Design, Construction and Optimization of Forward Osmosis Membrane Bio-Reactor

By

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This thesis is dedicated to my parents, brother, sisters, my teacher

Dr. Sher Jamal Khan and my friends

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List of Abbreviations

AL-DS	Active Layer Facing Draw Solution
AL-FS	Active Layer Facing Feed Solution
AS	Activated Sludge
BOD	Biological Oxygen Demand
CEOP	Cake Enhanced Osmotic Pressure
CER	Cake Enhanced Resistant
CFV	Cross Flow Velocity
COD	Chemical Oxygen Demand
CP	Concentration Polarization
CTA	Cellular Triacetate
DBPs	Disinfection Byproducts
DI	De-ionized
DO	Dissolved Oxygen
DS	Draw Solution
DSV	Draw Solution Starting Volume
EC	Electrical Conductivity
ECP	External Concentration Polarization
EPA	Environmental Protection Agency
EPS	Extracellular Polymeric Substances
ETDA	Ethylene Di Amine Tetra Acetic Acid
FO	Forward Osmosis
FO-MBR	Forward Osmosis Membrane Bio-Reactor
FS	Feed Solution
HRT	Hydraulic Retention Time
ICP	Internal Concentration Polarization
MBR	Membrane Bio-Reactor
MF	Microfiltration
MLSS	Mixed Liquor Suspended Solids
MLVSS	Mixed Liquor Volatile Suspended Solids
NF	Nanofiltration
NOM	Natural Organic Matter
OMBR	Osmotic Membrane Bio-Reactor
PRO	Pressure Retarded Osmosis
PSA	Particle Size Analyses
PVC	Poly Vinyl Chloride
RBC	Rotating Biological Contractor
RO	Reverse Osmosis
SBR	Sequencing Batch Reactor
SOUR	Specific Oxygen Uptake Rate
SRT	Specific Retention Time
TDS	Total Dissolved Oxygen
TFC	Thin Film Composite
TN	Total Nitrogen

TOC	Total Organic Carbon
TOD	Total Oxygen Demand
TP	Total Phosphorous
TS	Total Solids
UF	Ultrafiltration

ABSTRACT

The forward osmosis membrane bioreactor (FO-MBR) is an emerging alternative to conventional MBR, which can be used for both potable and non-potable reuse applications. FO-MBR combines the conventional MBR and forward osmosis (FO) processes. FO membrane has the capability of high range of contaminants removal, and has a lower fouling tendency than pressure driven membranes which results in less frequency of membrane cleaning. Due to low hydraulic pressure required for operation, the energy demand is exceptionally low, which makes FO-MBR system cost effective technology for wastewater treatment. In this study laboratory scale FO-MBR batch setup was developed using external hollow fiber membrane module (SMTC, Singapore) to optimize different operational parameters and their effect on the process was investigated. Operational parameters include temperature, osmotic backwashing, cross flow velocity of the system and draw solution (DS) volumes and concentrations were optimized. This system was modified to semi-continuous FO-MBR after all the parameters were optimized on batch setup. All the optimized parameters were cross checked on the semi-continuous system and was further improved to a continuous FO-MBR. Different salts were studied to investigate reverse solute transport and compared to select the most appropriate draw solution in FO-MBR for wastewater treatment. Internal concentration polarization is a major issue in FO-MBR, also discussed in this study. Results showed that change in initial volume of draw solution (DS) has no effect on the process. Increase in cross flow velocity increased the flux, but system cannot accommodate higher velocities beyond 150 ml/min, therefore cross flow velocity was optimized to a value of 150 ml/min. Increase in DS concentration from 0.5M to 2.0M increase the flux but further increase in molar concentration from 2M to 3M, the conductivity drop increases abruptly. Beyond 3M, change is almost constant which causes reduction of average flux, so optimized value was 2M. For osmotic backwashing draw solution was replaced by DI water. It was noted that osmotic backwashing was ineffective for change in flux. The flux was found to be 7.24 LMH at 22^0C and 7.18 LMH at 30^0C. This revealed that the temperature effect on flux is negligible. FO-MBR system was operated with $MgCl_2$ and KCl as draw solutions and MLSS of 6 g/L, it was observed that KCl has higher flux of 4.61 LMH than $MgCl_2$ which has a flux of 3.95 LMH. Although KCl has higher flux than $MgCl_2$ but its reverse solute transport is significantly higher which affect the system process severely. $MgCl_2$ was the most appropriate salt for wastewater treatment in FO-MBR setup.

Chapter 1

INTRODUCTION

1.1 Background

Water is the most important resource available to human kind. Exponentially growing population and rapidly increasing economic development, the world is fronting extraordinary challenges of water and energy supplies. Both water deficiency and energy crises have overwhelmed many communities around the world (Elimelech and Phillip, 2011). It is accounted for that more than 1.2 billion individuals on the planet need access to clean and safe drinking water, and 2.6 billion need sufficient sanitation (Montgomery, 2007). Though 71% of the earth surface is consists of water, only approximately 1% of the world total water is considered fresh potable water (Gleick, 1997). This potable fresh water needs to address the issues for everyday life of 7 billion individuals, agriculture and the continually increasing industries. In future 1.8 billion individuals will be in absolute water scarce countries or regions by 2025, and 66% of the world's population could be submerged under water strained conditions (UNDESA, 2013).

Pakistan is currently under water stressed conditions with water availability of 1200 m3/capita/year and is moving towards water scarcity 1000 m^3/capita/year. 32,500 hectares of land has been irrigated with wastewater and wastewater treatment is approximately 8% in Pakistan by 2011 (Sato et al., 2013). Building of new water reservoirs is not politically, socially and economically viable. Therefore, wastewater reclamation and reuse can be sustainable solution for domestic, agricultural and industrial purposes in Pakistan.

Due to more strict regulations, broad treatment of wastewater is turning out to be progressively essential. Increase in land cost in densely populated cities of Pakistan does not favor the use of nature land treatment technologies. Because conventional technologies require more land foot prints, produce poor quality effluents and create unaesthetic conditions in the area. Options for urban wastewater treatment in Pakistan include: conventional activated sludge process, moving bed biofilm reactor (MBBR) process, membrane bio-reactor (MBR) process. This study focused on the development of MBR technology.

Membrane bioreactor is combination of biological process with membrane filtration to provide direct solid liquid separation. In MBR system, the membranes are immersed in biological reactor and continuously aerated to provide oxygen to the biomass. MBR is promising technology for a wide range of organics and suspended solids removal. MBRs overcome conventional wastewater treatment technologies by several potential advantages, such as a reduced footprint and widespread decomposition of wastewater producing high quality treated water. The overall discharge does not hold any turbidity as by the ultra- or microfiltration (UF/MF) membranes. Therefore, recycling of biologically treated wastewater is feasible, both technically and economically (Lozier, 2000).

Regardless of several promising advantages over conventional wastewater treatment technologies, MBRs have numerous shortcomings. MBRs energy consumption is relatively high as compared to conventional wastewater treatment. Despite of this, membrane fouling is major operational problem, with both MF/UF membranes as well as the followed (spiral wound) RO membranes. In RO, membrane fouling is originated by the occurrence of natural organic matter (NOM) (Li and Elimelech, 2004) and bio-fouling (Vrouwenvelder and Kooij, 2001).

An advanced dense osmotic membrane bioreactor (OMBR) is presently under improvement. As an unconventional to MBRs, forward osmosis membrane bioreactor (FO-MBR), is the combination of biological and forward osmosis (FO) processes, merged in one system (Achilli et al., 2009). Osmosis is a natural energy process in which the net movement of solvent molecules takes place across a semi-permeable membrane. Osmotic pressure is the driving force in the FO process, generated by the osmotic gradient when a highly concentrated solution flows along one side of the membrane versus a low concentrated feed on the other side. Since the driving source in the FO process is natural osmosis, the energy demand is considerably lower as compared to other pressure driven membrane processes. Therefore, FO is an innovative membrane process that can possibly be used as an unconventional energy-saving alternative to other membrane processes.

Generally, the FO-MBR process includes two steps. First step consists of permeate extraction from highly contaminated feed source using appropriate draw solution (DS), which has high osmotic pressure. Second step deals with the separation of DS from the treated water.

1.2 Problem Statement

This study is based on the design and construction of FO-MBR and its optimization of different operational parameters: operating temperature, osmotic back flushing and chemical cleaning, feed and draw solution rates are optimized for wastewater treatment. The draw solute type and concentration, that is equally capable of extracting the water from brackish/wastewater was developed. Reverse solute transport is a major issue in FO-MBR, and also studied in this study. Because some draw solutes can seriously inhibit the microbial mass in the bio reactor and also increase the salinity of feed solution, which ultimately will cause decrease in treatment efficiency.

1.3 Objectives of Study

Objectives of the study are:

- To design and install the FO-MBR setup at IESE-NUST.
- To enhance bioprocess and membrane performance by system optimization to handle organics and nutrients removal.
- To investigate reverse salute transport in FO-MBR by using different salts as draw solutions.

1.4 Scope of Study

- The study is limited to lab scale only.
- Synthetic wastewater simulating domestic/industrial/brackish wastewater was used in this study.
- Inorganic salts are used in this study to choose the suitable draw solution for water/ wastewater treatment.
- KCl and $MgCl_2$ used in reverse salt transport studies.

Chapter 2

LITERATURE REVIEW

2.1 Wastewater and Impact on Environment

2.1.1 Wastewater Quality Parameters and Composition

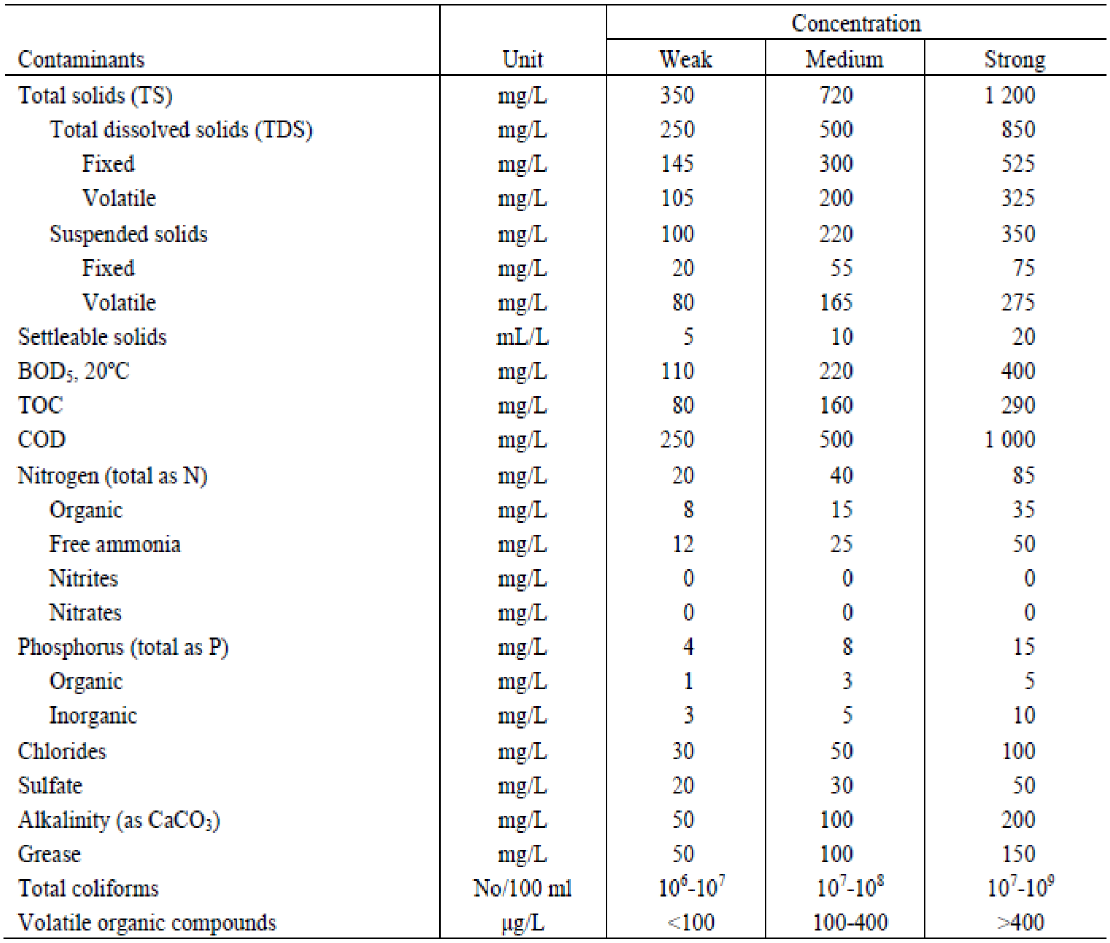
Physical, chemical and biological characteristic of wastewater may be attributed to its quality. Physical parameters contain of temperature, odor, color, turbidity, and unsolvable matters such as oil, lubricants and solids. Solids can be additionally classified into suspended and dissolved solids as well as volatile (organics) and fixed (inorganics) fractions (Metcalf and Eddy, 2003). Chemical parameters of wastewater may be classified by their organic and inorganic portion. Organic chemical parameters contain biochemical oxygen demand (BOD), chemical oxygen demand (COD), dissolved oxygen (DO), and total organic carbon (TOC). Parameters that deal with inorganics of wastewater are pH, hardness, NO^{-3}, NO^{-2} and NH_3-N, sulfates, sulfides, phosphate, chlorides, salinity, alkalinity and a variety of other nutrients and trace elements. Biological parameters are viruses, coliform, fecal coliform and other pathogens. Both time and local conditions are responsible for change in constituents and their concentrations. Typical concentration ranges for different contaminants present in wastewater are presented in Table 2.1. Contaminants are categorized as weak, medium and strong depending on its concentration.

2.1.2 Untreated Wastewater Discharge; Negative Effects on Environment

Generally, one of the main sources of pollution is the untreated effluents discharge from wastewater treatment system. The adverse impacts of these untreated effluents to individuals, animals, plants and aquatic ecosystem from detrimental elements which are found in them have been published both at national and international levels.

Some of these effects can contain death of sea-going life, algal blossoms, habitant obliteration from sedimentation, and expanded water stream and other short and long haul danger from compound contaminants; in combination with chemical accumulation and amplification at larger amounts of the natural food chain (Gazzette, 2010).

Table 2.1: Characteristics of untreated domestic wastewater



Contaminants	Unit	Concentration		
		Weak	Medium	Strong
Total solids (TS)	mg/L	350	720	1 200
Total dissolved solids (TDS)	mg/L	250	500	850
Fixed	mg/L	145	300	525
Volatile	mg/L	105	200	325
Suspended solids	mg/L	100	220	350
Fixed	mg/L	20	55	75
Volatile	mg/L	80	165	275
Settleable solids	mL/L	5	10	20
BOD_5, 20°C	mg/L	110	220	400
TOC	mg/L	80	160	290
COD	mg/L	250	500	1 000
Nitrogen (total as N)	mg/L	20	40	85
Organic	mg/L	8	15	35
Free ammonia	mg/L	12	25	50
Nitrites	mg/L	0	0	0
Nitrates	mg/L	0	0	0
Phosphorus (total as P)	mg/L	4	8	15
Organic	mg/L	1	3	5
Inorganic	mg/L	3	5	10
Chlorides	mg/L	30	50	100
Sulfate	mg/L	20	30	50
Alkalinity (as $CaCO_3$)	mg/L	50	100	200
Grease	mg/L	50	100	150
Total coliforms	No/100 ml	10^6-10^7	10^7-10^8	10^7-10^9
Volatile organic compounds	μg/L	<100	100-400	>400

Source: Metcalf and Eddy (2003)

The significant chemical contaminations in wastewater are nitrogen, phosphorus, heavy metals, cleansers, pesticides and hydrocarbons. Of these chemicals, the two which is most basic and limiting one are nitrogen and phosphorus (Larsdotter, 2006). The undesirable nitrogen present in wastewater discharge has harmful ecological impacts and also badly affects public health. The occurrence of nitrogen in wastewater release can be undesirable in light of the fact that it has natural effects furthermore influence general wellbeing. In general these incidences are accompanied by the throwing away of community sewage and application of fertilizers and pesticides to agricultural lands. The dangers that all these occurrences impersonated, reveals that nitrogen must be expelled from wastewater before it release (Kurosu, 2001). Essentially, the vicinity of nitrogen and phosphorus in fresh water can likewise make ecological conditions that support the development of toxin delivering cyanobacteria and green growth. The resulting pollutants can cause gastro problems, liver damage, nervous system disorder and skin irritation (WHO, 2006). In addition, production of algal blooms and plant growth in streams, ponds, lakes, reservoirs and estuaries and along shoreline cause eutrophication. These algal blooms are responsible for depletion of DO and contribute to serious water quality problems (EPA, 2000).

2.1.3 Wastewater Treatment and Reuse; A Sustainable Option

Water is one of the most important resources available to human kind; however it is under continuous danger due to variation in climate, exponentially growing population and waste. The most encouraging efforts to stalk the global water scarcity, is the reclamation and reuse of industrial and municipal water. The Water Reuse Association (WRA) defines reused, recycled, or reclaimed water as “the water that is used many times before it is added back to the natural water cycle”. Thus, the reusing of water is the reuse of treated wastewater for advantageous purposes, for example, watering system of rural terrains and scene, latrine flushing, mechanical procedures and ground water bowl energize. Water recovery and reuse make groups competent to wind up less reliant on surface and ground water sources and can diminish the preoccupation of water from delicate biological systems. In addition, water reuse may diminish the supplement loads from wastewater releases into conduits, accordingly decreasing and anticipating contamination. This "new" water source might likewise be utilized to recharge overdrawn water sources and restore or restore those already decimated. Since the urban regions of numerous creating nations are becoming quickly, environmental sanitation frameworks must be executed that are feasible and can adjust and develop with the group's sanitation needs (Chittoor, 2013).

2.2 Wastewater Treatment Technologies

Physical, chemical and biological techniques are utilized to expel contaminants from waste-water. With a specific end goal to accomplish diverse levels of contaminant evacuation, individual waste-water treatment methods are joined into a mixture of frameworks, delegated primary, secondary, and tertiary waste-water treatment. More thorough treatment of waste-water incorporates the evacuation of particular contaminants and additionally the evacuation and control of supplements. Regular frameworks are additionally utilized for the treatment of waste-water in area based applications. Sludge resulting from waste-water treatment operations is dealt by different methodologies as shown in Figure 2.1, with a specific end goal to decrease its water and organic content and make it suitable for end disposal and reuse.

2.2.1 Physical Unit Operations

Physical processes are the first treatment strategies in which physical strengths are utilized to remove contaminants from wastewater. Solids are expelled from wastewater as it courses through screens or channel media, or solids are evacuated by gravity settling or air flotation. Particles captured with air float to the surface and can be evacuated. These contaminants generally incorporate vast masses like plastic bags, animals, floating masses and trash etc.

2.2.2 Chemical Unit Operations

Chemical processes utilized as a part of waste-water treatment are intended to realize some type of change by means of chemical reactions. They are constantly utilized as a part of conjunction with physical unit operations and biological processes. In general, physical unit processes have low inherent draw backs as compared to chemical unit processes because of their additive nature. That is to say, there is normally a net increment in the broke up constituents of the waste-water. This can be a critical component if the waste-water is to be reused. This area examines the primary compound unit procedures, including synthetic precipitation, adsorption, disinfection, De-chlorination and different applications.

2.2.3 Biological Unit Processes

Biological unit procedures are utilized to change over the finely partitioned and broke up natural matter in wastewater into flocculent settleable organic and inorganic solids. In these procedures, microorganism, especially bacteria, change over the colloidal and broke down carbonaceous natural matter into different gasses and into cell tissue which is then evacuated in sedimentation tanks. Biological processes normally utilized as a part of conjunction with physical and chemical processes, with the primary goal of diminishing the organics (measured as BOD, TOC or COD) and supplement content (outstandingly nitrogen and phosphorus) of wastewater.

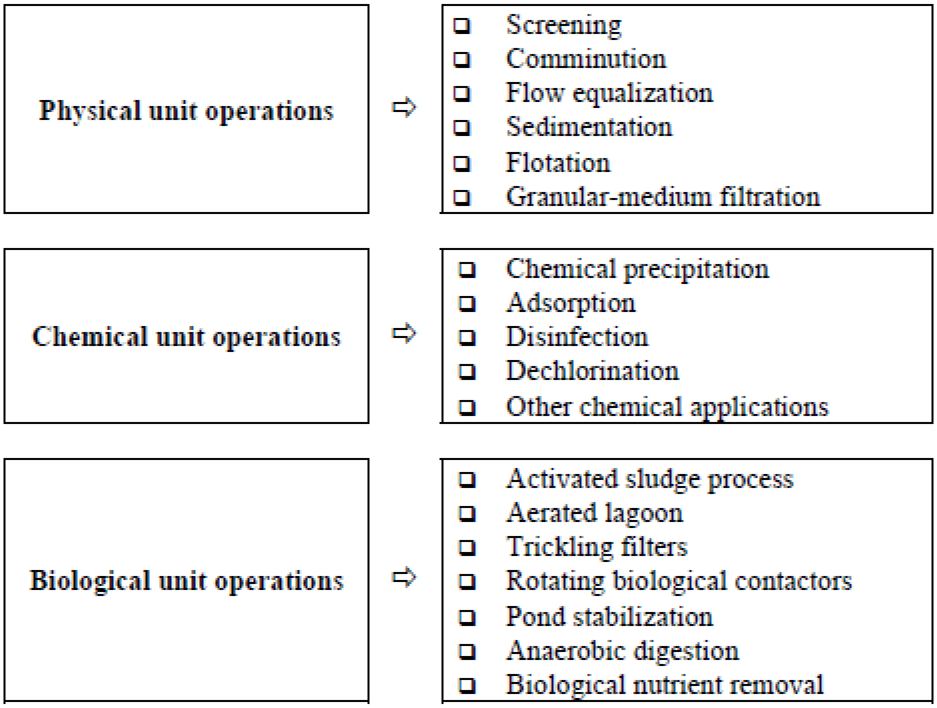


Figure 2.1: Wastewater treatment methods

2.3 Membrane Bio-reactor (MBR)

Water stressed conditions and stringent environmental regulations are raising the importance of wastewater treatment. To generate high quality water which is low in suspended solids, bacterial contamination and turbidity, makes membrane bioreactor (MBRs) an attractive process for wastewater treatment (Stephenson, 2000). In MBRs conventional biological treatment processes combine with membrane filtration to provide an advance level of organics, nutrients and suspended solids removal (Lawrence, 2002). In a submerged MBR the membranes are immersed in a biological reactor and permeate is extracted by creating a vacuum. This allows outside in flow of treated water which is free from suspended solids (Judd, 2006).

MBRs have a few particular advantages over conservative wastewater treatment innovations, such as reduced footprint and an extensive decomposition of wastewater resulting in high quality product water. So the reuse of MBR treated effluent becomes both technically and economically viable (Le-Clech, 2006). In spite of a few reasonable advantages over ordinary wastewater treatment advances, MBRs have a few downsides. The energy consumption of MBRs is comparatively high than the conventional wastewater treatment technologies. Aside from this, operational issues happen due to membrane fouling, with both micro-filtration and ultra-filtration (MF/UF) (Li and Elimelech, 2004). Fouling decreases process flux and increases the frequency of membrane cleaning and membrane substitution (Le-Clech, 2006).

2.3.1 Membrane Fouling

Membrane fouling is the result of deposition and aggregation of rejected contaminants from the feed stream on the membrane (Escobar et al, 2005). It is a standout amongst the most difficult issues of the innovation, which diminishes the execution of membrane filtration because of fouling, has obstructed the endless use of MBR processes for wastewater treatment (Bouhabila et al., 2002). The seriousness of membrane fouling is dictated by the joined impact of different physical, chemical, and biological functioning components and can be affected by the operational flux. In addition, “Materials buildup on a membrane surface, which cannot be removed by cross-flow, back flushing, or back pulsing, can prompt irreversible grip, bringing about permanent permeability loss or membrane fouling” (Escobar et al, 2005).

Fouling phenomena on the membrane surface and inside the pores diminish the long-term steadiness of flux efficiency. Permeate back flushing and chemical cleaning are standard methods connected to minimize these impacts and balance out general permeability of the membrane systems, but result in losses of net filtration productivity and conceivable harm to the membrane by cleaning agents (Wintgens and Rosen , 2003).

2.3.2 Classification of Fouling

Classification of membrane fouling developed by deposition of constituents can be depicted by three modes: 1) pore narrowing, 2) pore plugging, and 3) gel/cake formation (Tchobanoglous et al, 2003). Modes of membrane fouling are shown in Figure 2.2.

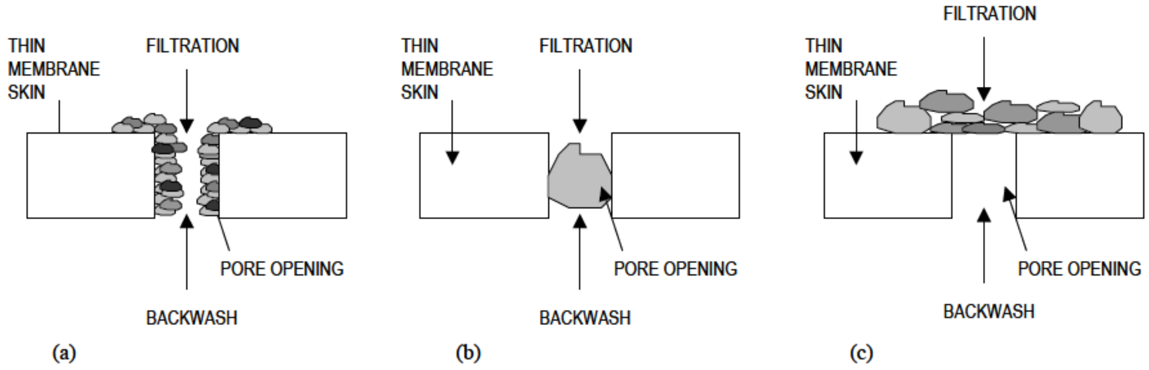


Figure 2.2: Membrane Fouling modes (a) Pore Narrowing, (b) Pore Plugging, and (c) gel/cake formation (Bourgeous et al, 1999).

2.3.3 Types of Membrane Fouling

Membrane fouling is a composite phenomenon which depends on type and size of floc particle, characteristics of sludge and system hydrodynamics. Generally it be classified into three categories based on their cleaning mechanisms: (Meng et al., 2009).

1. Removable fouling
2. Irremovable fouling
3. Irreversible fouling

- **Removable Fouling**

  Fouling that can be effectively disposed of by usage of physical cleaning (e.g., back flushing). The removable fouling is caused by loosely attached foulants and is credited to the development of cake layer.

- **Irremovable Fouling**

  Irremovable fouling needs chemical cleaning to be removed. Pore blocking and strongly attached contaminants during filtration created irremovable fouling.

- **Irreversible Fouling**

  Irreversible fouling means changeless fouling which can't be evacuated by any approaches.

2.3.4 Pretreatment Techniques

Pretreatment is the key step in avoiding the membrane fouling and long term use of membranes. The target of pretreatment to a RO system is to uproot particles, lessen organics and give a feed that won't bring about bio fouling in the RO/NF components. Whilst traditional pre-treatment innovation can be viable, it should be carefully designed, and thoroughly operated. Upsets, due to feed variability or contamination, will be exchanged to the RO, sometimes with desperate consequences. Most cases of RO framework disappointment can be put down to pre-treatment failings, either in outline or operation. The expense to correct these weaknesses, and the lost production which results, debilitates to give RO a terrible name at times UF/MF guarantees that essentially higher fluxes are achieved from the RO, with considerably less fouling, decreased chemical usage, and better on-stream time. Pretreatment can generously influence the force needed by RO.

Forward Osmosis

Forward osmosis (FO) has been considered as advanced membrane technology for wastewater reclamation reuse (Chung et al., 2012; Zhao et al., 2012). In contrast to pressure driven membrane processes, FO is a low energy natural osmotic pressure driven process that contains a semi-permeable membrane and an osmotic agent i.e. draw solution (DS). The semi permeable membrane act as a obstacle that discards the solute particles, solids or other contaminants but allows the solvent to pass through, while the DS has a higher potential resulting in high osmotic pressure that extracts water from the feed across the membrane (Cai et al., 2011; Zhang et al., 2012). The driving force in the FO process is an osmotic pressure developed by the osmotic gradient, when a high concentration of a DS courses through dense, semi permeable membrane on one side and a low concentration of feed solution (FS) along the other side (Hancock, 2013).

Osmosis progressions have been discovered for numerous prospective uses extending from water production, wastewater reclamation and reuse, food processing, pharmaceutical application to energy creation. As early as 1976, Loeb et al. explored salinity incline energy reaping by pressure retarded osmosis (PRO). In the late 1990s, Petrotos et al. considered the procedure parameters for the osmotic amassing of tomato juice. In 2005, Cath et al. joined direct osmosis, osmotic refining, and membrane refining for metabolic wastewater treatment in space. Subsequently in 2006, McCutcheon et al. connected the FO process for desalination utilizing a novel draw solute. The FO procedure has additionally been used in a membrane bioreactor system, called the forward osmotic membrane bioreactor (FO-MBR). The FO-MBR requires generously less backwashing and has higher aggregate natural carbon (TOC) evacuation proficiency when contrasted with ordinary MBRs (Zhang et al., 2012). The potential applications of FO in various fields are illustrated in Figure 2.3.

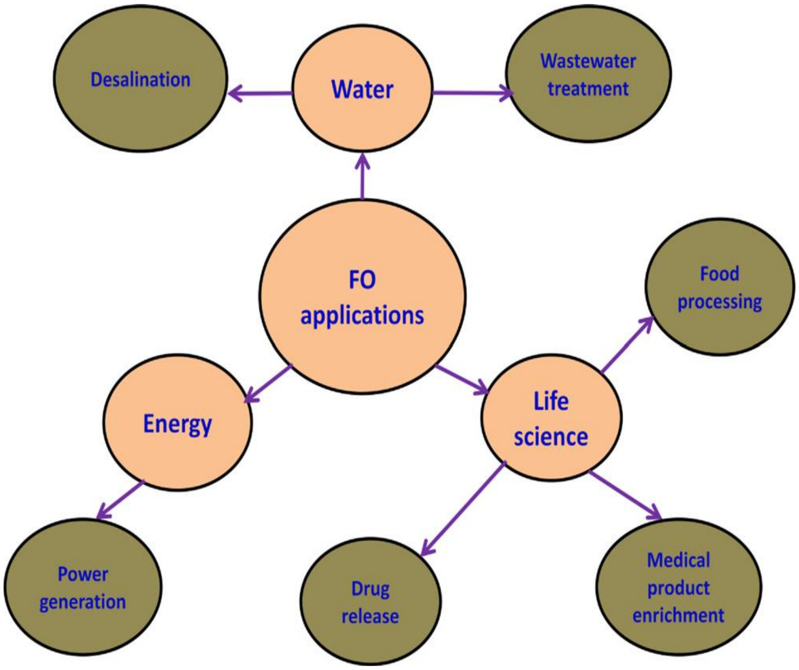


Figure 2.3: Potential applications of FO process in various Fields (Zhao et al., 2012).

Regardless of the great efficiency of FO procedures, there are two main challenges which hamper the applied uses of FO process. On is the identification of appropriate DS which has the properties of high osmotic potential, low viscosity, high diffusivity, simply replenished and reused, non-toxic and chemically compatible with membrane material, low permeability through the semi permeable membrane to improve the water extraction, to minimize the reverse solute transport which reduces the loss of DS and make the method cost effective and minimize the fouling. The other challenge is the manufacturing of suitable membrane material which can reduce the concentration polarization, reverse transport of draw solute and fouling effect (Achilli et al., 2010).

2.4.1 Classification of FO Process

Osmosis is the transport of solvent through a porous semi-permeable membrane from a region of high solute concentration to a region of lower solute concentration in solvent. The driving force in the FO process is the osmotic pressure developed by the osmotic gradient, when the high concentration of osmotic agent present on the one side of the semi porous membrane and low concentrated feed on the other side of the membrane.. This osmotic pressure made an entry over the membrane that just permits the water to go through, however rejects a large portion of the solute particles. FO utilizes the osmotic potential difference (Δπ) over the membrane, as opposed to hydraulic pressure differential (as in RO), as the main thrust for transport of water through the membrane. The FO procedure results in convergence of FS and weakening of very focused DS.

Pressure Retard Osmosis (PRO) can be seen as a intermediary procedure in the middle of FO and RO, where hydraulic pressure is connected in, as opposed to the osmotic gradient like RO and the net water flux is still toward the concentrated DS as in the FO process. Classifications of FO processes are shown in the Figure 2.4.

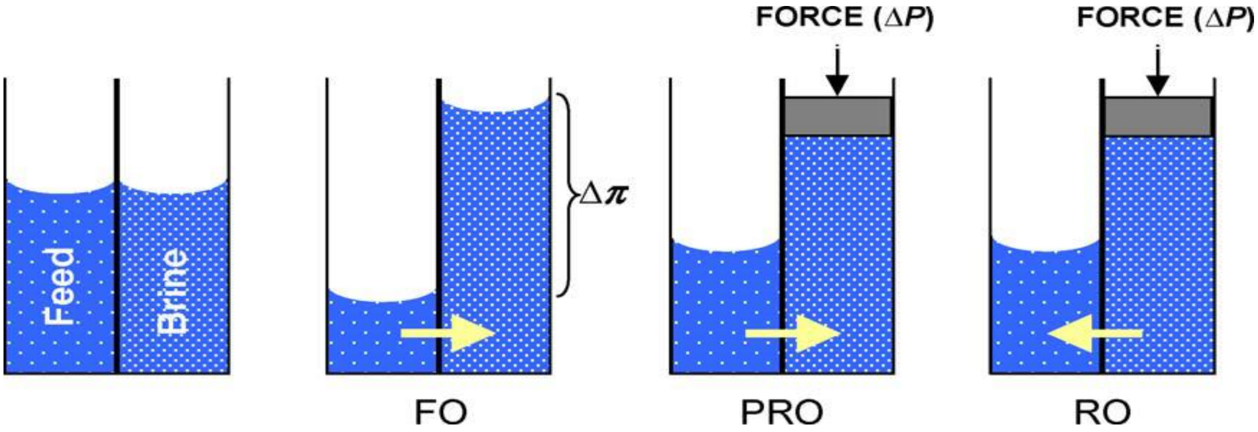


Figure 2.4: Classification of FO process (Cath et al., 2006).

Water flows in FO, PRO, and RO. For FO, ΔP is nearly zero and water diffuses to the concentrated fluid that is under the positive pressure of ($\Delta\pi > \Delta P$). For RO, water diffuses to the less concentrated fluid side because of hydraulic pressure ($\Delta P > \mathit{\Delta}\pi$).

The general mathematical statement portraying water transport in FO, RO, and PRO is

$J_w = A(\sigma \mathit{\Delta}\pi - \mathit{\Delta}P)$

Where J_w is the water flux, A the water permeability constant of the membrane, σ the reflection coefficient, and $\mathit{\Delta}P$ is the applied pressure. For FO, $\mathit{\Delta}P$ is zero; for RO, $\mathit{\Delta}P > \mathit{\Delta}\pi$; and for PRO, $\mathit{\Delta}\pi > \mathit{\Delta}P$. The flux headings of the infiltrating water in FO, PRO, and RO are described in Figure 2.5. Flux headings and main thrusts for the three procedures were portrayed in the early 1980s by Lee et al. The FO point, PRO zone, and RO zone, alongside the flux inversion point, are represented in Figure 2.5.

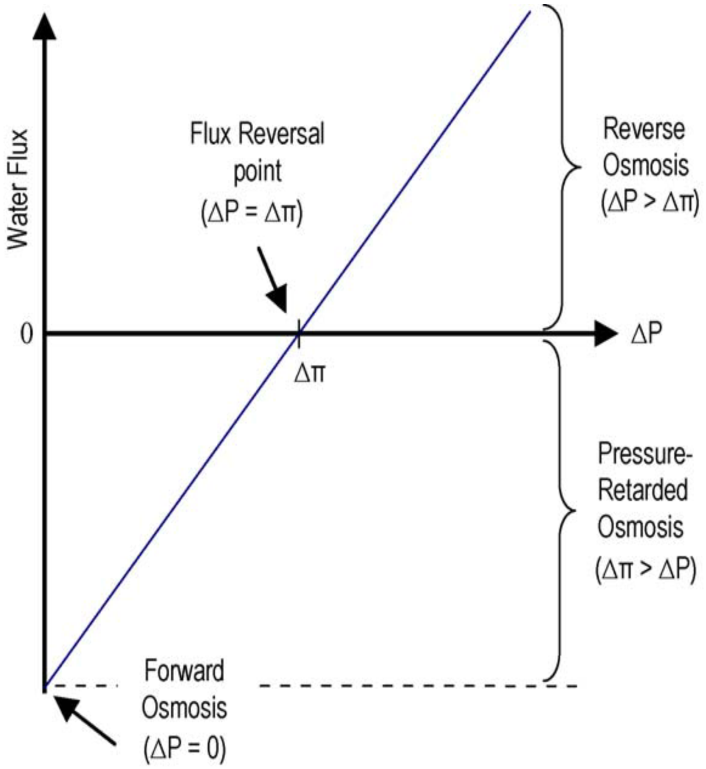


Figure 2.5: Permeating water flux direction in FO, PRO and RO (Cath et al., 2006).

In FO, PRO and RO processes, water flux direction and magnitude is the function of applied pressure. At zero hydraulic pressure FO happen. When the difference between applied pressure and the flux reversal point is zero, and then PRO take place. The zone of RO is where the hydraulic pressure difference is higher than the osmotic pressure difference (Cath et al., 2006).

2.4.2 Advantages of Forward Osmosis

FO has an extensive variety of potential preferences, predominantly because of its operation at low or no hydraulic pressures which is mandatory for this osmotically determined process (Holloway et al., 2005). FO has the promising technology for achieving low energy consumption, results in lowering costs of operation, if appropriate DS and their replenishment methods can be practically and economically established (Elimelech and Phillip, 2011). Development of replenishment methods could be one of the most attractive points of FO, in the energy crises and water stressed areas. Studies have demonstrated that FO has the ability of wide variety of contaminants removal (Cath et al., 2010) and relatively ensure a low membrane fouling than the pressure determined membrane processes. Fouling in FO is mostly reversible (Mi and Elimelech, 2010) and can decreased by streamlining the hydrodynamics i.e. increasing cross flow velocity (Lee et al., 2010). Principally due to high osmotic pressure created by high osmotic gradient through the semi-permeable membrane, high water flux and high water extraction is also achieved by the FO process. Hence, FO is an innovative membrane process that can possibly be used as an energy-saving and fouling unconventional to ordinary membrane processes (Achilli et al., 2009).

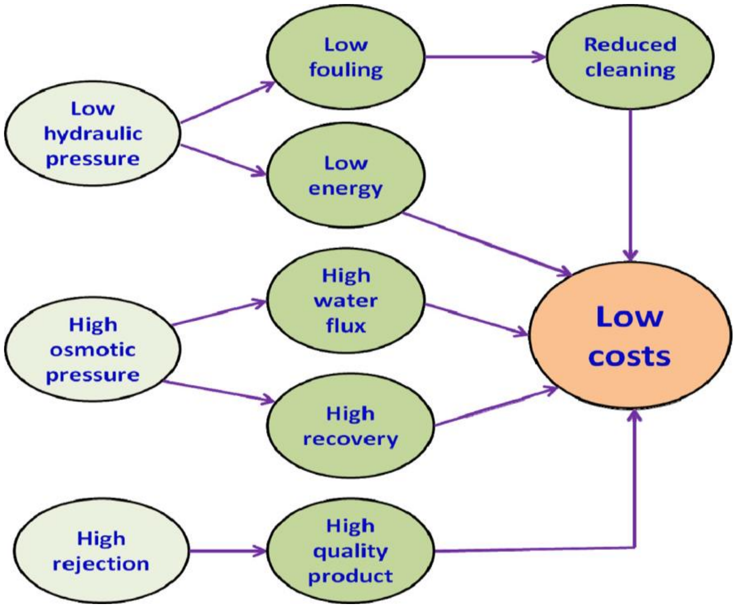


Figure 2.6: Advantages of FO process used in wastewater treatment (Zhao et al., 2012).

2.4.3 FO as Low Energy Alternative

As pretreatment of RO many options are present containing assimilation of FO with RO desalination process (Bamaga et al., 2011). The FO pretreatment has been utilized to desalinate feeds extending from brine water to brackish water (McCutcheon et al., 2005; Bamaga et al., 2009). The fundamental driver of utilizing the integrated FO–RO process for pretreatment of crude water is the expected lessening in the desalination cost. This reduction in cost is accredited to lower energy consumption for pretreatment, less pretreatment processes, lower preservation expense of RO components, reduction/exclusion of chemical cost, and decrease in RO membrane spare cost. It is due to the fact that pressure involved in FO process is the flow resistance in the membrane assembly, the apparatus utilized is exceptionally straightforward and membrane backing is less of a problem (Cath et al, 2006).

2.4.4 Draw Solution in Forward Osmosis

In FO process, the driving force is the result of the concentrated DS present on the permeate side of the semi permeable membrane. Different expressions are used by different scientists in the literature to name this solution comprising draw solution, osmotic agent, osmotic media, driving solution, osmotic engine, sample solution, or just brine. The essential criteria should be considered when selecting a DS; specifically, (1) high osmotic pressure which may encourage a high water flux; (2) insignificant reverse draw solute transport which reduces the regeneration cost; (3) simplicity in recovery of the diluted DS which reduces energy requirement and general operation cost (Phuntsho et al., 2011; Achilli et al., 2010; Ling et al., 2010; Ge et al., 2011). Other considerations include high solubility in solvent, nontoxicity and solid state at surrounding temperatue etc. (Phuntsho et al., 2011; Achilli et al., 2010).

In spite of the fact that FO has been progressively investigated for some applications, there are a few research territories expected to make headway with the FO process including identification of an appropriate draw solution (DS) such as ammonia-carbon dioxide, water soluble magnetic nanoparticles (Yip et al., 2010; Wang et al., 2010; Ling et al., 2010). Numerous endeavors have been dedicated to find suitable draw solutes. Sulfur dioxide as volatile solute, aqueous aluminum sulfate with certain salts added for ease of separation by precipitation, different sugars, for example, glucose and fructose were additionally investigated as draw solutes. In the mid 2000's, a water-dissolvable blend of ammonium bicarbonate was found as a draw solute and a high water flux was acquired because of its low sub-atomic weight and high dissolvability. The draw solute can be recuperated and disintegrated to ammonia and carbon dioxide upon warming at 65 °C (McCutcheon et al., 2005). On a basic level, utilizing small atoms, salts and electrolytes may not be economical and practical due to the challenges of recuperation and salt spillage, notwithstanding inciting stopping up in the supporting layer and bringing about serious fouling and internal concentration polarization (Hancock and Cath, 2009; Phillip et al., 2010).

Exceptionally hydrophilic nano-size magnetic particles have been planned and tried in FO forms (Ling et al., 2010; Ge et al., 2012). Poly-acrylic acid was used to activate these magnetic nanoparticles can harvest extraordinary osmotic pressure and high water flux could achieved. Agglomeration was observed when these magnetic nanoparticles were recycled by magnetic separators. To recuperate some of the FO performance, the size of agglomerated magnetic nanoparticles can effectively reduce by ultra-sonication. However, the resultant magnetic possessions were debilitated under ultrasonic procedures and in this way endangered recovery productivity in magnetic fields.

Another important concern with FO process is the reverse solute transport of draw solute from DS side towards the FS side (reverse diffusion); it is in accordance with the normal concept of osmosis. Cornelissen et al., (2008) observed that under similar operating conditions the draw solute which has more diffusion coefficient generates more osmotic pressure and hence high water flux in FO-MBR is observed. Moreover with increase in DS concentration the water flux increases. The FO membrane creates a hindrance in the reverse transport and stops it on the DS side. But with the smaller sized solute the chances of reverse transport increases. The reverse transport is important in FO-MBR because biomass can be greatly affected by possible toxicity of draw solute. The draw solute caught by the fouling layer additionally adds to the improved osmosis pressure on the feed side. The improved osmotic pressure inside of fouling layer diminished the net driving force, therefore brought about significant decay of flux (Zhen-Yu et al., 2012).

2.4.5 Membranes for Forward Osmosis

In general any thick, non-permeable and specifically porous material can be used for the manufacturing of FO membrane. The required properties for FO membranes would be the highly thick material of the dynamic layer for the high dismissal of solute particles, a tinny membrane with least porous material of the support layer to minimize the concentration polarization. These characteristics resulting in high water flux, lessened membrane fouling and give high mechanical quality to tolerate hydraulic pressure when used for PRO. The membranes that can achieve the desired characteristics will lead to enhance the efficiency in present applications and advancement of new applications for FO process (Cath et al., 2006).

The main hindrance in osmotic advancement is internal concentration polarization (ICP) (McCutcheon, 2005; Tang, 2010). Both dilutive and concentrative ICP may be assigned to the dispersion of solutes that decrease the osmotic gradient in low dismissals membranes that outcome in osmotic pressure contrasts for a FO system (Tang, 2010; McCutcheon, 2006). Membranes with low structure parameters (S), tortuosity, porosity and relation between thicknesses are favored to minimize the ICP (Wei, 2011). Hence, FO membranes with execution of high water porousness, high solute dismissal and low ICP are one of the real research points in FO zone (Chou, 2010). It was observed that the commercial membranes like RO and asymmetric cellulose triacetate (CTA) FO membranes couldn't give these basic properties in the meantime. RO membranes having low flux however give high solute dismissal when utilized as a part of FO mode. As contrast to RO, CTA membranes have moderately low water flux and solute dismissal (Wei, 2011; Ma, 2012). In this way, focusing on the accurate FO layer is a critical point in FO research regions. Asymmetric membranes with a thin permeable specific layer on top of profoundly permeable support layer are regularly utilized as a part of FO processes (Qi, 2012). As compare to other FO membranes a thin film composite (TFC) FO membrane have confirmed the high flux performance and improved solute rejection (Wang, 2009; Wang, 2010; Chou, 2010).

Lately, developments in nanotechnology have steered to the improvement of nano-structured materials, which may formulate the foundation for innovative FO membranes. Different studies have validated that tinny film nano-composite (TFN) membranes may considerably augmented the membrane characteristics i.e. selectivity, stability and permeability in different osmotic processes (Kim, 2011). TFN RO membranes have been manufactured by integrating the pure metal, metal oxide and zeolite nano particles into the polyamide rejection layer (Lee, 2010). In many literatures, it was observed that Carbon nanotubes (CNTs) have improved properties in some factors such as modulus, tensile strength, permeability and water flux. CNTs also have multiplied great attractions as a one of the TFN RO membranes additive because of the resemblance between their liquid transport resources and those of water transport directs in membranes (Kulprathipanja , 2003 ; Rahimpour, 2011).

Recently, many researchers have studied the appropriateness of the CNT membranes for the sea water desalination (Dumée, 2012; Xiang, 2012). However it was still useful to investigate the CNTs in the rejection layers of the FO membranes. The main limitation in using CNTs is their low solubility in the solvent and low hydrophilicity. In 2013, Amini and co-workers improved their performance by using functionalized multi-walled carbon nanotubes for surface modification and functionalization of CNTs. They found that the water flux and salt rejection both in FO and PRO mode were concurrently enhanced in the novel orchestrated TFN FO films. Further investigate that due to improved structural and rejection properties TFN membranes have larger prospective for FO application (Amini, 2013).

2.4 Challenges in Forward Osmosis

Forward osmosis developments have been extensively recommended and investigated for many practical applications but still it has some considerable challenges. These inevitable challenges include concentration polarization, reverse solute diffusion and membrane fouling (Yip and Elimelech, 2011).

2.5.1 Concentration Polarization (CP)

Concentration polarization occurs both in pressure driven and forward osmosis (FO) membrane processes, and is very common and difficult to remove its effect (McCutcheon and Elimelech, 2006). In FO membrane processes it is the result of concentration difference between the highly concentrated draw solution on one side of the asymmetric membrane and low concentrated FS on the other side. There are two categories of concentration polarization (CP) phenomena takes place in FO processes i.e. external concentration polarization (ECP) and internal concentration polarization (ICP).

2.4.1.1 External Concentration Polarization (ECP)

Generally ECP happens at the surface of the dense support layer of the membrane. The only difference in pressure and osmotically driven processes is that concentrative ECP occurs in pressure driven membrane processes while both concentrative and dilutive

ECP takes place in naturally driven processes depending on the membrane configuration. When the FS fronting the active layer of the membrane concentrative ECP take place, whereas dilutive ECP happens when the DS facing the membrane active layer. ECP diminishes the net main thrust at the interface of membrane active layers towards the FS side or the osmotic pressure decreased at the active layer towards the DS side. Still, the confrontational of ECP on the treated water flux can be remediated by increase the cross flow velocity or turbulence or by optimizing the water extraction (Cath, 2006; Lee, 2010).

In osmotically driven membrane processes almost low or no hydraulic pressure applied therefore, ECP encouraged membrane fouling and affect the water flux as compare to pressure driven processes. It was observed that the ECP has a lower effect on FO processes and is not the intention behind the lower than the normal flux in such processes (McCutcheon, 2006).

2.4.1.2 Internal Concentration Polarization (ICP)

The main interfering phenomena in osmotically driven membrane processes are ICP. Because the effects of ICP on permeate flux in FO is very high (Gray, 2006; McCutcheon, 2006). The initial FO studies investigated that 80% decrease could occur in permeate flux due to the phenomena of ICP (Mehta and Loeb, 1978). Like ECP therefore two sorts of ICP also occurs, specifically dilutive ICP and concentrative ICP which take place in membrane porous backing layer depending on the membrane configration as shown in Figure 2.7.

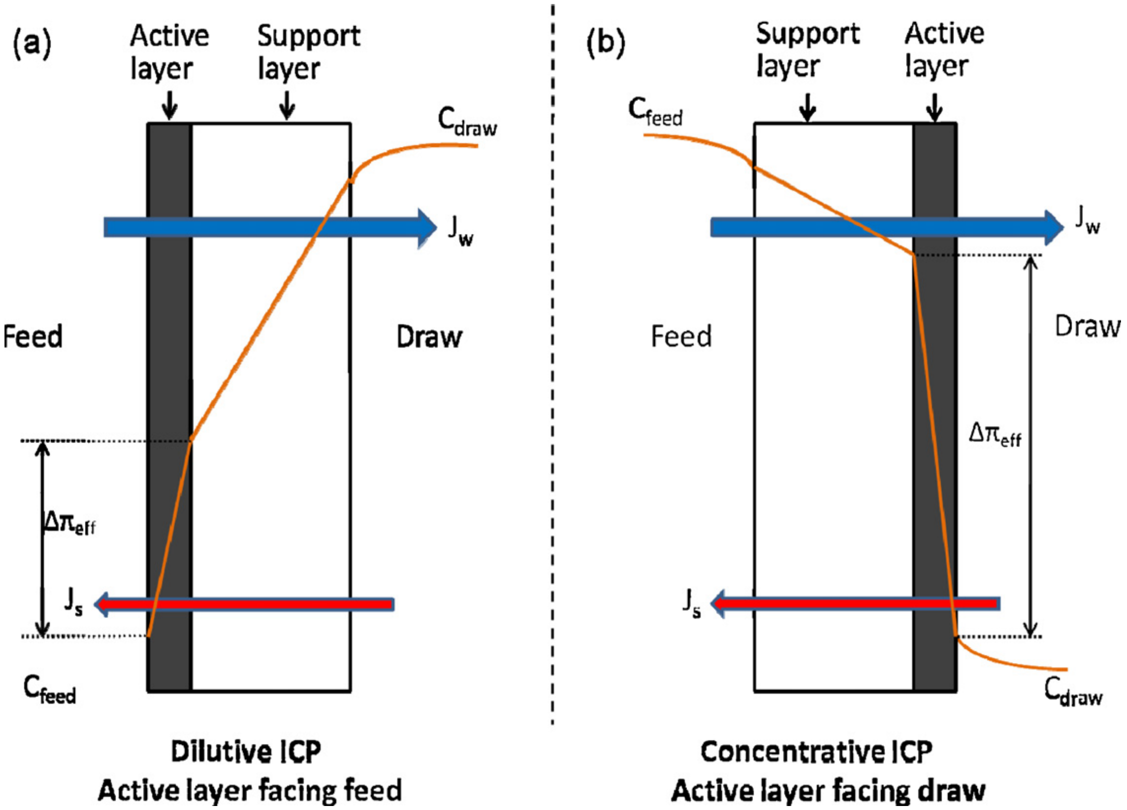


Figure. 2.7: Dilutive and concentrative ICP through an asymmetric FO membrane (Zhao and Zou, 2011).

In the FO mode, when the FS facing the active layer and DS facing the membrane support, dilutive ICP will result in the porous layer of the membrane as the water flux is from the FS to the DS side. While in PRO mode, when the DS is facing the active layer of the membrane and FS against membrane support layer, resulting in membrane concentrative ICP, since the solute in the feed stream gathers inside of the permeable support layer of the membrane. The effect of ICP on FO permeate flux has been modeled by following classical solution-diffusion theory (McCutcheon and Elimelech, 2007). In the FO mode, when the FS is facing the active layer of the membrane, dilutive ICP dominate he flux (J_w), and it can be represented by the equation (2.1):

$$J_w = \frac{1}{K} \ln \frac{A\pi_{\text{draw}} + B}{A\pi_{\text{feed}} + B + J_w} \tag{2.1}$$

In pressure retard osmosis mode the dominance of concentrative ICP on the permeate flux can be represented by the equation (2.2):

$$J_w = \frac{1}{K} \ln \frac{A\pi_{\text{draw}} + B - J_w}{A\pi_{\text{feed}} + B} \tag{2.2}$$

Where B is the membrane solute permeability coefficient and solute resistivity is represented by K, the solute capability to diffuse into or out of the membrane porous layer, and shows the rate of ICP in the porous layer. When the K is smaller it means ICP is lower and hence greater the water flux (J_w). K is defined (Cath, 2006; Yip, 2010) as:

$$K = \frac{t\tau}{\varepsilon D} = \frac{S}{D} \tag{2.3}$$

Where ε, τ, t and S are the porosity, tortuosity, membrane thickness, and structural parameter, respectively, and D is the diffusion coefficient for the solute. S is structural fundamental parameter of a membrane which is responsible for the measurement of ICP rate in the membrane porous layer by membrane properties such as porosity, tortuosity, and membrane thickness. Therefore the characterization of membrane structural parameter S for newly developed must be important. The estimation of S can be accomplished by putting FO test results in equation (1) and (2) (Tang, 2010; Phillip, 2010). Lately, Zhoa and Zou associated the ICP to the solute properties that includes particle size, viscosity and diffusion of the solute and also introduced the new idea of contrictivity (Zhoa and Zou, 2010). The resultant equation can be expressed as:

$$K = \frac{t\tau}{\delta \varepsilon_{\text{eff}} D} \tag{2.4}$$

In equation 2.4, a new parameter δ represents the constrictivity factor and ε_{eff} is the effective solute transport through membrane porosity. If for the large particles of the solute, small pores are not available then overall porosity of the membrane is greater than the ε_{eff} of the membrane. This new factor δ may be defined by the ratio of solute particle diameter and membrane pore diameter (λ)

$$\lambda = \frac{\text{molecule diamter}}{\text{pore diameter}} < 1 \qquad (2.5)$$

Constrictivity defines the rate of dispersion by varying the thickness in the permeable structure as a result of more prominent vicinity to the normal pore wall (Grathwohl, 1998).

2.5.2 Membranes Fouling

Similar to CP, membrane fouling is one of the most significant and unavoidable challenge to the all membrane processes (Lee et al., 2010, Tang et al., 2011). Lower the membrane fouling high water flux, lower cleaning frequency which result in longer membrane life, and in the same manner make the process cost effective both in capital and operational cases. However the membrane fouling of FO processes is not in resemblance with the pressure driven membrane processes due to the minimum hydraulic pressure requirements in FO.

Cath et al. are the first, that they studied the membrane fouling in FO processes. They concluded that the FO might have low fouling tendency than the other pressure driven membrane processes since they would not found any sign of fouling which effect the permeate flux in their studies (Cath et al., 2005). Since from the last decade FO has been used in osmotic membrane bio-reactor (OMBR) for the treatment of waste water because of its low fouling and low energy requirement (Achilli et al., 2009). When

OMBR was operated in the FO mode by Cornelissen et al. to treat the activated sludge, they reported that there is no reversible and irreversible fouling was found (Cornelissen et al, 2008). In 2009, Achilli et al. operated submerged OMBR for long term (28 days) studies and found that the membrane fouling is the principal reason for reduction in flux (Achilli et al., 2009). From this it can be inferred that layer fouling exist in FO processes and it may be reversible in long term operations.

In 2010, Mi and Elimelech found that both organic and inorganic fouling happens in FO. Furthermore, they compared FO and RO processes membrane fouling, and observed that the fouling of both processes were different from each other regarding the reversibility and cleaning efficiency of membrane (Mi and Elimelech 2010). In the same year, Lee et al. examined that membrane fouling in FO is about totally reversible whereas in RO it is unchanged. However they certify FO fouling to the quickened cake-enhanced osmotic pressure (CEOP), which is the result of draw solute reverse solute diffusion across membrane to the FS. The mechanism is demonstrated in Fig. 2.8 (Lee et al., 2010).

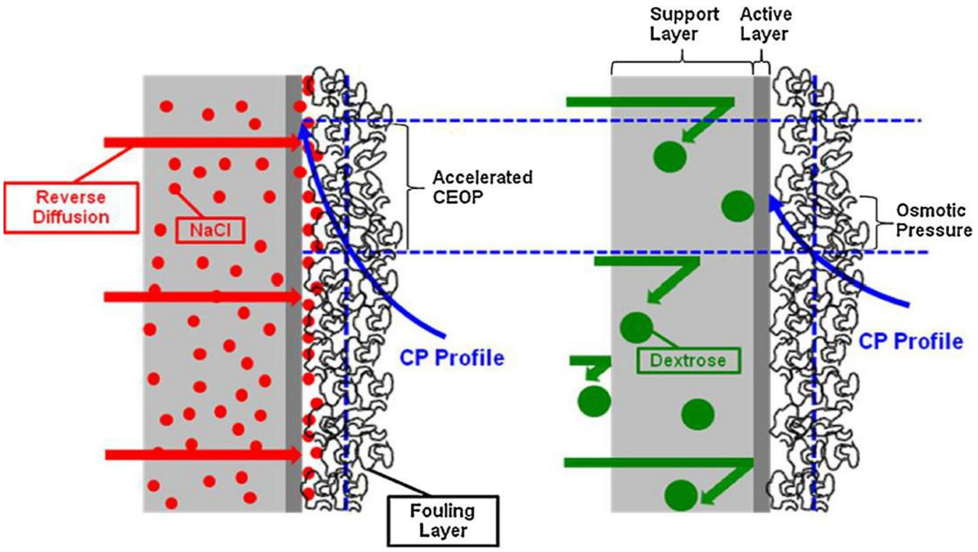


Figure 2.8: Illustrations of the Effect of Draw Solute (CEOP) in FO for two DSs: (a) NaCl (b) Dextrose (Lee et al., 2010).

In the FO mode, particles of solute build up on the active layer due to reverse solute transport, causing the CP which decreases the osmotic gradient across the membrane. The smaller the hydrated radius (i.e. NaCl) of the draw solute results in high CEOP than the larger hydrated radius (i.e. dextrose). It was also investigated that draw solute reverse solute transport could augment the CEOP influence and intensify the fouling (Lay et al., 2010). More ever, it was stated that FO membrane fouling can meaningfully be reduced by enhancing cross flow velocities (Lee et al., 2010).

2.5.3 Reverse Solute Transport

Reverse solute transport from the highly concentrated DS towards the low concentrated FS is also inevitable in FO processes. Reverse solute transport occurs due to the concentration difference through the membrane. In 2010, Lee et al. and Lay et al. interrelated the reverse solute transport to the membrane fouling and reported that reverse solute transport can intensify the CEOP effect exacerbate FO fouling (Lee et al., 2010; Lay et al.,2010;). Therefore, multivalent ion solutions with low reverse transport due to their larger size are preferred in some uses where high refusal is needed (Cath et al., 2006). Though, multivalent ions such as Ca^{+2} and Mg^{+2} after reverse transports may hamper with the foulants in the FS, which results in the enhancement of membrane fouling (Zou and Xio, 2011). More ever, due to their larger sizes, multivalent ion produces more severe ICP because of lower solution diffusion coefficients (Zhao and Zou, 2011). The particular reverse solute transport is define by the ratio between the solute reverse flux and treated water flux, and suggested as the membrane selectivity (Hancock and Cath, 2009). In 2010, it was investigated that, reverse solute diffusion is determined from the selectivity of the membrane active layer, but it is free from properties of draw solute and membrane (Phillip and Yong, 2010). This investigation could help the manufacturer in developing a new FO membrane. This can minimize reverse solute transport and make FO efficient. Additionally, using multivalent ion DS may reduce the reverse solute transport but it enhances the ICP which results in aggravated fouling must be noticed (Zou and Xiao, 2011). Moreover, utilizing a multivalent particle solution as the DS may minimize the reverse solute dissemination and thus lessen membrane fouling, yet the resultant higher ICP and the possibly expanded danger of fouling (S. Zou, Y. Gu, D. Xiao, 2011) must be considered carefully.

2.6 Forward Osmosis Membrane Bio-Reactor and its Treatment Efficiency

The forward osmosis membrane bioreactor (FO-MBR) is an emerging alternative to conventional MBR, which can be used for both potable and non-potable reuse applications. FO-MBR combines the conventional MBR and forward osmosis (FO) processes as shown in Fig. 2.9 (Achilli et al., 2009).In FO-MBR wastewater is nourished into a reactor as FS which is constantly aerated to provide oxygen to the biomass present in the system. Usually, the FO process results in dilution of DS and concentration of FS (Cath et al., 2006). FO membrane has the capability of high refusal of extensive variety of contaminants and has a lower membrane fouling tendency than pressure-driven membranes which results in less which brings about less recurrence of layer cleaning. Due to low hydraulic pressure required for operation the energy demand is exceptionally low, which makes FO-MBR system cost effective technology for wastewater treatment (Holloway et al., 2005). FO is not the eventual process in most of the wastewater treatment applications; however it can be used as a high level pretreatment step before an definitive replenishment process. Moreover, RO treatment system can provide dual barrier purification, if FO used as pretreatment to RO.

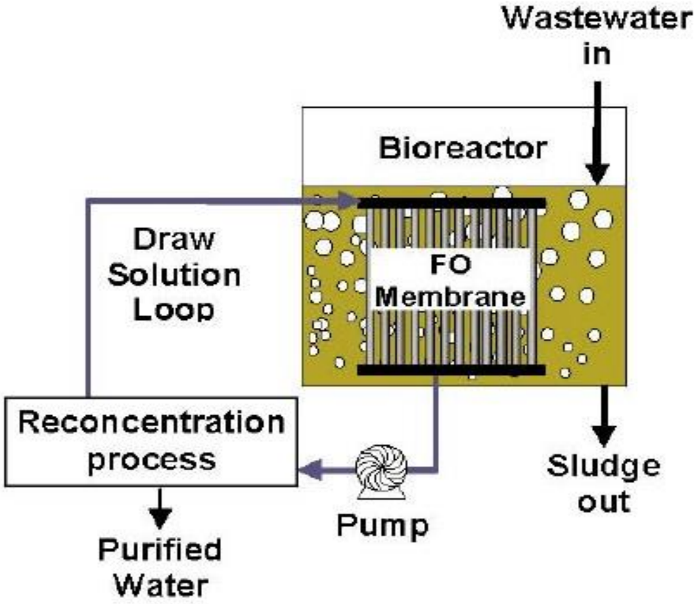


Figure 2.9: Schematic Diagram of an FO-MBR system (Achilli et al., 2009).

For making FO-MBR a practical and cost effective method, the FO membranes performance has to be optimized. In 2008, Cornelissen et al. investigated that with each step Celsius increase in operating temperature of the FO-MBR the water flux increases by 2.4% and by orienting membranes active layer towards the DS side, the water flux can be increased as compared with active layer towards the FS. In 2012, a study by Li et al. investigated the FO membrane fouling tendency during desalination of sea water. They revealed that higher cross flow velocity across membrane provides greater shear stress which inhibits the development of a fouling layer on the membrane surface. Likewise, high cross stream speed diminishes ECP on both sides of the film by upgrading the reverse transport and convection of salts from the surface of the layer or fouling layer to the mass feed or DS. They also attributed silica in the form of mono-silicic acid (H_4SiO_4)

to be the major foulant. Silica fouling is one of the unresolved issues when dealing with brackish water which contains silica in high concentration. Achilli et al., in 2009, operated an FO-MBR with various draw solution concentrations and three cellulose tri acetate FO membranes. They used synthetic wastewater of COD 4500 mg/L and gave a 3.5 d HRT to MLSS of 5500 mg/L. The reverse transport of salt after 8 hours was 100 mg/L in the MLSS. They revealed that membrane with loosest matrix showed highest water flux and highest reverse salt transport also. They proposed that after an introductory period of irreversible fouling happening in initial 14 days, after the fact periods of fouling are reversible and water flux can be kept up at a consistent level over the long haul. Still there are many areas needed to be optimized for effective FO-MBR operation.

2.7 Membrane Cleaning and Backwashing in FO-MBR

Membrane fouling and concentration polarization are the two important phenomena's on which membrane life span and water flux are primarily dependent (Sablani et al., 2001). Factors that affect membrane fouling include flow+ rate, feed solution pretreatment, membrane physical properties and cleaning water features. Lower cross flow velocity across the membrane resulting in increase in concentration polarization and fouling, consequently rapid decrease in flux and increase in cleaning frequency (Goosen et al., 2004).

Filter backwashing or air scouring can be used to detach some of the foulants, but for most the foulants chemical cleaning may be employed. Chemical cleaning is essential part of membrane cleaning which is cost effective and has profound efficiency. Normally manufacturers provide recommendations for membrane chemical cleaning (Kaiya et al., 2000). The ultimate goal of membrane cleaning is to acquire the introductory flux of the membrane and to evacuate the foulant aggregated on the surface of the membrane and inside of the membrane assembly (Wang and Lee, 2006).

2.7.1 Air Scouring Cleaning

Two air stone diffusers on both side of the chamber for length of time of 15 minutes at stream rate of 4166 mL/min in the FS tank, delivering 3.131 of air for every liter of FS. The defined stream rate does not damage the membrane material and remove all the accumulated foulants on the surface of the membrane. Linares et al. investigated FO membrane reversible fouling by using two different perspectives with air scouring. The membrane was initially cleaned from inside and afterward DI water was utilized as feed to clean the membrane and flux was calculated once again. Both of these methods are in situ cleaning techniques (Linares et al., 2012).

2.7.2 Chemical Cleaning

The chemicals used for membrane cleaning should loosen, dissolve the microscopic foulants and keep it in dispersion in the solution. Also, avoid spacer fouling, disinfect all wetted surfaces and should be friendly to membrane material (Tragardh et al., 1989). To remove the attached biofilm, membrane was flushed with the Milli-Q water for 48 hours. After flushing the membrane with biofilm is soaked in the solution of HNO_3 at pH of 2 for duration of 1 hour to dissolve the organic foulants. Bench scale FO/RO flow rate setups was used to measure the water permeability and mass transfer co-efficient after each cleaning (Wang and Shi, 2010).

MATERIALS AND METHODS

3.1 Introduction

This research study was comprised of three phases as shown in Figure 3.1

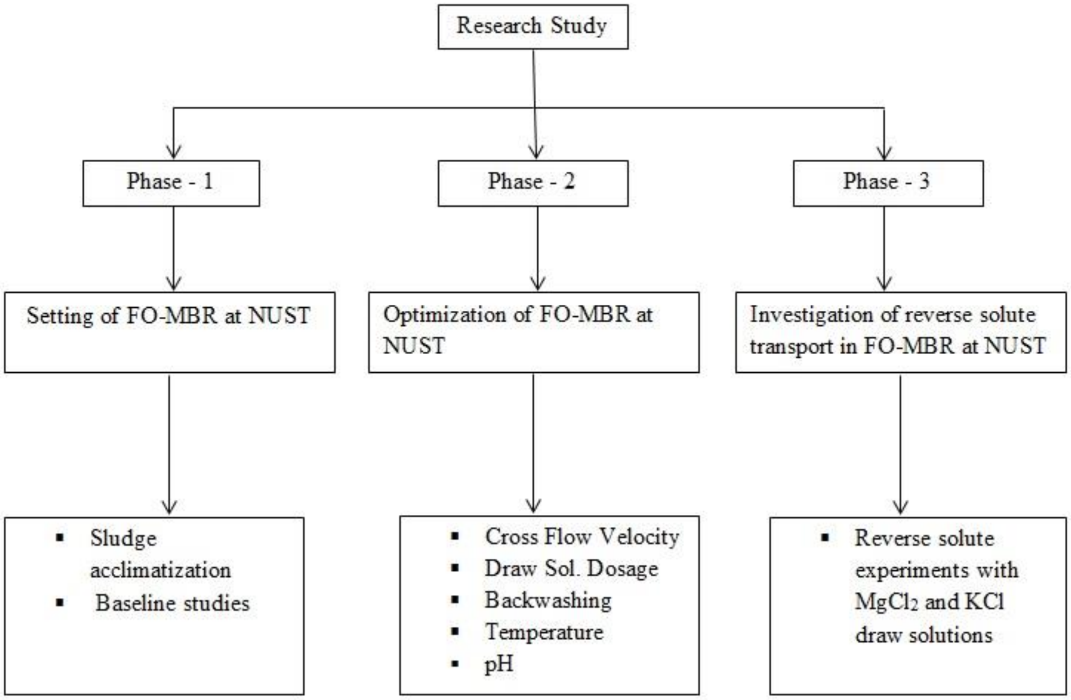


Figure 3.1: Phases of research study

Phase 1: This period of study comprises of the acclimatization of biomass and establishment of bench scale Forward Osmosis membrane bio-reactor (FO-MBR) at IESE-NUST. Protocols for all analytical and operating parameters like COD, ammonium nitrogen, nitrates, nitrites, $PO4^{3-}$ -P, MLSS and MLVSS, PSA, SOUR and EPS are studied and practiced.

Phase 2: This phase comprised of optimization of different parameters of FO-MBR which includes Draw solution initial volume, Cross flow velocity, molar concentration and backwashing mechanism. Cleaning protocols were developed for physical, base and acid cleaning.

Phase 3: In this phase reverse solute transport was investigated by using common salts as draw solutions in FO-MBR.

3.2 Synthetic Wastewater

In this study DI water was used as feed for batch setup i.e. optimization of different parameters for FO-MBR. Synthetic wastewater was used as influent with COD: N: P ratio of 100:10:2 for Continuous FO-MBR to investigate reverse solute transport by using different as draw solutions for wastewater treatment. The composition of synthetic domestic wastewater used in this study is described in Table 3.1. The synthetic wastewater has COD value of 500 mg/L; glucose was used as carbon source which is easily biodegradable. Ammonium chloride (NH_4Cl) of 50 mg/L and potassium di hydrogen phosphate (KH_2PO_4) of 10 mg/L was used as a source of nitrogen and phosphorus respectively. The pH in reactor was maintained between 7-8 using $NaHCO_3$. The other minor nutrients include calcium chloride ($CaCl_2$), Magnesium chloride ($MgCl_2$) and Potassium Chloride (KCl), each of quantity 10 mg/L was added to the synthetic waste water.

Table 3.2: Composition of synthetic wastewater

Components	Formula	Quantity (mg/L)
Glucose	$C_6H_{12}O_6.H_2O$	500
Ammonium chloride (NH_4Cl)	NH_4Cl	50
Potassium di hydrogen phosphate	KH_2PO_4	10
Calcium chloride	$CaCl_2$	10
Magnesium Sulphate	$MgSO_4.7H_2O$	10
Magnesium chloride	$MgCl_2$	10
Potassium Chloride	KCl	10
pH Buffer	$NaHCO_3$	200

3.3 Seed Sludge & Acclimatization of Biomass

Seed sludge was taken from municipal wastewater treatment plant of I-9 Islamabad, Pakistan. The sludge was collected from aeration tank of the treatment plant. This sludge was having MLSS concentration of 2000 mg/L during the start-up of the experiment and it was acclimatized with domestic synthetic wastewater for extent of two to three months in the waste water lab of IESE-NUST, Islamabad, under ambient temperature (25-30oC) before seeding of the bench scale FO-MBR. The sludge was acclimatized in relation with MLSS/MLVSS, pH, DO, removal of COD and total nitrogen. The sludge was aerated by supplying air and continuously mixed by using diffused aeration system. The acclimatization of Seeded sludge was carried out in sequencing batch reactor. The acclimatization protocol for seeded sludge is shown in the Figure 3.2.

Figure 3.2: Seeded sludge acclimatization protocol

3.4 Experimental Setup and Operating Conditions

3.4.1 Batch FO Process

The experimental setup of hollow fiber batch FO process is shown in Figure 3.3 and 3.4. Two poly-acrylic tanks each of volume 7 liters served as feed and draw solution reservoirs. The thin film composite polyamide hollow fiber membrane from Singapore Membrane Technology Centre (SMTC) was connected to the tanks using master flex piping. Physical characteristics of the membrane are given in Table 3.2.There are two modes of hollow fiber membrane module. When the FS face the active side of the membranes called AL-FS, and when active layer faces the DS is called AL-DS. The active layer was coated inside the hollow fibers and since the particles size of sludge particles was greater so only possibility was the AL-DS configuration. There are two peristaltic pumps which were used to cycle the DS and FS in the system on both active layer and porous support layers of the FO module respectively. A conductivity meter was used manually, both in Draw and feed solution tank to monitor the change in conductivity with time interval of 1 hour. To measure the permeate flux which is the change in mass of DS in the DS tank was placed on the electric balance. The balance was connected to the computer which records flux after every second. Flow meters were installed to measure the flow rates of draw and feed solutions.

Table 3.2: Specification of hollow fiber membrane module

Item	Value	Unit
Water permeability coefficient	2.7	LMH/bar
Solute permeability coefficient	0.13	LMH
Outer diameter of one hollow fiber	1.32	mm
Effective length of one hollow fiber	280	mm
No. of fibers in one module	15	-
Membrane area of module	17408.6	mm^2

As the system started osmosis occurred due to concentration gradient. This concentration gradient is the result of difference in the TDS contents of the DS and FS. During the osmosis the FS passes through the porous support layer of the membrane and resulted in treated water. This treated water or permeate was added to DS cycle and flowed to DS tank. This addition of permeate to DS results in dilution of the DS. The residual waste water was returned back to FS tank. The process was continued until the membrane was fouled and its flux was reduced to a value of 10% less than its initial value.

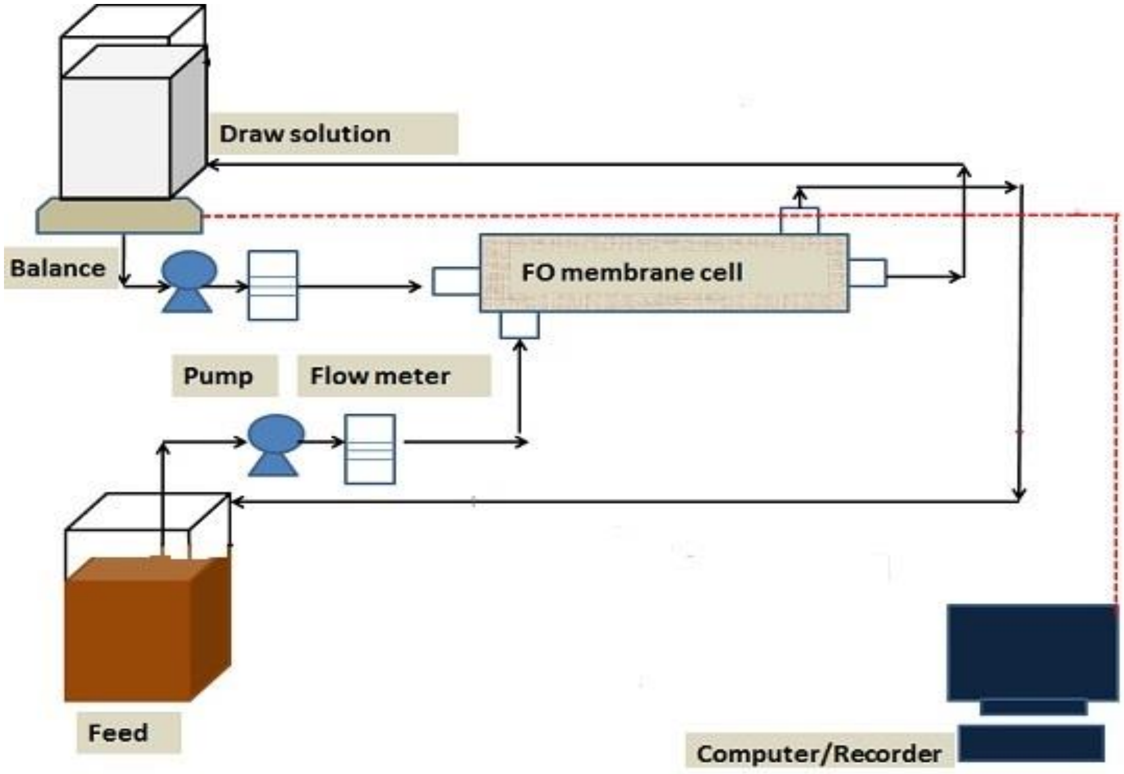


Figure 3.3: Schematic diagram for experimental setup of batch FO-MBR process

Figure 3.4: Laboratory scale batch FO process setup

3.4.2 Semi-Continuous FO Process

When treated water was added to the DS in batch setup, the conductivity or TDS content of DS was reduced and the TDS of feed solution was increased. Consequently the flux was reduced which ultimately slow down the osmosis and a time would reach that the process goes in reverse direction. To maintain the conductivity of draw solution, system was converted to semi-continuous system.

A timer was installed which was used to ON the pump for 1 minute after every 15 minutes. A secondary concentrated (5M) draw solution container was also used to re-concentrate the draw solution. Feed solution gets concentrated due to water treatment which reduces the flux for the continuous constant flux. The schematic and laboratory scale semi- continuous FO setup is shown in the Figure 3.5 and 3.6 respectively.

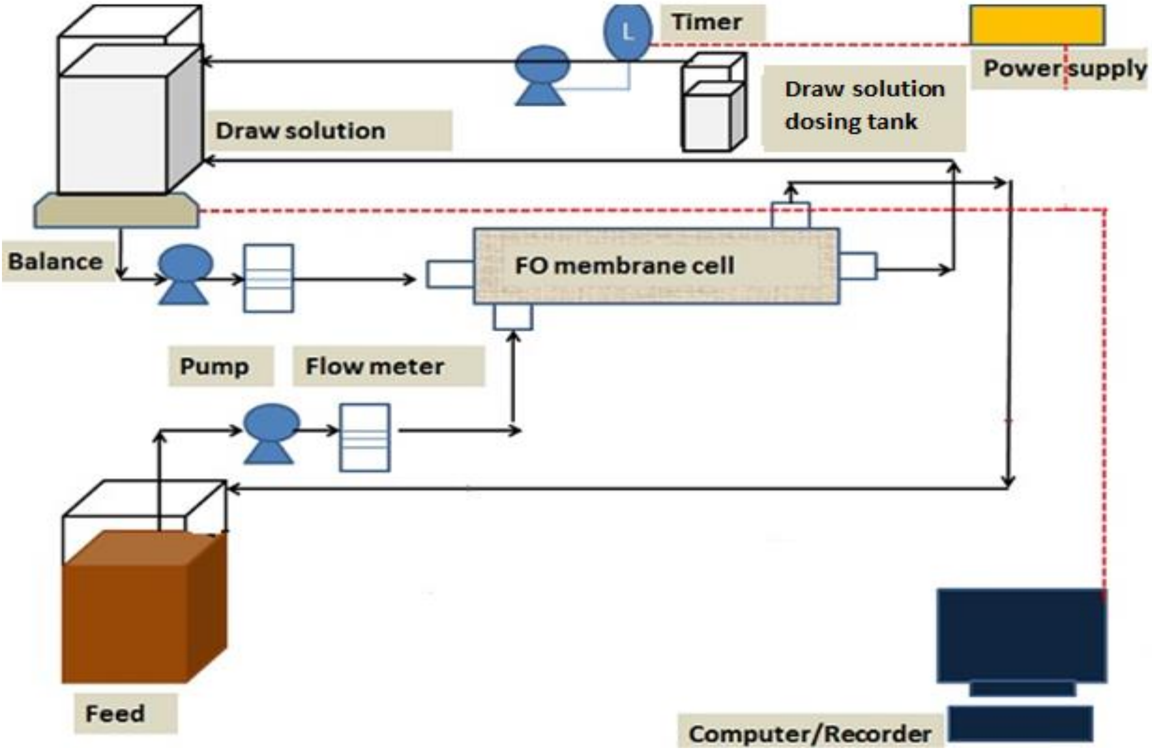


Figure 3.5: Schematic diagram for experimental setup of semi-continuous FO process

Figure 3.6: Laboratory scale semi-continuous FO process setup

3.4.3 FO-MBR Process

For smooth and continuous flux the system was further modified to the continuous system. In continuous system a secondary feed storage container was placed, and a control tank is also connected with the FS to control the level of feed FS in tank. The relay and sensor mechanism was installed to control the flow of feed solution from feed storage tank to control tank and from control tank to the FS tank. The feed in FO-MBR is synthetic wastewater. The composition of synthetic wastewater is discussed in section 3.2. The schematic and laboratory scale FO-MBR setup is shown in Figure 3.6 and 3.7.

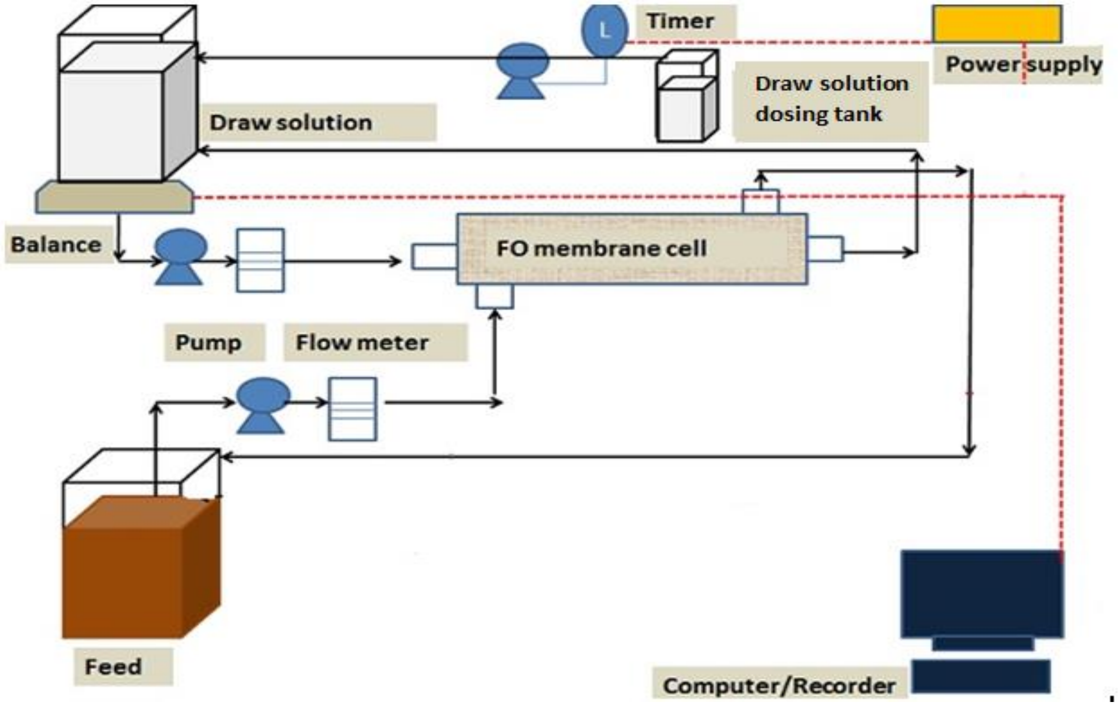


Figure 3.7: Schematic diagram of experimental setup of FO-MBR

Figure 3.8: Laboratory scale FO-MBR setup

3.5 Operating Parameters and Analytical Methods

The list of operated parameters that were analyzed, method adopted to determine each of that parameters and equipment or materials used is reported in Table 3.4.

3.5.1 Conductivity

Electrical conductivity (EC) is measure of the capability of a solution to pass electrical current. Ions present in the solution are responsible for the transport of electrical current; increase in concentration of the solution increases its conductivity. Total dissolved solids (TDS) can be measured by substituted the calculated values of EC. To check appropriateness of water for irrigation purpose it is very important parameter to be determined first. EC is used to determine the salinity of treated wastewater to be used for irrigation. In SI units it is represented by millisiemens per meter (mS/m).

Estimation of TDS of water test taking into account measured EC is given in the equ: 3.1.

$$\text{TDS (mg / L)} = \text{EC(dS /m)} \times (0.55 - 0.70) \,.\,.\,.\,.\,.\,.\,.\,.\,.\, (3.1)$$

The conductivity meter (Oakton PC 300, Singapore) was used to determine the conductivity of sample in mS/cm.

3.5.2 Total Organic Carbon (TOC)

Total organic carbon (TOC) examination developed from the need to break down wastewater and metropolitan water from organic matter. Estimation of TOC is a considerably more quick strategy to govern the organic matter content in water and wastewater, which is specifically identified with aggregate organic content.

The determination of TOC is important environmental monitoring parameter that provides a rapid indication of the contents of organic substances present in the sample.

Natural organic matter reacts with the active chlorine compounds to yield chlorinated disinfection byproducts. TOC analysis emerged as a rapid and accurate alternative to the classical but lengthy BOD & COD analyses.

3.5.3 Chemical Oxygen Demand (COD)

COD is a measure of the oxygen required by a strong oxidizing agent comparable to the organic matter that is prone to oxidation. In other words COD is the indirect measure of the amount of organic composites present in water. Larger quantities of organic matter in wastewater mean higher Chemical Oxygen Demand (COD). So in case of heavy organic matter contamination present in wastewater entering in a water body of robust ecosystem will result in depletion of dissolved Oxygen ultimately that will further result in lesser availability of oxygen for aquatic life present in that water body. Due to depletion of dissolved oxygen living organisms present in water start dying and result in more Chemical Oxygen Demand (COD). So COD is an important wastewater parameter as it disturbs the aquatic ecosystem extensively.

Table 3.3: Analytical parameters, methods and equipment/material

Parameter	Method	Equipment/Material	Reference
MLSS-MLVSS	Filtration-Evaporation	1.2 µm glass microfiber filter (GF/C, Whatman®); 105°C oven (MLSS); 550°C muffle furnace (MLVSS)	APHA (2005)
COD	Close reflux	COD tube; 150°C oven	APHA (2005)
Conductivity	-	Conductivity meter (Oakton PC 300, Singapore)	-
Total dissolved solids (TDS)	-	TDS meter (Oakton PC 300, Singapore)	-
pH	-	pH meter (Oakton PC 300, Singapore)	-
Specific oxygen uptake rate (SOUR)	Rate of DO depletion	DO meter (YSI, Model 5100, USA)	Xing et al. (2001); Mathieu and Etienne (2000); APHA (2005)
Soluble EPS	Centrifugation	Centrifuge (SIGMA Laborzentrifugen, Sigma 204, Germany)	Zhang et al. (2006)
Bound EPS	Cation exchange resin (CER) method	Centrifuge (SIGMA Laborzentrifugen, Sigma 204, Germany)	Frolund et al. (1996)
PSA	Laser light scattering	Particle size analyser (LA-300, Horiba, Japan)	
$NO3^{-}$-N, $NO2^{-}$-N	Ultraviolet Spectrophotometry	Spectrophotometer (DR/2400, Hach, USA)	APHA (2005)
$NH4^{-}$N	Ultraviolet Spectrophotometry	Spectrophotometer (DR/2400, Hach, USA)	APHA (2005)
PO4-P	Ultraviolet Spectrophotometry	Spectrophotometer (DR/2400, Hach, USA)	APHA (2005)

3.5.4 pH

pH meter (Oakton PC 300, Singapore) was used to measure the pH. The pH meter probe was inserted in the draw solution and feed solution tank after every hour to check the effect of draw solute on the biomass present in the feed solution, during reverse solute transport.

3.5.5 Particle size distribution (PSD)

A laser scattering particle size distribution analyzer LA-300 (Horiba, Japan) was used to measure the PSD of the samples. For particle size distribution analysis, fresh samples of activated sludge were directly taken from the FO-MBR feed tank and sonicated for 5 min at 25 ^{o}C in sonication bath before analyzing in particle size distribution analyzer.+

3.5.6 Specific oxygen uptake rate (SOUR)

The oxygen demand of biological suspended sample i.e. activated sludge is determined by SOUR test. Oxygen uptake rate measurement is a valuable tool for assessment and guideline of the process efficiency. Oxygen uptake rate estimations can give much data concerning treatment plant execution, wastewater qualities, degradability of uncommon concentrated streams and in addition parameters required for numerical models, keeping in mind the end goal to anticipate conceivable advancements of a treatment plant. Likewise it is valuable for every day operation control.

3.6 Membrane Cleaning

3.6.1 Osmotic Backwashing

Osmotic backwashing were performed by replacing DS (NaCl) to DI water. Before changing the draw solution to DI water the module and piping system were flushed with DI water for 1-2 minutes and was wasted after flushing. All the experiments were performed for duration of 8 hours comprising of 7 hours of positive system filtration and 1 hour backwashing. The Net positive volume of water extracted from the FO module was calculated by subtracting the total volume of water used for backwashing from the sum of positive system filtration volume.

Net volume extracted (ml) = sum of positive volumes (ml) - sum of backwash volume (ml)

3.6.2 Physical Cleaning

The module was opened and the rust layer was removed on the influent draw solution side manually by hands covered with gloves. Remove all solids from the piping by flowing clean water through them.

3.6.3 Chemical Cleaning

- **Base Cleaning**

Base cleaning was performed by using Sodium Hydroxide solution. The solution was prepared by solving 300g of NaOH in 10 liters of water (30 g/L or 0.75M). The solution was used both as draw and feed solutions simultaneously to clean the membrane from active and porous support layer sides. Cleaning was continued for 5 hours at low Cross flow velocity of 30 ml/minutes. Flux recovery experiments were performed after base cleaning of the membrane.

- **Acid Cleaning**

For getting complete flux recovery the acid cleaning was followed by base cleaning. Nitric Acid (HNO3) with 0.5M concentration was used as cleaning solution. The pH of the solution was kept above 2, to avoid any physical damage to the membrane material. The solution was run through the membrane module for 2 hours in the same way as during base cleaning. After acid cleaning the DI water was flushed for 2 hours and flux recovery experiment were performed.

Table 3.4: Manufacturer flux recovery protocol for hollow fiber FO membrane

FO Membrane cleaning mode comparison	**Methodology adopted**	**Total Time of cleaning (hrs)**	**Flux Recovery (%)**
SMTC (Zhang et al.,2012): Submerged membrane in FO-MBR	1. Flushing membrane surface with Millipore water for 48 hrs. 2. Membrane soaked in HNO3 solution at 2 pH for 1 hr.	50	10 97.8
Modified method in this study:	1. Removing cake/scaling layer manually after opening the module. 2. Flushing DI water for 1 hr. 3. Flushing 0.75 M (30g/100ml) NaOH for 2 hrs. 4. Flushing DI water for 30 minutes. 5. Flushing 0.2M HNO_3 for 1 hr. 6. Flushing DI water for 1 hr.	6	93

Chapter 4

RESULTS AND DISCUSSION

4.1 Introduction

This chapter presents the results and analysis of different experiments for FO-MBR optimization. The data is shown in the form of tables and graphs followed by detailed discussions.

4.2 Batch FO Process

4.2.1 Influence of Initial DS Volume on Flux

To find the relationship between the draw solution starting volumes and flux a series of experiments were performed under different operating condition as presented in the table.

Table 4.1: Operating conditions for starting volume of DS optimization

Operating Conditions					
Sr. No.	**Conc. (M)**	***DSV (L)**	****CFV (ml/min)**	*****FS**	**Avg. Flux(LMH)**
1	2	1	40	DI	11.8
2	2	0.5	40	DI	12.1
3	1	0.5	40	DI	5.91

*DSV Draw solution starting volume **CFV Cross Flow Velocity ***FS Feed Solution

The results shown in Figure 4.1 reveals that when the molar concentration of the DS was kept constant 2M the decrease in Draw solution initial volume from 1L to 0.5 L has no effect on the flux. But at constant Draw solution initial volume of 0.5L, decrease in molar concentration for 2M to 1M decreases the flux by about 50%. Therefore, the average flux depends on molar concentration rather than the starting volume. So for the next experiments starting volume was chosen to be 0.5L.

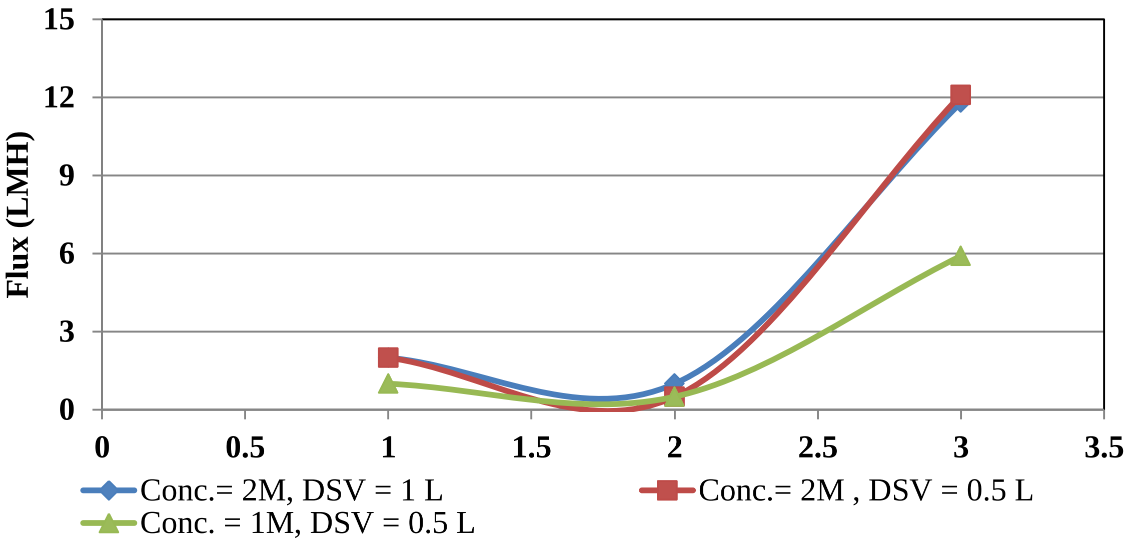


Figure 4.1: Relationship between DS initial volume and Conc. Vs Flux

4.2.2 Influence of Cross Flow Velocity on Flux

Cross flow velocity is an essential factor to be optimized in the FO-MBR. It is usually believed that increase in cross flow velocity may reduce ECP, and hence increases the flux. So, flux is directly corresponding to the cross flow velocity upto some extent, but after diminishing the ECP completely, increase in cross flow velocity is not effective to enhance the flux. In a study by Qin et al. (2009), 0.5M NaCl was used as DS and cross flow velocity was carried from 0.1 to 0.7 m/s. A gentle increment in flux was seen with enlargement in cross flow velocity and level off when the flow pattern comes to be turbulent. This could be accredited to a high solute concentration of the DS, consequential in a countable involvement of dilutive ECP to the flux (Qin et al., 2009). Positive effect of changing hydrodynamic conditions on fouling mitigation in FO is reported in other studies as well (Boo et al., 2013).

For determining the relation between cross flow velocity and flux, a series of experiments were performed under different operating conditions as presented in Table

4.2. By keeping 1 molar concentration and 0.5 L DS initial volume constant, cross flow velocity of 50 ml/min resulted in flux of 5.91 LMH. Increase in cross flow velocity to 100 ml/min increased the flux from 5.91 LMH to 7.89 LMH. Further increase in cross flow velocity to 150 ml/min increased the flux by 50% from 7.86 LMH to 11.76 LMH as shown in Fig. 4.2.

Table 4.2: Operating conditions for cross flow velocity optimization

Operating Conditions						
S. No.	**Molar Conc: (M)**	***DSV (L)**	****CFV (ml/min)**	*****FS**	**Flow Direction**	**Avg. Flux(LMH)**
1	1	0.5	40	DI	Concurrent	5.91
2	1	0.5	100	DI	Concurrent	7.86
3	1	0.5	150	DI	Concurrent	11.76

*DSV Draw solution starting volume **CFV Cross Flow Velocity ***FS Feed Solution

When the DS faces the active layer and FS faces the porous support layer of the membrane, this configuration consequences concentrative ICP on the feed side and Dilutive ICP on the DS side. This ECP can be reduced by adequate cross flow and turbulence (Gadelha et al., 2014). ECP decreases the dynamic force due to reduced osmotic pressure at the surface of the membrane active layer on the DS side, or increase the osmotic pressure at the interface towards the FS side. Still, the confrontational effect of ECP on the permeate flux can be avoided by enhancing the flow turbulence or flow rate (Cath et al., 2006). So increase in cross flow velocity minimized the ECP and played an significant role in enhancing the permeate flux. The cross-flow velocity was further raised to 200 ml/min; however the system could not accommodate such high cross flow velocity. So cross flow velocity value was optimized at 150 ml/min.

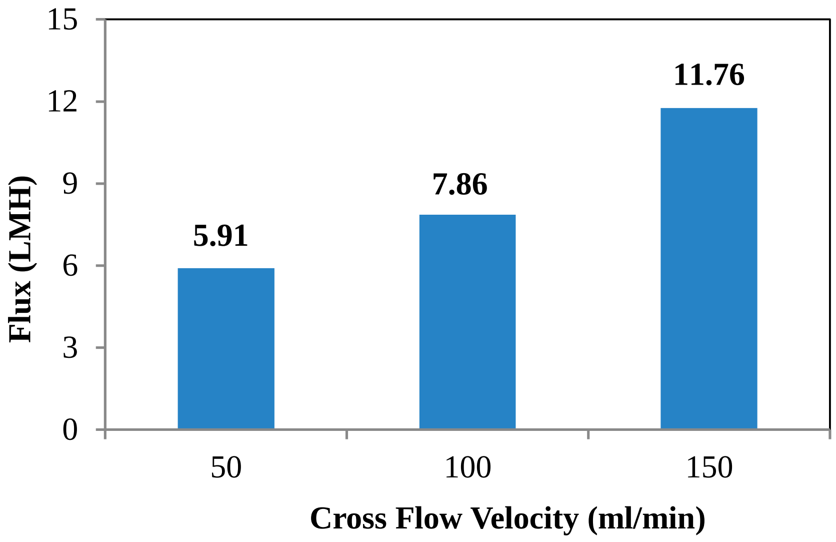


Figure 4.2: Relationship between DS Cross Flow Velocity Vs Flux

4.2.3 Influence of Variation in DS Molar Concentration

Operating conditions for the optimization of molar concentration are given in Table 4.3. Fig. 4.3 demonstrates the variation in flux and conductivity of feed solution, with variable DS concentrations of 0.5, 1.0, 2.0, 3.0, 4.0 and 5.0 M NaCl. As DI water was used as FS having zero conductivity so, increase in its conductivity was reflective of reverse salt transport from the DS. Since AL-DS configuration was used, so there cannot be any concentrative ECP and concentrative ICP and major flux decline may only be due to dilutive ECP and dilutive ICP. The increase in flux with DS concentration was not directly proportional and it declined with increasing concentration. Such non-linear affiliation between flux and DS concentration in FO, is reported in the literature (Tang et al., 2010). Table 4.3 shows that average flux increased linearly as the molar concentration amplified from 0.5 to 2.0 M.

Table 4.3: Experimental analysis of Draw Solution concentration

S. No.	Draw Solution conc. (M)	Average Flux (LMH)	Drop in conductivity of D.S. mS/cm (% drop)	Increase in conductivity of F.S. µS/cm (% increase)	Reverse transported conductivity FS µS/cm (% drop)
1	0.5	5.8	20	41	212
2	1	7.8	77	50	440
3	2	10	270	75	572
4	3	5.3	348	73	1280
5	4	4.3	426	71	960
6	5	3.9	Over range	N/A	881

But further increase in molar concentration it stayed constant up to 4M followed by a decline onwards. Since the flux beyond 2M is not significant. So 2M was the optimized value for molar concentration for hollow fiber FO membrane. Figure 4.3 shows that with increase in molar concentration, increased the osmotic pressure difference between DS and FS which reduce the flux. It was also observed that percent increase in conductivity of FS relatively proportional to the concentration of DS. Since the FS was DI which had zero conductivity, any increase was only due to reverse transport of solute. Conductivity increase of FS from 2M to 3M is very abrupt; later on it goes down but not significantly. Therefore, it is recommended to use DS concentration at maximum of 2M to avoid reverse solute transport and net flux decline.

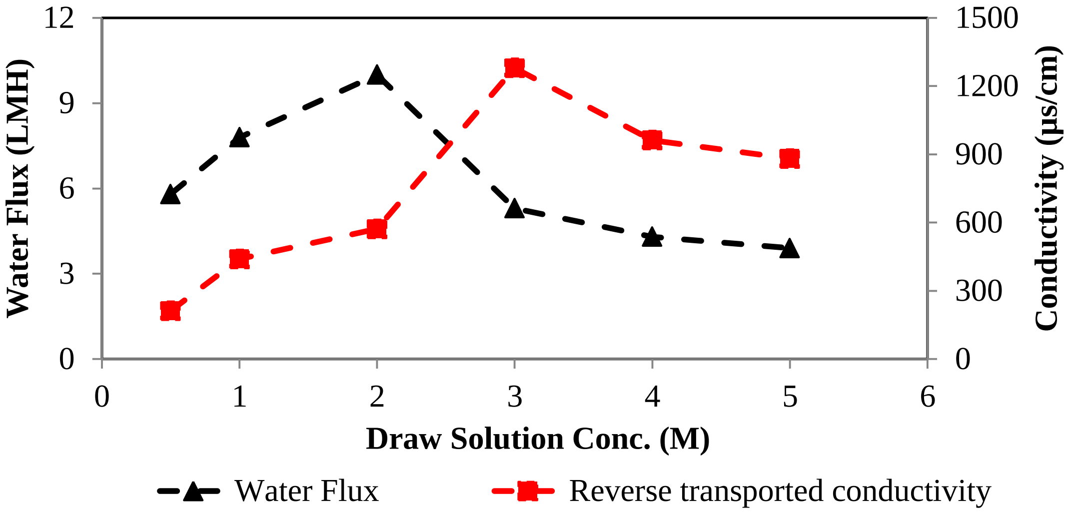


Figure 4.3: Variation in water flux and reverse transported conductivity with concentration

4.2.4 Effect of temperature change

By keeping other conditions similar, the effect of temperature variation was found on the resultant flux. The flux was found to be at 7.24 LMH at 22^0C and 7.18 LMH at 30^0C. This revealed that there is no need of going at high temperature.

4.2.5 Membrane Cleaning

4.2.5.1 Osmotic backwashing

Table 4.4 summarizes the results of osmotic backwashing experiments; the methodology is discussed in section 3.6.1. the osmotic backwash approach adopted in this study was more realistic and practicable compared to the studies that used DI water in replacement of DS and some weak NaCl solution in replacement of the FS (Achilli et al., 2009) or performed only with model foulants and not with the mixed sludge (Kim et al., 2012). In this study it was expected that when the DS was replaced with DI water, the DI water will start flowing in reverse direction and the mass of the FS/activated sludge will increase gradually. And it will remove the fouling layer, caused by the accumulation of sludge particles, from the membrane surface. Due to the practical limitations of hollow fiber membrane used, AL-DS configuration was used, which is more prone to ICP by activated sludge as compared to AL-FS mode. So from this it can be concluded that the fouling in PRO mode is irreversible as compared to FO mode which is reversible, for hollow fiber membranes.

The DS used in this study 2M NaCl and the FS was mixed sludge. Looking at the sum of filtrate volumes extracted it may be discovered that the osmotic backwashing for 20 and 30 minutes was ineffective compared to the 60 minutes backwash, because of negative water flux during backwash and adding more complexity to the system. This negative flux during the 20 and 30 minutes backwash may be attributed to the gradient inside the FO membrane established by 2M NaCl. This gradient was so strong that even rinsing it with DI water, before backwash, could not remove its effect completely. Also, the mixed sludge had not such a high osmotic pressure to establish its own gradient in the membrane. So, it may be inferred that the osmotic backwashing is not practical at least with the hollow fiber FO-MBR.

Table 4.4: Osmotic backwashing for hollow fiber FO membrane

Exp. No.	**Condition**	**Cycles/ day**	**Positive 1 (ml)**	**Positive 2 (ml)**	**Positive 3 (ml)**	**Sum of positive volume (ml)**	**Backwash 1 (ml)**	**Backwash2 (ml)**	**Backwash 3 (ml)**	**Net Positive Volume (ml)**
1	**420 min positive + 60 min backwash**	**1**	201	N/A	N/A	201	17	N/A	N/A	**184**
2	**210 min positive + 30 min backwash**	**2**	108	73	N/A	181	-48	-19	N/A	**248**
3	**140 min positive + 20 min backwash**	**3**	80	58	64	202	-33	-10	8	**237**

4.2.5.2 Chemical Cleaning

Membrane cleaning was optimized by trial and error method. Various concentration of cleaning solution and cleaning intervals were studied for attaining maximum flux recovery. The detailed methodology was discussed in section 3.6.3. Results of hollow fiber membrane chemical cleaning are shown in Table 4.4 with the methodology applied its operating conditions and the process efficiency.

Table 4.5: Results of hollow fiber membrane cleaning

Method	Condition	Efficiency
Base Cleaning (NaOH, 0.75M)	Duration = 4hr to 5hr CFV = 30 ml/min	70%
Acid Cleaning (HNO_3 , 0.5M)	Duration = 6hr pH => 2	93%
SMTC (Zhang et al.,2012): Submerged membrane in FO-MBR	Duration = 50 hr. pH = 2	97%

The flux recovery was tested with submerged hollow fiber FO module; taking 50 hours cleaning and attaining flux recovery is reported (Zhang et al.,2012). In this protocols developed in this study, the cumulative cleaning time is only 5 hours and flux recovery was 93% for externally connected hollow fiber membrane module. So, this protocol is much improved than the previous one in terms of robustness and cost.

4.2.6 Dynamics of hollow fiber FO membrane

Table 4.5 summarizes the results when synthetic domestic wastewater was used as the feed solution and 2M NaCl as draw solution, in batch mode, to identify the dynamics of hollow fiber FO membrane. In all the experiments the volume of draw and feed were 0.5L and 2.5L respectively. Composition of the synthetic wastewater is listed in Table 3.1.

the actual values are the experimental values and the calculated values are normalized with water volume added in the draw solution or water volume subtracted from the feed solution.

From the results of TOC it may be revealed that if there was no passage of TOC from feed to draw, then the draw TOC should have reduced continuously with operation time due to dilution with treated water. But in first hour almost 34 mg/L TOC was transferred in the draw solution. It depicts that this FO membrane cannot remove TOC from the wastewater by just simple filtration. The constant values of TOC from 2nd to 6th hour of operation shows that the maximum TOC was transferred in the first hour and then the TOC did not passed through the membrane. It may be assumed that the membrane initially allowed the organics to pass through it and then due to the combined effects of ECP and ICP the pore clogging occurred and the rest of the organics were not able to pass through the membrane. The passage of 3 mg/L of TOC to DS during FO-MBR operation was also observed in another study (Achilli et al., 2009). By comparing last values of actual (218.4) and expected (293) feed TOC it is clear that almost 74.6 mg/L TOC was transferred to the draw solution in the whole experiment. So the TOC removal efficiency is around 74%.

The conductivity results in the Table 4.5 reveal that the conductivity was only due to the inorganics and not due to organics, almost 1.11 mS/cm NaCl reverse transported towards the feed solution in the first hour only. Due to same expected ICP the reverse transports was stopped and draw solution conductivity decreased and feed increased as per expectation. In another study transfer of 10 mS/cm conductivity in first 12 days operation of a continuous FO-MBR; due to reverse solute was reported. After that the conductivity was stabilized due to sludge wastage (Zhang et al., 2012). It shows that the conductivity increase in FO-MBR may be controlled easily and it may not affect the processes on the feed side. Similar trend may be observed with TN as well, which was also stabilized after first hour. From these results it may be revealed that the first hour of the system is highly critical and all major changes occur in that. The critical nature of the first hour in FO-MBR fouling and steady state achievements also reported by other researchers (Qin et al., 2009), which support this study of understanding for hollow fiber FO membrane dynamics.

Table 4.6: Direct treatment of synthetic wastewater with hollow fiber FO membrane

Time (hr)	Actual Feed Cond. (mS/cm)	Actual Draw Cond. (mS/cm)	Draw cond. If no salt passed membrane (mS/cm)	Feed cond. If no salt passed membrane (mS/cm)	Actual Feed TOC (mg/L)	Actual Draw TOC (mg/L)	Draw TOC if no organics passed through membrane	Feed TOC if no organics passed through membrane	Feed TN (mg/L)	Draw TN (mg/L)	Volume of treated water added in draw (ml)
0	0.38	139.9	139.9	0.38	240	0	0	240	93	4.01	0
1	0.98	105.6	106.9	0.40	214.2	34.56	2.3	255	79.23	33.92	154 (154)
2	1.13	94.8	93.1	0.42	220.1	22.05	2.04	266	78.76	35.51	251 (97)
3	1.22	88.9	83.3	0.43	221.5	18.46	1.82	277	77.97	33.99	339 (88)
4	1.40	80.5	76.4	0.45	220	14.48	1.67	287	76.98	36.38	415 (76)
5	1.51	75.9	71	0.47	220.5	10.51	1.55	297	76	38.78	485 (70)
6	1.59	74.3	66.9	0.48	218.4	12.08	1.46	306	74.03	41.72	545 (60)

4.3 Semi-Continuous FO process

4.3.1 Comparison of Batch and Semi-Continuous FO process

In batch setup the conductivity of DS decreased abruptly at the start of the experiment due to high water extraction as shown in Figure 4.4. Later on the decrease in DS conductivity was gradual till the minimal flux. While in the semi-continuous FO system, conductivity of DS falls at early stage due to high water extraction, but later on it goes on increasing with time till it was stabilized for almost constant conductivity of DS as shown in Figure 4.5. So from the comparison it can be inferred that the Semi-Continuous FO process almost give constant conductivity of DS and the process goes smoother as compare to Batch FO process. All the optimized parameters were cross checked for semi-continuous FO process. On the basis of this investigation the system was further modified to the FO-MBR process.

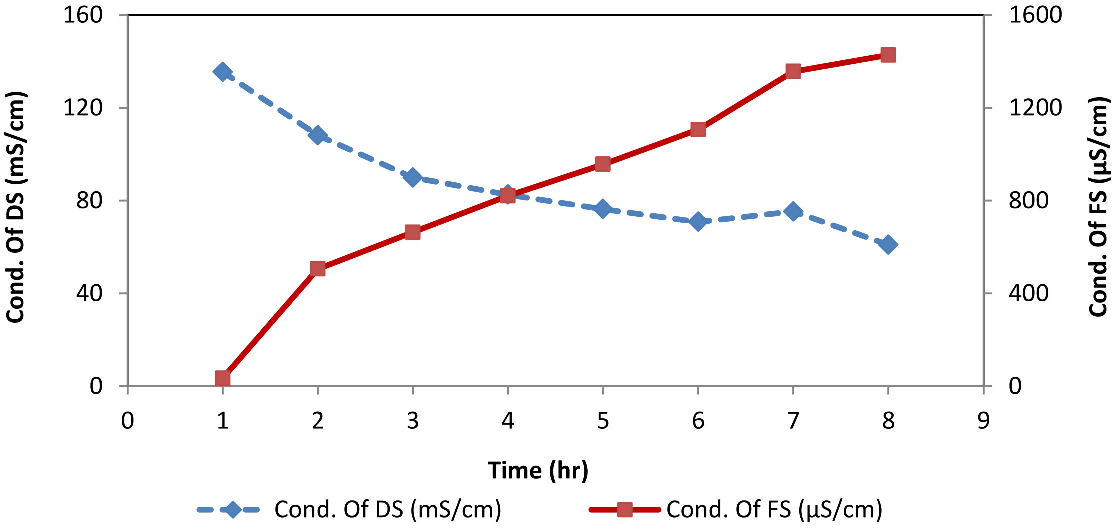


Figure 4.4: Conductivity graph for Batch FO process

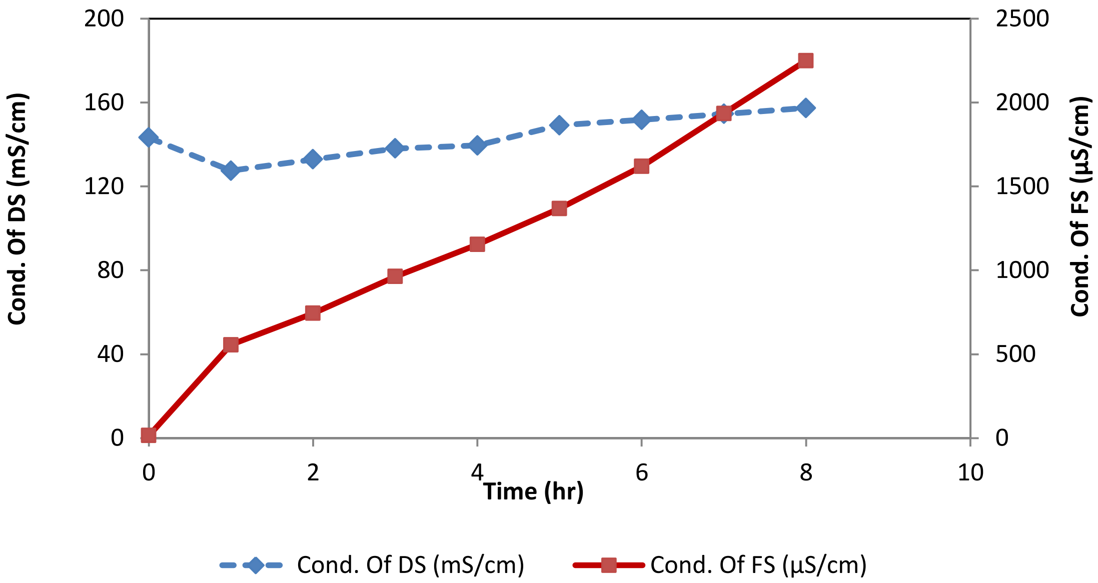


Figure 4.5: Conductivity graph for semi-continuous FO process

4.4 Continuous FO-MBR System

4.4.1 Comparison of salts for FO-MBR

Experiments were performed on Continuous FO-MBR system under optimized conditions with activated sludge (MLSS= 6g/L) used as feed solution. $MgCl_2$ and KCl were used as draw solutions. All the experiments were performed for duration of 48 hours with the DS facing the membrane active layer (AL-DS) under optimized operating conditions. The volume of FS was 3L facing support layer of membrane. As the water was extracted from the feed solution tank, fresh synthetic wastewater starts flowing from feed storage tank to FS tank in order to prevent the increase in conductivity of FS and maintain the biological process in terms of organics and nutrients requirements.

The flux obtained from $MgCl_2$ was 3.95 LMH. From the Figure 4.6, it can be observed that the conductivity of feed solution is almost constant throughout the experiment which shows very low reverse solute transport. Therefore, $MgCl_2$ can be separated from diluted draw solution by using RO and reused. While on the other contrary, KCl achieved high average flux than $MgCl_2$. But the trend of KCl conductivity as shown in Figure 4.7, declines in early hours of the experiment due to severe reverse solute transport resulting in the conductivity increase of feed solution throughout the experiment. This highly transported KCl may be difficult to recover from the FS.

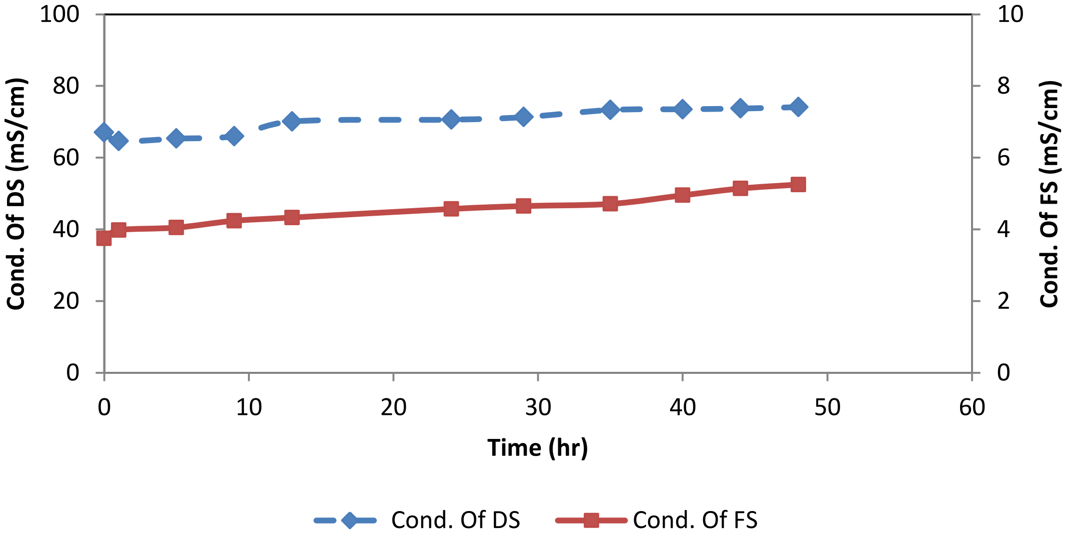


Figure 4.6: Relationship between conductivity of DS and FS for $MgCl_2$

From the comparison of Figure 4.6 and 4.7, it is clear that the KCl have higher flux of 4.61 LMH than $MgCl_2$ which has a flux of 3.95 LMH. Flux in FO-MBR depends mostly on internal concentration polarization (ICP) and reverse solute transport. ICP depends on the diffusivity, particle size and viscosity of DS either or FS depending on AL-FS or AL-DS configuration. Mg^{+2} ion is divalent catian; it has low diffusivity and larger particle size so it is difficult for Mg^{+2} ion to pass through the membrane, therefore its reverse solute transport was very low. This reverse solute transport is reduced by internal concentration polarization (ICP). The larger size Mg^{+2} cannot pass through the active layer of the membrane and accumulated on it. Concentrative ICP occurs as the solute in the feed solution accumulates within the membrane support layer and the draw solution particles concentrated near the surface of the active layer of the membrane. Due to this osmotic pressure going to decrease which reduces the flux and the time would reach that the process stop.

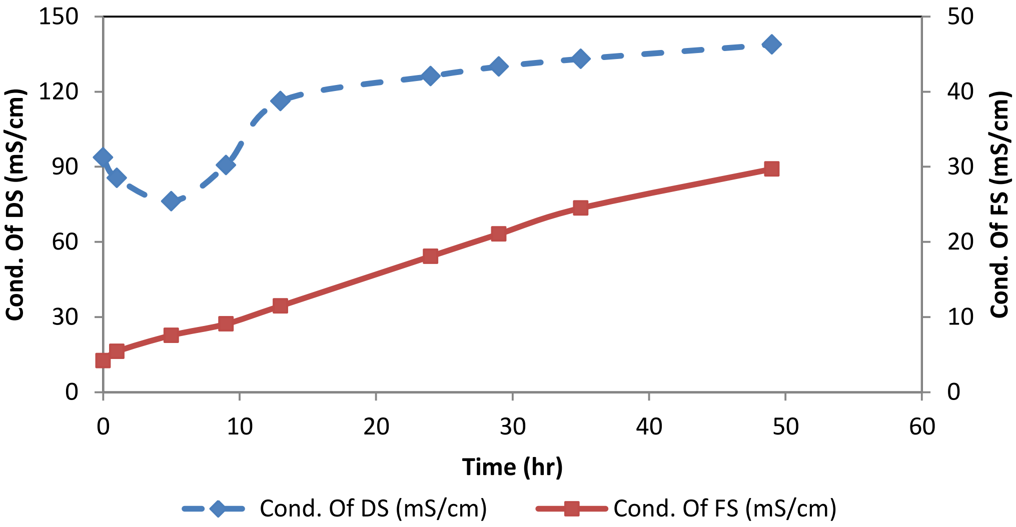


Figure 4.7: Relationship between conductivity of DS and FS for KCl

KCl has smaller molecular size, high diffusivity and low viscosity therefore it has the capability to pass over the membrane active layer easily and causes the reverse solute transport in the starting hours of the process. Reverse solute transport is more severe in early hours of operational time of experiment due to which conductivity of draw solution falls in early hours as shown in Fig. 4.7. Although KCl has higher flux than $MgCl_2$ but its reverse solute transport is significantly higher which affect the system process severely. The replenishment of KCl is low because the salt particles are transported to the feed solution due to reverse solute transport. In 2013 a study by Nawaz et al., concluded that chlorides of bivalent metals like Ca^{+2} and Mg^{+2} support microorganism's growth in the bioreactor, more than the chlorides of monovalent metals like Na and K. Commonly, chloride salts have no harm to the biomass in the FO-MBR and can be used without any danger (Nawaz et al., 2013). So $MgCl_2$ was recommended as compared to KCl as draw solution in FO-MBR process. It is preferred for future studies to used polymeric, divalent, multivalent ions.

4.4.2 FO-MBR Treatment Performance

Biological performance of FO-MBR system was assessed by evaluating carbon and nutrients removal. FO-MBR experiments were performed in PRO mode. Activated sludge of 6g/L was used as the FS and continuously aerated to provide oxygen to the biomass present in the system. Experiments were performed for duration of 48 hours.

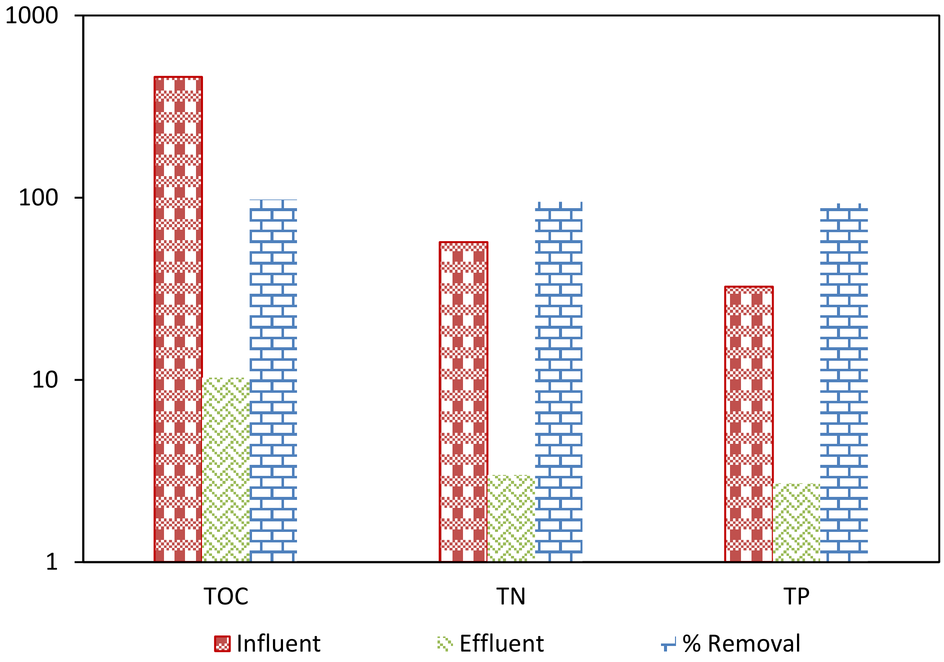


Figure 4.8: Influent, effluent and removal efficiencies of TOC, TN and TP for FO-MBR.

The average nutrients removal efficiency in the FO-MBR is shown in the Figure 4.8. Average concentrations of TOC, TN and TP in the influent were 460 ±5 mg/L, 55±5 mg/L and 30±5 mg/L respectively. After 48 hours of biological degradation and FO membrane filtration the average concentration of the TOC, TN and TP in supernatant collected from biological reactor was condensed to the values of 10±2 mg/L, 3±0.5 mg/L and 2.5±0.5 mg/L, respectively. In a study by, FO-MBR was operated for seven days in continuous operation with MLSS of 3.7 g/L and reported TOC removal of 87 % (Alturki et al., 2012). Due to high concentration of DS, it was not possible to measure exact values of organics and nutrients concentration of the treated water sample. Thus, the exact organics and nutrients removal effectiveness of the FO-MBR system couldn't be straightforwardly determined. TOC removal effectiveness of 87% by the reactor confirmed that that the system was biologically active during the experiment.

Biological degradation reduce the concentrations of organics and nutrients in the bioreactor, while FO hollow fiber FO membrane accumulates these constituents, as the semi-permeable membrane rejects the nutrients. Table 4.7 shows the nutrients removal efficiencies of both the FO-MBR and standalone batch FO process. These results depict that biological degradation in FO-MBR works effectively to reduce the TOC, TN and TP overcoming the concentrated FS by FO process only. For TOC and $NH^{4\,+}$-N removal by the FO membrane, in this study, both the TOC and $NH^{4\,+}$-N rejections are comparable to published results by Holloway et al. (2007). Researchers reported for FO-MBR, the TOC and NH4 $^{+}$ -N removals are considerably higher than those found in conventional MBRs, where removals up to 95% are classic. For the FO-MBR system followed by RO, greater than 99% removal can be achieved for both TOC and $NH^{4\,+}$-N (Judd, 2006).

Table 4.7: TOC, TN and TP removal efficiencies at various stages of the FO- MBR system

Organics and Nutrients	**% rejection FO membrane**	**% removal of FO- MBR process**
TOC (mg/L)	74%	98%
TN (mg/L)	62%	95%
TP (mg/L)	N/A	93%

Chapter 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Following conclusions were drawn from this study:

- Flux depends on molar concentration rather than draw solution starting volume. The DS starting volume was recommended 0.5L.
- The flux varies linearly with cross flow velocity. Since membrane cannot accommodate cross flow more than 150 mL/min. So cross flow velocity was optimized to a value of 150 mL/min.
- Flux rises linearly as the molar concentration goes on increasing but with the increase in flux beyond 2M, the conductivity drop increases abruptly. Therefore molar concentration was optimized to 2M.
- Osmotic backwashing was ineffective for change in flux in hollow fiber membrane modules. Base cleaning followed by acid cleaning is recommended for cleaning.
- First hour of the FO system is very crucial, all the nutrients and solute reverse transport occurred in First hour of the FO batch system.
- PRO mode of hollow fiber FO membrane more prone to irreversible fouling as compare to FO mode.
- $MgCl_2$ was the most suitable salt for waste water treatment as compared to KCl due to low reverse solute transport and high replenishment.
- TOC, TN and TP removal efficiencies for FO-MBR were 97.8 %, 95% and 93%.

5.2 Recommendations

The following recommendations are made for future study:

- Chlorides of sodium and calcium can be compared for selecting the most suitable draw solute for waste water treatment.
- FO-MBR can be used as pretreatment to RO process.
- Comparison of hollow fiber membrane and flat sheet membrane can be studied.
- Effect of reverse solute transport can also be studied on MBR microorganisms.

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