

Fertilizer Drawn Forward Osmosis (FDFO) Membrane Process for Textile Dyes Removal



BY

ZAHRA SAEED

MUHAMMAD QASIM

MOHAMMAD ALI CHAUDHRY

A thesis submitted in partial fulfillment of the requirements for the degree of

Bachelors of Engineering

In

Environmental Engineering

Institute of Environmental Sciences and Engineering (IESE)

School of Civil and Environmental Engineering (SCEE)

National University of Sciences and Technology (NUST)

It is certified that the contents and forms of the thesis entitled

**REMOVAL OF TEXTILE DYES USING FERTILIZER
DRAWN FORWARD OSMOSIS PROCESS**

Submitted by

ZAHRA SAEED KHAN

NUST201305127BSCEE10213F

MUHAMMAD QASIM KHAN

NUST201307976BSCEE10213F

MOHAMMAD ALI CHAUDHRY

NUST201307936BSCEE10213F

Have been found satisfactory for the requirements of the degree of

Bachelors of Engineering in Environmental Engineering

Supervisor: _____

Engr. Arsalan Khalid

Lecturer

IESE, SCEE, NUST

DEDICATED

TO

OUR LOVING FAMILIES

AND

FRIENDS

It wouldn't have been possible without their prayers and constant support.

ACKNOWLEDGEMENT

We have no words to express our deep sense of thankfulness and countless gratitude to **ALMIGHTY ALLAH**, the compassionate and merciful, who bestowed on us His blessings and gave us courage to complete the present studies and dissertation.

We have no words to express our sincere gratefulness to our respectable and worthy supervisor **Engr. Arsalan Khalid**, Institute of Environmental Sciences and Engineering, for his keen potential interest, skillful guidance, constructive criticism, and ever encouraging attitude throughout the course of research work.

We feel that our words cannot give an appropriate shelter to our expressions about **Dr. Sher Jamal**, HOD Institute of Environmental Sciences and Engineering, who provided his skillful guidance, financial assistance and valuable suggestions throughout the project as the Mentor.

We would like to thank **MK SONS Private Limited** for providing us with their data and also the dyes used in the research study.

We also wish to pay our heartiest gratitude to **Sir Aamir khan, Sir Mamoon and Sir Basharat**, Institute of Environmental Sciences and Engineering, who provided the much-needed support and assistance in Lab work.

We are also very thankful to **Mr. Usman, Mr. Tabish, Mr. Amir and Ms. Ammara Haider**, Institute of Environmental Sciences and Engineering, for their guidance and support as senior PhD and Masters Students. We are very grateful to the staff of the Waste Water Lab and Chemistry lab, for the technical assistance. Last but not least, we shall ever pride on having very accommodating and earnest friends, seniors and class fellows.

LIST OF FIGURES:

- ✚ Fig a. Osmotic process diagram
- ✚ Fig b. FDFO concept diagram
- ✚ Fig c. Solubility of fertilizers
- ✚ Fig d. Osmotic pressures of different fertilizers
- ✚ Fig e. Commonly used fertilizers
- ✚ Fig f. Process flow diagram of experimental set up
- ✚ Fig g. Experimental lab setup
- ✚ Fig 1. Pure water Flux
- ✚ Fig 1 (a). Viscosity of draw solutions
- ✚ Fig 2. Reverse solute flux
- ✚ Fig 3. Water flux when dyes used as feed solution
- ✚ Fig 4. Effect of Reactive Blue dye concentration on FO performance
- ✚ Fig 5. Effect of Direct Orange dye concentration on FO performance
- ✚ Fig 6. Effect of dye solution pH on FO performance
- ✚ Fig 7. End concentration of feed solution
- ✚ Fig 7 (a). Calibration curve of Reactive Blue dye
- ✚ Fig 7 (b). Calibration curve of Direct Orange dye
- ✚ Fig 8. Flux Recovery of FO process
- ✚ Fig 9. Google map image for Khurianwala Faisalabad

LIST OF TABLES:

- ✚ Table 1. Fixation degree of different dye classes on textile support
- ✚ Table 2. Fertilizer classification according to Nutrients
- ✚ Table 3. Nitrogen concentration in final diluted draw solute and the dilutions required to make it suitable for plant growth.

LIST OF ABBREVIATIONS:

FO	Forward osmosis
FDFO	Fertilizer drawn forward osmosis
RSF	Reverse solute flux
SOA	Sulphate of Ammonium
DAP	Di Ammonium Phosphate
MF	Micro Filtration
UF	Ultra Filtration
NF	Nano Filtration
RO	Reverse Osmosis
UV	Vis Ultra violet visible spectrophometer
DI	De Ionized water

ABSTRACT:

A novel fertilizer drawn forward osmosis (FDFO) membrane treatment process was demonstrated for the first time for the treatment and reuse of textile wastewater. The proposed FO process recovers water from wastewater through osmosis, in return the reducing the volume of the feed stream with an enhanced dye concentration. This was achieved using a fertilizer as a draw solution in order to eliminate the need of separation or regeneration of draw solution as in case of other FO processes. This diluted fertilizer solution can be used directly for fertigation. In this particular study, performance of two different fertilizers namely Ammonium Sulphate and Di ammonium phosphate were tested against two different dyes classes; reactive blue and direct orange. Both Fertilizers Ammonium Sulphate $(\text{NH}_4)_2\text{SO}_4$ and Di-Ammonium phosphate $(\text{NH}_4)_2\text{HPO}_4$ at 0.5M concentration showed good performance with water flux of 11.78 LMH and 13.25 LMH respectively at the end of 6 hours' experiment. The Flux increased with increasing Molar concentrations but the RSF increased simultaneously. 100% rejection of Dyes through FO membrane was observed. Remarkable reverse fouling behavior was observed as Initial Flux Recovered after all runs with physical flushing only. The impressive rejection of dyes, satisfactory water flux and adequate final nutrient concentration which requires minimal dilution in the final FDFO product water to meet the plant requirement indicates great potential of FDFO as a textile wastewater treatment technology along with the added benefit of water reuse and conservation.

Table of Contents

CHAPTER 1: INTRODUCTION	11
1.1 Textile hazards and need for its treatment	11
1.2 Existing treatment technologies and FO	11
1.3 Objectives of the study	12
1.4 Significance of the study	13
CHAPTER 2: LITERATURE REVIEW	14
2.1 Textile wastewater	14
2.2 Dye classification	14
2.3 Textile wastewater and its impacts	15
2.4 Conventional treatment processes	17
2.4.1 Biological	17
2.4.2 Chemical	18
2.4.3 Physical	18
2.5 Forward osmosis	19
2.6 Concept of fertigation	22
2.7 Dye and fertilizer selection	23
2.7.1 Dye selection:	23
2.7.2 Fertilizer selection:	26
CHAPTER 3: MATERIALS AND METHODS	31
3.1 Materials	31
3.1.1 Experimental setup:	32
3.1.2 Equipment used	33
3.2 Methodology:	35
3.2.1. Determination of preliminary data:	37
3.2.2. Assessment and performance evaluation of FO process with Dye Solutions:	39
3.2.3 Assessment and performance evaluation of FO process with change in pH of dyes solution	40
CHAPTER 4: RESULTS AND DISCUSSION	41
4.1 Pure water flux of different draw solutions:	41
4.2 Reverse solute flux (RSF) of different draw solutions:	42
4.3 Water Flux when dyes used as feed solution	44

4.4 Effect of dye concentration on water flux	45
4.5 Effect of feed solution pH on water flux	46
4.6 Rejection of Dyes and Concentration of the dye in the feed solution at the end of 6-hour experiment.....	48
4.7 Membrane cleaning and Flux Recovery	50
4.8 Nutrient Concentrations in the Final FDFO Product Water	51
CHAPTER 5: CONCLUSION AND RECOMMENDATIONS.....	54
5.1 Conclusion.....	54
5.2 Recommendation.....	54
REFERENCES:.....	55
Appendix 1: Sample Excel calculation data sheet.....	58
Appendix 2: Nitrogen calculation:	59

CHAPTER 1: INTRODUCTION

1.1 Textile hazards and need for its treatment

Textile industry is one of the largest manufacturing industries in Pakistan, which contributes 8.5% to the GDP of the country. These industries usually consume large amounts of water specifically in wet processing such as desizing, scouring, mercerizing, bleaching, dyeing, printing and finishing. Wastewaters produced by these processes have variable compositions of textile dyes, mineral oils, suspended solids and electrolytes. The most harmful amongst which is the dyeing effluent because of the presence of toxic and non-biodegradable dyes (Carmen & Daniela, 2010).

High percentages of dyes in the industries do not have a good fixation and are released directly into the wastewater streams (Mattioli et al., 2005). The presence of even small quantity of dyes impacts the environment by increasing the toxicity, COD and BOD levels significantly and is damaging to human health, aquatic life and is also esthetically displeasing (Chequer et al., 2013; Kant, 2012; Shaikh & Engineering, 2009). These complex contaminants actually hamper plant growth by adding color to the wastewaters, which are extremely difficult to degrade through conventional treatment technologies as ozonation, bleaching, activated sludge and electrochemical method (Eng et al., 2014).

1.2 Existing treatment technologies and FO

Earlier studies show that membrane technologies like MF, UF, NF and RO have proven to be effective in treating textile industry effluents, but these treatment methods have their advantages and disadvantages. Out of all these, Nano filtration having properties between RO and UF is considered to be very efficient in color rejection, salt retention and producing high permeate water flux (Prof, Petrinić, & Hélix-nielsen, 2014). But this has a limitation of considerably high operation and maintenance cost due to fouling.

Forward osmosis is relatively a newer technology which is an “osmotically driven membrane process”. It has previously been used for water and wastewater treatment. It has numerous other applications as osmotic power generation, desalination/concentration, emergency drinks and fertigation (Cath, Childress, & Elimelech, 2006). Forward osmosis has shown great potential in treating diverse range of impaired water sources, because as compared to other membrane technologies it does not require external hydraulic pressure, but water

moves under osmotic pressure from less concentrated feed side to the more concentrated draw side through a semi permeable membrane.

Many chemicals organic based, inorganic based, magnetic Nano particles, micelles and dendrimers have been used as draw solutes but the major problem is the recovery of pure water from diluted draw side and the regeneration of the draw solute (Chekli, Phuntsho, Shon, Kandasamy, & Chanan, 2016). So, to curtail that issue concept of fertilizer drawn forward osmosis (FDFO) or fertigation is introduced. In which the fertilizer is used as the draw solute to generate high concentration gradient for feed water to move towards draw side (Nasr & Sewilam, 2016; Phuntsho et al., 2012; Taylor et al., n.d.; Zou & He, 2016). And once it gets diluted it can be directed into the streams without any subsequent separation technique. This process has many benefits because the diluted water is nutrient rich and can be applied to the plants and crops.

Here in this research we have investigated the removal of the textile dyes using two different types of fertilizers namely Ammonium sulfate (SOA) and Di-ammonium-phosphate (DAP). Choice of fertilizers was made following the criteria of their popularity, osmotic pressures and solubility in water. This research can be of a significant contribution in countries like Pakistan which is an agricultural as well as an essential textile producing country. This is a sustainable technology as the wastewater from the textiles can end up in agriculture fields.

1.3 Objectives of the study

Our Objectives include;

- Investigating the performance of commercial fertilizers as draw solutes for forward osmosis membrane process
- Understanding the effects of parameters of forward osmosis membrane process on water flux and dyes rejection

1.4 Significance of the study

Global water scarcity is major issue faced worldwide, which therefore calls for timely investment on research to find out new and robust methods to purify water at low energy and cost. If low cost wastewater technologies are made available, it can make a drastic impact on the agriculture sector especially for countries like Pakistan where agriculture and textile industry sectors are providing major contribution for economic development of the country.

CHAPTER 2: LITERATURE REVIEW

2.1 Textile wastewater

Textile industry consumes large quantities of water and chemicals in wet processing, dyeing, printing and finishing. This delivers only a certain number of colorants and chemicals, rest being discharged as wastewater. This is due to degree of fixation and improper uptake of water soluble and insoluble dyes. Depth of shade, method of application, pH and material to liquor ratio are control factors for dye application for different type of substrate material.

Pollutants in wastewater vary with each industry depending upon the methods applied and chemicals used. Most common pollutants are biodegradable organic matter, heavy metals, toxic organic compounds, suspended and dissolved solids. Due to high color color intensity and variable composition, textile wastewaters are difficult to treat.

Dyes are complex molecular structure substances which are stable and are hard to degrade in wastewater. They are classified according to their chemical nature and fiber application. Acid, Basic, Direct and Reactive dyes being used for cellulosic fiber and disperse dyes for polyester or synthetic fiber.

2.2 Dye classification

Dyes are classified according to their chemical nature and fiber application. Some of the common dye groups are as follows;

Reactive dyes: Reactive dyes are most commonly used for dyeing and printing cotton fibers. They have better color and brighter shades than direct dyes. They have a simple molecular structure. Most of them contain an azo group which is basically a metallized azo, formazan, triphendioxazine, pthalocyanine and anthraquinone. These dyes react with the fiber as name indicates and forms a covalent bond due to ester or ether linkages under suitable conditions. They are soluble in water.

Direct dyes: Most of the dyes in this group are polyazo compounds, along with some stilbenes, pthalocyanines and oxazines; they have high affinity for cellulosic fibers due to this chemical property. To improve their wash fastness dyestuffs are chelated with metal

(copper or chromium) salts. They are also treated with formaldehyde or a cationic dye complex resin. They are soluble in water in presence of electrolytes.

Disperse dyes: The molecular structures of these dyes consist of azo and anthraquinonoid groups which have low molecular weight which help them in forming stable aqueous dispersions. They are non-ionic dyes, insoluble in water that is why they are applied to hydrophobic fiber such as polyester, polyamide, polyacrylonitrile, polypropylene etc. and also to dye nylon, cellulose acetate and acrylic fibers through micro fine aqueous dispersion.

Vat dyes: The main structural groups of vat dyes are anthraquinone and indigo. They are water insoluble dyes but are made soluble through process of vatting in which they are converted to their leuco compounds by reduction and solubilization with sodium hydroxide and sodium hydrosulphite solution.

Acid dyes: These are water soluble dyes and anionic in nature. They are applied on nylon, wool, and silk and modified acrylics. Also used for paper dyeing, leather dyeing, food color, cosmetics and inkjet printing

Basic dyes: These are cationic and water-soluble dyes. They are used for coloring of paper, polyacrylonitrile, modified nylon and polyester. They are also used with silk, wool and tannin-mordant cotton when brighter shades are required.

Sulfur dyes: They are water insoluble anionic dyes and are used for cotton fibers. They are made water soluble by reduction process under alkaline conditions using sodium sulphide as a reducing agent. These dyes are economically attractive due to their low cost and good wash fastness property. (Kyzas, Kostoglou, Lazaridis, & Bikiaris, 2013)

Reactive dyes, being most commonly used dyes for cellulosic fibers, have lowest degree of fixation and nearly half of these dyes are released into the effluent.

2.3 Textile wastewater and its impacts

Presence of the toxic compounds in textile wastewater are not only damaging to the environment but also pose serious threat to human health and aquatic life. Among all these chemicals, dyes are the most critical pollutants.

2.3.1 Health impacts:

They cause acute toxicity which involves oral ingestion and inhalation, skin and eye irritation, and skin sensitization. Evidence suggests that reactive dyes cause contact dermatitis, allergic conjunctivitis, rhinitis, occupational; asthma or other allergic reactions in workers.

Other major long-term potential health hazard of certain textile dyes is genotoxicity. Genotoxic chemicals include mutagens, carcinogens and teratogens. Mutagens produce mutations in living organisms; they may or may not be carcinogens. Almost 40% of colorants used globally have organically bound chlorine which is a known carcinogen.

Dyes not only are a hazard themselves but also carry along harmful compounds as toluene, ethyl benzene, di chlorobenzene, naphthalene, phenol, nitro phenol, 4-dimethylphenol, pentachlorophenol and p-chloro-m-cresol as trace organic impurities.

The textile wastewater effluent is a concern for environment as it has a low oxygen concentration due to presence of hydrosulfides and also acts as a hindrance to the passage of light thereby impacting the aquatic life growth. This effluent is detrimental to the water ecosystem and human health.

2.3.2 Environmental impacts

Dyes as mentioned above are long lasting in as they are highly stable to heat and light and don't degrade easily. Even the presence of small concentrations of them colors the effluent due to their brilliance. Their light absorption property reduces the photosynthetic activity of algae and other aquatic plants which in turn affects the food chain.

The foul smell and bad appearance of effluent is due to colloidal matter and oily scum, this increases turbidity and reduces light penetration necessary for photosynthesis. Also, the depleted oxygen poses a serious threat to marine life.

This effluent if led to the fields, it clogs the soil pores reducing its productivity. Soil texture is hardened and root penetration is hindered. If allowed to flow in drains and rivers, it affects the water quality and making it unfit for human use (Kant, 2012).

2.4 Conventional treatment processes

Public perception of water quality is greatly influenced by the color. So, the removal of color from wastewater is often more important than the removal of the soluble colorless organic substances. Removal of the dyes from the textile wastewater is often very costly, but a stringent environmental legislation has stimulated the textile sector in developing wastewater treatment plants.

Because of these harmful impacts of the dyes and stringent regulations implied in the recent years it is required by the industries to treat their effluent before discharging them into the streams and rivers. Some of the conventional treatment process employed to treat these effluents are classified into three different categories as; Physical, Chemical and biological methods.

Due to the complex nature of effluents there is no single process that can treat all the contaminants. Each process has their significant advantages and disadvantages. These processes are combined to optimize their efficiency as in the effective removal of pollutants, low energy costs and minimum sludge production and its ease of disposal.

Brief overview of the conventional treatment technologies are as mentioned below:

2.4.1 Biological

It is the most economical technology as compared to the physical and chemical methods. This involves the biological degradation of contaminants because microorganisms such as bacteria, yeasts algae and fungi are able to accumulate and degrade different pollutants. These biodegradation methods comprise fungal decolourization, microbial degradation, adsorption by living or dead microbial biomass and bioremediation systems. Biological treatment has drawback of considerable land area requirement, long treatment times and large amounts of sludge produced at the bottom of the tanks that need to be disposed of (Robinson, McMullan, Marchant, & Nigam, 2001). Its constraints involve diurnal variations, toxicity of some chemicals and less flexibility in design and operation. Optimum color removal is not achieved through this process due to the stability and complex nature of dye components; many organic molecules are recalcitrant due to their synthetic origin. Notably azo dyes due to their xenobiotic nature are not degraded.

2.4.2 Chemical

Chemical methods include coagulation or flocculation combined with flotation and filtration, precipitation-flocculation with Fe (II)/Ca (OH)₂, electro flotation, electro kinetic coagulation, conventional oxidation methods by oxidizing agents (ozone), irradiation or electrochemical processes. These chemical techniques are often expensive, and although the dyes are removed, accumulation of concentrated sludge creates a disposal problem. There is also the possibility that a secondary pollution problem will arise because of excessive chemical use. Recently, other emerging techniques, known as advanced oxidation processes, which are based on the generation of very powerful oxidizing agents such as hydroxyl radicals, have been applied with success for the pollutant degradation. Although these methods are efficient for the treatment of waters contaminated with pollutants, they are very costly and commercially unattractive. The high electrical energy demand and the consumption of chemical reagents are common problems.

2.4.3 Physical

Physical treatment process involves adsorption and membrane separation techniques (Reverse osmosis, Nano filtration and electro dialysis). In accordance with extensive research done previously, it is concluded that liquid-phase adsorption is a popular adsorption technique which produces high quality effluent due to its proper design. This provides an attractive alternative exclusively if the adsorbent is inexpensive and the effluent doesn't need pretreatment. It is preferred due to the less initial cost, flexibility and simplicity of design and insensitivity to toxic pollutants. It also does not produce harmful substance as end product (Chequer et al., 2013).

Membrane process as Nano filtration has been commonly used as textile wastewater effluent treatment. Ong et al., 2014 concluded that Nano filtration membrane shows 98% and above rejections and high-water fluxes. They also concluded that the molecular weight of the dye affects the water flux. A dye with a smaller molecular weight has a higher tendency in reducing the flux. The membrane shows robust performance in terms of flux and rejection under cycles of chemical cleaning during the lab-scale and pilot-scale evaluations. The major disadvantage of the membrane processes is that they have a limited lifetime before membrane fouling occurs and the cost of periodic replacement must thus be

included in any analysis of their economic viability. Another major disadvantage is of extensive energy required as they're all pressure driven processes.

Whereby, to deal with this limitation of high energy requirement the forward osmosis process was introduced that will be explained in the later section.

2.5 Forward osmosis

As the name suggests this process works on the natural principle of osmosis, which is how plants and trees take water up from the soil. This is a low energy process as it exploits a natural principle.

As indicated in Fig a. (Nicoll., 2013.) This works by having two solutions of different concentrations separated by a selective semi-permeable membrane. Pure water flows from a less concentrated solution to a more concentrated side diluting it as a result and leaving the salts behind due to the membrane selectivity.

This process requires two different solutions separated by a selective membrane just like in reverse osmosis. These two solutions are called feed solution and draw solution. Feed solution is basically the low concentrated solution from which the water needs to be extracted and draw solution is the high salt concentration solution that provides osmotic gradient to the fluid to move from less concentrated side to more concentrated side and dilute it. This process takes place at atmospheric pressure, with variations such as pressure enhanced osmosis and pressure retarded osmosis. These can be understood from the figure shown below (Fig a).

Forward osmosis process does two things;

- It concentrates the low osmotic pressure solution
- It dilutes the high concentrate solution

In forward osmosis membrane processes, the driving force for water separation is quantified by the osmotic pressure difference between solutions on either side of the forward osmosis membrane: higher osmotic pressure difference → higher rate of water diffusion. In ideal solutions with low solute concentration, the osmotic pressure difference ($\Delta\Pi$) can be approximated by the Morse equation:

$$\Delta\pi = iRT\Delta M$$

- i is The Van't Hoff factor, which reflects the dissociation multiple of the solute species in question. For a dilute solution of sodium chloride, the Van't Hoff factor is equal to 2 because 1 mole of NaCl dissociates into 2 moles of solutes in aqueous solution.
- R is the gas constant in $L \cdot atm \cdot K^{-1} \cdot M^{-1}$
- T is the temperature of the solution in Kelvin [K]
- M is the molarity of the solution in Molar [M]

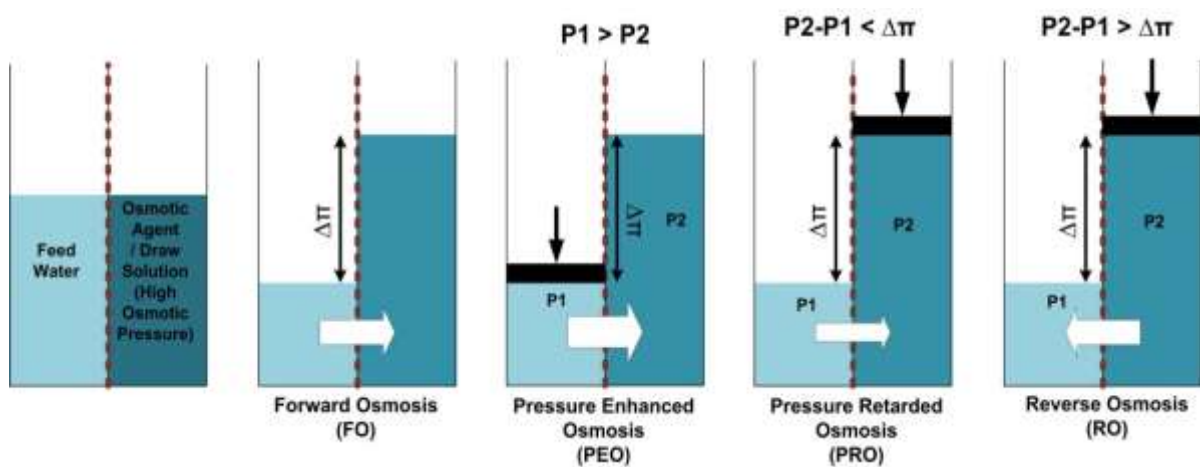


Fig a. Osmotic processes

And as a result, ions are rejected both in forward flow and reverse flow movement. Fouling is less of a problem in FO because it's a natural process and fluid moves according to the natural osmotic gradient this will be discussed in later sections.

FO Applications: Forward osmosis is a newer technology and is not fully established yet. It has multiple applications some of which are described below. All of them are not put into practice on a large scale but are studied or practiced at lab scale or pilot scale. The applications are diverse in range where forward osmosis process is deployed, some of them are single step and in others they are used in combination with other processes.

Some of its applications include osmotic power generation, desalination, cooling tower makeup water, emergency drinks, fertigation and fracture water makeup using flow back water.

FO performance: Performance of forward osmosis membrane process is judged similar to other membrane processes i.e. in terms of water flux, Rejection and Reverse solute transport.

Water flux defines the rate of transport of water across the membrane under the driving force of osmotic pressure.

$$J_w = A (\Delta P - \Delta \Pi)$$

- A is the “pure water permeability coefficient” – an intrinsic membrane property
- ΔP is the difference in hydraulic pressure across the membrane
- $\Delta \Pi$ is the difference in osmotic pressure across the membrane

Rejection is a measure of how much contaminant have been retained on the feed side and reverse solute transport/reverse salt transport is a measure of the salts that have penetrated through the membrane from draw to the feed side, the formula for calculations will be explained in later section.

Forward osmosis membrane consists of a thin active or rejection layer fused with an underlying micrometer size support layer to provide mechanical support and overall strength. Therefore, the performance is governed by physical properties of both rejection layer and underlying support layer.

FO Draw solute: Forward osmosis process requires a high concentrated draw solution to provide osmotic gradient for which various draw solutes have been used in numerous studies. Draw solute (DS) properties such as osmotic pressure and water solubility affect the performance of the process. Some of the draw solutes are generally classified as

- Organic based
- Inorganic based
- Magnetic Nano particles

- Ionic polymer hydrogel particles
- Micelles close to the Kraft point
- Dendrimers

The problem here is the regeneration of draw solute or its separation from the diluted draw solution. Because as the pure liquid moves from the feed to the draw and dilutes it, it's still not usable in any form unless it acquires further processing of separation of draw solute from pure liquid. This recovery process shouldn't be energy intensive otherwise FO is not comparable with other pressure driven processes.

2.6 Concept of fertigation

Fertigation is the injection of fertilizers, soil amendments, and other water-soluble products into an irrigation system. It is the idea of using liquid fertilizer for the crops rather than using it in granular or pellet form. It is practiced extensively in commercial agriculture on high value crops such as vegetables, fruit trees, turf and ornaments.

Fertigation has certain benefits over conventional fertilizer application techniques because:

- It reduces the amount of fertilizers, chemicals and water required
- It enhances the nutrient absorption rate
- It also prevents leaching of chemicals into the water supply.
- It minimizes the loss of fertilizer as the application of nutrients can be controlled at the precise time and rate necessary

When water, energy and the environmental issues are all inter related, a treatment technology that consumes much lower energy is essential especially for large scale irrigation. So, the idea of fertilizer drawn forward osmosis was introduced keeping in view the energy requirement of draw solute separation in forward osmosis. This idea makes use of fertilizer as a draw solute which upon dilution can be used directly in fields for agricultural purposes and hence does not require any subsequent separation. Fertilizers are extensively used in agricultural production making them an ideal choice as draw solutes. This diluted fertilizer solution can also be used for hydroponics.

Hydroponics is the method of growing plants in soil less conditions or aquatic based environment, using mineral nutrient solutions in a water solvent. Some researchers have used fertilizer drawn forward osmosis diluted fertilizers for hydroponics plant growth and have been successful. For example, Chekli et al., 2017 observed the growth of lettuce through hydroponics.

Fig b. shows the concept of Fertilizer drawn forward osmosis as suggested by the research paper (Zou & He, 2016).

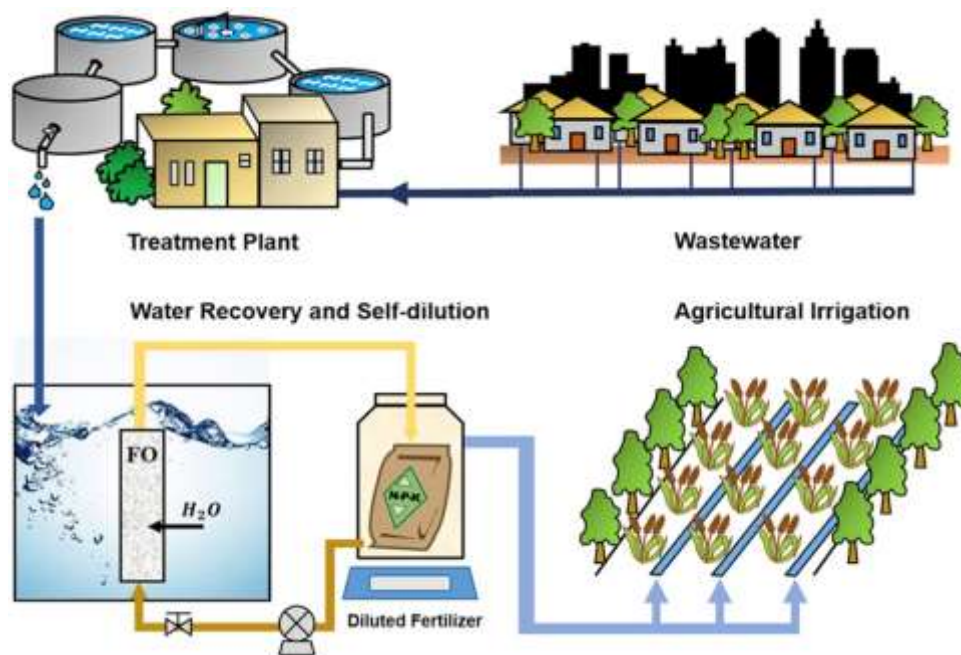


Fig b. Fertilizer drawn forward osmosis concept

Fertilizer drawn forward osmosis is applicable only if fertilizers possess certain properties. Not every fertilizer is suitable for this use. Therefore, the selection criteria for the two fertilizers used in this study, namely ammonium sulphate and di ammonium phosphate are explained below.

2.7 Dye and fertilizer selection

2.7.1 Dye selection:

We selected two dyes from two different dye groups as their representative. The choice of dye group was made on the basis of their scale of application, degree of fixation, loss in effluent and keeping in view the variety of dyes being used in the textile industry. Further details are explained in this section.

Table 1. Fixation degree of different dye classes on textile support

Dye class	Fibre type	Fixation degree, %	Loss in effluent, %
Acid	Polyamide	80-95	5-20
Basic	Acrylic	95-100	0-5
Direct	Cellulose	70-95	5-30
Disperse	Polyester	90-100	0-10
Metal complex	Wool	90-98	2-10
Reactive	Cellulose	50-90	10-50
Sulphur	Cellulose	60-90	10-40
Dye-stuff	Cellulose	80-95	5-20

As indicated in Table 1 (Carmen & Daniela, 2010), two of the most commonly used dye groups in the textile industry namely Reactive dyes and Direct dyes have the lowest degree of fixation to the fabric and which is why most of the dyes are lost into the effluent without getting attached to the fiber. This colored effluent is undesirable and requires proper treatment. Also, the loss of these expensive dyes cost the industrialists an extra price. Therefore, the research for concentrating this effluent dye stream for reuse purposes is still on board.

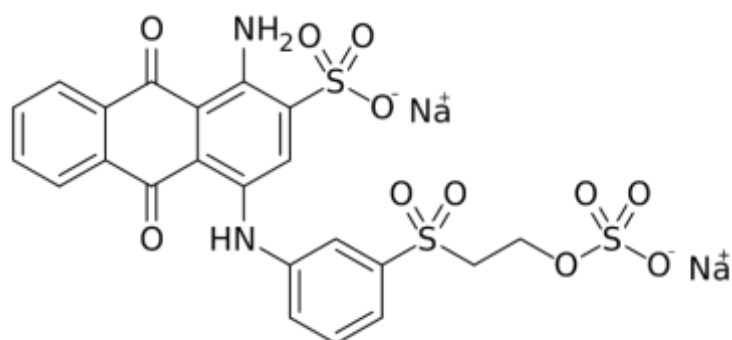
Reactive Blue:

Reactive dyes are extensively used in textile industry, fundamentally due to the ability of their reactive groups to bind to textile fibers by covalent bonds formation. These characteristics facilitate the interaction with the fiber and reduce energy consumption. The major environmental problem associated with the use of the reactive dyes is their loss in the dyeing process. The fixation efficiency is in the range 60–90% (Table 1). Consequently, substantial amounts of unfixed dyes are released in wastewater. Textile wastewater is characterized by high chemical oxygen demand (COD), low biodegradability, high-salt content and is the source of aesthetic pollution related to color. Government regulation imposes limits on color, as it reduces light penetration in receiving water bodies.

Reactive dyes form a reactive vinyl sulfone ($-\text{SO}_3-\text{CH}=\text{CH}_2$) group, which creates a bond with the fibers. However, the vinyl sulfone group undergoes hydrolysis (i.e. a spontaneous reaction that occurs in the presence of water), and because the products do not have any affinity with the fibers, they do not form a covalent bond (Prof et al., 2014). Therefore, a

high amount of dye constituents is discharged in wastewater. For instance, the half-life of hydrolyzed Reactive Blue 19 is about 46 years at pH 7 and 25°C (Carmen & Daniela, 2010).

Chemical structure of Remazol Reactive Blue dye is;



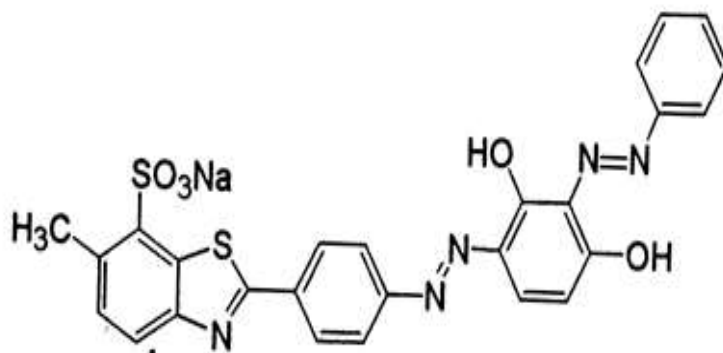
Its molecular formula is $C_{22}H_{16}N_2Na_2O_{11}S_3$ and its molar mass is $626.53 \text{ g}\cdot\text{mol}^{-1}$ ("CID 17409 Pubchem," n.d.)

Direct Orange:

Direct dyes are aromatic azo compounds which are solubilized by the introduction of sulphonic acid groups into the aromatic nuclei and are used in the form of sodium salts. Azo dyes have always been the major chemical class of dyes with which relatively long and linear molecular structures. Good wet fastness properties of direct dyes on cotton are generally believed to be due to the unique linear structure which allows them to aggregate within the cellulose structure once they have penetrated the fiber. The dyeing mechanism of cellulose fiber with direct dyes depends primarily on the pore structure of the fibers and dye properties such as diffusion and substantivity.

Dyes that are made from these chemicals may break down to form them again, after they are absorbed into the body, so they are not safe to be exposed to. Both benzidine and o-dianisidine are suspected cancer-causing chemicals.

The direct dye we selected was direct orange 32, it has a double azo bond and rest of the details is given below.



Its molecular formula is $C_{26}H_{18}N_5NaO_5S_2$ and its molar mass is $567.57 \text{ g}\cdot\text{mol}^{-1}$ (“WorldDyeVariety,” n.d.)

2.7.2 Fertilizer selection:

Mineral fertilizers are mainly chemical products. The main representatives of this group are concentrated mineral fertilizers, which are divided into

1. One-component (straight) fertilizers – contain one nutrient as a major. They may also comprise accompanying ions, respectively microelements. They are divided into nitrogen, phosphoric acid, potassium, calcium and magnesium fertilizers.
2. Multi-component (compound) fertilizers – fertilizers containing at least two or more major nutrients, may include accompanying ions and microelements. According to the nutrient content they are divided into fertilizers – double ones containing 2 major nutrients (NP, NK, PK), triple (full), fertilizers with micronutrients and special group consists of fertilizers containing sulphur.

Table 2. Fertilizer classification according to Nutrients

Nitrogenous	Phosphate	Potash
Urea	Di ammonium phosphate (DAP)	Muriate of potash
Ammonium sulphate	Super phosphate	Sulphate of potash
Sodium sulphate	Ammonium hydrogen phosphate	
Ammonium nitrate		

Choice of fertilizers was made keeping in mind the following criteria;

- Solubility: Solubility is an important parameter because less soluble fertilizers might settle at the bottom of the tank, hence lowering the potential to draw water from feed side. Also, high solubility in fertigation helps fertilizers to absorb into plant roots easily. Figure below indicates the solubility of different fertilizers and SOA and DAP have justifiable solubility.

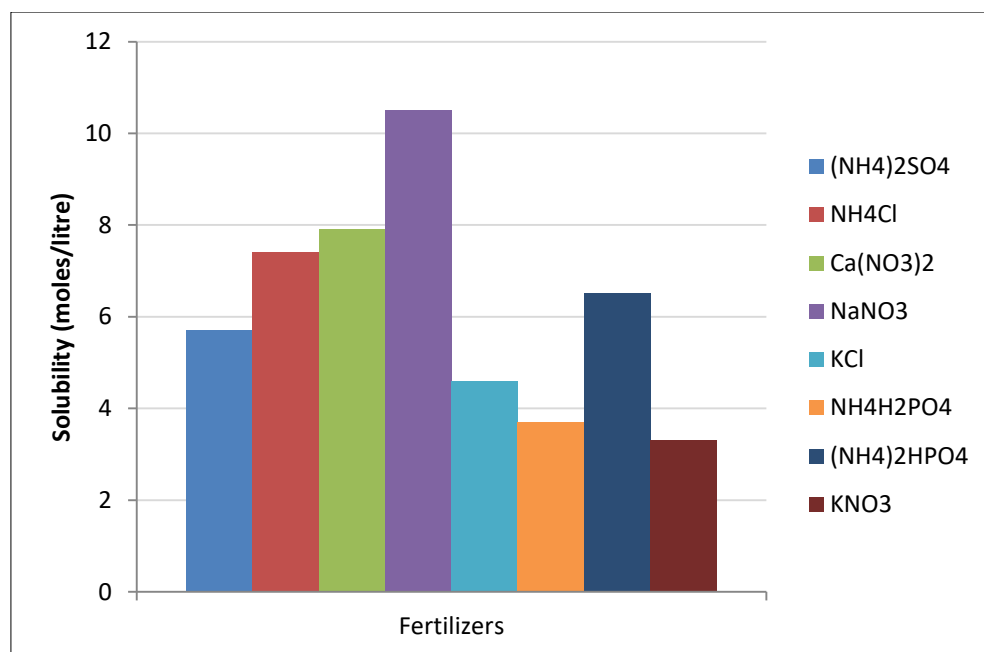


Fig c. Solubility of fertilizers in water (Phuntsho, Kyong, Hong, Lee, & Vigneswaran, 2011)

- Osmotic pressure: Osmotic pressure is the colligative property of the solution and is independent of the number and type of species formed. Fig d shows the osmotic pressure of different fertilizer draw solutions at increasing concentrations (Phuntsho et al., 2011). Ca(NO₃)₂ has the highest osmotic pressure at 2 M concentration followed by (NH₄)₂SO₄, NH₄Cl, and KCl. KNO₃ showed the lowest solubility and osmotic pressure amongst the selected fertilizers.

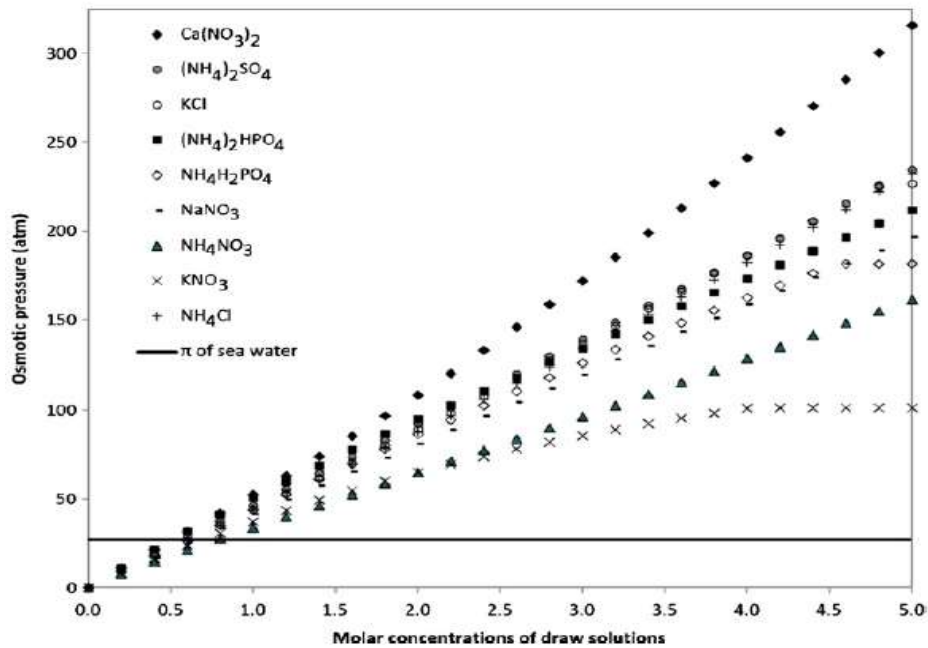


Fig d. Osmotic Pressure of different fertilizer solutions at 2 M concentration generated by OLI stream analyzer

- Popularity: DAP and SOA are most commonly used fertilizer around the globe. Although Urea is also commonly used but it isn't desirable as a draw solution because urea has low molecular weight and is highly soluble in water, it does not dissociate in water or form charged species and therefore it was found to have very low osmotic potential and high reverse solute flux.

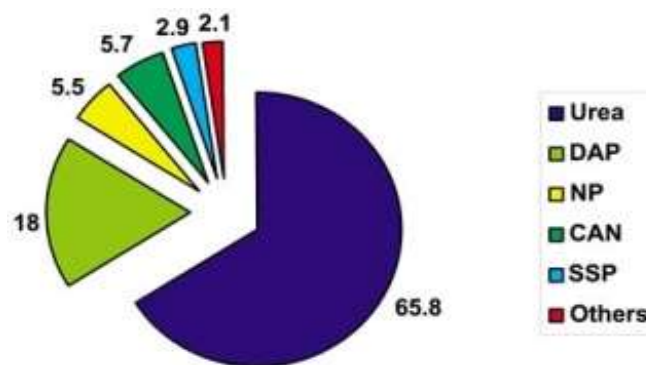
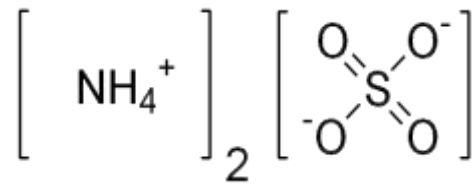


Fig e. percentage of fertilizers used commonly ("Fertilizer use by crop in Pakistan", 2004.)

Ammonium Sulphate/Sulphate of Ammonia (SOA):

Ammonium sulphate was one of the most important N-fertilizers but because it contains 21% of N and 24% of Sulphur. It is soluble in water and nitrogen in this fertilizer is readily

available to crops. This fertilizer has an acidifying effect; therefore, its continuous use may be advantageous on alkaline soils. Chemical structure of SOA is;



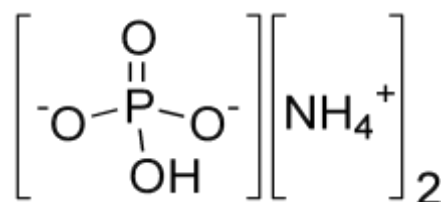
It provides an excellent source of S which has numerous essential functions in plants, including protein synthesis. Because the N fraction is present in the ammonium form, ammonium sulfate is frequently used in flooded soils for rice production, where nitrate-based fertilizers are poor choice due to denitrification losses.

Ammonium sulfate exhibits a high osmotic pressure due to the formation of a large number of species in aqueous solution. At a 2 M concentration, osmotic pressure of ammonium sulfate is estimated to be 92.1 atm, which is comparatively higher to that of seawater (~28 atm).

Di Ammonium Phosphate (DAP):

DAP is the most commonly used phosphate fertilizer; It contains 18% of N and 46% of Sulphur. The solubility of DAP is more than 95%, which is highest among the phosphatic fertilizers available in the country. Due to high solubility, it can also be used through fertigation as well as by foliar application. Its nitrogen to phosphorus ratio (1: 2.5) makes it an ideal fertilizer for Basal application to meet the initial requirement of most of the crops. Having an ultimate acidic effect on the soil, it is well suited for our alkaline soils.

Chemical structure of DAP is;



DAP fertilizer is an excellent source of P and N for plant nutrition. The ammonium present in DAP is an excellent N source and is gradually converted to nitrate by soil bacteria, resulting in a subsequent drop in pH. Therefore, the rise in soil pH surrounding DAP granules is a

temporary effect. This initial rise in soil pH neighboring DAP can influence the micro-site reactions of phosphate and soil organic matter.

DAP and DAP blends are used on a range of crops in broad-acre farming, cereals, sugar cane, sowing pastures, dairy pastures, fodder crops and also in horticultural crops; for example, vegetables and tree crops.

CHAPTER 3: MATERIALS AND METHODS

3.1 Materials

The setup functions on the combination of a Feed Solution (FS) and the Draw Solution (DS). They were circulated within the membrane housing which was designed and prepared for an active area of 42 cm². Flow rates were kept at an equal rate of (550 ml/min) with two peristaltic pumps (Longer Man pump) and the changes in mass from the Feed side to the Draw side were registered using an automated mass balance (Shimzadu). For real time data collection, a computer system was connected to this mass balance in order to record the changes in mass on a spreadsheet.

Feed solution

For the Feed solution two textile dyes namely Reactive Blue and Direct Orange both in the concentration range of 100 to 1000mg/L were used and upon requirement their respective pH was varied using 1 Molar concentrated solutions of Sodium Hydroxide (NaOH) and 1 Molar solution of Hydrochloric acid (H₂SO₄). These agents were incorporated into the feed solution to assess the effects of variable pH on overall performance of the membrane process.

Draw Solution

In this study, two fertilizers selected for the study, namely Ammonium Sulfate (SOA) and Di Ammonium Phosphate (DAP) were used in the range of 0.5 to 3 M concentration. These solutions were prepared separately in distilled water to provide a pure feed stream for the process.

Other chemicals:

Sodium Chloride (NaCl) was another major chemical used in the study as its multiple solutions were prepared to determine the baseline flux values which assisted in the comparative assessment of FO membrane process where the feed is a textile dye containing stream of water. NaCl was used to form Draw solutions with concentrations ranging between 0.5 to 3 Molar solutions.

3.1.1 Experimental setup:

A comprehensive setup established to cover the parameters of the study was constructed with the core principal of being simple, precise and integrated.

Two tanks (5 liter each) were used to act as a sum for the Feed solution and Draw solution.

The inlet and outlet of a peristaltic pump (BT300-2J Longer Pump) was submerged in the Feed tank as well as the Draw tank, these pumps allow the precise control of flow rates for small values of discharge.

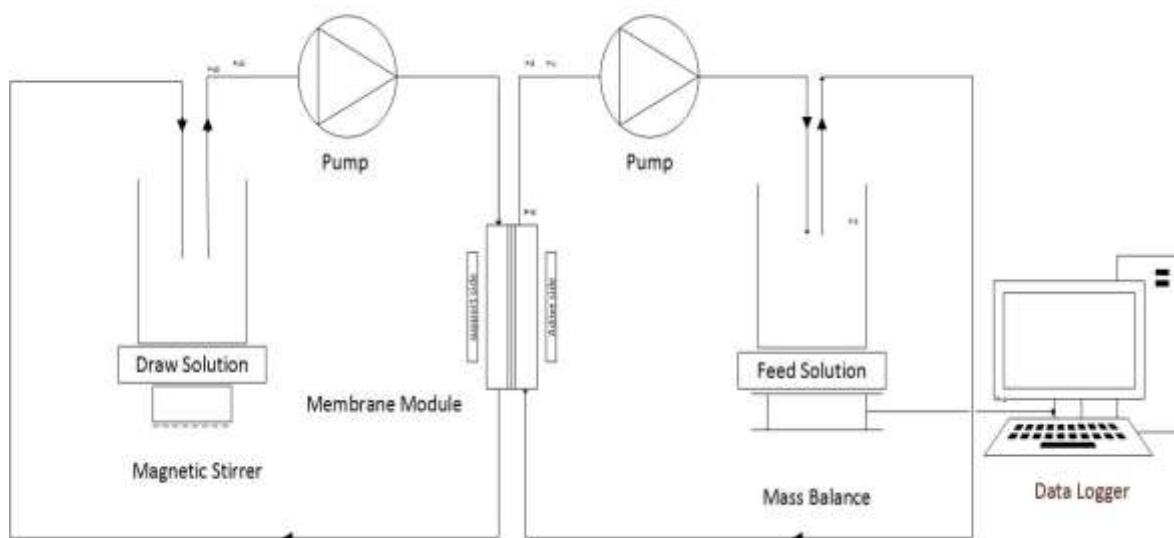


Fig f. Process flow diagram of experimental setup (generated using MS Visio)

A custom Flat Sheet Membrane Module of active area 42cm^2 was built and attached in sequence of the individual flow circuits. The membrane placed within this housing was a Thin Film Composite with Poly-Amide Coating. Here the Active side of the membrane sheet was kept facing the Feed Stream thus maintaining the FO mode in contrary to PRO mode for all experiments completed.

A magnetic stirrer (PC 420D CORNING) was kept under the Draw tank to make sure all the fertilizers and salt added remains dissolved thus maintaining a homogenous blend of fertilizer solution. A mass balance (UW6200H SHIMADZU) was kept under the Feed tank to record the loss in mass of the Feed tank which would later be used to determine the variation in Permeate Flux through the duration of each run cycle. This scale was connected via RS232C Data Cable to the Computer System which plotted these periodic readings into a spreadsheet program.



Fig g. Experimental Lab Setup

3.1.2 Equipment used

In order to record and interpret the parameters required for the conclusion of results, different techniques were employed to extract this information in a comprehensive manner. The equipment used include:

Mass Balance (*UW6200H SHIMADZU*)

The mass balance used during the experimental runs allowed for very accurate readings as well as the permission to connect it to a computer system and record readings at a fix time interval specified by the user. These values for change is mass per unit time were used to derive the water flux and multiple values over the six hours duration were used to form graphs depicting the trend lines for these fluxes.

pH and Temperature Probe (*Cyber Scan 500ph*)

This tool was employed to monitor both the pH and temperature of the Feed Stream before, during and after each run to see the changes brought about in the values within the Feed Stream. For the runs conducted where the pH of the Feed stream was ignored the instrument was not used with reference to pH but temperature alone.

During runs in which pH had to be brought to specific levels the tool was used to prepare the specific solution upon the required addition of 1 M solution of both acid and Base.

UV-Spectrophotometer (*Model T-60U range 190-1100nm*)

The principal mechanism for the equipment is the direct relation between the concentration of the specific particle and the quantified amount of light that has been absorbed by that particle at a specific wavelength that is unique for different types of particles. Light at only a certain characteristic wavelength is absorbed and this absorbance is proportional to the concentration of the particles in solution.

In this study, the solutions of known dye concentration were prepared from 1000 mg/L to 10 mg/L and tested in the UV-Spectrophotometer for absorbance, upon determining the specific absorbance values for each known concentration, a straight-line calibration curve was plotted and the equation was determined. Then, the unknown concentrations of Dye in the Draw solutions were determined by testing a sample of Draw solution after each run in the UV-Spectrophotometer and obtaining its absorbance. The equation determined from the calibration curve was applied for determining the concentration of dye present in the Draw solution. This led to the Rejection value achieved by the membrane process.

Conductivity meter (*inoLab ph/conductivity 720*)

Conductivity, defined as the ability of an electrolyte solution to conduct electricity, was a major principle used to determine the amount of fertilizer that had travelled from the Draw stream into the Feed stream. As the fertilizer is fundamentally a salt that forms ions in a solution, these ionic solutions form electrolytes. The concentration of these ions present in the solvent is directly proportional to the conductivity of this solution.

After the completion of each baseline run where the feed stream was pure water, the conductivity of distilled water which had been determined prior to the experiment was subtracted from the conductivity after the completion of the run.

As the only constituent of this solution was fertilizer from the Draw stream, the conductivity value was an accurate representation of the fertilizer concentration in the Feed stream. Conversion to attain values from micro Siemens to units of concentration was performed to depict greater clarity.

Viscometer (*Redwood Viscometer*)

The Forward Osmosis Membrane process performance is affected by the viscosity of the solutions that are run along the membrane interface. As the viscosity increases the resistance offered to incoming permeated water also increases, this results in a decreased overall water flux.

To assess and understand the extent to which this occurs in the case of Ammonium Sulfate and Di Ammonium Phosphate, solutions at different molar concentrations were prepared. Sodium Chloride solutions were also prepared in the concentration range of 0.5 to 3 M solutions. The differences in viscosity were then used to justify the differences in water flux for different Draw solutions.

Total Nitrogen (*Total Kjeldahl Nitrogen Apparatus*)

These experiments were performed to assess the final amount of Nitrogen present in the Draw Stream after each run. This value of nitrogen has to be assessed as some salt permeates towards the Feed side during experiment, this is referred as the reverse solute flux (RSF).

TKN values also showed the extent to which the nitrogen has been diluted as this was used to further understand how much dilution would be required in order to make this draw stream water adequate for direct application to plant and crops.

3.2 Methodology:

Cross-flow velocity

To determine the ideal Cross Flow Velocity, a value must be derived that fulfills the requirements for the particular membrane assembly (Devia et al., 2015). A cross flow velocity too low will result in thicker boundary layer formation which will aid concentration polarization. A fall in permeate flux will result due to this concentration polarization phenomenon. If the cross-flow velocity is kept at an inadequately high value than the chances of physical damage to the membrane itself are high. Thus, a value in the range of 5 to 10 cm/s was desired for this membrane housing of active area 42 cm².

- ❖ For a flow rate = 550 mL/min = 550 cm³/min
Width of inlet = 4.2 cm
Depth of inlet = 3 mm = 0.3 cm

$$\text{Cross Sectional Area} = 4.2 \times 0.3 = 1.26 \text{ cm}^2$$

Now,

$$\text{Flow Rate} = \text{Cross Flow Velocity} \times \text{Inlet Cross Sectional Area}$$

$$\text{Flow Rate}/\text{Inlet Cross Sectional Area} = \text{Cross Flow Velocity}$$

$$\begin{aligned} 550/1.26 &= \text{Cross Flow Velocity} = 436.51 \text{ cm/min} \\ &= 7.275 \text{ cm/s} \end{aligned}$$

❖ $\text{Cross Flow Velocity} = 7.275 \text{ cm/s}$

Operating conditions

A similar experimental environmental was maintained for the multiple experimental runs performed. The slight difference in conditions for the experimentation made a negligible impact as the membrane system is an enclosed one and ambient conditions within the lab could be kept at a near constant.

These conditions can be summed up as:

- Temperature = $24 \pm 1^\circ\text{C}$
- Cross Flow velocity = 7.275 cm/s
- Run Time = 6 Hours
- Membrane Forward Flushing = 1 Hour
- Feed Volume = 2 Liters
- Draw Volume = 0.5 Liters

The sequence of each individual experiment followed the basic steps of

- Preparing a Draw solution with fixed volume of 0.5 Liters and a Feed Solution at a Fixed Volume of 2 Liters.
- Conduction of the experimental run for a duration of 6 hours
- Upon Completion of the 6 hours run the system would be drained and flushed with sufficient distilled water
- The Feed and Draw Tank would then be filled with 1 Liter of distilled water and the system would be shifted to a higher flow rate and kept in sequence for approximately 1 hour. This would be the forward flushing phase of the experimental run to clean out any foulant and remains throughout the membrane system.

Formulas Used:

Experimental flux (L/m²h-LMH):

$$j_w = \frac{\Delta m}{\Delta t} \frac{1}{A_m} \quad (1)$$

Where Δm is the mass change, Δt is the test time duration which is 6 h and A_m is the effective membrane area which is 0.042 m².

Rejection (%)

$$R = 1 - \frac{C_d \times V_d / V_p}{C_f} \quad (2)$$

where C_d (ppm) is the dye concentration in the draw solution at the end of each FO test, V_d (L) is the final volume of draw solution, V_p (L) is the volume of the permeate water and C_f (ppm) is the heavy metal concentration in the feed solution.

Reverse solute flux (g/m²h)

$$J_s = \frac{\Delta C_t V}{\Delta t} \frac{1}{A_m} \quad (3)$$

Where ΔC_t (g/L) and V (L) are the changes of salt concentration and feed solution volume.

Water Recovery (%)

$$J_w = \frac{J_w^f}{J_w^i} \times 100 \quad (4)$$

Where J_w^f is the final water flux while, J_w^i is the initial water flux (Cui, Ge, Liu, & Chung, 2014; Han et al., 2016).

For calculations and sample data sheet consider Appendix 1. The sequence of the overall progression of different phases of study is in the order of:

3.2.1. Determination of preliminary data:

Baseline experiments

To assess the flux performance of the Thin-Film Composite (TFC) Membrane with Poly Amide Coating, baseline experimental runs were performed with Sodium Chloride (NaCl) as a general procedure to verify the specifications of the commercial grade membrane. For all baseline experimentation, the feed stream is always kept as distilled water and the

concentration of salt in the Draw Stream may be varied. These baseline runs were also performed for the Fertilizers under study. The procedure has been elaborated under this section.

a. *Calibration curves for dyes*

To quantify and calculate the rejection of dye for the experimental runs, UV-Spectrophotometer (*Model T-60U range 190-1100 nm*) was used.

b. *Viscosity of the draw solutions*

Small sample solutions of 0.5 M, 1 M, 2 M and 3 M concentration were prepared for Sodium Chloride (NaCl), Ammonium Sulfate (SOA) and Di Ammonium Phosphate (DAP). These multiple solutions were then tested using Viscometer (*Redwood Viscometer*) and their numerical values were noted down in a spreadsheet program for further interpretation.

c. *Pure water flux for Sodium Chloride (NaCl)*

To establish the baseline water and reverse solute flux values and to define a reference value for comparative reasons, controlled 6 hour runs were performed by using distilled water as a feed stream and different molarities of NaCl as draw stream, i.e. 0.5 M, 1 M, 2 M and 3 M.

d. *Pure water flux for Ammonium Sulfate (SOA) and Di Ammonium Phosphate (DAP)*

In order to determine the baseline water flux, reverse solute flux and optimum values of highest water flux with least reverse solute flux, 6 hours' experiments were performed with 0.5 M, 1 M, 2 M and 3 M solutions for both SOA and DAP as draw solutions and distilled water as feed solution. The results were interpreted to determine a single concentration of SOA and DAP that would be used for further experimental runs where dye would be the Feed Solution.

3.2.2. Assessment and performance evaluation of FO process with Dye

Solutions:

Dye concentration:

Through the consultation of published literature and the wastewater characteristics report of the textile manufacturing industry *Mk. Sons Pvt. Limited*, concentration of textile dyes were specified at 100 mg/L and 1000 mg/L for both Reactive Blue and Direct Orange dyes. This allowed for an accurate representation of Dye concentration in the textile wastewater found in the effluents of textile industries. Each concentration was tested with NaCl, SOA, and DAP as the objectives of the study.

a. *FO Performance with Sodium Chloride as draw solution and both Reactive Blue and Direct Orange dyes as feed solution*

Experimental runs, lasting the duration of 6 hours each, were performed with Sodium Chloride as the Draw Solution at a fixed concentration of 0.5M with combinations of 100 mg/L and 1000 mg/L for Reactive Blue and Direct Orange dyes. The resulting values of permeate flux were brought in comparison with the pure water flux achieved by Sodium Chloride and interpreted for performance potential.

b. *FO Performance with Ammonium Sulfate and Di Ammonium Phosphate as draw solution and Reactive Blue and Direct Orange dyes as feed solution*

In this study, 0.5 M solutions of both fertilizers were prepared separately and experimental runs for each dye at concentrations of 100 mg/L and 1000 mg/L were conducted. The data produced by these runs was of major significance as this would determine the practicality of fertilizer as a usable Draw Solution or fertigation to be a viable method in the extraction of clean water from contaminated water stream of textile industry. Comparative study was performed with this information and the produced values were assessed in light of the pure water fluxes achieved for the same fertilizers in previous experimentation.

c. *Determining the TKN values at the end of experimental runs of different Fertilizers with the Textile Dyes selected for study*

Total Kjeldahl Nitrogen analytical determinations were performed according to “Standard Methods” (APHA, AWWA and WEF, 1998). The TKN values determined in this phase for 6 hour runs would be the equivalent of the nitrogen concentrations we would achieve if this setup were to be shifted from a lab scale model to a pilot or commercial scale. The significance of these values would come in use during the discussion of FO setup as a viable commercial technology of the future.

3.2.3 Assessment and performance evaluation of FO process with change in pH of dyes solution

In the final stages of experimentation, the effect of change in pH of dye solutions was observed where the draw solutions of NaCl, SOA, and DAP at 0.5 M concentration were used. Using a few drops of 1 M Sodium Hydroxide (NaOH) and Hydrochloric Acid (HCl) solutions, pH of the 100 mg/L solutions were adjusted to pH 10 from original pH of 6.60 and 6.85 for Reactive Blue and Direct Orange dye solution, respectively. The comparative analysis at pH 10 and original pH was performed and reported in later sections. The added base and acid volumes were negligible with respect to overall volumes of feed solutions.

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Pure water flux of different draw solutions:

Experimental pure water flux or the baseline flux for both SOA and DAP fertilizer solutions and NaCl solution for 6 hours' experiment is shown in Fig.1. Pure water flux is the flux calculated when de ionized water is used as feed water to determine the water extraction potential of the draw solute and the loss of draw solute in form of reverse solute diffusion, the results of which are discussed in next section. An ideal draw solution for the FO process should have a high water but a low reverse solute flux.

In Fig. 1, the performance of the fertilizer draw solutions was compared with NaCl solution at four different concentrations i.e. 0.5 M, 1 M, 2 M and 3 M. At low molar concentrations of 0.5 M and 1 M, the increase in flux is linear but at the higher concentrations the flux is not linear as in case of osmotic pressure (Phuntsho et al., 2011)(Nasr & Sewilam, 2016) (section 2.7). We found that the jump in flux decreased for each sequential raise in molarity.

This poor correlation of the flux and osmotic pressure and flux indicates that experimental flux is influenced by other factors than osmotic pressure. Although, the osmolality is a measure of active solute that contributes to the osmotic pressure, but the non-linearity might be due to the type of species formed in the draw solution. (Phuntsho et al., 2011)

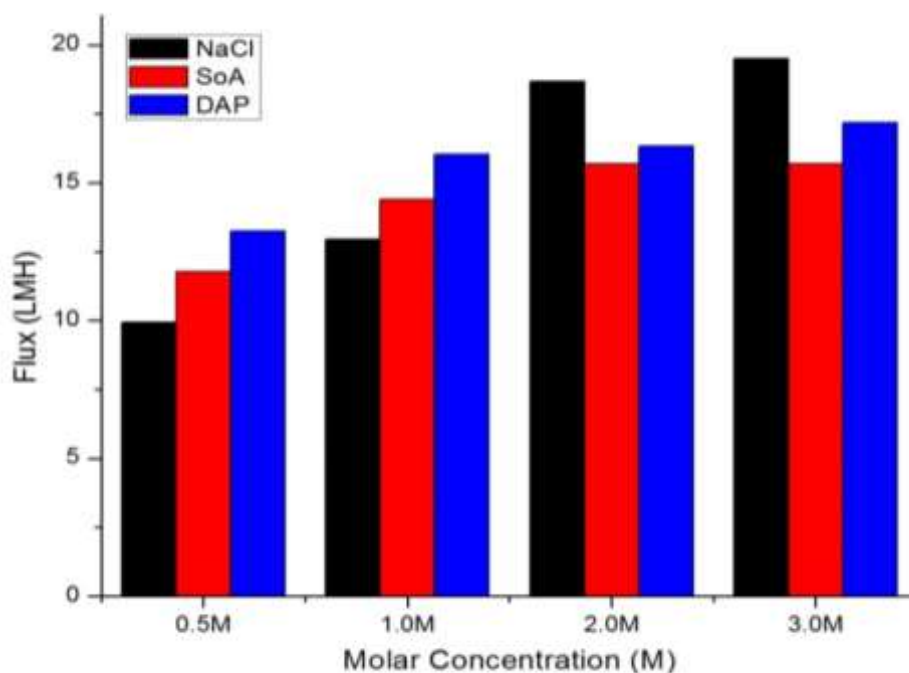


Fig1. Pure water Flux when feed is distilled water and draw solution is NaCl/fertilizer.

The nature of species influences the severity of CP in the FO process significantly. Since, the experiments were run in FO mode where draw solution faces the support layer, the fertilizer molecules have tendency to create the Concentration Polarization hence reducing the flux. (Kant, 2012)(Lay, Wang, & Fane, 2015).

Another observation was that at higher concentrations of NaCl solution, flux increased significantly but not in case of fertilizers. This might be due to increase in viscosity of fertilizers solutions due to the higher molecular weight of fertilizers. These results are in according with the viscosity of draw solutions determined experimentally using the viscometer [Fig 1 (a)].

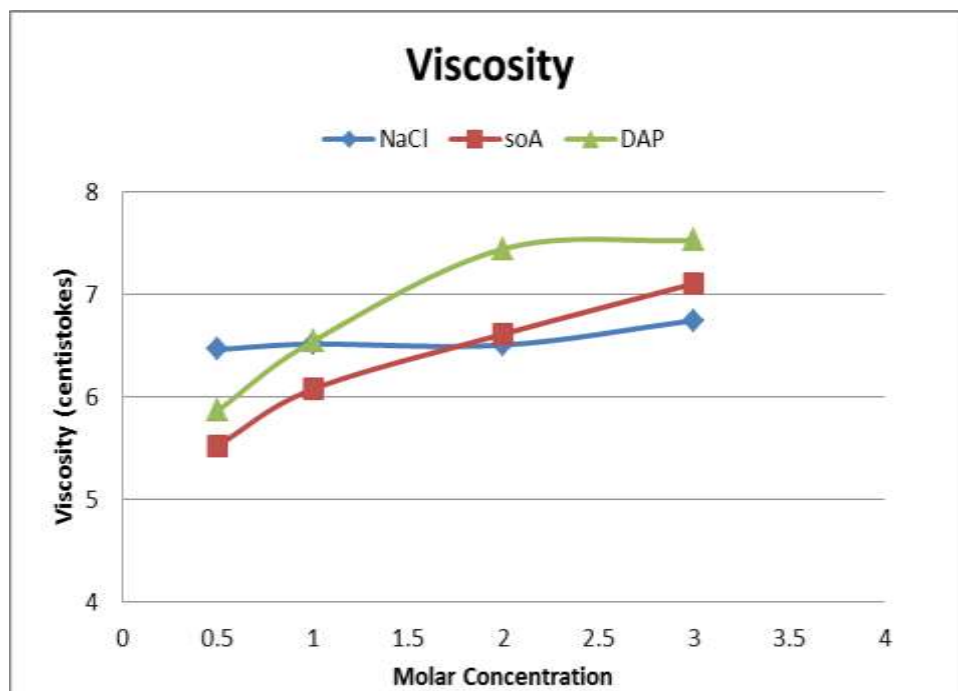


Fig 1 (a). Viscosity of Draw Solution at 0.5 M, 1 M, 2 M and 3 M Concentration

4.2 Reverse solute flux (RSF) of different draw solutions:

As the water moves from high concentration to the low concentration, draw solutes similarly have the tendency to move from draw side to the feed side. This is because no membrane acts as perfect barrier and reverse salt permeation is inevitable (Lay et al., 2015). This is an imminent disadvantage in case of FO process as it makes the feed concentrate management complicated because of the presence of unnecessary components. Also due to

the transfer of the solute on the opposite side, osmotic pressure of the draw solution decreases subsequently reducing water extraction potential (Hancock & Cath, 2009).

The basics and models for understanding of reverse salt permeation are described earlier (Phillip, Yong, & Elimelech, 2010). Our objective was to analyze the performance of fertilizers, for that RSF was determined through measuring electrical conductivity (EC) at the beginning and at the end of 6-hour experiment using Conductivity meter.

We observed the correlation of fertilizer molar concentration and RSF, and found out that RSF increased with increasing molarity. The 0.5 molar solutions showed the least amount solute transfer to the feed side precisely 5.71 gmh, 5.67 gmh and 5.94 gmh for NaCl, SOA and DAP, respectively. SOA showed lowest RSF as compared to DAP and NaCl which is in accordance with the studies conducted previously (Phuntsho et al., 2011).

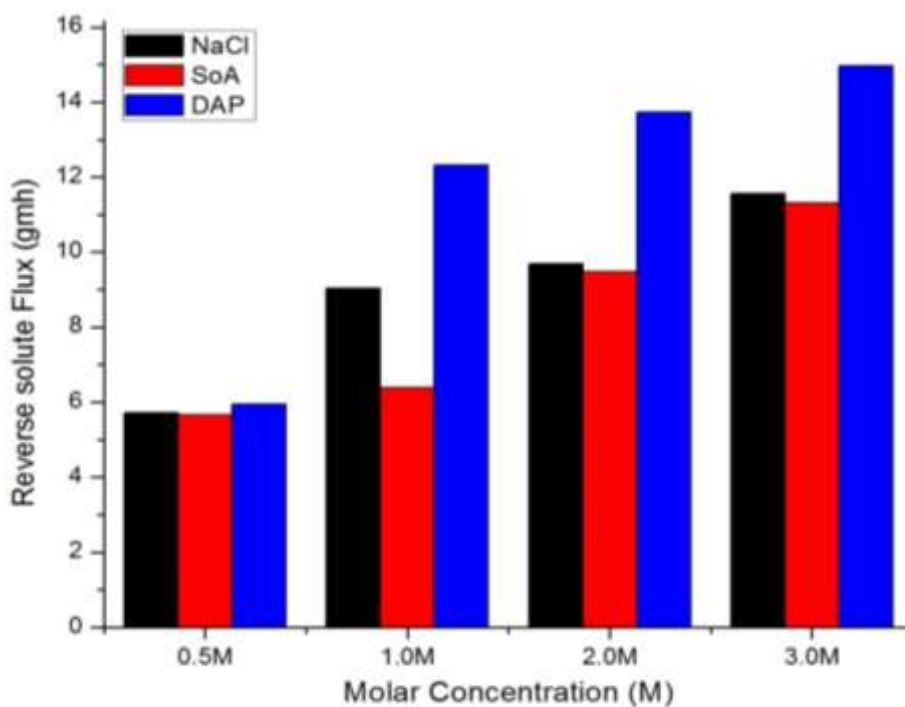


Fig2. Reverse solute flux (gmh) when feed is distilled water and draw solution is NaCl/fertilizer.

Loss of nutrients by reverse diffusion of draw solutes during FDFO Process affect the nutrient concentration of the end water product. This loss of fertilizer is also a drawback in terms of economics because in order to maintain the osmotic pressure on the draw side, constant feeding of fertilizer will be required. Performance of fertilizer in terms of RSF

should be evaluated particularly in case of Nitrogenous or phosphate fertilizer because these two compounds are major source of eutrophication in the receiving water bodies.

4.3 Water Flux when dyes used as feed solution

After the baseline experiments, De ionized (DI) water were replaced with dye feed solution. Concentration of the feed solution was fixed initially at 100 mg/l with regard to the low strength textile wastewater (Carmen & Daniela, 2010). The concentration of the dye was initially kept low also in order to avoid the fouling that it may cause on the membrane surface.

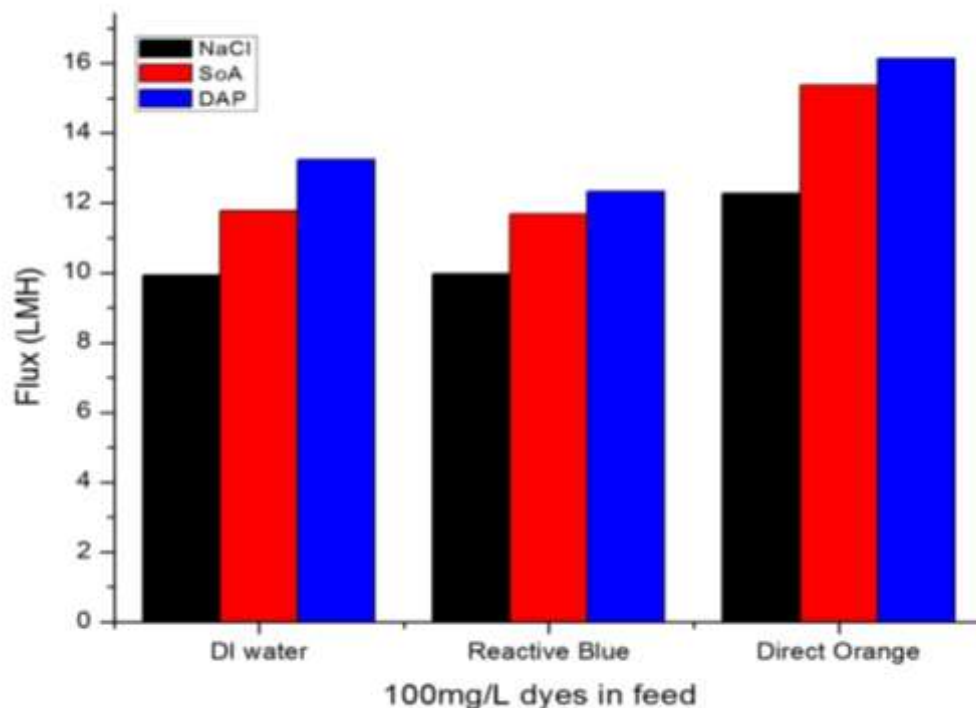


Fig3. Water Flux at 100mg/l concentration of reactive blue and direct orange dye

After concluding an ideal concentration of 0.5 M from the previous assessments, runs with Reactive Blue and Direct Orange dyes were performed and their fluxes were determined. By keeping the concentration at a fix 100 mg/L for both dyes difference in their fluxes can be seen in Fig. 3. Flux in case of Reactive Blue dye was lesser in comparison to the DI water because of the lowering of the osmotic pressure difference due between both sides (Han et al., 2016). But in case of Direct Orange dye, the flux was higher. The reason for this irregularity might be due to the change in membrane after the experiments with reactive blue dye, another possible reason might be due to Room temperature change from 18°C to

21°C at time of Reactive Blue and Direct Orange as previously studied by (Wang & Xie, 2014), where the flux increased with increase in solution temperature.

4.4 Effect of dye concentration on water flux

In the next step, we investigated the effect of dye concentration on the performance of FO membrane under FO mode. Fig. 4 and Fig. 5 show the decrease in water flux with increasing the Blue and Orange dye concentrations from 100 mg/L to 1000 mg/L, respectively. The increase in concentration was made in order to replicate real textile wastewater of medium to high strength. The decrease in flux is possibly caused due to two different factors; firstly the increase in osmotic pressure of the feed solution at higher concentration of dyes and secondly due to the enhanced attachment of dyes on the polyamide surface (Han et al., 2016).

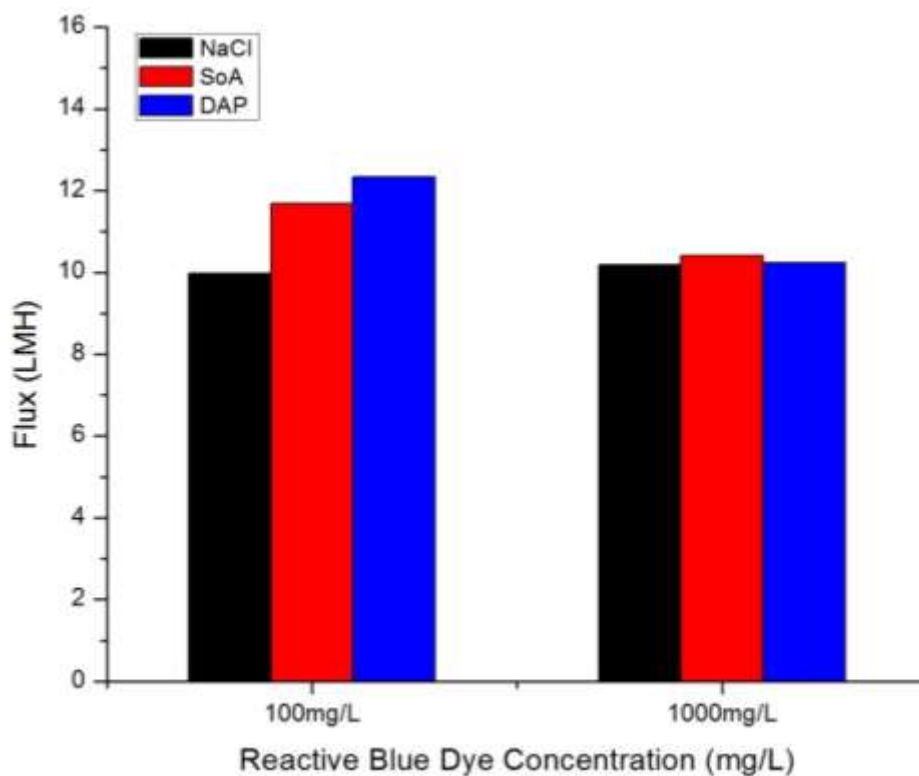


Fig4. Effect of Reactive Blue dye concentration on Flux

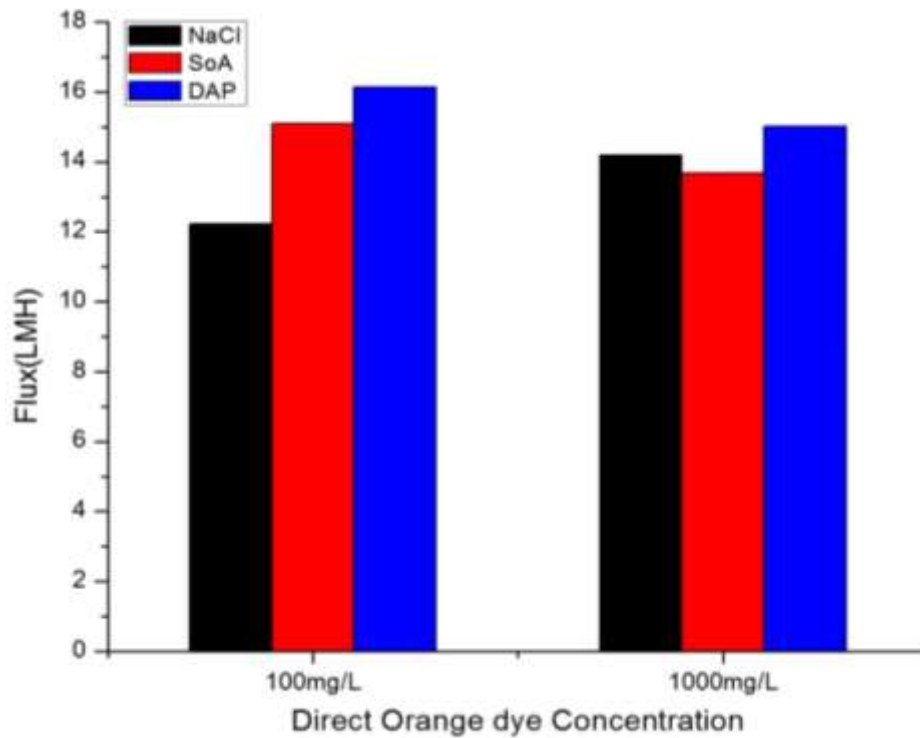


Fig5. Effect of Orange dye concentration on Flux

It was also identified that the flux decreased with the increase in concentration but the degree of decrease was not same for both the dyes. For example, for 0.5 M SOA draw solute the decrease in flux for Reactive Blue dye was 10.9% while for Direct orange dye it was 9.3%. Similar observation was noted when 0.5 M DAP was used as draw solute. This is probably due to lesser molecular weight of the Direct Orange dye (section 2.7) as compared to the Reactive Blue dye (Han et al., 2016).

4.5 Effect of feed solution pH on water flux

Textile wastewater usually has an extremely variable composition with fluctuating quality standards as BOD, COD, pH, color, temperature and salinity. These characteristics vary from industry to industry depending on the dyes being used and fabric being produced. But mostly textile dyeing effluents are basic in nature (Babu, Parande, Raghu, & Kumar, 2007; Imtiazuddin, Mumtaz, & Mallick, 2012), their pH is usually greater 6.

This basic pH is due to the chemicals added in the dyeing bath for better fixation of dyes. Salts added in extensive amounts to maintain the alkaline pH range are sodium nitrate, sodium sulfate, sodium hydroxide and sodium chloride in the dye bath. Reactive dyes form a reactive vinyl sulfone ($-\text{SO}_3-\text{CH}=\text{CH}_2$) group in alkaline conditions i.e. (pH 9-12), which

then forms a bond with fiber. But the bond is not covalent due to the immediate hydrolysis of the vinyl sulfone group (Carmen & Daniela, 2010; Eng et al., 2014; Naser, Haque, & Islam, 2015).

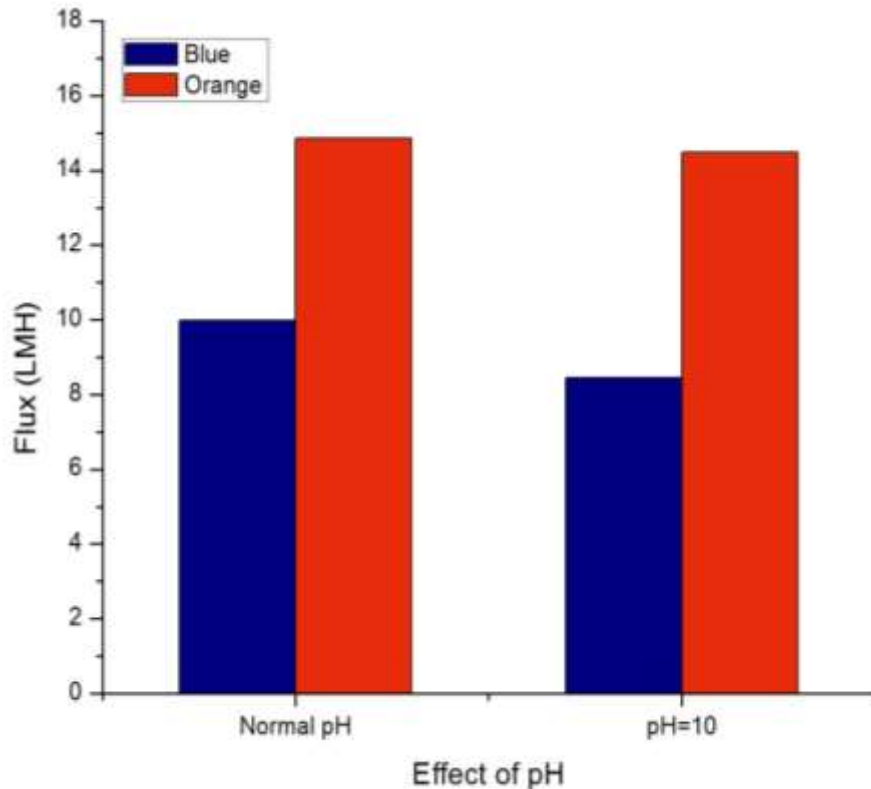


Fig.6 Effect of pH on Water Flux when NaCl is used as draw solution

Actual pH of Reactive Blue dye is 6.60 ± 0.2 and that of Direct Orange dye is 6.85 ± 0.2 . We increased the pH to 10 by adding 1M NaOH solution. In this segment, we determined the effect of pH on the water fluxes for both subjected dyes against 0.5M NaCl as a draw solution, and the flux values were compared with the same dye feed solutions but at a higher pH of 10. As the results show the flux for Reactive Blue dye dropped from 9.98 LMH to 8.45 LMH, while for Direct Orange dye the Flux dropped from 14.86 LMH to 14.48 LMH. Fig. 6 shows no significant change occurred due to this change in pH up to 10 as suggested in a previous study by Wang & Xie, 2014 who concluded that this minimal change in the membrane flux due to the pH change might be related to the filtration mechanism. Because the osmotic pressure is the driving force in FO, pH could not influence the flux notably. This gives FO an edge over Nano filtration (NF) membranes where initial feed pH influences the rejection (Zeng, Tanaka, Suzuki, & Fujii, 2017).

4.6 Rejection of Dyes and Concentration of the dye in the feed solution at the end of 6-hour experiment

We developed the calibration curves for both the dyes using UV-vis spectrophotometer to determine the rejection of the dyes. Fig. 7 (a) shows the Calibration curve for Reactive Blue dye, for which the absorbance at difference concentrations was determined at Wavelength of $\lambda = 608\text{nm}$.

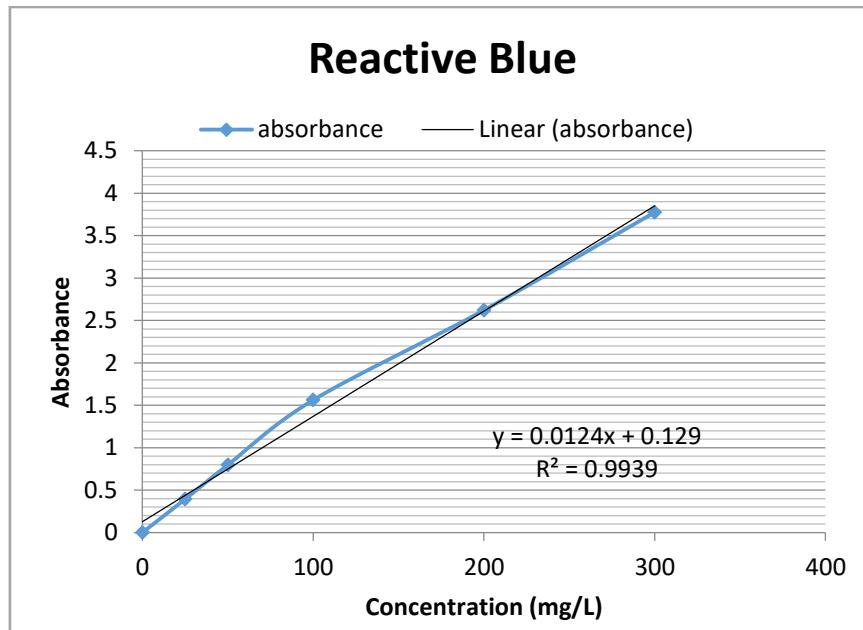


Fig. 7 (a) Calibration curve for Reactive Blue dye

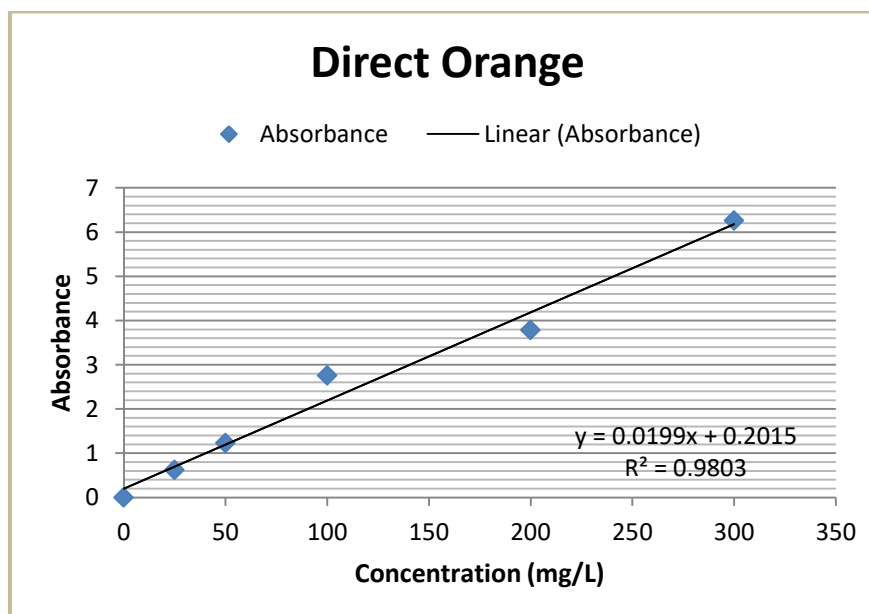


Fig. 7 (b) Calibration curve for Direct Orange dye

While Fig. 7 (b) shows the Calibration curve for direct orange dye, whose absorption was determined at Wavelength of $\lambda = 489\text{nm}$. Both the calibration curves are linear and show reasonable goodness of fit. The absorption of the draw side sample at the end of experiment showed nearly zero absorbance which turned out to indicate a 100% rejection of both dyes also concluded previously by (Han et al., 2016) which is a milestone in textile dye removal technology as compared to other popular technologies as Activated sludge and Nano Filtration where complete dye removal has never been achieved before (C. Liang, Sun, Li, Ong, & Chung, 2014; Mirbolooki, Amirnezhad, & Pendashteh, 2017).

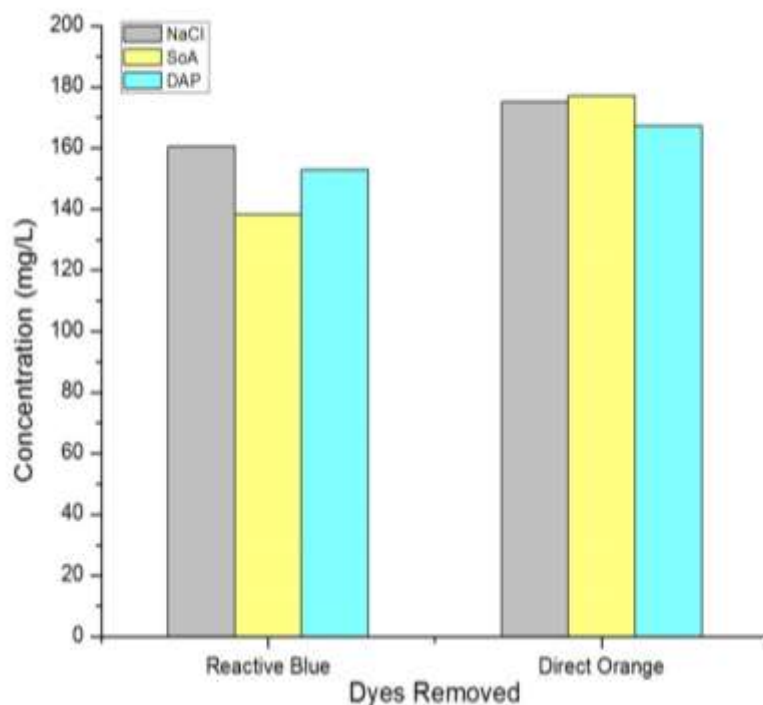


Fig7. Concentration of Feed side after 6 hours using 0.5M NaCl/SoA/DAP as Draw Solution

Fig7. Shows the final concentration of the respective dye on the feed side after six hour runs was determined and it can be seen that reactive blue resulted in a lower concentration as it offered a lesser flux. Runs with direct orange produced a more concentrated feed side as more water permeated. This resulted in a lesser feed volume and a more concentrated feed stream. This concentrate can be further processed by either integrating it with coagulation-flocculation (Han et al., 2016) or by simple drying techniques.

This all over suggests the potential of FO for concentrating the dye effluent stream and make it reusable as in case of NF (Chollom, Rathilal, Pillay, & Alfa, 2015) but it has an edge over other membrane processes because it isn't an energy intensive process ("Kerusha et al.," 2014). And also this makes FO a suitable textile wastewater treatment technology because the amount of solid waste generated after treatment is very less as compared to commonly used Activated Sludge treatment process where sludge management after treatment is significant issue (Eng et al., 2014; Mirbolooki et al., 2017).

4.7 Membrane cleaning and Flux Recovery

After all the performance experiments, we determined the flux recovery by conducting a final run with a 0.5 molar NaCl solution after the membrane had been used for over 20 runs that last 6 hours or more each. The values achieved were quite in-line with the ones achieved with a new membrane and this advocates for the potential of FO membranes to allow for much better flux recovery and last much longer regarding service life ("Kerusha et al.," 2014)

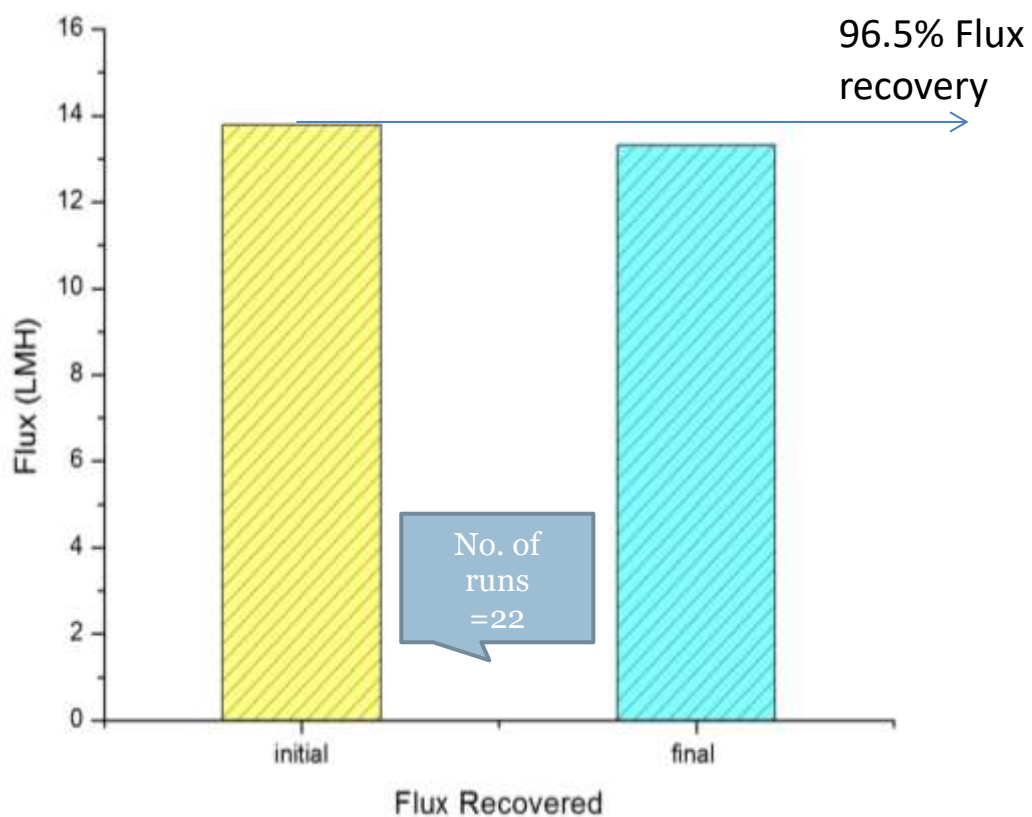


Fig 8. Baseline Flux with 0.5M NaCl Draw Solution

We observed a 96.5% flux recovery at the end of all the runs, These results demonstrate how the membrane fouling of FO thin film composite membrane under the FO mode is mild and loose and is irreversible which can easily be removed without chemical cleaning. (Han et al., 2016).

The minimal amount of fouling caused after each run was cleaning using physical method of forward flushing using distilled water on both sides by increasing its cross flow velocity for one hour to remove the particles from the surface. (Arnal, García-fayos, & Sancho, 2009)

FO membrane has an upper hand to other membrane technologies for textile wastewater treatment in terms of membrane fouling as it is a natural process while other processes as Nano filtration are pressure intensive which cause foulants to surge into the porous membrane surface and cause membrane fouling (C.-Z. Liang, Sun, Li, Ong, & Chung, 2014)

4.8 Nutrient Concentrations in the Final FDFO Product Water

After fixing the molar concentration of draw solution at 0.5 M because of the optimum flux and minimum reverse solute flux, we carried further experiments after baseline performance tests. Section 2.1 suggest that increasing the molar concentration of the draw solution can increase the water flux, water extraction potential from the feed side, but there is ultimately a limit to which osmotic pressure can continue occurring. So, draw solution can only extract water until osmotic pressure reaches equilibrium on both sides. Beyond this point any draw solute is unable to extract water from the feed side and the diluted draw solute is still not appropriate for fertigation (Phuntsho & Kyong, 2012). Similarly, in our case at the end of our 6-hour experiment diluted feed solution still had concentration higher than that required for direct fertigation.

We determined the nitrogen concentration in the diluted draw solution side at the end of our experiment (Appendix 2). The final concentration of N in diluted draw solution was 274.05 mg/L and 1348.15 mg/L for DAP and SOA, respectively. This is higher than that required by all the crops (Phuntsho et al., 2012) , and these fertilizers are salts and can there increase the electrical conductivity for water, which can then be damaging to sensitive crops.

Therefore, in order to meet the nutrient requirement of the plants further dilutions of fresh water will be required. The table 3. below shows dilution required for 8 different plants if SOA or DAP were used as fertilizers. This indicates that DAP requires lesser dilution can therefore be preferred over SOA, as this is used for multiple crops as well. Another conclusion we made was that if the process was to last for more than 6-hours, until the osmotic equilibrium was reached, then fertilizers might be diluted enough to be used directly (Phuntsho et al., 2016; Taylor et al., 2015)

Table 3. Nitrogen concentration in final diluted draw solute and the dilutions required to make it suitable for plant growth.

Ammonium Sulphate $\text{NH}_4^+ = 1733.3 \text{ mg/l}$ $\text{N} = 1348.12 \text{ mg/l}$			Di-Ammonium Phosphate $\text{NH}_4^+ = 352.35 \text{ mg/l}$ $\text{N} = 274.05 \text{ mg/l}$		
Crops/Fruit Fields	Nitrogen Requirement (mg/l)	Dilution Required (Times)	Crops/Fruit Fields	Nitrogen Requirement (mg/l)	Dilution Required (Times)
Hydroponic Tomato	190	7.09	Hydroponic Tomato	190	1.44
Rice	168.28	8.01	Rice	168.28	1.62
Potato	131.75	10.2	Potato	131.75	2.08
Cucumber	200	6.7	Cucumber	200	1.37
Pepper	190	7.09	Pepper	190	1.44
Strawberry	50	26.9	Strawberry	50	5.48
Melon	200	6.7	Melon	200	1.37
Roses	170	7.9	Roses	170	1.61

If the nutrient concentration does not meet the crop requirement, then it requires further dilution which could only be done easily if the site has access to a source of irrigation water as in case of this study conducted by Phuntsho et al., 2016 where mine impaired water was used for farms nearby.

This can also be possible in many locations in Pakistan where industrial sites are closer to the agricultural lands. As in case of Faisalabad, the textile Hub of Pakistan. The map below shows the Industrial zone near to the Agricultural areas.



Fig. 9 Faisalabad industrial zone (source "Google Map Fsd," n.d.)

CHAPTER 5: CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

- Both Fertilizers Ammonium Sulphate $(\text{NH}_4)_2\text{SO}_4$ and Di-Ammonium phosphate $(\text{NH}_4)_2\text{HPO}_4$ at 0.5 M concentration showed good performance with water flux of 11.78 LMH and 13.25 LMH respectively at the end of 6 hours' experiment. This means DAP has a better performance as compared to SOA.
- The Flux increased with increasing Molar concentrations but the RSF increased simultaneously.
- 100% rejection of Dyes was observed.
- Initial Flux Recovered after all runs showing low fouling tendency of FO membranes.

5.2 Recommendation

Forward Osmosis has the potential to treat textile wastewater; as this experimentation showed 100% rejection of both Reactive Blue and Direct Orange dye using fertilizer as draw solutions and making water reusable for direct fertigation. Fertilizers showed good performance in terms of high Flux and low RSF. Limitations lie in the further dilution of Fertilizer for direct application, and concentrating the feed stream. For that, here are some prospects to be researched in future:

- Trying high loading Textile wastewater with fertilizer draw solutions.
- Trying treated FDFO water for hydroponics and testing plant growth dynamics.
- Using Blended Fertilizer as draw solutes to balance out NPK and minor nutrients for direct fertigation.
- Upscaling Laboratory Scale to Pilot Scale Plant.
- Research about Concentrate management techniques.

REFERENCES:

- Arnal, J. M., García-fayos, B., & Sancho, M. (2009). Membrane Cleaning.
- Babu, B. R., Parande, A. K., Raghu, S., & Kumar, T. P. (2007). Cotton Textile Processing : Waste Generation and Effluent Treatment, *153*, 141–153.
- Carmen, Z., & Daniela, S. (2010). Textile Organic Dyes – Characteristics , Polluting Effects and Separation / Elimination Procedures from Industrial Effluents – A Critical Overview.
- Cath, T. Y., Childress, A. E., & Elimelech, M. (2006). Forward osmosis : Principles , applications , and recent developments, *281*, 70–87. <https://doi.org/10.1016/j.memsci.2006.05.048>
- Cekli, L., Kim, J. E., El Saliby, I., Kim, Y., Phuntsho, S., Li, S., ... Kyong Shon, H. (2017). Fertilizer drawn forward osmosis process for sustainable water reuse to grow hydroponic lettuce using commercial nutrient solution. *Separation and Purification Technology*, *181*, 18–28. <https://doi.org/https://doi.org/10.1016/j.seppur.2017.03.008>
- Cekli, L., Phuntsho, S., Shon, H. K., Kandasamy, J., & Chanan, A. (2016). A review of draw solutes in forward osmosis process and their use in modern applications, *3994*(May). <https://doi.org/10.1080/19443994.2012.672168>
- Chequer, F. M. D., Oliveira, G. A. R. de, Ferraz, E. R. A., Cardoso, J. C., Zanoni, M. V. B., & Oliveira, D. P. de. (2013). Textile Dyes: Dyeing Process and Environmental Impact. In M. Günay (Ed.), *Eco-Friendly Textile Dyeing and Finishing*. Rijeka: InTech. <https://doi.org/10.5772/53659>
- Chollom, M. N., Rathilal, S., Pillay, V. L., & Alfa, D. (2015). The applicability of nanofiltration for the treatment and reuse of textile reactive dye effluent, *41*(3), 398–405.
- Cui, Y., Ge, Q., Liu, X., & Chung, T. (2014). Novel forward osmosis process to effectively remove heavy metal ions. *Journal of Membrane Science*, *467*, 188–194. <https://doi.org/10.1016/j.memsci.2014.05.034>
- Devia, Y. P., Imai, T., Higuchi, T., Kanno, A., Yamamoto, K., & Sekine, M. (2015). Effect of Operating Conditions on Forward Osmosis for Nutrient Rejection Using Magnesium Chloride as a Draw Solution, *9*(6), 691–696.
- Direct orange 32. (n.d.). Retrieved from <http://www.worlddyevariety.com/direct-dyes/direct-orange-32.html>
- Eng, J. C., Technol, P., Ghaly, A. E., Ananthashankar, R., Alhattab, M., & Ramakrishnan, V. V. (2014). Chemical Engineering & Process Technology Production , Characterization and Treatment of Textile Effluents : A Critical Review, *5*(1), 1–18. <https://doi.org/10.4172/2157-7048.1000182>
- Fertilizer use by crop*. (n.d.). Retrieved from <http://www.fao.org/docrep/007/y5460e/y5460e07.htm>
- Forward osmosis for application in wastewater treatment : A review ScienceDirect Forward osmosis for application in wastewater treatment : A review. (2014), (May 2016). <https://doi.org/10.1016/j.watres.2014.03.045>
- Google Map Fsd. (n.d.). Retrieved from [https://www.google.com/maps/place/Mksons+\(pvt\)+LTD/@31.4853349,73.2864958,2695m/data=!3m1!1e3!4m5!3m4!1s0x0:0x78c2819a7ed5570e!8m2!3d31.4853349!4d73.2864958](https://www.google.com/maps/place/Mksons+(pvt)+LTD/@31.4853349,73.2864958,2695m/data=!3m1!1e3!4m5!3m4!1s0x0:0x78c2819a7ed5570e!8m2!3d31.4853349!4d73.2864958)
- Han, G., Liang, C., Chung, T., Weber, M., Staudt, C., & Maletzko, C. (2016). Combination of forward osmosis (FO) process with coagulation / flocculation (CF) for potential treatment of textile

- wastewater. *Water Research*, 91, 361–370. <https://doi.org/10.1016/j.watres.2016.01.031>
- Hancock, N. T., & Cath, T. Y. (2009). Solute Coupled Diffusion in Osmotically Driven Membrane Processes. *Environmental Science & Technology*, 43(17), 6769–6775. <https://doi.org/10.1021/es901132x>
- Imtiazuddin, S. M., Mumtaz, M., & Mallick, K. A. (2012). Pollutants of Wastewater Characteristics in Textile Industries, 554–556.
- Kant, R. (2012). Textile dyeing industry an environmental hazard, 4(1), 22–26.
- Kyzas, G. Z., Kostoglou, M., Lazaridis, N. K., & Bikiaris, D. N. (2013). Decolorization of Dyeing Wastewater Using Polymeric Absorbents - An Overview. In M. Günay (Ed.), *Eco-Friendly Textile Dyeing and Finishing*. Rijeka: InTech. <https://doi.org/10.5772/52817>
- Lay, W., Wang, R., & Fane, A. G. (2015). Coupled effects of internal concentration polarization and fouling on flux behavior of forward osmosis membranes during humic ... *Journal of Membrane Science*, 354(1–2), 123–133. <https://doi.org/10.1016/j.memsci.2010.02.059>
- Liang, C.-Z., Sun, S.-P., Li, F.-Y., Ong, Y.-K., & Chung, T.-S. (2014). Treatment of highly concentrated wastewater containing multiple synthetic dyes by a combined process of coagulation/flocculation and nanofiltration. *Journal of Membrane Science*, 469, 306–315. <https://doi.org/http://dx.doi.org/10.1016/j.memsci.2014.06.057>
- Liang, C., Sun, S., Li, F., Ong, Y., & Chung, T. (2014). Treatment of highly concentrated wastewater containing multiple synthetic dyes by a combined process of coagulation / flocculation and nanofiltration. *Journal of Membrane Science*, 469, 306–315. <https://doi.org/10.1016/j.memsci.2014.06.057>
- Mattioli, D., Florio, L. De, Giordano, A., Tarantini, M., Enea, S., Ipts, M. A., ... Centexbel, I. D. V. (2005). E-WATER, 1–18.
- Mirbolooki, H., Amirnezhad, R., & Pendashteh, A. R. (2017). Treatment of high saline textile wastewater by activated sludge microorganisms. *Journal of Applied Research and Technology*, 15(2), 167–172. <https://doi.org/https://doi.org/10.1016/j.jart.2017.01.012>
- Naser, A., Haque, A., & Islam, A. (2015). The contribution of different vinyl sulphone-reactive dyes to an effluent. *Integrative Medicine Research*, 9(4), 594–600. <https://doi.org/10.1016/j.jtusci.2015.03.010>
- Nasr, P., & Sewilam, H. (2016). Investigating fertilizer drawn forward osmosis process for groundwater desalination for irrigation in Egypt. *Desalination and Water Treatment*, 3994(November), 1–11. <https://doi.org/10.1080/19443994.2016.1170639>
- Nicoll, P. G. (n.d.). FORWARD OSMOSIS – A BRIEF INTRODUCTION.
- Ong, Y. K., Li, F. Y., Sun, S.-P., Zhao, B.-W., Liang, C.-Z., & Chung, T.-S. (2014). Nanofiltration hollow fiber membranes for textile wastewater treatment: Lab-scale and pilot-scale studies. *Chemical Engineering Science*, 114, 51–57. <https://doi.org/http://dx.doi.org/10.1016/j.ces.2014.04.007>
- Phillip, W. A., Yong, J. S., & Elimelech, M. (2010). Reverse Draw Solute Permeation in Forward Osmosis: Modeling and Experiments. *Environmental Science & Technology*, 44(13), 5170–5176. <https://doi.org/10.1021/es100901n>
- Phuntsho, S., Eun, J., Johir, M. A. H., Hong, S., Li, Z., Ghaffour, N., ... Kyong, H. (2016). Fertiliser drawn

- forward osmosis process : Pilot-scale desalination of mine impaired water for fertigation. *Journal of Membrane Science*, 508, 22–31. <https://doi.org/10.1016/j.memsci.2016.02.024>
- Phuntsho, S., & Kyong, H. (2012). Fertiliser drawn forward osmosis desalination : the concept , performance and limitations for fertigation, *2050*, 147–168. <https://doi.org/10.1007/s11157-011-9259-2>
- Phuntsho, S., Kyong, H., Hong, S., Lee, S., & Vigneswaran, S. (2011). A novel low energy fertilizer driven forward osmosis desalination for direct fertigation : Evaluating the performance of fertilizer draw solutions. *Journal of Membrane Science*, 375(1–2), 172–181. <https://doi.org/10.1016/j.memsci.2011.03.038>
- Phuntsho, S., Shon, H. K., Majeed, T., Saliby, I. El, Vigneswaran, S., Kandasamy, J., ... Lee, S. (2012). Blended Fertilizers as Draw Solutions for Fertilizer-Drawn Forward Osmosis Desalination.
- Prof, A., Petrinić, I., & Hélix-nielsen, A. P. C. (2014). Towards new membrane-based technologies for water treatment and reuse in the textile industry, *63*, 251–258.
- Pubmed.chem. (n.d.).
- Robinson, T., McMullan, G., Marchant, R., & Nigam, P. (2001). Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative. *Bioresource Technology*, 77(3), 247–255. [https://doi.org/http://dx.doi.org/10.1016/S0960-8524\(00\)00080-8](https://doi.org/http://dx.doi.org/10.1016/S0960-8524(00)00080-8)
- Shaikh, A., & Engineering, T. (2009). Environmental issues related with textile sector, (October), 36–40.
- Smart fertilizer. (n.d.). Retrieved from <http://www.smart-fertilizer.com/>
- Taylor, P., Majeed, T., Sahebi, S., Lotfi, F., Kim, J. E., Phuntsho, S., ... Shon, H. K. (n.d.). Desalination and Water Treatment Fertilizer-drawn forward osmosis for irrigation of tomatoes, (April 2015), 37–41. <https://doi.org/10.1080/19443994.2014.931524>
- Wang, W., & Xie, Y. (2014). Effects of pH and temperature on forward osmosis membrane flux using rainwater as the makeup for cooling water ... *DES*, 351(September), 70–76. <https://doi.org/10.1016/j.desal.2014.07.025>
- Zeng, C., Tanaka, S., Suzuki, Y., & Fujii, S. (2017). Impact of feed water pH and membrane material on nanofiltration of perfluorohexanoic acid in aqueous solution. *Chemosphere*, 183, 599–604. <https://doi.org/https://doi.org/10.1016/j.chemosphere.2017.05.132>
- Zou, S., & He, Z. (2016). Enhancing wastewater reuse by forward osmosis with self-diluted commercial fertilizers as draw solutes. *Water Research*, 99, 235–243. <https://doi.org/10.1016/j.watres.2016.04.067>

Appendix 1: Sample Excel calculation data sheet

Date: 3rd March' 17	time	Time Difference (hr.)	Mass (grams)	Volume (L)	change mass (gram)	Volume Change (L)	Water Flux (L/m ² /hr)	Concentration (g/L)	reverse solute flux (g/m ² /h)
Feed: Distilled water	15:20	0.1667	2232.45	2.23245	0.23	0.00023	0.328505727	0.015744	9.4818867
Draw: 0.5L-2M SOA	15:30		2232.22	2.23222	11.86	0.01186	16.93946925		
Time: 3:20 p.m.	15:40		2220.36	2.22036	11.66	0.01166	16.65381209		
132.14g in 500ml	15:50		2208.7	2.2087	11.81	0.01181	16.86805496		
temp=17°C	16:00		2196.89	2.19689	12.01	0.01201	17.15371211		
	16:10		2184.88	2.18488	11.88	0.01188	16.96803496		
	16:20		2173	2.173	11.89	0.01189	16.98231782		
	16:30		2161.11	2.16111	12.09	0.01209	17.26797498		
	16:40		2149.02	2.14902	12	0.012	17.13942926		
	16:50		2137.02	2.13702	12	0.012	17.13942926		
	17:00		2125.02	2.12502	11.94	0.01194	17.05373211		
	17:10		2113.08	2.11308	11.8	0.0118	16.8537721		
	17:20		2101.28	2.10128	12.44	0.01244	17.767875		
	17:30		2088.84	2.08884	11.71	0.01171	16.72522638		
	17:40		2077.13	2.07713	11.79	0.01179	16.83948925		
	17:50		2065.34	2.06534	11.75	0.01175	16.78235781		
	18:00		2053.59	2.05359	11.63	0.01163	16.61096352		
	18:10		2041.96	2.04196	11.64	0.01164	16.62524638		
	18:20		2030.32	2.03032	11.6	0.0116	16.56811495		
	18:30		2018.72	2.01872	11.64	0.01164	16.62524638		
	18:40		2007.08	2.00708	11.42	0.01142	16.31102351		
	18:50		1995.66	1.99566	11.46	0.01146	16.36815494		
	19:00		1984.2	1.9842	11.49	0.01149	16.41100351		
	19:10		1972.71	1.97271	22.79	0.02279	32.55063273		
	19:20		1949.92	1.94992	11.42	0.01142	16.31102351		
	19:30		1938.5	1.9385	11.38	0.01138	16.25389208		
	19:40		1927.12	1.92712	11.28	0.01128	16.1110635		
	19:50		1915.84	1.91584	22.48	0.02248	32.10786414		
	20:00		1893.36	1.89336	11.07	0.01107	15.81112349		
	20:10		1882.29	1.88229	11.43	0.01143	16.32530637		
	20:20		1870.86	1.87086	11.09	0.01109	15.83968921		
	20:30		1859.77	1.85977	11.14	0.01114	15.91110349		
	20:40		1848.63	1.84863	11.11	0.01111	15.86825492	0.16	

Appendix 2: Nitrogen calculation:

Diammonium phosphate (DAP)

NH_4^+ concentration in the final FDFD product water

$$\text{NH}_4^+ = 352.35 \text{ mg/L}$$
$$\text{Nitrogen content} = \frac{14}{18} \times 352.35$$
$$= 274.05 \text{ mg/L}$$

Plants nitrogen requirement and dilutions required;

- * Hydroponic tomato = 190 mg/L
dilution required = $\frac{274.05}{190} = 1.44$ times
- * Rice nitrogen requirement = 168.28 mg/L
dilution required = $\frac{274.05}{168.28} = 1.62$ times

Similarly for others;

potato	=	$274.05 / 131.75$	=	2.08
cucumber	=	$274.05 / 200$	=	1.37
pepper	=	$274.05 / 190$	=	1.44
strawberry	=	$274.05 / 50$	=	5.48
melon	=	$274.05 / 200$	=	1.37
Roses	=	$274.05 / 170$	=	1.61

Plant nutrient requirement source: ("Smart fertilizer," n.d.)

Ammonium Sulfate (SOA)

NH_4^+ concentration in final FDFO product water = 1733.3 mg/L

$$\begin{aligned}\text{Nitrogen content} &= \frac{14}{18} \times 1733.3 \\ &= 1348.12 \text{ mg/L}\end{aligned}$$

Plant nitrogen requirement and dilutions required;

* Hydroponic tomato = 190 mg/L

$$\text{dilution required} = \frac{1348.12}{190} = 7.09 \text{ times.}$$

* Rice nitrogen required = 168.28 mg/L

$$\text{dilution required} = \frac{1348.12}{168.28} \text{ mg/L} = 8.01 \text{ times.}$$

Similarly for others;

$$\text{Potato} = \frac{1348.12}{131.75} = 10.2$$

$$\text{Cucumber} = \frac{1348.12}{200} = 6.7$$

$$\text{pepper} = \frac{1348.12}{190} = 7.09$$

$$\text{Strawberry} = \frac{1348.12}{50} = 26.9$$

$$\text{Melon} = \frac{1348.12}{200} = 6.7$$

$$\text{Roses} = \frac{1348.12}{170} = 7.9$$

