freshwater resources is critical for ensuring a sustainable water supply (Giagnorio et al., 2019). Also, there is a dire need to investigate the reuse potential of treated wastewater for various industrial and potable water reuse applications (Manikandan et al., 2022). The textile industry is one of the largest water consumers, with approximately 230 to 270 tons of water used per ton of fabric, contributing to 20% of industrial wastewater production (Al-Mamun et al., 2019; He et al., 2020; Tavangar et al., 2019). The textile wastewater has a high pH, chemical oxygen demand (COD), and intense color, and it can deteriorate the water quality of receiving drains as well as the groundwater due to infiltration (Han et al., 2016; Khalid et al., 2021; Nawaz and Khan, 2013). The untreated disposal of textile wastewater in water receiving bodies can also negatively impact flora and fauna (Lellis et al., 2019; Saini, 2017).

The primary dyes released from the textile industry are disperse, vat, and reactive, among which 70% are sparingly soluble (Disperse and Vat dyes) (Arslan-Alaton and Turkoglu, 2008; Berradi et al., 2019). The disperse and vat dyes are first adsorbed and then diffuse monomolecularly into the fiber. They do not undergo any chemical change during the dyeing process, and their reuse is possible after recovery (Ketema and Worku, 2020). Immense concentrations (around 10 to 20%) of the disperse and vat dyes are lost during spent dyebath disposal (Ammayappan et al., 2016). Furthermore, a textile industry with a production capacity of 8000 kg per day spends US\$ 480-1200 on dyestuff (Badani et al., 2009). Hence, to improve the profitability of the textile industry, some method or technique is required which can not only remove the dyes from the dyebath effluent but can also reconcentrate them for reuse in subsequent coloring batches. The textile industrial zones are now leading towards minimum liquid and hazardous chemicals discharge solutions (Moreira et al., 2022).

1.2 Problem Statement

The minimum liquid discharge (MLD) is not possible with conventional biological or physico-chemical processes, which are dye destructive and generate hazardous sludge

by-products, and which are not safe for environmental discharge (Petrinić et al., 2015). Also, some dyes become carcinogenic on breaking down into small fragments during biodegradation (Pereira and Alves, 2012; Pinheiro et al., 2022). Hence, MLD is not achievable when mixing different process streams originating from the same textile industry.

By reconcentrating and reusing the dyebath effluent, the remaining streams can be easily treated biologically in less time, with less energy and no hazardous sludge generation. A feasible option for the reconcentration of dyebath effluent is to apply a membrane filtration based non-destructive technique that involves no hydraulic pressure. In this context, forward osmosis (FO), an osmotic-driven membrane process, can be used to concentrate valuable products from process wastewater (Im et al., 2021; Malik et al., 2021). No hydraulic pressure is needed in FO and the concentration difference between the two streams serves as the driving force (Son et al., 2020; Wang et al., 2021). Some previous studies explored dye recovery using FO, but either the dye type was not reusable (e.g., azo dyes) or the regeneration of diluted draw solution (DS) was required, which is an energy-intensive process (Li et al., 2020; Li et al., 2019). Also, the DS used in these studies (e.g., fertilizers) can reverse transport and impede the quality of reconcentrated dyebath effluent for further reuse (Mendoza et al., 2022). So, an ideal DS for dye recovery should depict lower reverse solute flux (RSF) and should be directly reused without any need for regeneration.

1.3 Significance and Novelty

Surfactants as a DS can produce a stable osmotic pressure above critical micelle concentration (CMC), and their RSF is 100 times less than NaCl, primarily due to their large molecular size (Nawaz et al., 2016; Roach et al., 2014). Based on the research gaps, there is a need to investigate the potential of surfactants as a DS for reconcentrating vat and disperse dyebath effluents for direct reuse in coloring the next batches. This will partially save fresh water and new dyes requirement for preparing the dyebath for the next batches. It can also contribute to the reduction of the per-item cost of production. In addition, being a non-destructive method, it will prevent the generation of intermittent harmful by-products and their discharge into the environment.

This study evaluated the surfactant driven forward osmosis (SDFO) process by measuring the dye rejection through the FO membrane, flux generation capability, and RSF of SDS and TEAB against the simulated dyebath wastewater as feed solution (FS). The impact of critical operational factors like temperature and crossflow velocity (CFV) was evaluated. The key foulants were identified, and the impact of their interaction with the active groups on the membrane AL were investigated. Lastly, the structural properties of recovered dyes were compared to the unused dyes to evaluate their chemical integrity and reuse potential. It is the first comprehensive and practical study in this area and can serve a pivotal role in the recovery and reuse of dyes from dyebath effluents.

1.4 Research Objectives

The key objectives of study are as follows:

1. Optimization of flux in surfactant driven forward osmosis at different cross flow velocities, temperatures and concentrations of feed and draw solutions
2. Investigation of reverse solute flux (RSF), dye reconcentration, diluted surfactant concentration and mass transfer across FO membrane
3. Characterization of fouling /scaling on membrane surface
4. Investigation of dye structural properties after reconcentration

LITERATURE REVIEW

2.1 Water Scarcity as a Global Issue

Water covers around 70% of earth among which only 3 percent is considered as fresh water. From this three percent only one third is accessible as rest is in frozen form. Every passing year lowers the global freshwater percentage due to industrial and urban development. According to statistics around 2.1 billion people do not have access to safe drinking water, the percentage of people suffering from water scarcity is shown in **Figure 2.1** (Unicef, 2019) and by 2050, 4 billion people will suffer from water scarcity (Orimoloye et al., 2021).Water availability also controls agriculture development and food security. The freshwater extraction resource is overpassing the boundary by 10% (Giordano et al., 2019).
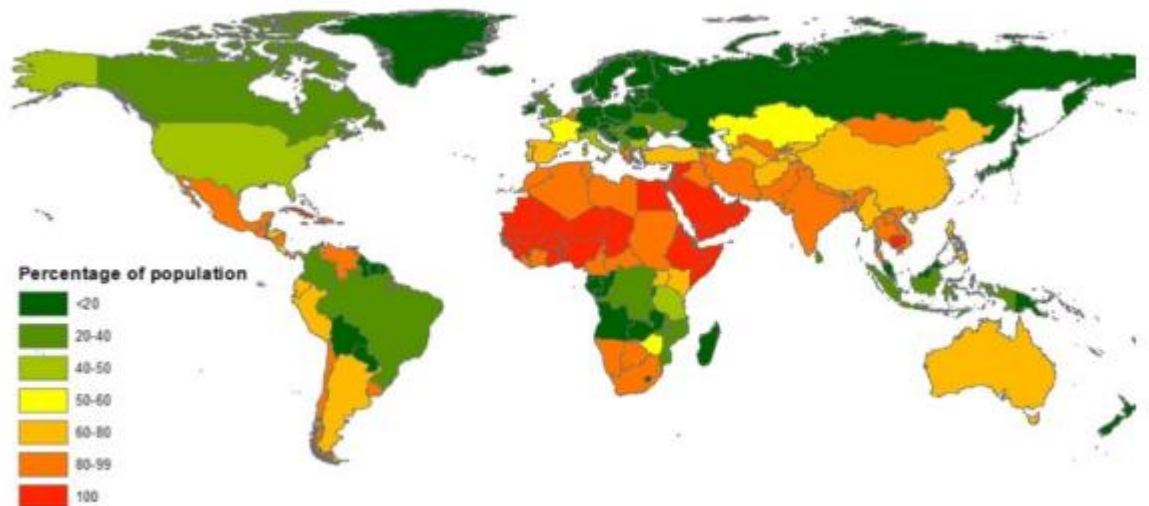
Figure 2.1: Global water scarcity faced by population at least one month per year

(Water footprint network)

Currently one of the main reasons for water scarcity is the overconsumption of water for domestic, industrial and agricultural purposes (AghaKouchak et al., 2021). Climate change and global warming is another factor affecting water scarcity. It not only contributes to rise in sea level by melting glaciers but it also increases the evaporation rate from surfaces of water bodies. According to Clausius–Clapeyron-relation, this evapotranspiration phenomenon also causes extreme weather events to occur with increased intensity and frequency (Skliris et al., 2016). Considering all these factors,

water crisis is enlisted as the largest future risk worldwide (Sharma and Soederberg, 2020). Due to alarming situation of water shortage, "clean water and sanitation" is indicated as the sixth sustainable development goal (SDG 6) which aims to improve water quality, capacity building and water use efficiency (Northey et al., 2019).

In order to mitigate the water scarcity, various options are available including conservation of fresh water, infrastructure projects and reuse/reclamation of wastewater for non-potable utilization (Capodaglio, 2021). Industrial sectors consume 21% of available total fresh water, so to cope with the water scarcity issues and environmental concerns, its treatment is hot topic for researchers and scientists. Basically, wastewater treatment has two main purposes. Firstly it is treated to fulfill the environmental compliance and secondly for water reuse which is a modern concept for overcoming water scarcity (Kharraz et al., 2022; Salgot and Folch, 2018).

2.2 Need for Wastewater Reuse

With the rising demand for water, reclamation and reuse of wastewater is becoming an ever-increasing trend over the last decade (Grant et al., 2012). The reuse of wastewater lowers the volume as well as the risk of wastewater discharged to the environment and also reduces the ecosystem pressure imposed by the withdrawal of fresh water, So reclaimed water is not considered a pure form of waste that can pollute the ecosystem, but it is actually a resource that can improve water sustainability on the planet (Tong and Elimelech, 2016).

2.3 Textile Industry as a Major Consumer of Water

On global level textile sector has a key reputation in the world's economy and satisfaction of individual needs. Textile industries are water demanding comprising of various processes involving considerable water consumption (Niinimäki et al., 2020). An average size textile mill having 8000 kg production per day utilizes 1600 metric cubes of fresh water daily. While among these statistics major portion of water is consumed by the dyeing and printing section (Kant, 2012; Khan and Malik, 2014).

According to the World Bank assessments almost 17 to 20% of worldwide industrial wastewater is produced by dyeing and finishing units of textile sector (Holkar et al., 2016). Textile effluent contains recalcitrant compounds like dyes, fixing agents. oils, latex and glues, so its handling and treatment with conventional treatment systems is very difficult (Yukseler et al., 2017). From the above discussion it can be inferred that

textile wastewater treatment and reuse can save a noticeable amount of water to overcome issues of water scarcity and protection of ecosystem.

2.4 Processes Involved in the Textile Industry

Textile industry involves different processes to convert raw fabric into a final product. **Figure 2.2** shows the major processes for wet processing in textile industry.
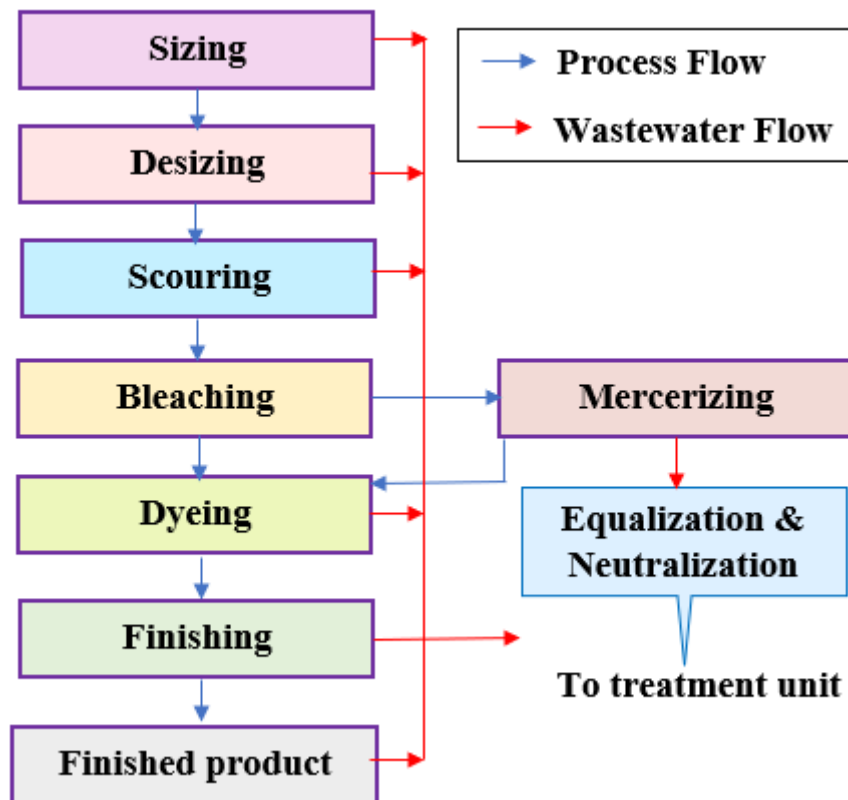
Figure 2.2: Flow chart for wet processing of fabric (Sahoo et al., 2012)

Sizing of fabric is done to enhance the stiffness by adding sizing agents including cellulose and starch. While desizing process is actually done to remove the excess amount of cellulose with the help of enzymes and alkalies. After that oil and grease is removed from fabric with the addition of surfactants. Hydrogen peroxide and sodium hypochlorite are added as bleaching agents to remove the natural color of fabric. After that strength and brightness of fabric are improved by the process of mercerizing. Acid washing is done to remove excess alkali. After that coloring and finishing of fabric are done (Sahoo et al., 2012).

Textile industry consumes a considerable amount of water at different stages, as a result waste effluent is generated from every process as shown in the above flow chart. But

the main consumers of water are manufacturing processes including dyeing and finishing. On the basis of toxic wastewater generation, it is a dominant cause of environmental and aquatic pollution in different industrial zones or settlements (Mia et al., 2019).

2.5 Nature and Type of Textile Dyes

The most significant constituent of textile industry are textile dyes and approximately 0.1 million dye types are available commercially. The worldwide production of textile dyes is around 1 million tons/year from which 0.28 million are disposed into water bodies due to process inefficiencies hence polluting both surface and groundwater. Dyes mostly consist of chromophores and auxochromes; Chromophores are responsible for the color of dye while auxochromes maintain and strengthen that color. The six major types of textile dyes are shown in **Figure 2.3**.
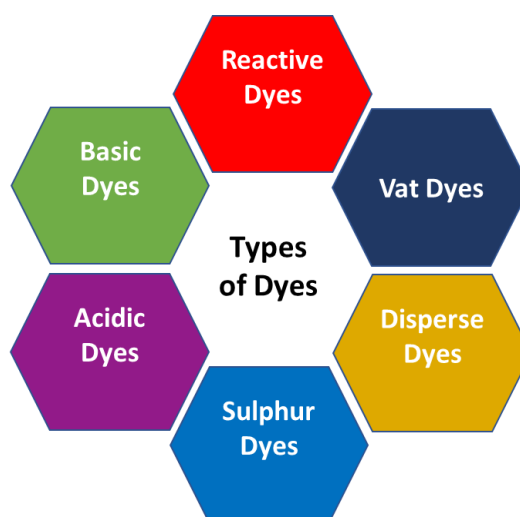
Figure 2.3: Main dye classes used in textile industry

Reactive dyes are commonly used for cotton and viscose fabric. They form new chemical compounds while coming in contact with the fabric. 95% of reactive dyes belong to azo class and contain recalcitrant compounds (Pal, 2017). Basic dyes contain amino groups and are cationic in nature which are mainly applied to silk and wool fabric. They are water- soluble and acetic acid is mostly used in dyebath to enhance the coloring efficiency (Bartczak et al., 2022). Acidic dyes are suitable for nylon, silk and wool having anionic nature and water solubility in acidic dyebath. The phenomenon of dye absorption is by forming ionic bonds with fabric (Ujiie, 2015). Sulphur dyes are non-ionic and water insoluble in nature. They are applied to fabric with the help of

reduction /oxidation process resulting in the formation of sulphonic bonds with cellulosic fibers (Periyasamy and Militky, 2020).

Disperse dyes are used for dyeing acrylics, triacetates, and mainly polyester fibers. Disperse dyeing does not require any fixing agents as it is done by the phase change phenomena depending upon temperature. They are not readily water soluble and around 50% of disperse dyes belong to the azo class while 25% are from anthraquinones, nitro and methine. Disperse dyeing is done in acidic medium and most suitable for fibers with hydrophobic nature due to good fastness properties of these dyes (Koh, 2011; Song et al., 2020). Vat dyes are sparingly water soluble and applied particularly on cellulosic fibers. These dyes are most widely used because of their excellent water and light fastening capability (Khatri et al., 2017).

2.6 Potential of Resource Recovery in Textile Dyebath

One of the important points in textile effluent pollution is the low fixation of dyes due to inefficiencies in textile processes. It has been found that mainly reactive, vat and disperse dyes are present in textile wastewater among which 70% are recoverable (Arslan-Alaton and Turkoglu, 2008; Berradi et al., 2019). The disperse and vat dyes are first adsorbed and then diffuse monomolecularly into the fiber. They do not undergo any chemical change during the dyeing process, and their reuse is possible after recovery (Ketema and Worku, 2020). Furthermore, a huge amount of water is lost as a treated effluent in conventional processes and became a part of water bodies that further need polishing for reuse. It is possible to recover and reuse the water on source for non-potable purposes (Yaqub and Lee, 2019). Studies are also conducted to recover salts and heavy metals like chromium and nickel from textile effluent (Chaouqi et al., 2019).

2.7 Recent Progress in Textile Dyebath Effluent Treatment and Reuse

2.7.1 Physico-Chemical Techniques

Different physico chemical methods were developed previously for the treatment of textile wastewater including coagulation flocculation, adsorption, and ion-exchange

Coagulation and flocculation methods are well suitable for the removal of disperse dyes while having low efficiency in case of vat and reactive dyes (Holkar et al., 2016). This

technology has limitations like high chemical cost, low dye removal performance and sludge production (Liang et al., 2014).

Adsorption technology gives significant dye removal results in the case of textile effluent treatment. The selection parameters for adsorption includes high affinity, surface area and desorption properties. While limitations include high cost and difficulty in the recycling of adsorption media (Jadhav and Srivastava, 2013). Another main point is the pollutants i.e., dyes cannot be reused and pollutants ultimately remain in the environment (Galán et al., 2013).

Ion exchange method can be used to remove cationic and anionic pollutants from wastewater. This technology involves the use of synthetic resins. This technology has found good results in water softening but is not efficient in dye removal. There is no loss of adsorbents by this technology, it is found workable in case of water-soluble dyes like reactive dyes but not in the case of water insoluble dyes (Hassan and Carr, 2018).

2.7.2 Biological Techniques

Biological processes are conventionally used for the treatment of textile wastewater. Mostly the aerobic processes like activated sludge process and sequencing batch reactor are applied commonly but they have various disadvantages like toxicity towards the microorganisms, high energy demand, land requirements and high hydraulic retention times (Sarayu and Sandhya, 2012). While in the case of anaerobic treatment of textile effluent, production of aromatic amines affects the process. So in the long run pollution is only converted from one form to another (Haider et al., 2018).

2.7.3 Chemical Techniques

Chemical techniques are applied on industrial effluents mainly for the removal of toxic metals, dyes, pollutants, and odor. Chemical oxidation using ultraviolet light and oxidant is proven for dye removal. Studies have been done and it is analyzed that hydrogen peroxide (H_2O_2) in combination with UV light is the most commonly used oxidant for textile effluent treatment. The oxidant properties of chlorine dioxide (ClO_2) are also found effective for dye removal (Asghar et al., 2015). Fenton process solution of hydrogen peroxide and ferrous ion is used as a catalyst to oxidize the contaminants from wastewater. It shows maximum color removal efficiency of 98% and COD removal of 85% at pH=3 in textile effluent stream. The limitation of fenton process is the production of byproducts i.e., iron sludge due to the combined flocculation process

of fenton reagents and molecules of dyes (Ayyaru and Dharmalingam, 2014). Furthermore, the inhibition effect of dyes and emulsification effect of surfactants found in textile wastewater can affect the dye removal efficiency to some extent (Ledakowicz et al., 2012). Textile wastewater can also be treated by ozonation which involves breaking of dyes conjugate bonds utilizing ozone gas. The major advantages include the use of ozone in gaseous form, no reduction in the volume of wastewater and zero solid waste sludge generation (Miralles-Cuevas et al., 2017). While the main limitation includes production of toxicants in effluent, short half-life, and high cost. Furthermore, it has been noticed that ozonation is fast at alkaline conditions (approximately 8.5 pH) (Gosavi and Sharma, 2014). Photo catalysis is another simple technique that can degrade organic pollutant from wastewater into carbon dioxide, and smaller molecules and inorganic pollutants into harmless substances. In solar photo fenton process at 60 mg loading of catalyst up to 95% decolorization and 82% mineralization was achieved (Shindhal et al., 2021). Mostly TiO_2 catalyst are used in dye effluent treatment, but they also have some limitations like poor thermal stability, difficult aggregation and recovery of nano particles (Soares et al., 2014).

2.7.4 Membrane Techniques

The common membrane processes used for the treatment of textile wastewater are shown in **Table 2.1** along with membrane characteristics and permeate flux potential.

Microfiltration (MF) is mostly used in textile industry as a pre-treatment process before the application of tertiary treatment. Basically the pore size of MF is larger which allows total dissolved solid (TDS) to pass through it while suspended solids can be retained with the help of this separation technique (Ellouze et al., 2012). The flux of 150 LMH was previously studied by using these membranes. It was mostly used as a pre-treatment for nanofiltration. 50% COD while 28% salinity removal was observed using MF (Ayadi et al., 2016).

Ultrafiltration (UF) membranes have smaller pore size as compared to MF. UF is mostly applied as a pre-treatment to reverse osmosis (RO) or nanofiltration (NF). While now a days it is has also applied in the domain of salts and dyes fractionation from textile wastewater to achieve the benefits of resource recovery (Jiang et al., 2018). It was found that the UF technology allows the passage of NaCl and Na_2SO_4 and can reject reactive and direct dyes. Past studies show 99% desalination and 97% dye

rejection efficiencies. So, it proves the promising nature of UF in salts and dye fractionation during textile wastewater treatment (Jiang et al., 2018). A tight UF ceramic membrane has the potential of recovering reactive dyes and salt sources separately from the discharged textile wastewater but it is more compatible with negative ions as compared to positive ion dyes due to electrostatic interactions with ceramic membranes (Ma et al., 2017)

NF is a membrane separation technique that shows higher efficiency as compared to UF in terms of rejection and also shows higher performance when compared to reverse osmosis (RO) membrane. NF membrane is suitable for charged dyes and metals present in textile effluent due to electrostatic repulsion (Ong et al., 2014). The color and COD removal at 15 bars was found to be 95% and 98%, respectively by using NF membrane. NF can be used to treat textile wastewater and reuse of process wastewater is also possible (Cebeci and Torun, 2017). Hybrid NF and bipolar membrane electrodialysis were examined to reconcentrate direct and reactive dyes along with acid and base recovery. They have achieved 99% dye rejection (Lin et al., 2015) but NF applies mechanical strength in terms of hydraulic pressure and due to shear force dyes integrity can be affected (Samhaber and Nguyen, 2014).

RO is used for the rejection of monovalent salts, chemical auxiliaries, and hydrolyzed dyes (Kumar et al., 2013). Almost 99.9% color and COD rejection is achieved by using reverse osmosis on biologically treated textile effluent, however direct filtration through RO cause reversible fouling. It has been noticed that almost 80% of water recovery can be achieved by using RO at 45 to 60 LMH flux which can be reused in the next batch of dyeing (Balcik-Canbolat et al., 2017). The limitation of RO includes that at higher concentrations the osmotic pressure is important, and it increases the energy requirement which in turn rises the operational cost (Kumar et al., 2013).

Membrane Distillation (MD) is a temperature driven process which is best suitable to textile wastewater as textile effluent is released at a high temperature of 60-80℃ which results in low energy requirements (Keskin et al., 2021). Studies have been done earlier on the application of MD in textile wastewater treatment and it has been found that 12 to 15 LMH flux and 100% dye rejection can be achieved that can be further improved by using hybrid systems. The major concerns in this technique are membrane fouling and wetting encountered during the operation (Reddy et al., 2022).

Membrane bioreactor (MBR) is basically a hybrid process consisting of biological process (aerobic or anaerobic) and membrane filtration. The land space and sludge production can be reduced by using MBR with high concentrations of biomass in the system and can cope with fluctuations in the effluent quality. It has been reported that MBR at 1.3 h hydraulic retention time (HRT) can remove COD, color and TSS by 91, 99 and 80%, respectively (Yang et al., 2020). Anaerobic MBRs are more efficient in term of methane production and less energy requirements but in the case of dyes anaerobic processes can convert pollutants into toxic by-products (Jegatheesan et al., 2016).

Table 2.1: Common membrane processes used for the treatment of textile wastewater

Membrane Type	Size	Driving Force	Flux (LMH)	Reference
Microfiltration	0.1-10 μm	Hydraulic pressure	150	(Ayadi et al., 2016).
Ultrafiltration	0.005–0.1 μm	Hydraulic pressure	70-120	(Srivastava et al., 2011)
Nanofiltration	0.001-0.01 μm	Hydraulic pressure	50-60	(Fersi and Dhahbi, 2008)
Reverse Osmosis	0.0001 μm	Hydraulic pressure	45-50	(Balcik-Canbolat et al., 2017)
Membrane Distillation	100 nm -1 μm	Temperature Difference	12-15	(Reddy et al., 2022)
Membrane Bioreactor	Depends on membrane type	Hydraulic pressure/ Temperature Difference/ Hydraulic osmotic pressure	7-10	(Jegatheesan et al., 2016)
Forward Osmosis	0.4-1 nm	Osmotic Pressure	13-14	(Korenak et al., 2019)

2.8 Forward Osmosis for Reconcentration of Textile Dyebath

2.8.1 Forward Osmosis (FO)

Osmosis is a process by which water moves from one solution to another due to concentration difference. FO follows the same phenomena with the help of semi-permeable membrane. Flux in FO depends upon the concentration difference between draw solution and feed concentration.

2.8.2 Advantages of FO

FO has many advantages over other membrane technologies such as no hydraulic pressure (Kook et al., 2018), higher contaminants rejection (Amin et al., 2016), lower membrane fouling because flow resistance is only responsible for the drop in hydraulic pressure within the membrane module. The fouling in FO is mostly reversible and osmotic backwashing can recover the membrane efficiency (Liu and Mi, 2012).

2.8.3 Disadvantages of FO

Attaining high flux in case of large-scale FO systems is difficult while use of thin film composite TFC membranes and some new draw solutions seems effective (Chekli et al., 2017). Fouling is a major problem in membrane-based processes, while in FO it is very low but still exists in the form of internal concentration polarization (ICP) on the support layer and external concentration polarization (ECP) on the active layer (Lay et al., 2012).

2.9 Forward Osmosis: Basic Principles and Terminologies

2.9.1 Flux

Flux is the measure of solvent permeability through the membrane, and it can be expressed as:

$$J_w = A(\Delta\pi - \Delta P) \ \dots \ (1)$$

Where J_w is Permeate flux, water permeability coefficient is denoted by A, $\Delta\pi$ is difference in osmotic pressure between feed and draw solution, and ΔP is difference in hydraulic pressure across the membrane.

2.9.2 Difference between FO, PEO, PRO and RO

In equation (1) when hydraulic pressure difference is zero the process is referred as forward osmosis, when draw solution is subjected to hydraulic pressure it is known as pressure enhanced osmosis (PEO), when $\Delta\pi$ is greater than ΔP, the phenomena is called pressure retarded osmosis (PRO) and when ΔP is greater than $\Delta\pi$. reverse osmosis (RO)

takes place. It is assumed that FO is applied for water treatment purposes while PRO for osmotic pressure applications. In PRO membrane, the active layer is faced towards draw solution side as shown in **Figure 2.4** (Albergamo et al., 2019; Han et al., 2015).
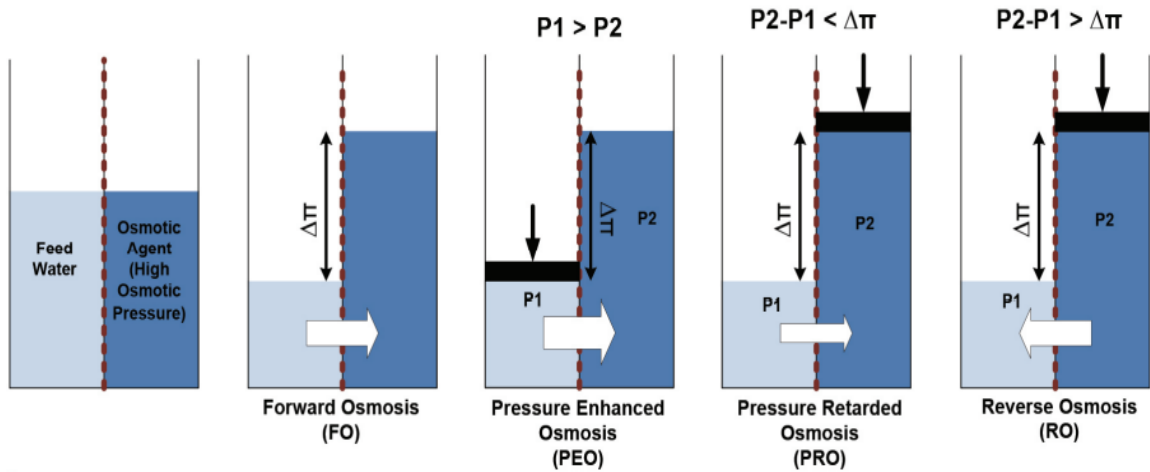
Figure 2.4: Osmotic processes for semi permeable membrane (Nicoll, 2013)

2.9.3 Solute Flux

The solute flux is presented by J_s and can be presented by Fick's law.

$$J_s = B\Delta c \ \ldots. (2)$$

In equation (2), B is the coefficient of solute permeability while transmembrane concentration is presented by Δc. It is depicted from the above equation that solute diffuses from the higher concentration side to the lower concentration. It is mostly observed in RO where solute from feed water diffuses toward the product water whereas in FO diffusion takes place in forward as well as backward direction depending upon feed and draw solution concentrations. This phenomenon can affect the microbes present in feed solution in the case of osmotic membrane bioreactor and may cause scaling when draw solution is recycled (Cornelissen et al., 2008; Hancock and Cath, 2009).

2.9.4 Concentration Polarization

The permeate flux as described in equation (1) depends upon the osmotic pressure across the active layer of the membrane rather than the bulk osmotic pressure of feed and draw solution. It has been observed that actual permeate flux is always less than the theoretical it is due to concentration polarization. Two types of concentration polarization are found in FO as shown in **Figure 2.5**; external concentration polarization (ECP) is found on the dense active layer of the membrane while internal

concentration polarization (ICP) on the porous support layer. If the support layer is towards feed solution side, then concentrative ICP takes place while if its toward draw solution side then phenomena of dilutive ICP can be observed (Zhao and Zou, 2011).

Concentration polarization can be modelled by using equation (3) for FO water fluxes without consideration of any hydraulic pressure or membrane flux (Loeb et al., 1997).

$$J_w = (1/k) \ln (\pi_{Hi}/ \pi_{Low}) \ldots (3)$$

In equation (3) solute diffusion friction within support layer of membrane is presented by K, while π_H and π_{Low} are the feed and draw bulk osmotic pressure.

K is a constant and can be defined as

$$K = t\tau/\varepsilon D_x = S/D_x \ldots (4)$$

Equation (4) represents thickness of membrane, τ is tortuosity, porosity is denoted by ε, D_x is solute diffusion coefficient while S is the structural parameter. It has been noticed that structural parameter directly affects the magnitude of ICP as well as flux. So thin and open structured membranes are more suitable for FO than thick and torus (Zhao et al., 2012)
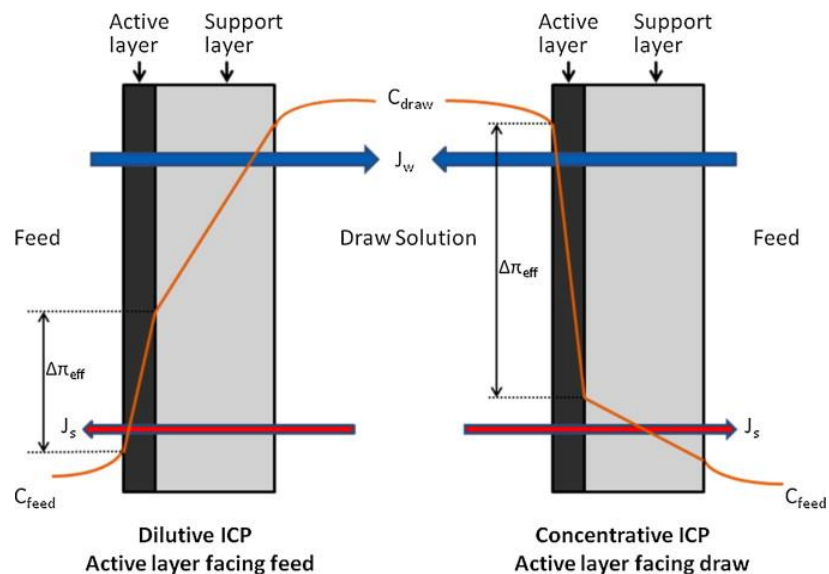
Figure 2.5: Internal Concentration Polarization in Forward osmosis

2.9.5 Membrane Fouling

One of the major problem in membrane based treatment systems is membrane fouling (Hu et al., 2005). It might result due to variety of particles present in contaminated feed solution like inorganic compounds, colloidal particles, organics in dissolved form or

microorganisms (Herzberg and Elimelech, 2007; Schneider et al., 2005). Fouling of membrane results in membrane cleaning requirements which as a result increases the operational cost. Therefore, for efficient membrane process, fouling should be minimized. It has been previously studied that fouling in case of FO is much less than RO processes and most often it is reversible (Lee et al., 2010). Furthermore, in case of FO organic fouling can be controlled by increasing the cross flow velocity. The reasons for low fouling in FO were found to be due to low water flux, application of smooth and hydrophilic membranes and no or very low hydraulic pressure (Lay et al., 2010).

2.10 Application of Forward Osmosis in Textile Effluent Reconcentration Using Various Draw Solutions

Many previous studies have discussed on forward osmosis for the treatment of textile wastewater. The potential application of the symmetric forward osmosis membranes was examined for sustainable concentration and recovery of valuable dyes from textile wastewater using a 1.5 M Na_2SO_4 draw solution and a concentration factor of 10 was achieved (Li et al., 2019). FO-MD was used to treat textile wastewater with a concentration factor of 10 and to regenerate Na_2SO_4 from the draw solution (Li et al., 2020). Fertilizer drawn forward osmosis was analyzed for treating textile wastewater by using KCl as draw agent with 5 LMH flux and 0.85 RSF (Karunakaran et al., 2021). Rejection of antimony from textile wastewater was examined by using forward osmosis and up to 99% rejection was achieved by using NaCl as a draw solution. Anaerobic fertilizer drawn FO-MBR was assessed for textile wastewater treatment by using Mono Ammonium Phosphate (MAP), Ammonium sulfate (SOA) and Mono Potassium Phosphate (MKP) blended draw solutions and it showed up to 8 LMH flux and 25 to 75 Pt-Co color was left in FO permeate but an increase in reverse solute flux adversely affected microbial activity (Abbasi et al., 2021). It has been observed that most of the studies need draw solution regeneration hence increasing energy cost and when we use fertilizers as draw solutions, reverse solute flux can negatively impact the feed concentrate quality (Mendoza et al., 2022). Reactive and basic dyes were used as draw solutes for textile wastewater treatment, the mixture of dyes and salts produced relatively high osmotic pressure and direct use of diluted DS needs further research. So based upon the above discussion a different draw solution for textile wastewater treatment is needed which should not have limitations of regeneration and have minimum reverse solute flux (Sheldon et al., 2018).

2.11 Surfactants as Beneficiary Draw Solution for Dye Wastewater

Surfactants are blends of amphiphilic and organic molecules presenting both hydrophilic and hydrophobic group having dual structural units. Surfactants as a DS can produce a stable osmotic pressure above critical micelle concentration (CMC) with fluxes of 4-13 LMH and 100 times less RSF than NaCl, primarily due to their large molecular size (Nawaz et al., 2016; Roach et al., 2014). Above CMC, due to constant osmotic pressure, surfactants can produce stable FO fluxes even with declining DS concentration, however, below CMC they behave like inorganic DS (Cai, 2016; Gadelha et al., 2014). Surfactants are used as antistatic, untangling, and softening agents in different textile processes like scouring, lubrication, dyeing, and finishing. Therefore, the diluted surfactant DS can be directly reused without regeneration in some other unit process within the same textile industry (Sivaramakrishnan, 2013).

METHODOLOGY

3.1 Composition and Characterization of Synthetic Wastewater

In this study, high-strength textile dyebath effluent was simulated as FS with recipes described in **Table 3.1**. The dyes and dyebath effluent recipe used in the study were provided by two industrial partners, Dilltex Pvt. Ltd., Pakistan, and DyStar Pvt. Ltd., Pakistan; therefore, either the chemical formula or trade names are stated in the study. The average characteristics of synthetic dyebath effluents (denim + polyester) prepared in this study and their justification from the literature are also added in **Table 3.1**. Two classes of dyes were targeted i.e., vat and disperse. Firstly, operational conditions were optimized using vat dye (denim dyebath effluent), and then the optimized conditions were applied to different concentrations of disperse dye (polyester dyebath effluent). These two dyes were used because, unlike other dye classes, these dyes do not chemically react with fiber during the dyeing process, hence increasing the possibility of reuse after recovery. All other chemicals were purchased from Sigma-Aldrich, UK, with lab-grade quality.

Table 3.1: Composition and characteristics of synthetic textile dyebath effluents

Sr. no.	Constituents	Formula	Concentration
	Denim dyebath effluent		
1	Sodium dithionite	$Na_2S_2O_4$	1.31 g/L
2	Sodium hydroxide (50%)	NaOH	1.22 mL/L
3	C1 vat blue	$C_{16}H_{10}N_2O_2$	1.5 g/L
	Polyester dyebath effluent		
1	Trisodic phosphate	Na_3PO_4	1 g/L
2	Sera gal PLP	-------	0.5 mL/L
3	Ammonium sulphate	$(NH_4)_2SO_4$	2 g/L
4	Acetic acid	CH_3COOH	0.5 g/L
5	Disperse orange 30	$C_{19}H_{17}Cl_2N_5O_4$	1 g/L
6	Sodium hydroxide (32%)	NaOH	3 mL/L
7	Sodium hydrosulphite	$Na_2S_2O_4$	3 g/L

Sr. no.	Parameter	Denim dyebath effluent	Polyester dyebath effluent	References
1	pH	9.8 ± 0.8	3.8 ± 0.2	(Aygun et al., 2021)
2	COD (mg/L)	$16,465 \pm 1000$	$4,200 \pm 700$	(Miled et al., 2010)
3	Color (Pt-Co)	$7,150 \pm 200$	$16,000 \pm 2,000$	(Ünlü, 2008)
4	Conductivity (mS/cm)	4.2 ± 0.5	8.9 ± 0.6	(Ünlü, 2008)
5	TDS (mg/L)	$2,390 \pm 200$	$2,500 \pm 200$	(Hussein, 2013)
6	Turbidity (NTU)	50 ± 15	60 ± 10	(Cerqueira et al., 2009)

Note: The characteristics of synthetic dyebath effluents are an average of three batches

3.2 Draw Solutions

In this research, surfactants (SDS and TEAB) were used as DS owing to their stable flux and lower RSF. Both surfactants were purchased from Sigma-Aldrich, UK with lab grade quality. Given below are the details of surfactants targeted as DS.

3.2.1 L Sodium Dodecyl Sulphate (SDS)

SDS also known as sodium lauryl sulphate is an organic compound having formula $CH_3(CH_2)_{11}OSO_3Na$ and its molar mass is 288.38 g/mol. It is an orgo sulphate salt with density of $1.01 g/cm^3$ and CMC of 0.008mol/L. The permeate flux of 5-6 LMH was previously achieved using 0.5 M SDS as draw solution with RSF of 5.24×10^{-4} mol/m^2/h (Gadelha et al., 2014). SDS is a surfactant widely used in textile processing

as a detergent depending upon its properties like low cost, high water solubility, and dirt removal (Niraula et al., 2014).

3.2.2 Tetraethyl Ammonium Bromide (TEAB)

TEAB is a quarterly compound of ammonium having chemical formula $C_8H_{20}N^+Br^-$ and molar mass of 210.16 g/mol. It is water soluble having CMC of 0.16 mol/L and has density of 1.4 g/cm^3. As studied earlier, TEAB is a cationic surfactant and can generate flux up to 9 LMH at 1 M concentration using CTA membrane, while the FS used was 5 g/L NaCl solution with low RSF of 7.87×10^{-5} gMH (Gadelha et al., 2014). Furthermore it is applied as surfactant and fabric softener in textile industry (Bajpai and Tyagi, 2006).

3.3 Description of Experimental Setup

3.3.1 Membrane Specifications

In all experiments, Polyamide-TFC flat sheet FO membrane was used from Toray Chemicals, Korea. The membrane was hydrophilic in nature with a contact angle of 90°. The coefficient for water permeability is 6.4 LMH/bar. The structural parameter of the support layer is 409 μm. Membranes were stored at laboratory temperature 24±1 °C in ultrapure DI water which was replaced weekly. AL-FS orientation was used in all experimental runs. The detailed characterization of these membranes are stated in previous studies (Abbasi et al., 2021; Manzoor et al., 2022).

3.3.2 Batch Study

In this study, two types of experiments were performed, batch and semi-continuous. The batch experimental setup photo is shown in **Figure 3.2**. It comprised of two variable speed peristaltic pumps (BT300-2J, Longer Pump, China), a standard membrane cell having two symmetric channels with dimensions (10.5 x 4 x 0.1 cm), a weighing balance (UX6200H, Shimadzu, Japan), temperature controller (TPM-900, Sanhng, China), hot plate (PC-420D, Corning, USA), two EC meters attached with FS and DS (HI2003 edge, HANNA instruments, USA) and a chiller. The FS and DS (1 L each) were pumped in a closed-loop channel in a counter-current flow direction. All the experiments were run in batch mode for 24 h with an active layer facing feed solution (AL-FS) configuration. Different CFV, temperatures, and DS concentrations were systematically optimized. A new membrane coupon was used from the same membrane sheet for each experiment.

3.3.3 Semi Continuous study

The optimized operational conditions from the batch experiments were used to operate a semi-continuous setup for 48 h. The initial volume of FS and DS was 1 L, and the surfactant concentration was maintained at 0.75 M by continuous dosing of concentrated DS (2 M SDS) at the rate of 1.25 mL/min with the help of a timer (DH48S, Omron, China). Furthermore, the level of FS was maintained constant by supplying DI water using a level sensor every time the remaining volume of FS reached 500 mL mark. The schematic diagram of semi-continuous setup is shown in **Figure 3.1,** and the actual setup is shown in **Figure 3.3**.
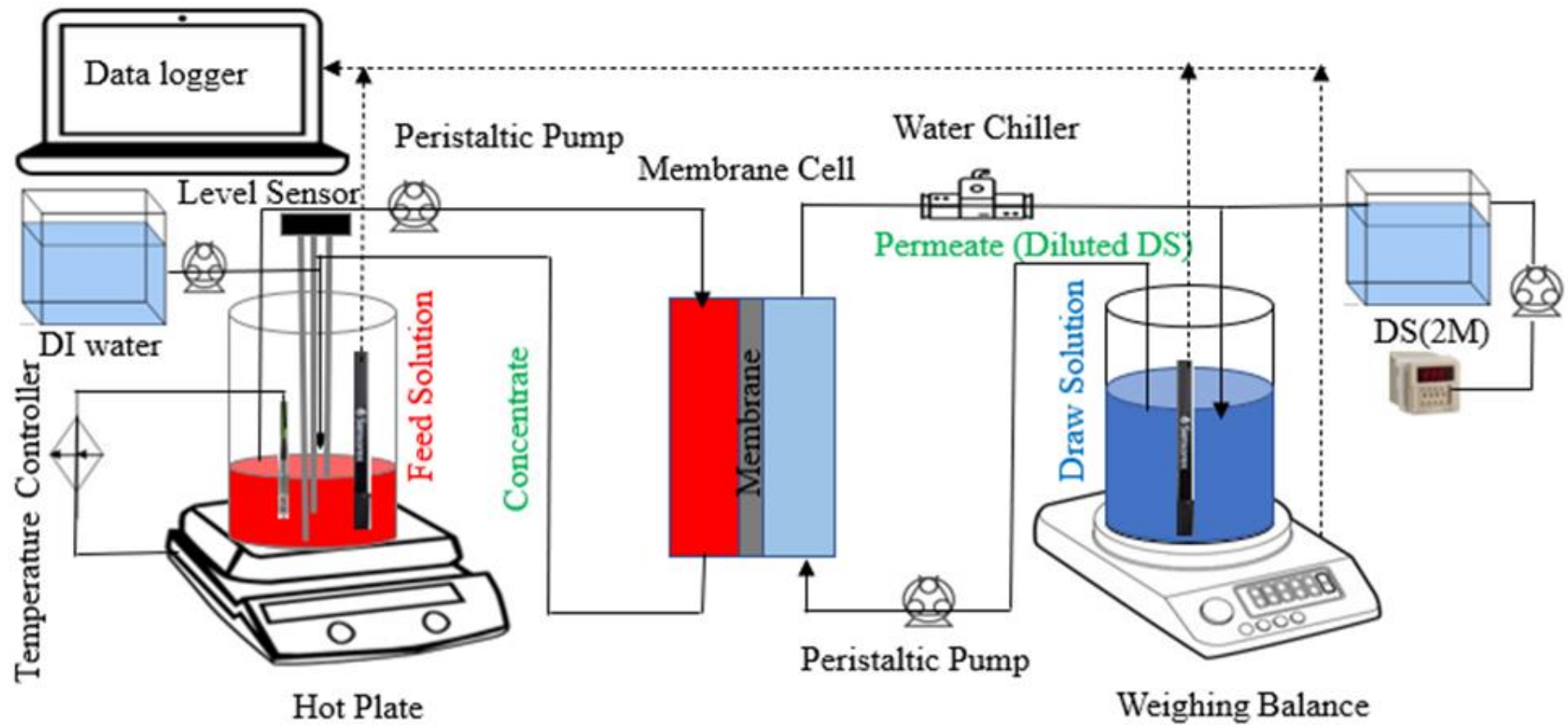
Figure 3.1: Schematic diagram of semi-continuous FO setup

Figure 3.2: Batch Mode FO Setup(1) Feed Solution Tank (2) Draw Solution Tank (3) Membrane Module(47cm2) (4) Hot Plate Stirrer (5) Weighing Balance (6) Conductivity Meter (7) Peristaltic Pump (8) Data Logger (9) Water Chiller (10) Temperature Controller

Figure 3.3: Semi-continuous FO setup (1) level sensor (2) time relay (3) concentrated DS (2M SDS) tank.

3.4 Analytical Methods

3.4.1 Calculation of Water Flux and Reverse Solute Flux

Water flux across the membrane was calculated by measuring the change in volume of the DS after each minute and the reverse solute flux was estimated by measuring the actual conductivity of feed and DS after every minute. Calculated values were obtained at each minute by dividing actual conductivity by the cumulative volume of FS and DS at the end of experiment. To estimate the amount of salt transfer, calculated conductivity values were subtracted from the original conductivity values (Nawaz et al., 2021).

3.4.2 Monitoring of pH, Color, COD, and Surfactant Concentration

After every run 200 ml of samples were taken from both FS and DS and stored at 4°C for analysis. The pH and COD of both FS and DS samples were measured before and after experiments to observe the mass transfer across the membrane. pH was measured by using a pH meter (Eutech Instruments Pte Ltd., pH 700, Singapore) while COD was measured using COD vials reactor (Hach -COD reactor, model 45600, UK). The color of the FS was measured before and after experiments by using the multiwavelength method (APHA, 2017) through spectrophotometer (SPECORD 200 PLUS UV/VIS Spectrophotometer, Germany) to measure the % dye reconcentration. To find the dilution factor and estimation of DS reuse in the textile industry, concentration of surfactant was measured by two phase titrimetric method using dimidium disulphine blue indicator and 0.004 M hyamine solution as titrant for SDS, while in case of TEAB , a similar methodology was adopted with the replacement of hyamine with 0.004 M SDS solution (Gadelha et al., 2014).

3.5 Membrane Characterization

Membrane characterization provides information about characteristics of fouling layer built across the membrane surface which helps in developing control strategies. Secondly membrane characterization is used to verify the membrane structural properties after cleaning (Gao et al., 2018). In cross flow FO systems for textile wastewater, mostly physical or chemical characterization methods are considered, among which some common techniques are used in this research as described below. After each experiment, the used membrane was dried and stored as shown in **Figure**

3.4. Each sample was cut into two parts; one was rinsed with DI water, and the other was left as such. Both parts were slowly air dried and stored for characterization.

Figure 3.4: Fouled membranes stored for characterization

3.5.1 SEM-EDX Analysis

Scanning electron microscope (SEM) is a kind of electron microscope, having magnification greater than optical microscope. It captures images by scanning surfaces through electron beam. These electrons when interact with the surface atoms produce signals carrying information about surface topology and chemical composition of membrane surface, the schematic illustration of principle is shown in **Figure 3.5** (Ghorbanpour and Wani, 2019). For more detailed analysis, energy dispersive x-ray spectrophotometer (EDX) is attached with SEM. It gives elemental composition of area imaged by SEM. Thus SEM-EDX provides structure, shape, and chemical composition of foulants present on the surface of fouled membrane which helps in identification of suitable cleaning techniques (Cardell and Guerra, 2016).
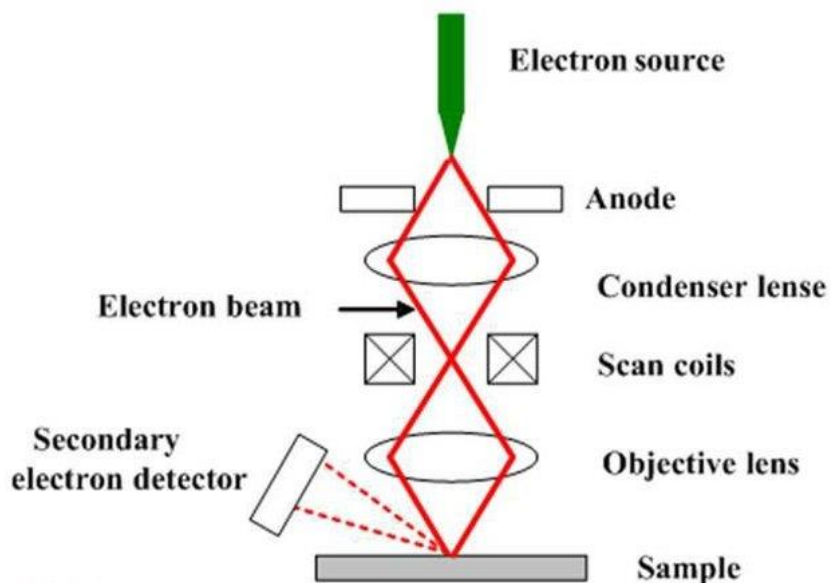
Figure 3.5: Principle of scanning electron microscopy analysis (Peiris, 2014)

The scanning electron microscopy-energy dispersive X-ray (SEM-EDX) imaging of fouled membranes (without rinsing) was done at 20 kV accelerating voltage using the microscope (JSM-6490LV, JOEL USA) to identify the key foulants on the membrane AL.

3.5.2 FTIR Analysis

Fourier transform infrared spectroscopy (FTIR) is used for determination of functional group on membranes to analyze the structural properties. Examples of functional group includes OH^- (hydroxyl)and C=O (Carboxyl). It works by targeting infrared radiations to samples by using reference solvent (Wypych, 2019). Some of the radiations are absorbed while another pass through the sample which are detected by a detector and spectrum is produced. Another method is attenuated total reflection (ATR) for FTIR analysis without using reference solvent. In this method, a spectrum of FTIR is generated through ATR crystal made from diamond. It will result in production of evanescent waves. Then reflected beam is perceived and analyzed to produce FTIR spectra as shown in **Figure 3.6**.(Sun, 2008).
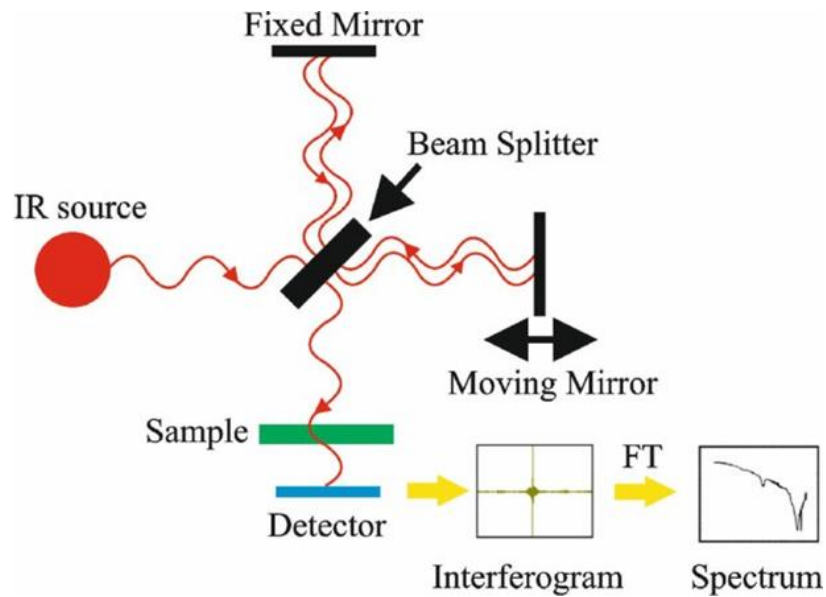
Figure 3.6: Principle of Fourier Transform Infrared Spectroscopy (Mohamed et al., 2017)

In this research, the membrane samples after rinsing with DI water were subjected to Fourier transform infrared spectroscopy (FTIR) using spectrometer (Alpha-P Bruker, USA) fitted with a diamond Attenuated Total Reflection (ATR) crystal to determine ionic peaks of the rinsed AL.

3.5.3 AFM Analysis

Atomic Force spectroscopy (AFM) is a high resolution technique used for surface examination of membrane. As compared to other spectroscopy techniques, it has advantages to provide both surface topology as well as surface roughness by producing 3D images (Erinosho et al., 2018). AFM works on principle of measuring force between probe and the sample, where probe is composed of cantilever having sharp tip which tries to touch sample but will be deflected in case of forces of attraction between probe and the sample (Giordano, 2012). Laser beam is used to detect the deflection which when reflected forms image by passing through the photo detector as shown in **Figure 3.7**. AFM can help to identify the changes in fouled membrane surface or thickness after cleaning as compared to pristine membrane (Grant et al., 2008).
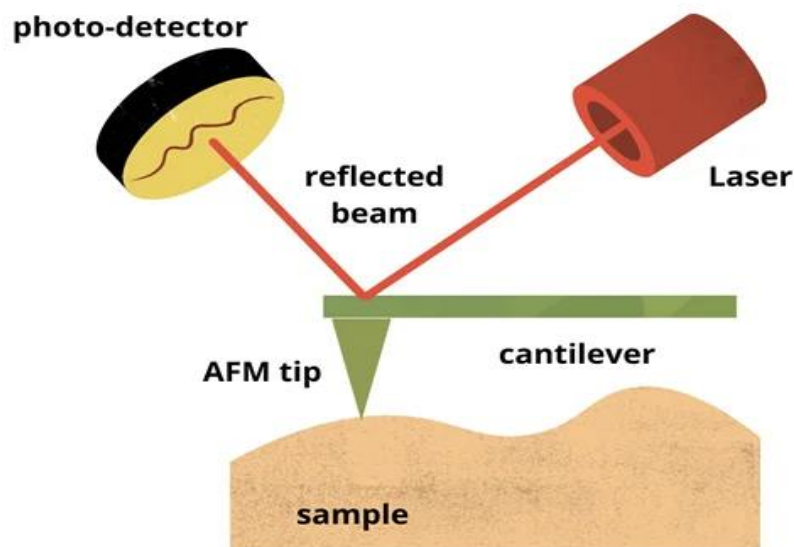
Figure 3.7: Principle of atomic force spectroscopy (De Oliveira et al., 2012)

The atomic force microscopy (AFM) was performed by scanning probe microscope (JSPM 5200, JOEL, USA) for analyzing the rinsed AL surface roughness used in different experiments. The area of 5.18 μm × 5.18 μm was scanned in each image.

3.6 Dye Characterization

Structural determination of newly synthesized or recovered substances is very important in textile industry to maintain the quality of fabric. Dyes are the main component of fabric manufacturing so its characterization before utilization is necessary. Different chromatographic and spectroscopic techniques can be used for this purpose. According to previous studies, NMR analysis is the most efficient method to identify the structure of dyes (Gao et al., 2016; Guha, 2020; Otutu and Asiagwu, 2019).

3.6.1 NMR Analysis

Nuclear magnetic resonance (NMR) analysis is a technique used for structure identifications of different materials. It provides quantitative analysis of chemical shifts, coupling constants, spin multiplication and atomic ratios which can determine structure of any compound (Chen et al., 2020). According to principle of NMR, a spectroscopy all nuclei are electrically charged so on the application of external magnetic field, energy transfer from lower energy level to higher can be achieved at a specific wavelength which coincides with radiofrequency waves produced by transmitter. The unabsorbed frequencies are detected by radio frequency detectors and

processed in the form of NMR spectra by a data processor as shown in **Figure 3.8** (Thomas et al., 2017).
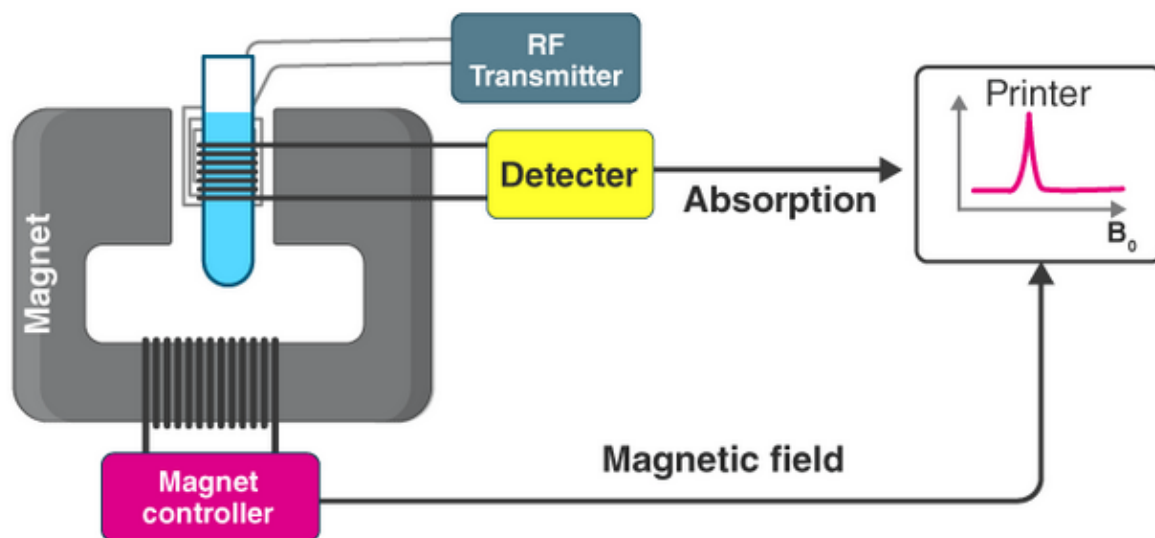
Figure 3.8: Principle of NMR spectrophotometry (Chen et al., 2020)

For selective experiments, 50 mL of reconcentrated feed sample was kept in a petri dish and oven-dried to get the powdered dye samples, as shown in **Figure 3.9**. The recovered dye was investigated for structural variation using nuclear magnetic resonance (NMR) spectrometric (Vance series Bruker, Switzerland (300 MHz)). The solvent used in the NMR analysis was Dimethyl Sulfoxide (DMSO) which is ideal for dissolving the dyes and not dissolving other chemicals present in the synthetic dyebath effluent. However, some impurities are expected to co-dissolve in the DMSO and affect the NMR peaks of recovered dyes compared to the original dye. NMR spectra were processed and analyzed using Bruker Topspin 4.1.1 software
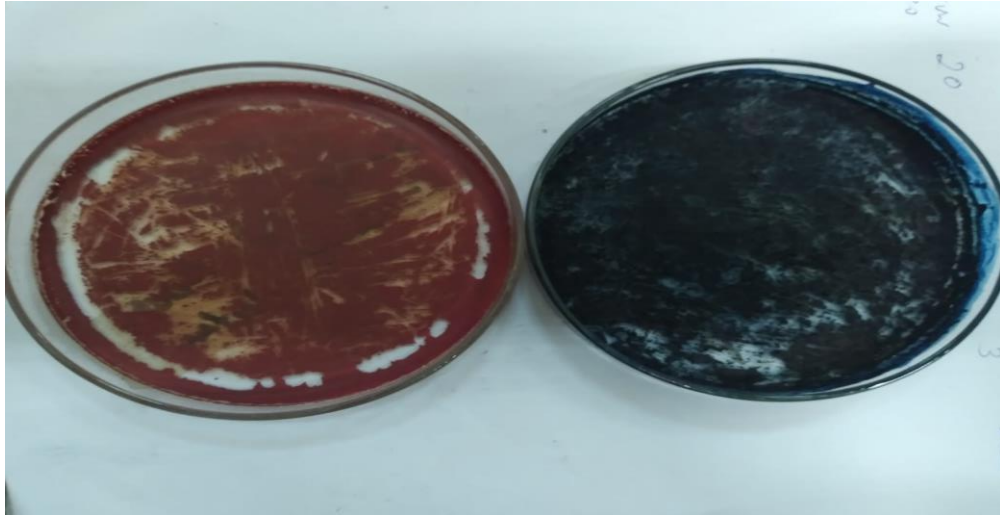
Figure 3.9: Oven dried Disperse and vat Dyes recovered from reconcentrated feed
solution

3.7 Membrane Cleaning

Every membrane coupon was used for two runs so after completion of the first-run, the
membrane was cleaned chemically. In the first step, membrane was rinsed with 0.5%
sodium hydrooxide solution after that acidic cleaning was done using 2% Citric acid
(Wang et al., 2015). The 95% flux recovery was achieved after cleaning. The membrane
coupon after cleaning is shown in **Figure 3.10**
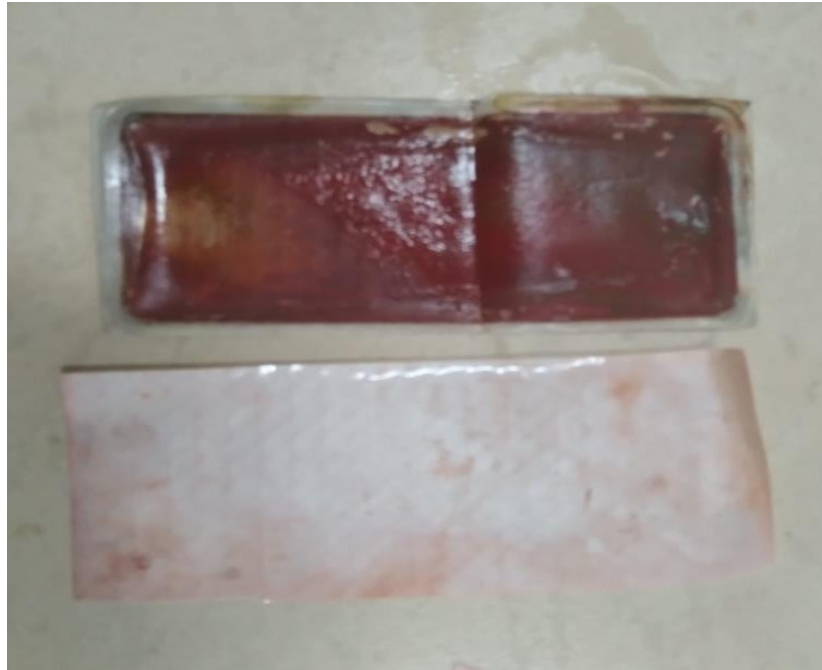
Figure 3.10: Fouled vs chemically cleaned FO membranes

RESULTS AND DISCUSSION

4.1 Phase 1: Performance Optimization of SDS as Draw Solution

4.1.1 Effect of CFV and Temperature

For experimental validation of the concept, different cross-flow velocities (CFVs) and temperatures were optimized for both FS and DS. In **Figure 4.1,** the dots denote the average hourly flux, and the trend line is fit to show the overall flux behavior in that particular experiment. The flux decline is due to the combined effect of the loss in osmotic pressure with the dilution of DS and concentrative external concentration polarization (ECP) on AL (Tayel et al., 2019). The flux increased with CFV from 8-16 cm/s but slightly reduced by further increase up to 24 cm/s. The rise in flux with increasing CFV is probably due to a reduction in ECP on AL by scouring effect (Ryu et al., 2020). Contrary to that, at a very high CFV, the FS stream gets lesser time to diffuse through the membrane (Regupathi et al., 2016; Zhang et al., 2021), and a higher shear force breaks down the FS particles to cause pore blocking (Nawaz et al., 2019). Due to these reasons, the flux at CFV of 24 cm/s was lower as compared to 16 cm/s.
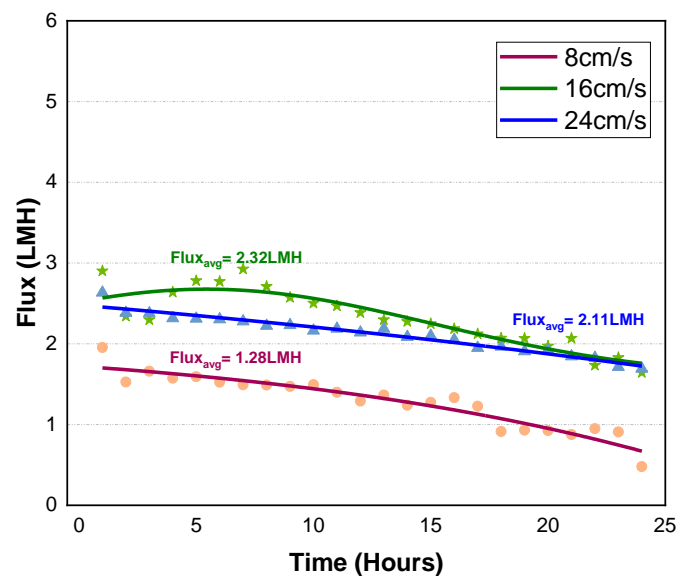
Figure 4.1: Flux values using different FS CFV at a fixed DS CFV of 8cm/s. Operating conditions: FS temperature=40°C, DS temperature=25°C; FS concentration=1.5g vat dye, DS concentration = 0.5 M SDS

Using the optimized FS CFV of 16 cm/s, the DS CFV was optimized, as shown in **Figure 4.2**. The maximum flux was obtained at 8 cm/s because on the DS side only

dilutive ECP happens, which is not the main flux limiting factor (Li et al., 2021; Pal et al., 2016). The low RSF of only 0.004 g/m^2/h (gMH) also suggests 8 cm/s as the optimum CFV of the DS.
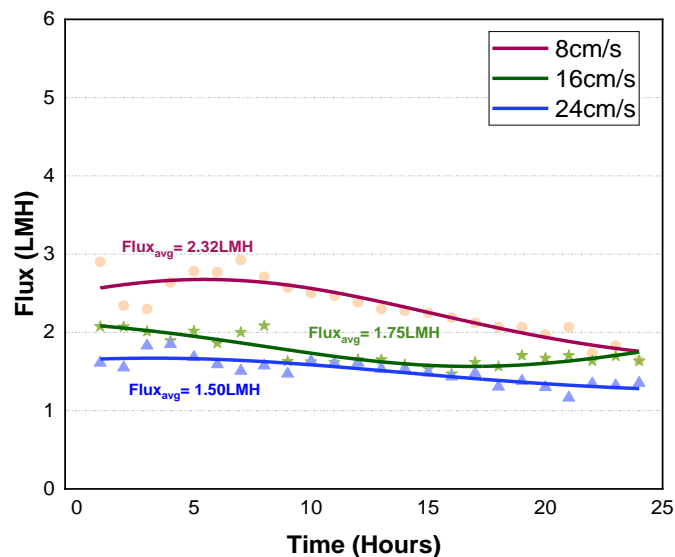
Figure 4.2: Flux at different DS CFV and fixed FS CFV = 16 cm/s.
Operating Conditions: FS Temp. =40°C, DS Temp. =25°C; FS Conc.= 1.5g Vat dye,
DS Conc. = 0.5M SDS

After CFV optimization, the FS and DS temperature were optimized, as shown in **Table 4.1**. The FS temperature was changed from 40 to 60°C as the temperature of denim dyebath effluent is generally between 60 to 80°C at the point of generation (Epolito et al., 2008). As shown in **Figure 4.3,** with increasing FS temperature from 40 to 60 °C, the flux increased by 43%, primarily due to decreased FS viscosity (Nawaz et al., 2022). The dynamic viscosity of water, which is the solvent in FS, is 0. 653mPa.s at 60°C and 0.4658 mPa.s at 40°C. The reduced viscosity positively affects the solution transport through the FO membrane resulting in a flux increase (Phuntsho et al., 2012). However, it is interesting to note that the RSF also slightly increased with increasing FS temperature. It could be because with increasing FS temperature, a more pronounced negatively charged fouling layer develops at the AL, attracting positively charged ions (Na$^+$) from the DS and resulting in RSF increase (Bell et al., 2017).
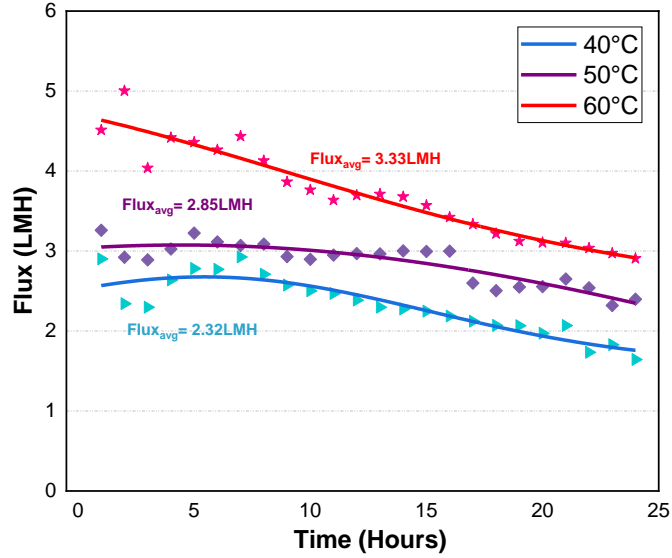
Figure 4.3: Flux at different FS temperature and fixed DS Temp.= 25°C. Operating Conditions: FS CFV = 16 cm/s, DS CFV = 8 cm/s; FS Conc.= 1.5g Vat dye, DS Conc.= 0.5M SDS.

Table 4.1: Summary of 24 h batch experiments to evaluate the system efficiency at different FS and DS CFV and temperatures using SDS as DS

Experimental conditions				Average flux	RSF	Dye Reconcentration	SDS Conc. in DS
CFV (cm/s)		Temp.(°C)		(LMH)	(gMH)	(%)	(g/L)
FS	DS	FS	DS				
8	8	40	25	1.28	0.017	30	36.24
16	**8**	40	25	2.32	0.004	51	35.22
24	8	40	25	2.11	0.019	45	35.40
16	16	40	25	1.75	0.007	36	31.26
16	24	40	25	1.50	0.009	39	29.44
16	8	50	25	2.85	0.022	55	24.34
16	8	**60**	25	3.33	0.020	58	30.33
16	8	60	**35**	3.50	0.012	66	30.02
16	8	60	45	3.24	0.013	57	29.22

The effect of DS temperature on permeate flux was negligible as shown in **Figure 4.4**. Ideally with increasing DS temperature the osmotic pressure should increase due to increase in solubility of ionic draw solutes. However, for surfactants, this is not the case. It is proven that the CMC of SDS varies between 8-10 mM when temperature is varied between 25-45°C (Chatterjee et al., 2001). Since the DS concentration in this study is 0.5 M, so it is way above the CMC (8 mM). At constant CMC, SDS shows a

constant osmotic pressure; that is why flux remained unchanged with DS temperature variation. While trends agree with previous prediction that at high temperature, flux suddenly drops at initial stages with viscosity variation when temperature is maintained at 45°C.

The flux of 3.5 LMH and RSF of only 0.012 gMH at 0.5 M SDS is comparable with other studies. RSF using 1 M KCl as DS for textile effluent reconcentration was found to be 6-7 gMH at 5 LMH flux (Karunakaran et al., 2021) while at 1 M mono-potassium phosphate as DS, RSF ranges between 2-3 gMH at 10 LMH flux (Chekli et al., 2017). Hence, the idea of utilizing SDS to generate stable and reasonable fluxes with dyebath effluent is validated.
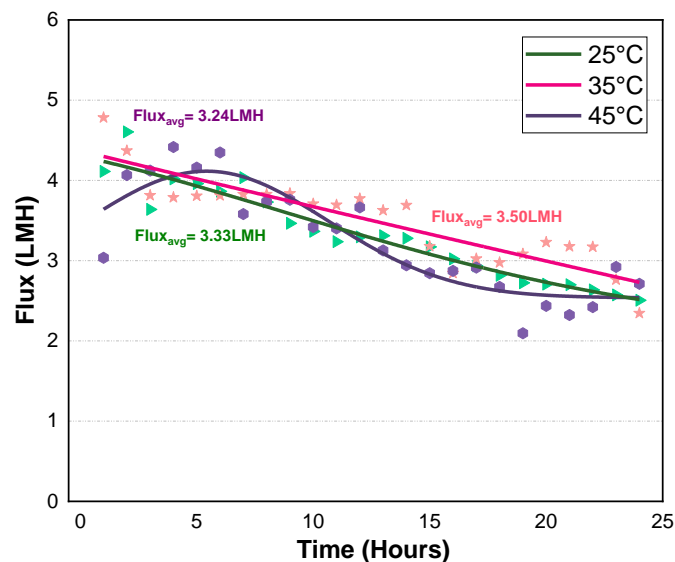
Figure 4.4: Flux at different DS temperature and fixed FS Temp.= 60°C. Operating Conditions: FS CFV = 16cm/s, DS CFV = 8cm/s; FS Conc.= 1.5g Vat dye, DS Conc.= 0.5M SDS.

a. COD Rejection

Up to 96% COD removal was found in all discussed runs regardless of the FS temperature and CFV. It proves that COD is primarily removed due to size exclusion here, which is independent of both temperature and CFV.

b. Dye Rejection and Recovery

As mentioned in Section 3.3 color measurement was performed for estimating the dye reconcentration after each experiment. **Table 4.1** shows adapted experimental conditions for optimization of average flux and dye recovery rate. It is evident from the data that along with higher flux, lower RSF and higher dye recovery were observed,

endorsing the selection of optimized parameters. In all experiments, 100% dye rejection took place showing no color in the DS. It can also be obvious from the direct relationship between percent dye reconcentration and flux data in **Table 4.1.**

c. pH Variation

An increase in pH of FS is noted after reconcentration. It might be due to fact that SDS is an anionic DS, so it attracts H^+ ions towards itself. It has been reported earlier that SDS has a stronger interaction activity with hydrogen ions of solvent molecules (Sachin et al., 2018). Another study observed pH of FS increases because of a decrease in the dissolution of CO_2 due to the increase in the salt concentration (Li et al., 2019). Later pH of the DS decreases with time as the overall pH of the system should be constant unless acid or base is added (Jegatheesan et al., 2016).

d. Diluted SDS Concentration

After every experiment, SDS concentration was analyzed, and the results are shown in **Table 4.1.** The SDS concentration was inversely related to the flux, and average concentration in DS was found to be at 31 g/L. SDS is basically a surfactant and emulsifier primarily used as a wetting agent and detergent in the textile industry to clean and prepare fabric for dyeing. It is mainly employed in desizing, scouring, and bleaching processes in concentrations around 2 g/L (Basit et al., 2018). Thus, the diluted SDS solution can be further diluted with fresh water to reuse in some of the mentioned unit operations or processes.

4.1.2 Impact of Dye Type, Concentration and SDS Concentration on System Performance

In the next stage the impacts of dye type and concentrations and DS concentrations were examined on the process performance. The recipes of denim and polyester dyebath effluents were used as described in **Table 3.1**, with different concentrations of vat and disperse dyes, as mentioned in **Table 4.2**. In this way the efficiency of the process was evaluated for a different dye type (disperse) and concentrations. As shown in **Table 4.2**, the flux was inversely proportional to the vat dye concentration, as dyes increase the potential of CECP on the AL and reduce the flux. Flux also depends upon DS concentration, in this case when concentration of DS is increased from 0.5 M to 0.75 M flux is increased due to rise in osmotic pressure difference but then decreased at a 1.0 M concentration. This happens due to an excessive osmotic gradient at the

beginning of the experiment, which swiftly attracts feed solutes to cause CECP on the AL. So, for vat dyes, 0.75 M SDS concentration was optimized and later subjected to different concentrations of disperse dyes. The flux, RSF and dye rejection results were found equally promising for the dispersed dyes (polyester dyebath) as well. It shows the stability of the proposed process for the dye reconcentration regardless of the dye type and concentration.

Table 4.2: Summary of 24 h batch experiments to evaluate the system efficiency at different FS type, dye, and SDS concentrations.

Experimental Conditions			Avg. Flux	RSF	Dye Reconcentration	SDS Conc. in DS
Dye conc. (g/L)	Dye Type	DS Conc. (M)	(LMH)	(gMH)	(%)	(g/L)
1.5	Vat	0.5	3.50	0.012	66	30.02
1.0	Vat	0.5	3.63	0.035	70	28.31
0.75	Vat	0.5	3.78	0.012	74	27.22
0.75	Vat	**0.75**	6.38	0.032	80	33.76
0.75	Vat	1.0	4.26	0.035	38	52.02
1.0	Disperse	0.75	3.62	0.019	60	41.36
0.75	Disperse	0.75	4.31	0.023	63	40.12
0.5	Disperse	0.75	4.61	0.015	67	32.88
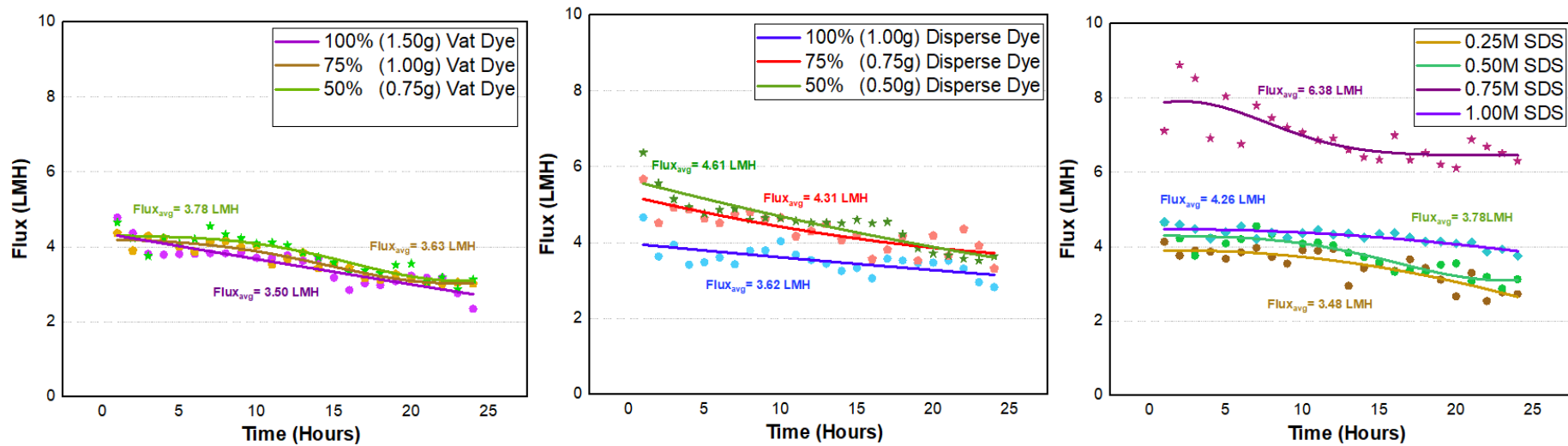
Figure 4.5: Impact of dye and SDS concentration on permeate flux

4.1.3 Impact of Dyebath Effluent on Membrane Chemistry

It is important to understand the dyebath effluent foulants interaction with the AL of FO membrane for the proposed process sustenance. If the foulants chemically interact with the FO membrane and impede its selectivity, the concept developed in this study could not be applied for dye reconcentration. For this, the fouled and cleaned membranes were subjected to a detailed characterization.

a. SEM-EDX Analysis

In **Figure 4.6,** SEM-EDX analysis of pristine and fouled membranes are shown. The main elements that appear in pristine membranes are carbon, oxygen, nitrogen, and sulfur as they are the building blocks of polyamide active layer and polyether sulfone support layer. On the fouled membranes, a thick fouling layer was observed, which was covering the membranes and was different in appearance under each operating condition. The leading elements found on the fouled membranes were carbon, oxygen, nitrogen, sulfur, and sodium. The carbon, nitrogen, and oxygen primarily came from the C1 vat blue dye and acetic acid. The sodium and sulfur came from sodium dithionite, sodium hydrosulphite, sodium hydroxide and ammonium sulfate. Furthermore, it is observed that at higher flux the fouling is comparatively high due to the deposition of dyes. The membrane can be chemically cleaned using 0.5 M sodium hydrooxide followed by 2% citric acid (Wang et al., 2015). The flux recovery of up to 95% was achieved by adapting this cleaning protocol. Detailed membrane characterization was performed to assess the impact of dye type and concentration on the AL. **Figure 4.7** shows the SEM-EDX images for fouled membranes on varying FS and DS concentrations. The key foulants were the same as for optimization of CFV and temperature experiments. Interestingly, the peaks of chlorine and phosphorus appeared when polyester dyebath effluent was used as FS **Figure 4.7 (e and f)**. Disperse dye 30, and trisodic phosphate might be the sources of chlorine and phosphorus. The spherical shape particles in SEM images refer to presence of chlorine and phosphorus. As mentioned earlier this type of fouling can be easily removed by chemical cleaning with sodium hydroxide and citric acid.

b. FTIR Analysis

The FTIR analysis was done for both the pristine membrane and fouled membranes (after rinsing with DI water), to find any changes in the active group's chemistry because of interaction with foulants. In **Figure 4.8** and **4.9,** the major peaks are

observed at wave numbers 3400, 1585, 1490, 1243, 1151, and 1105 cm^{-1} representing 0-H, N-H, C-C, C-N, O=S=O, and C-O bond respectively. These peaks are similar which shows that overall, there were no changes in the membrane active layer (Sark et al., 2021). There were minor changes in O-H weak peaks in a few experiments probably due to the remaining moisture content on the AL. However, there was no change in sharp peaks. Hence, the FO membrane is stable when used for dyebath wastewater reconcentration purpose and can be repeatedly reused after cleaning and there is no major chemical interaction between membrane active groups and foulants.
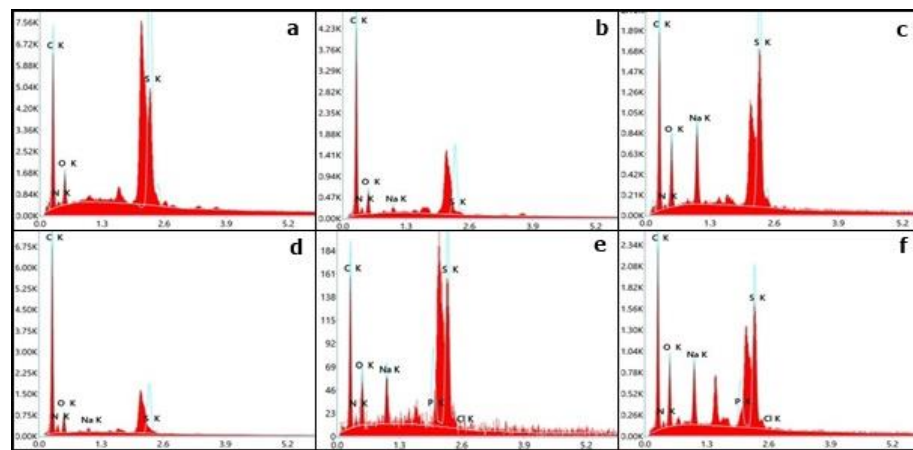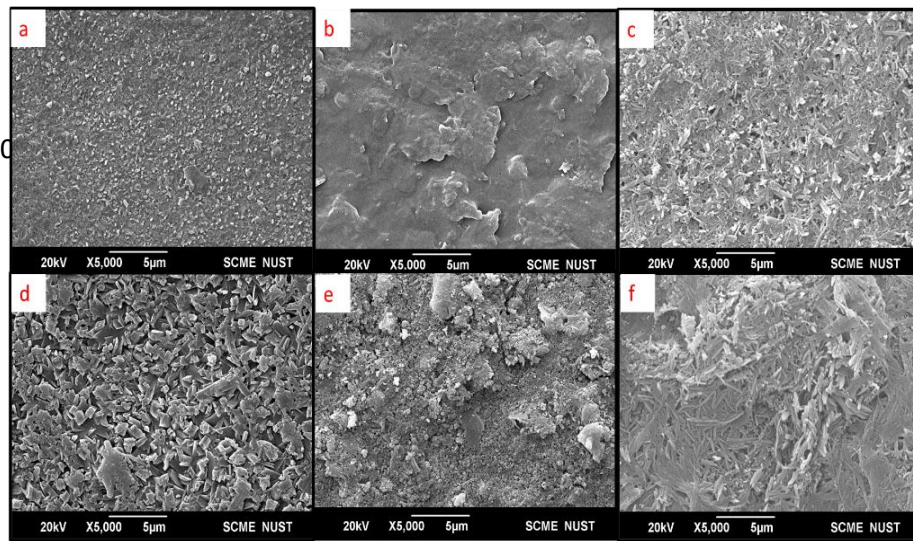
Figure 4.7: SEM-EDX analysis of AL of (a) pristine membrane. Fouled membranes after CFV and temperature optimization experiments (b) CFV (FS = 16 cm/s, DS = 8 cm/s) and temperature (FS = 40 °C, DS = 25 °C) (c) CFV (FS = 16cm/s, DS = 16cm/s) and temperature (FS = 40 DS = 25 °C) (d) CFV (FS = 16cm/s, DS = 8 cm/s) and temperature (FS = 50 °C, DS = 25 °C) (e) CFV (FS = 16 cm/s, DS = 8 cm/s) and temperature (FS = 60 °C, DS = 35 °C) (f) CFV (FS = 16cm/s, DS = 8cm/s) and temperature (FS = 60 °C, DS = 45 °C).
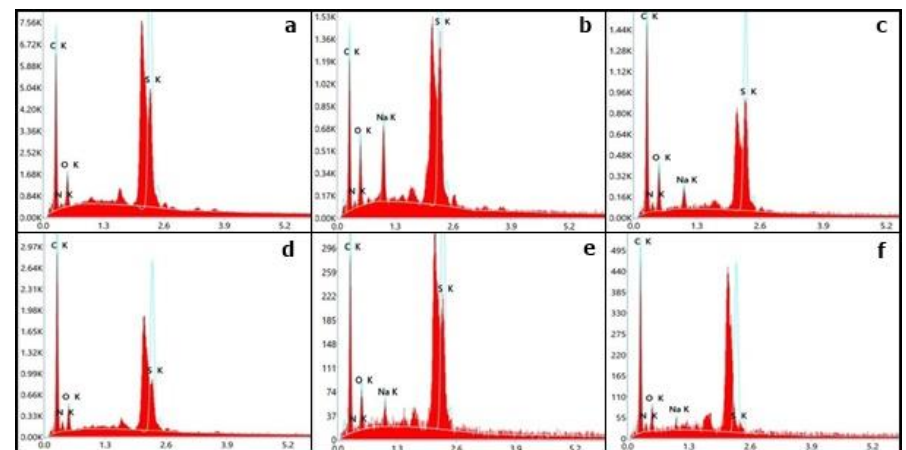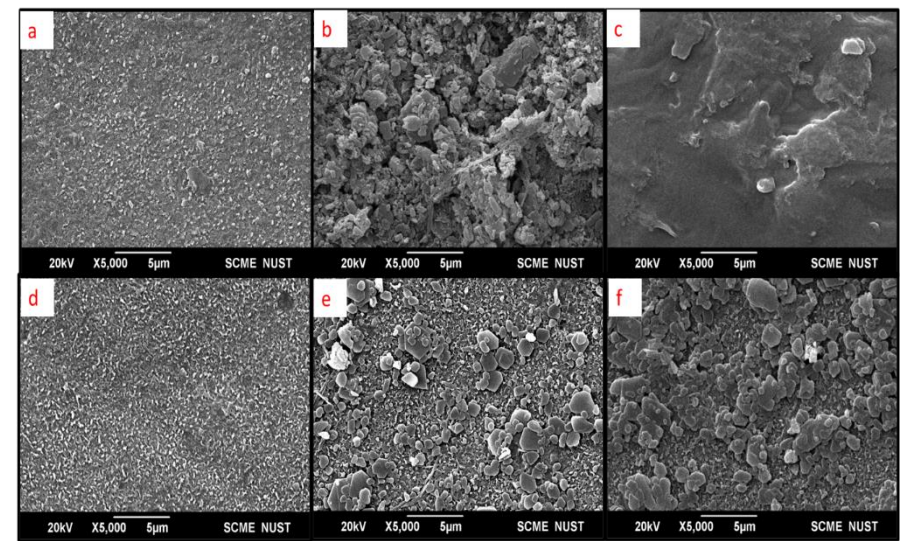
Figure 4.6: SEM-EDX analysis of AL of (a) pristine membrane (b) FS concentration = 0.75 g vat dye and DS = 0.5 M SDS (c) FS concentration = 0.75 g vat dye and DS = 1 M SDS (d) FS concentration = 0.75 g vat dye and DS = 0.75 M SDS (e) FS concentration = 1.0 g disperse dye and DS = 0.75 M SDS (f) FS concentration = 0.5 g disperse dye and DS = 0.75 M SDS
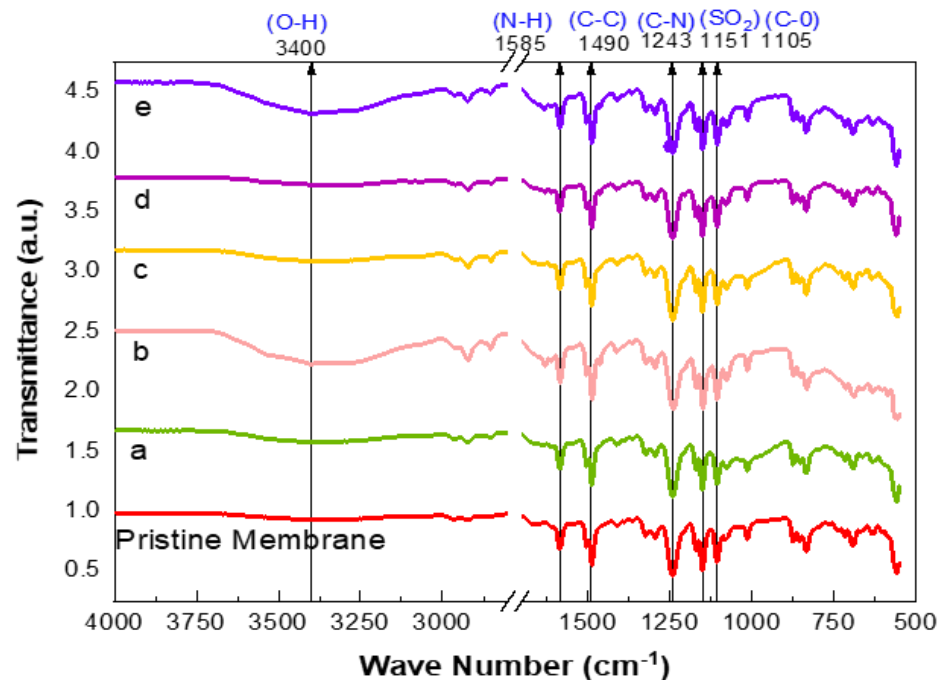
Figure 4.8: FTIR analysis of AL of pristine and fouled membranes after CFV and temperature optimization experiments. (a) CFV (FS = 16cm/s, DS = 8cm/s) and temperature (FS = 40 °C, DS = 25 °C) (b) CFV (FS = 16cm/s, DS = 16cm/s) and temperature (FS = 40 °C, DS = 25 °C) (c) CFV (FS = 16cm/s, DS = 8 cm/s) and temperature (FS = 50 °C, DS = 25 °C) (d) CFV (FS = 16 cm/s, DS = 8 cm/s) and temperature (FS = 60 °C, DS = 35 °C) (e) CFV (FS = 16cm/s, DS = 8cm/s) and temperature (FS = 60 °C, DS = 45 °C).
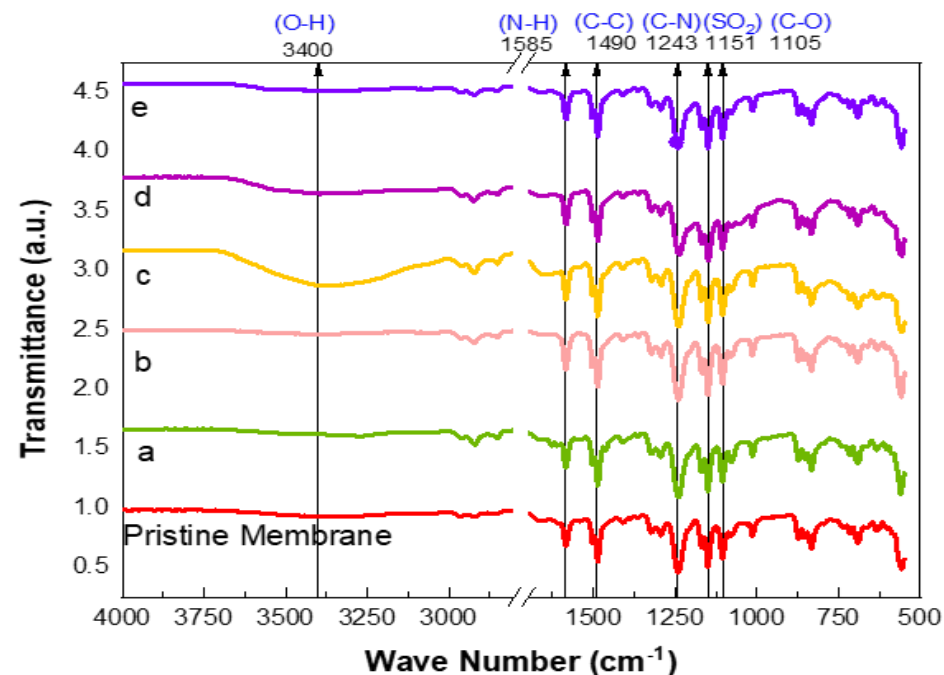
Figure 4.9: FTIR analysis of AL of pristine membrane. Fouled membranes after dye and SDS concentration optimization experiments (a) FS concentration = 0.75 g vat dye and DS = 0.5 M SDS (b) FS concentration = 0.75 g vat dye and DS = 1 M SDS (c) FS concentration = 0.75 g vat dye and DS = 0.75 M SDS (d) FS concentration = 1.0 g disperse dye and DS = 0.75 M SDS (e) FS concentration = 0.5 g disperse dye and DS = 0.75 M SDS.

b.   AFM Analysis

The AFM imaging was done on pristine membrane and fouled membranes (after rinsing with DI water), to find any changes in the mean square roughness of the AL. The AFM images with mean square roughness values are shown in **Figure 4.10**. The surface morphology of TFC polyamide membranes shows ridge and valley-like structures (Zhou et al., 2020). It is observed that the mean square roughness remained roughly the same before and after the use of membranes. Thus, from the SEM-EDX, FTIR and AFM imaging, it is proved that the FO membranes have excellent capability to remove the key contaminants present in the denim dyebath effluent. Also, the AL showed a good chemical stability against these foulants and did not react with them.
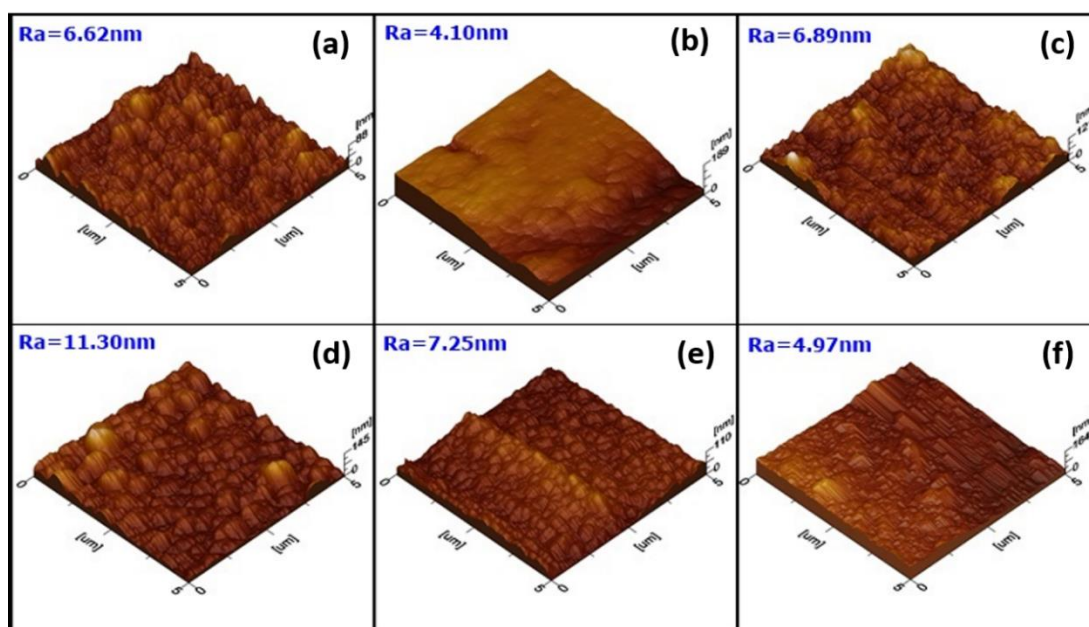
Figure 4.10: AFM analysis (a) Pristine membrane. Fouled membranes at (b) CFV (FS=16cm/s, DS=8cm/s) and temperature (FS=40°C, DS=25°C) (c) CFV (FS=16cm/s, DS=16cm/s) and temperature (FS=40°C, DS=25°C) (d) CFV (FS=16cm/s, DS=8cm/s) and temperature (FS=50°C, DS=25°C) (e) CFV (FS=16cm/s, DS=8cm/s) and temperature (FS=60°C, DS=35°C) (f) CFV (FS=16cm/s, DS=8cm/s) and temperature (FS=60°C, DS=45°C).

The AFM analysis results are shown in **Figure 4.11** describing unchanged surface roughness after different dye types and concentrations. It shows that the FO membrane was chemically stable regardless of dye type and concentration
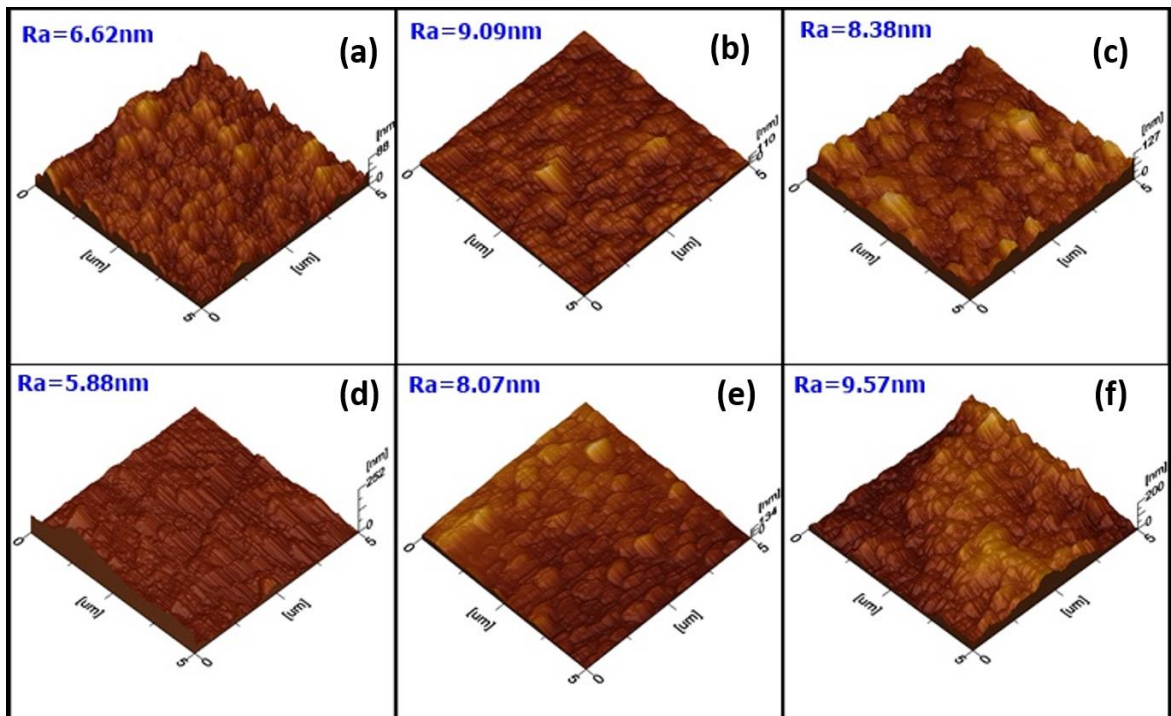
Figure 4.11: AFM analysis (a) Pristine membrane (b) FS concentration = 0.75 g vat dye and DS = 0.5 M SDS (c) FS concentration = 0.75 g vat dye and DS = 1 M SDS (d) FS concentration = 0.75 g vat dye and DS = 0.75 M SDS (e) FS concentration = 1.0 g disperse dye and DS = 0.75 M SDS (f) FS concentration = 0.5 g disperse dye and DS = 0.75 M SDS.

4.2 Phase 2: Performance Optimization of TEAB as Draw solution

4.2.1 Effect of Temperature Variation

a.   Water Flux and RSF

The temperature of TEAB was varied from 25 to 45°C while using 60°C preoptimized temperature for FS. It was found that on increasing temperature, the flux starts slightly increasing as shown in **Figure 4.12**. It might be due to decrease in viscosity with increasing temperature which enhances the diffusion of water molecules through membrane. Similar results are reported earlier while variation of DS temperature from 20 to 40°C (Xie et al., 2013). Furthermore, flux at 45°C i.e., 11.06 LMH is taken optimum because at 60°C maintained feed temperature, the average temperature noticed on draw solution side without using chiller was 45 ± 2°C so it can save energy as well in long run. The trends at 25°C and 45°C observed in **Figure 4.12** shows that flux initially decrease till 8 hours after that it becomes stable while at 45°C, the trend was comparatively steeper so this was another reason for optimization of flux at 45°C.

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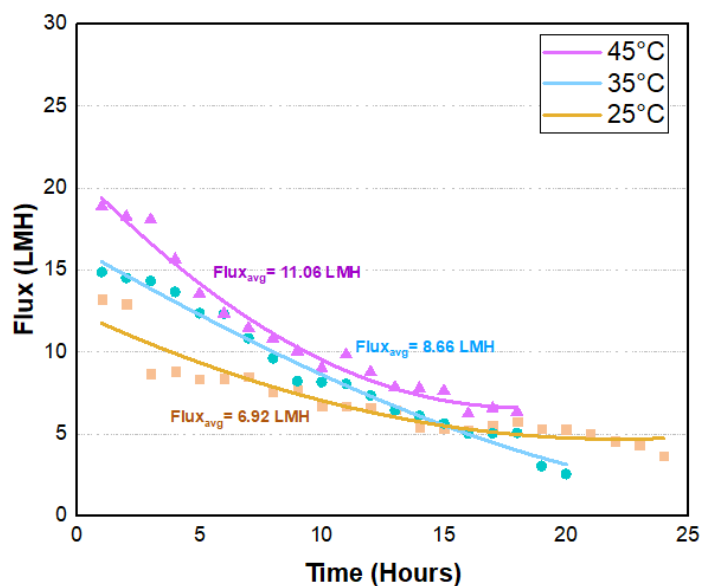
Figure 4.12: Flux values using different DS Temperature at a fixed FS temperature of 60°C, Operating conditions: FS concentration=1.5g vat dye, DS concentration = 0.5 M TEAB

The mass transfer was observed for Phase 2 and is shown in **Table 4.3**. The RSF found was 0.3-0.4 gMH at optimized conditions using TEAB as draw solution, which is almost 95% less than RSF using NaCl as draw solution (Chekli et al., 2017). Furthermore, the COD removal of greater than 95% is achieved as it is dependent on pore size.

Table 4.3: Summary of 24 h batch experiments to evaluate the system efficiency at different FS and DS temperatures and concentration using TEAB as DS

	Experimental Conditions			Avg. Flux	RSF	Dye Reconcentration	TEAB Conc. in DS
DS Temp.	Dye conc. (g/L)	Dye Type	TEAB Conc. (M)	(LMH)	(gMH)	(%)	(g/L)
25°C	1.5	Vat	0.5	6.92	0.19	95	66.56
35°C	1.5	Vat	0.5	8.26	0.34	97	50.42
45°C	1.5	Vat	0.5	11.05	0.40	97	45.06
45°C	1.5	Vat	0.5	11.05	0.40	97	45.06
45°C	1	Vat	0.5	11.81	0.42	96	50.18
45°C	**0.75**	Vat	0.5	13.04	0.44	97	47.19
45°C	0.75	Vat	0.5	13.04	0.41	97	47.19
45°C	0.75	Vat	**0.75**	18.06	0.43	98	63.75
45°C	0.75	Vat	1	25.30	0.47	98	89.78
45°C	0.75	Vat	0.25	8.68	0.28	95	29.9
45°C	1	Disperse	0.75	7.19	0.23	82	79.83
45°C	0.75	Disperse	0.75	9.95	0.25	87	76.30
45°C	**0.5**	Disperse	0.75	12.29	0.31	88	74.86

4.2.2 Impact of Dye Type, Concentration and TEAB Concentration on System Performance

Similar types of dyes as described in Phase 1 were applied in different concentrations to find the maximum gained flux in the scenario of TEAB. Flux has an inverse relation with the FS concentration as shown in **Figure 4.13.** It might be related to fact that an increase in FS concentration enhances external concentration polarization on active layer of membrane. While in case of draw solution as shown in **Figure 4.13,** when the concentration of TEAB was increased, the flux increased with an increase in osmotic pressure but at higher concentration, viscosity increases, and particles starts concentrating/fouling on membrane layer due to which flux was although high but not stable. So, 0.75 M was observed as optimized draw solution concentration.
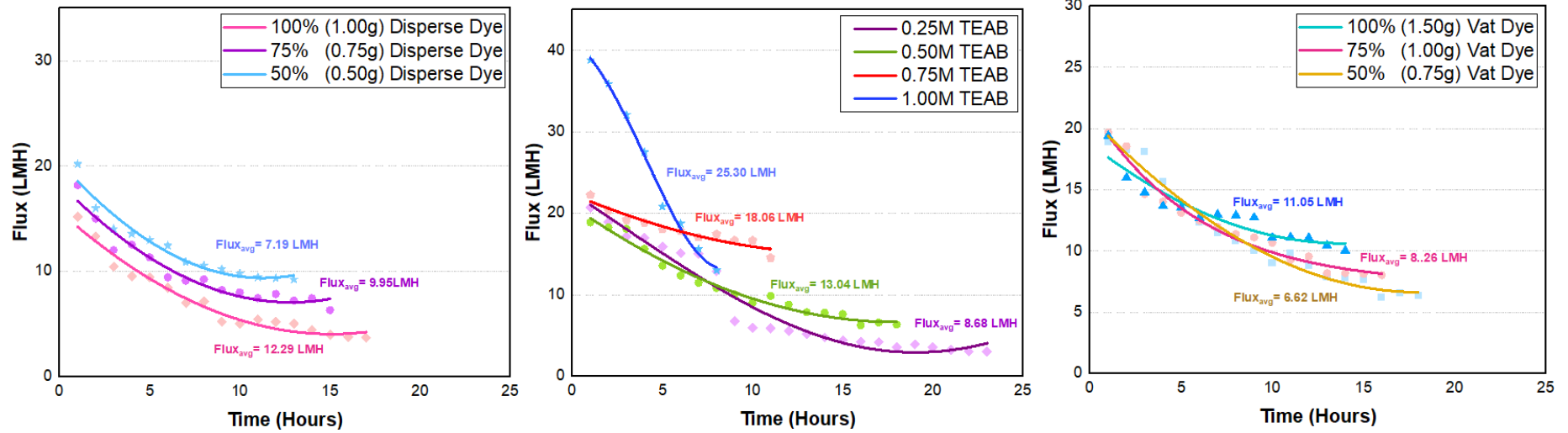
Figure 4.13: Effect of dyes and TEAB concentration on permeate flux

4.2.3 Mass Transfer Across Membrane

It has been observed that flux is comparatively higher for TEAB as DS i.e., 18 LMH. So, it is a phenomenon when forward flux increases as a result there is a rise in backward flux, but RSF is still less than other inorganic draw solutions like NaCl. The COD rejection was above 90% while dye recovery of 95 to 97% was achieved. Furthermore, 55-60 g/L of TEAB from diluted draw stream can be reused in different textile processes with dilution factor.

4.2.4 Membrane Characterization

Figure 4.14 shows SEM-EDX analysis for Phase 2 and similar foulants were detected as found in Phase 1 but as flux is higher, their concentration is somehow increased. But as discussed in Section 4.1, fouling is reversible by Basic-Acidic cleaning and up to 95 % flux can be recovered. Furthermore, **Figure 4.15** shows FTIR Analysis and almost same peaks were observed in selected optimized runs so the structure of membranes remained undisturbed. The surface morphology of TFC FO membrane is analyzed by AFM analysis as shown in **Figure 4.16** and it is found that average roughness remains almost same.
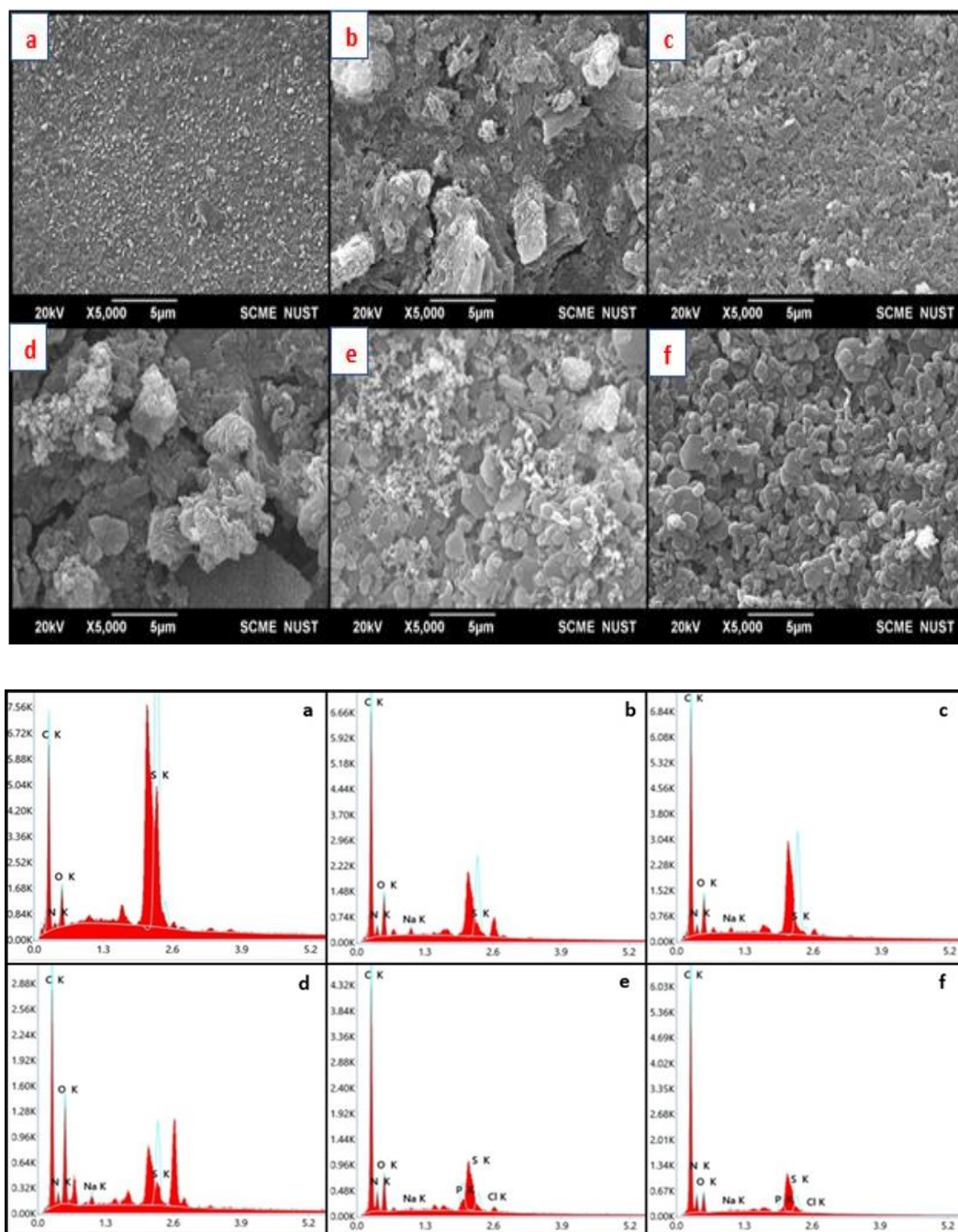
Figure 4.14: SEM-EDX analysis of AL of (a) pristine membrane. Fouled membranes (b) FS concentration = 0.50 g vat dye and DS = 0.5 M TEAB (c) FS concentration = 0.75 g vat dye and DS = 0.5 M TEAB (d) FS concentration = 0.75 g vat dye and DS = 0.75 M TEAB (e) FS concentration = 1.0 g disperse dye and DS = 0.75 M TEAB (f) FS concentration = 0.5 g disperse dye and DS = 0.75 M TEAB.
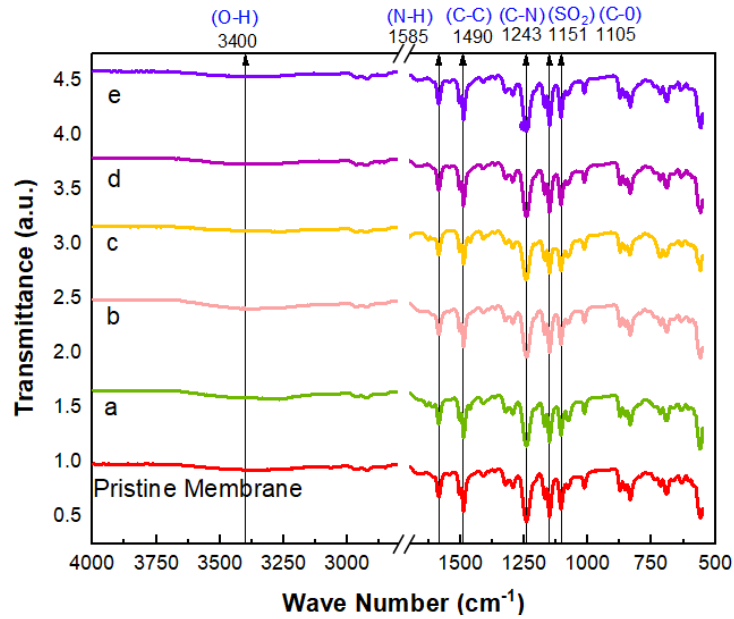
Figure 4.15: FTIR analysis of AL of (a) pristine membrane. Fouled membranes (b) FS concentration = 0.50 g vat dye and DS = 0.5 M TEAB (c) FS concentration = 0.75 g vat dye and DS = 0.5 M TEAB (d) FS concentration = 0.75 g vat dye and DS = 0.75 M TEAB (e) FS concentration = 1.0 g disperse dye and DS = 0.75 M TEAB (f) FS concentration = 0.5 g disperse dye and DS = 0.75 M TEAB.
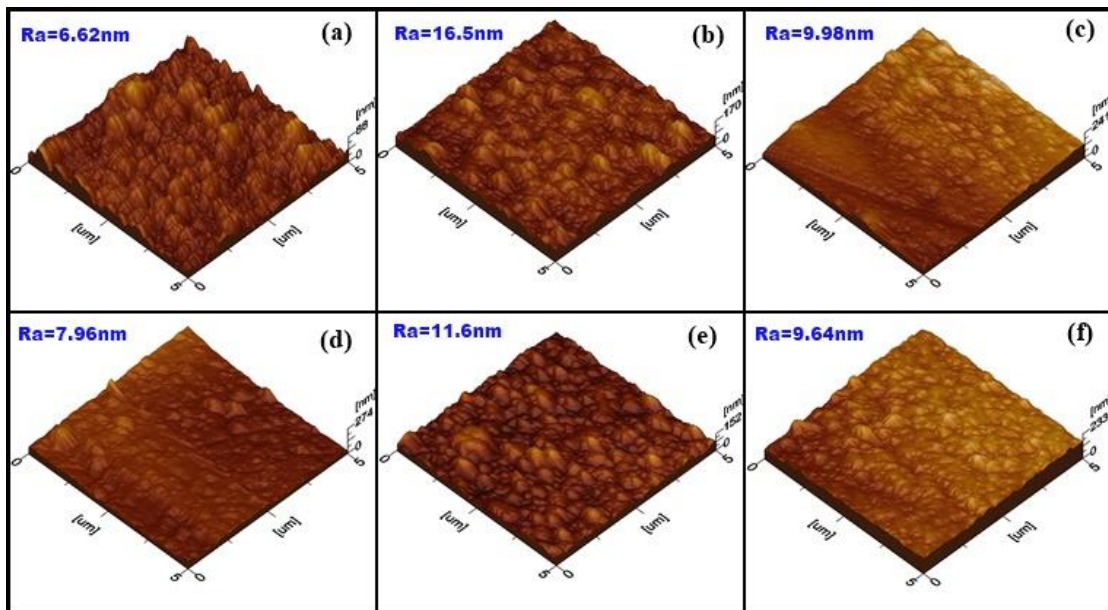
Figure 4.16: AFM analysis of AL of (a) pristine membrane. Fouled membranes (b) FS concentration = 0.50 g vat dye and DS = 0.5 M TEAB (c) FS concentration = 0.75 g vat dye and DS = 0.5 M TEAB (d) FS concentration = 0.75 g vat dye and DS = 0.75 M TEAB (e) FS concentration = 1.0 g disperse dye and DS = 0.75 M TEAB (f) FS concentration = 0.5 g disperse dye and DS = 0.75 M TEAB

4.3 Phase 3: Semi-Continuous Study Using Optimized SDS and TEAB Concentrations

The semi continuous study of 48 hours on pre optimized conditions shows that the flux in both cases is relatively stable and TEAB has higher value of flux as well as RSF but still remains less than other inorganic salts.
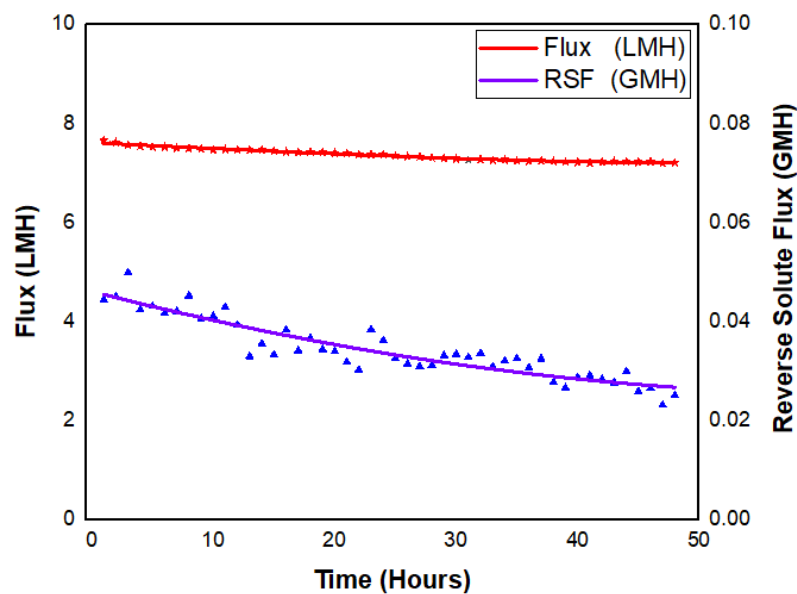
Figure 4.17: Semi continuous study using SDS as DS
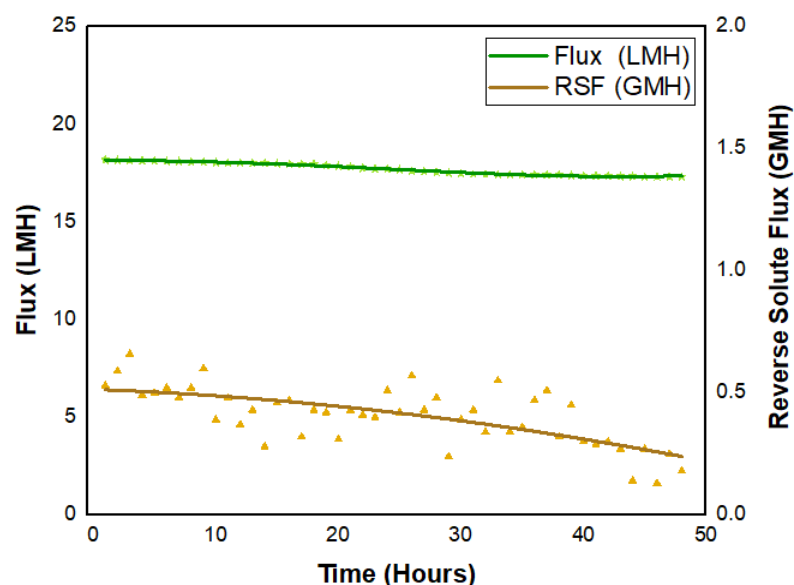
Figure 4.18: Semi continuous study using TEAB as DS

4.4 NMR Analysis for Recovered Dyes

Finally, the most critical aspect of this study was to identify the reuse potential of recovered dyes as shown in **Figure 3.9**. For this, proton nuclear magnetic resonance (^{1}HNMR) spectroscopic analysis was performed on the disperse orange dye (polyester dyebath) for the investigation of recovered dye structures as shown in **Figure 4.19**. The eight unique hydrogens were found in the spectra. The singlet formed at $\delta 1.14$ ppm belongs to the methyl group (CH_3) attached to the ester group. The peaks detected at $\delta 2.50$ ppm refer to CH_2-CN stretching while peaks at $\delta 2.82$ ppm and $\delta 3.49$ ppm corresponds to 2H atoms of CH_2-N having different neighbors. Signal at $\delta 3.76$ ppm commensurate with CH_2-O. Furthermore, it had been observed that all proton peaks of aromatic rings deshielded towards left due to their strong electronegative nature and formed at $\delta 6$ -8.5 ppm range. These peaks consist of three types of protons, depending upon their unique environment showing signals at $\delta 6.96$ ppm, $\delta 7.83$ ppm and $\delta 8.32$ ppm depicting hydrogen on benzene ring attached with N terminal of CN, hydrogen affiliated with carbon atoms attached with N-N and hydrogen atoms on benzene ring having Chlorine, respectively.

The stacked 1D ^{1}HNMR spectra of both original and recovered disperse dyes are shown in **Figure 4.19.** The characteristic signal of various protons confirms the structure of the recovered dye is analogous to the original one (>90%), which technically validates the concept that the recovered dye maintains its integrity during reconcentration and can be reused in the next batch of fabric dyeing.
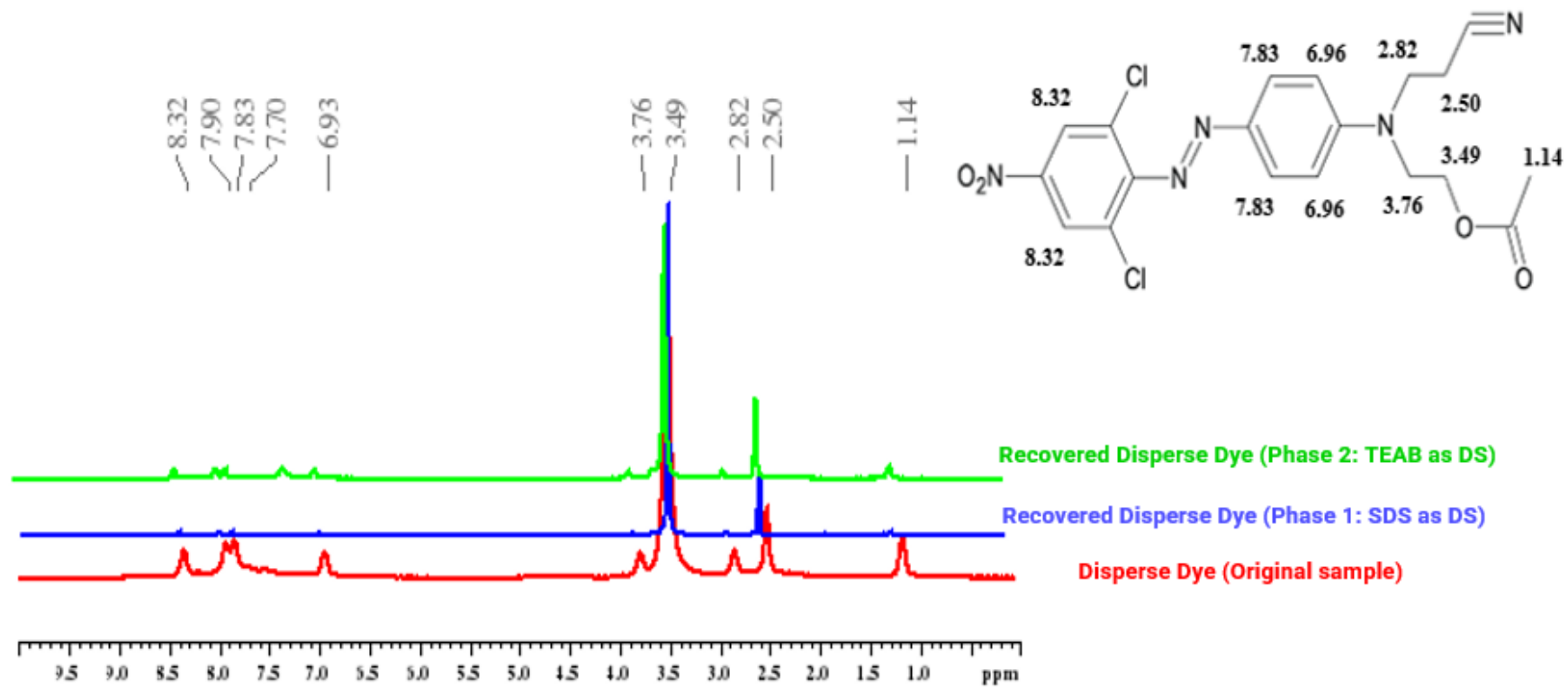
Figure 4.19: HNMR analysis of actual vs recovered dyes

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

This study experimentally proved the feasibility of dyebath effluent reconcentration and reuse potential with surfactant driven FO process. The proposed scheme achieves zero liquid and hazardous materials discharge. In both batch (24 h) and semi-continuous (48 h) experiments, the dye rejection was always 100% and no color was observed in the DS. Extremely stable water fluxes of around 7.5 LMH in case of SDS and 18 LMH of flux while using TEAB was achieved with negligible RSF of 0.03-0.1 gMH proving the potential of surfactants as ideal DS for this process. No regeneration is required for diluted surfactant with 30-35 g/L and 55-60 g/L of SDS and TEAB concentrations, respectively, and they can easily be reused in desizing, scouring, and bleaching after further dilution. The FS temperature was found to positively impact the flux which is ideal for the future onsite applications of the process as dyebath effluent is generated with >60°C temperature. The RSF of surfactants is 100 times less than NaCl due to the property of micelle formation. The FO membrane was found chemically stable after interacting with the dyebath effluent and no major change in AL groups or surface roughness was observed. The recovered dye shows great structural resemblance (>90%) to the original dye, which proves its reuse potential in the dyeing of the next batches. Hence, the proposed scheme has an excellent potential for dyebath effluent reconcentration and reuse, and it can be further explored in onsite applications.

5.2 Recommendations

Described below are the recommendations for future research.

1. Fabric fastening analysis of recovered dyes can be investigated for full scale implementation.
2. Dye reconcentration using acidic and basic dyes can be analyzed.
3. Potential of other surfactants can be studied for more economical benefits.

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