# Performance Evaluation of Fertilize-Drawn Forward Osmosis Membrane Bioreactor Treating Domestic Wastewater

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**(2018)**

# Performance Evaluation of Fertilize-Drawn Forward Osmosis Membrane Bioreactor Treating Domestic Wastewater

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

Master of Science in Environmental Engineering

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# CERTIFICATE

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

"**Performance Evaluation of Fertilize-Drawn Forward Osmosis Membrane Bioreactor Treating Domestic Wastewater**"

Submitted by

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has been found satisfactory for the requirement of the degree

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# LIST OF ABBREVIATIONS

| **Abbreviations** | **Description** |
|---|---|
| **AL-DS** | Active layer facing the draw solution |
| **AL-FS** | Active layer facing the feed side |
| **CER** | Cat-ion exchange resin |
| **CTA** | Cellulose tri-acetate |
| **CASP** | Conventional activated sludge process |
| **C-MBR** | Conventional membrane bioreactor |
| **CST** | Capillary suction time |
| **COD** | Chemical oxygen demand |
| **DCMD** | Direct contact membrane distillation |
| **DI** | Deionized |
| **DO** | Dissolve oxygen |
| **DS** | Draw solution |
| **EDTA** | Ethylenediaminetetraacetic |
| **ECP** | External concentration polarization |
| **EPS** | Extra-cellular polymeric substance |
| **FS** | Feed side |
| **FO-MBR** | Forward osmosis membrane bioreactor |
| **F/M** | Food to micro-organisms ratio |
| **HTI** | Hydration technology innovation |
| **HRT** | Hydraulic retention time |
| **HF** | Hollow fiber |
| **ICP** | Internal concentration polarization |

| | |
|---|---|
| **J** | Operational flux |
| **MLSS** | Mixed liquor suspended solids |
| **MLVSS** | Mixed liquor volatile solids |
| **NTU** | Naphthalometric turbidity unit |
| **OLR** | Organic loading rate |
| **OMBR** | Osmotic membrane bioreactor |
| **PSA** | Particle size analysis |
| **SOUR** | Specific oxygen uptake rate |
| **SRT** | Sludge retention time |
| **SEM** | Scanning electron microscopy |
| **SMBR** | Submerged membrane bioreactor |
| **TN** | Total nitrogen |
| **TDS** | Total dissolve solids |
| **TOC** | Total organic carbon |
| **TN** | Total nitrogen |
| **UF** | Ultra filtration |

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# Abstract

Reverse solute transport (RSF) of ions inside the bioreactor from the draw solution is the main problem of forward osmosis (FO). This RSF is significantly reduced when fertilizers with anions of larger hydrated diameter are used. Performance of three selected fertilizer-based draw solutes, ammonium sulfate (SOA), potassium hydrogen phosphate monobasic (MKP) and mono ammonium phosphate (MAP) was investigated in a forward osmosis membrane bioreactor (FO-MBR). For effective recovery of draw solutes and production of clean water, a direct contact membrane distillation (DCMD) setup was integrated with FO-MBR setup to form a hybrid (FOMBR-MD) system. Results demonstrated that the MAP significantly reduced the salinity buildup (0.113 g/m$^2$/hr (gMH)) inside the bioreactor, in comparison with SOA (0.568 gMH) and MKP (1.17 gMH), during FO operation. At constant molar concentration, SOA showed the highest initial water flux of 2.5 LMH followed by MKP (2.11 LMH) and MAP (1.97 LMH) during FO-MBR operation. Furthermore, MKP exhibited the shortest filtration run of 12 days due to increased salinity buildup inside the bioreactor which led to the rapid flux decline, and SOA showed relatively prolonged filtration runs followed by MAP of 17 and 15 days, respectively. It was found that MKP and SOA exhibited inhibitory effects on the mixed liquor characteristics in terms of biomass growth, particle size distribution and sludge filterability in contrast with MAP. Approximately 98±1% removal of COD and total phosphorus (TP) was achieved for all three fertilizers because of the synergic effect of dual barrier membranes. Only 90±2% removal of $NH_4^+$-N was found in case of ammonium-based fertilizers (i.e. SOA and MAP), while 99±1% removal was attained in case of MKP as draw solute. Based upon these findings, MAP was found to be the most viable draw solute for (FO-MBR) considering low RSF, moderate flux, prolong filtration cycle, high biomass growth, and treatment performance.

# Chapter 1

# Introduction

## 1.1. Background

Water is a precious resource for the survival of human life. Importance of water as a necessity to all living things cannot be exaggerated. The exponential increase in population and economic development causes the world to face challenges of water and energy supplies. Both water shortage and energy disasters have overwhelmed many societies around the world (Elimelech & Phillip, 2011). According to a survey report, it is estimated that 12,00 million people do not have clean and fresh water to drink (Montgomery & Elimelech, 2007). Nevertheless, 71% of earth surface consist of water only 1% of the total world water is fresh water (Gleick, 1997). Fresh potable water is the main aspect for determining the existence of human race. Increasing demand for fresh water are the results of the exponential growth of population and industries. The uneven distribution and water pollution also sever the water scarcity.

In Pakistan 32,500 hectare of land has been irrigated with wastewater and wastewater treatment is only about 8% by 2011 (Sato et al. 2013). So, there is a need for installation of wastewater treatment facilities at least to meet the water needs of horticultural and urban agriculture.

Stringent effluent water quality regulations require a high level of wastewater treatment. Nowadays, membrane technology has become a more attractive option for water reclamation and reuse. A densely populated area having high land cost doesn’t favor the use of conventional treatment technologies as it requires a large area and it’s also unaesthetic and produces a foul smell. In this regard, utilizing Microfiltration or Ultrafiltration MBR is gaining attention in which biological treatment follows membrane separation for effective removal of suspended organic matter. MBR is a very promising technology having low footprint. MBR is also preferred because of its consistent effluent quality as compared to the conventional wastewater treatment processes. Irrespective of several promising advantages of MBR over conventional wastewater treatment technologies, MBRs have several inadequacies. Intensive membrane fouling leads to rapid flux decline and requires frequent O&M cost (Wang et al. 2016; Wang et al. 2014).

Cornelissen et al. (2008) and Achilli et al. (2009) introduced a novel treatment technology Osmotic membrane bioreactor (FO-MBR). FO-MBR is a substitute solution that requires a lesser amount of energy and works on a natural osmotic process (Hankins et al. 2015). FO-MBR is a novel integration of Forward Osmosis and Biological treatment. Forward Osmosis is a process in which water moves from the feed through semi-permeable FO membrane on the bases of concentration gradient created by draw solution. In contrast, with conventional MBR using MF/UF membranes treat wastewater by applying high suction force which causes membranes to rapidly foul, FO-MBR withdraw treated water from less saline sludge into highly concentrated draw solution under natural osmotic force mitigating the energy consumption and fouling problems with increase in removal efficiency of trace organic compounds (Achilli et al. 2009; Holloway et al. 2015; Wang et al. 2016). Only reversible membrane fouling was found in OMBR studies, the membrane can achieve its original flux by simple tap water cleaning or by backwashing it using high potential solute on the feed side. A suitable draw solution assisted OMBR can substitute conventional MBR. There are also some limitations associated with FO-MBR like lower water flux, internal concentration polarization (ICP) and buildup of salinity in bioreactor because of reverse transport of draw solute into the bioreactor and rejection of solutes through FO membranes (Achilli et al. 2009; Lay et al. 2011; Zhang et al. 2012). Direct contact of FO membrane to the sludge containing varieties of microbial communities and organic and inorganic foulants of high strength feed not only result in decline in water flux as membrane resistance but also elevate the External Concentration Polarization (ECP) (Qiu and Ting, 2013; Wang et al. 2016; Yuan et al. 2015).

## 1.2. Problem Statement

Salinity buildup due to salts accumulation in bio tank inhibit the microbial community and diminish the sludge concentration resulting in lower biological treatment efficiency of the system. To control the salinity buildup in FO-MBR, many researchers have proposed solutions such as Wang et al. (2014) found that lowering the SRT lowers the salinity buildup and Chen et al. (2014) proposed that manually removal of salts from the supernatant of sludge at the end of each filtration run lowers the concentration of salts in bioreactor. Holloway et al. (2015) used UF membranes inside a bioreactor to lower the concentration of accumulated salts. Zhang et al. (2014); Qiu and Ting (2013) and Li et al. (2016) concluded that intensity of aeration in bio-tank and membrane surface modification also lowers the fouling intensity of membrane. Nguyen et al. (2016a) recently showed that moving carriers reduces the salts accumulation in the bioreactors which reduces the biofouling problem. The accumulation of solids due to rejection through the membrane and due to reverse transport of solute ensures the high treatment efficiency of the system. This saline atmosphere of bioreactor inhibits most of the microorganisms as they are not prone to halophilic conditions like denitrifying are comparatively more sensitive under saline conditions (Lay et al. 2010). Many researchers synthesized new draw solutions and prepared draw solutions by mixing two different salts to reduce the salts accumulation (Qiu and Ting, 2013). Nguyen et al. (2015) and Nguyen et al. (2016a) used a mixture of organic and inorganic salts as a result salinity buildup in bioreactor dramatically reduced. Reverse transport of organic salts in the bioreactor is very low. They act as a source of carbon to the sludge and very beneficial for methane production in the anaerobic process as they are easily degradable (Qiu and Ting, 2013; Ansari et al. 2015). Inorganic divalent ions have also shown relatively less leakage and show better flux performance (Nguyen et al. 2015).

This study focused to minimize the salinity buildup in a bioreactor by investigating the performance of fertilizer draw solutions. For the recovery of draw solute, Cross-flow DCMD (Direct contact membrane distillation) process was used. Hybrid FO-MBR-MD system was operated for the selected draw solutions till the fouling of the membrane.

## 1.3. Objectives of the Study

The key objectives of the study were as follows:

- To determine water flux and salt accumulation of selected fertilizers during FO operations
- Influence of fertilizer draw solutions on biodegradation of organics and nutrients in FO-MBR
- Evaluate the impact of fertilizer-based draw solutions on biomass characteristics in FO-MBR

## 1.4. Scope of the Study

A DCMD system was attached with FO-MBR to re-concentrate the diluted draw solution.

Performance of the fertilizer based draw solutes were examined at constant molar concentration of 0.25M i.e. Ammonium sulfate (SOA), Mon-ammonium phosphate (MAP) and Potassium hydrogen phosphate mono-basic (MKP).

Reverse transport impact of each fertilizer was observed in-term of Degradation of organic matter and Biomass characteristics of aerobic granular sludge. Fresh sludge from full scale MBR plant at NUST, Islamabad was used for each of the draw solute.

# Chapter 2

# Literature Review

## 2.1. Wastewater and Impact on Environment

### 2.1.1. Wastewater Quality Parameters and Composition

Wastewater quality is defined by its physical, chemical and biological properties. Physical parameters include odor, color, turbidity, temperature and particles that don't dissolve and remain suspended i.e. oil, lubricant, and solids. Solids further classified into suspended and dissolved solids as well as volatile and fixed fractions (Metcalf and Eddy, 2003). Chemical parameters categorized into organic and inorganic portions. Parameters for organic portion are Biological oxygen demand(BOD), Dissolve oxygen(DO), Chemical Oxygen Demand(COD) and total organic carbon (TOC) (Whetton et al. 1993). Inorganic chemical parameters are Ammonium Nitrogen ($NH_4$-N), Nitrate ($NO_3^-$), Nitrite ($NO_2^-$), hardness, pH, Sulfates, Sulfides, chlorides, phosphates, salinity, alkalinity etc. Biological parameters include viruses, pathogens, coliform, fecal coliform. Concentrations and constituent of wastewater are strongly dependent on temperature. Table 2.1. illustrate the typical concentrations of contaminants present in wastewater.

### 2.1.2. Untreated Wastewater Discharge; Negative Effects on Environment

Untreated wastewater discharge from wastewater treatment systems is one of the main sources of contamination in surface water reservoirs. This untreated effluent also adversely impacts aquatic life, animals and plants when this wastewater is directly used to irrigate the plants and can causes serious health problems to the humans as well as animals because wastewater contains very hazardous elements. The important chemical contaminants are nitrogen, phosphorus, pesticides, heavy metals, and hydrocarbons. Among them, nitrogen and phosphorus are the main limiting and basic contaminants. The increased amount of nitrogen in untreated effluent has harmful impact on aquatic life and it also affects the public health. To reduce the danger, nitrogen must be removed from wastewater before its releases into the wastewater (Kurosu, 2001).

**Table 2.1. Concentration of contaminant present in Domestic wastewater.**

| **Contaminants** | **Units** | **Concentration** | | |
|---|---|---|---|---|
| | | **Weak** | **Medium** | **Strong** |
| Total Solids (TS) | mg/L | 350 | 720 | 1200 |
| 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 | mg/L | 5 | 10 | 20 |
| $BOD_5$, 20°C | mg/L | 110 | 220 | 400 |
| TOC | mg/L | 80 | 160 | 290 |
| COD | mg/L | 250 | 500 | 1000 |
| Nitrogen (total N) | mg/L | 20 | 40 | 85 |
| Organic | mg/L | 8 | 15 | 35 |
| Free Ammonia | mg/L | 12 | 25 | 50 |
| Nitrates | mg/L | 0 | 0 | 0 |
| Nitrites | mg/L | 0 | 0 | 0 |
| Phosphate (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 |
| Sulfates | mg/L | 20 | 30 | 50 |
| Alkalinity as ($CaCO_3$) | mg/L | 50 | 100 | 200 |
| Grease | mg/L | 50 | 100 | 150 |
| Total Coliforms | mg/L | $10^6$-$10^7$ | $10^7$-$10^8$ | $10^7$-$10^9$ |
| Volatile Organic Compounds | µg/L | <100 | 100-400 | >400 |

Source: Metcalf and Eddy (2003)

The presence of nitrogen and phosphorus in freshwater can create ecological conditions that enhance the production of cyanobacteria having a property of producing toxin and it also favors green growth (WHO, 2006). This green growth causes the condition of eutrophication in fresh water. Particularly, algal blooms deplete the dissolved oxygen (DO) and degrade the water quality (EPA, 2000).

### 2.1.3. Wastewater Treatment and Reuse; A Sustainable Option

The most important resource for the survival of human life is the availability of water; nevertheless, it is under serious threat due to the climatic variation, growing population, and its wastage. The only possible option is to reclaim and reuse of municipal and industrial wastewater. The reuse of water is possible by using it for horticulture purposes, washing vehicles, flushing toilets etc. In addition, reuse of water may lessen the supplement loads from wastewater that releases into conduits, hence decreasing contamination.

## 2.2. Wastewater Treatment Technologies

The main purpose of water treatment is to remove the harmful pollutants from wastewater. For that, we must use different treatment methods. Broad categories of wastewater treatment include physical, chemical and biological treatment techniques. To achieve the high level of effluent quality, wastewater treatment is further divided into primary, secondary and tertiary treatment. Sludge resulting from wastewater treatment pass through thickening process by extracting water from it. The purpose of removing water from it is to make it suitable for disposal and reuse.

### 2.2.1. Physical Unit Operations

Physical process for wastewater treatment is the first approach to remove contaminants. Suspended particles or floating objects are separated from wastewater by using gravity settler or air flotation techniques.

### 2.2.2. Chemical Unit Operations

In this process, different chemicals are utilized to remove the contaminants from wastewater. This technique is used in conjunction with biological and physical treatment techniques. The physical process is more suitable to remove contaminants than chemical process as chemicals are additives in nature and sometimes form harmful byproducts which make them not safe for reuse.

### 2.2.3. Biological Unit Processes

In biological process, bacteria break the carbonaceous natural matter into gases and into cell tissues which can be removed in sedimentation tanks. The biological process can also be used as part of conjunction with chemicals and physical process.

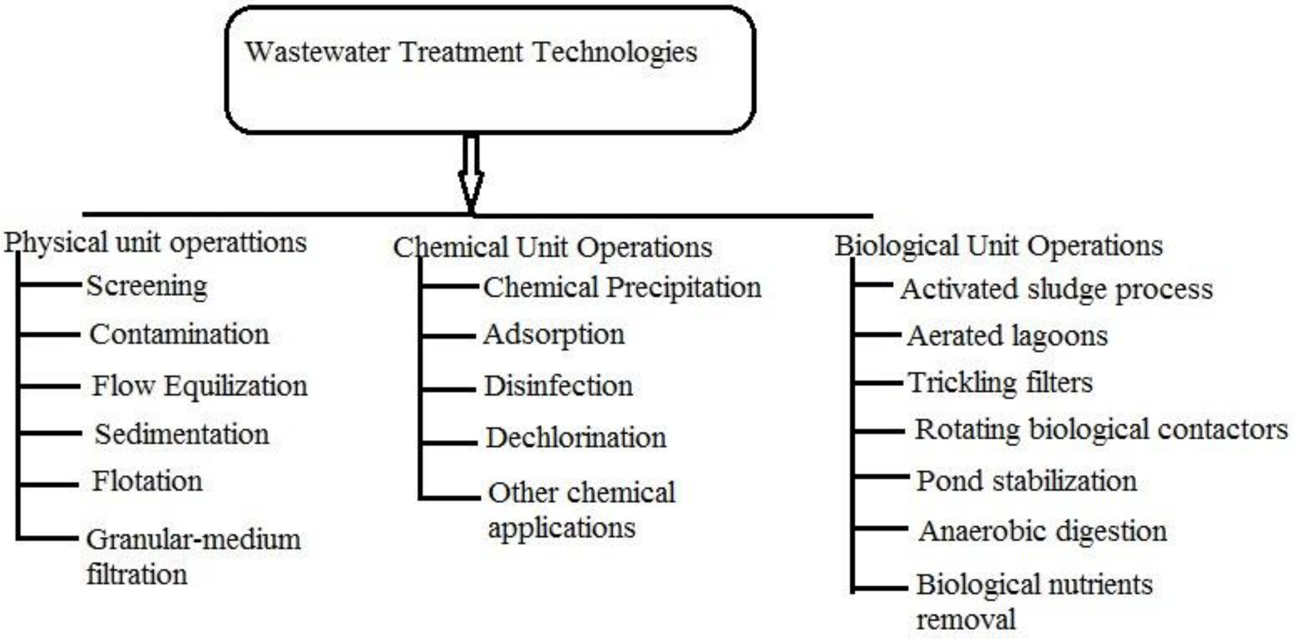


**Figure 2.1.** Wastewater treatment technologies.

## 2.3. Membrane separation Techniques

### 2.3.1. Introduction

Availability of fresh water is getting depleted day by day, so we need new measures to fulfill the water demand. To separate the materials from wastewater membrane technology is the best suitable option. Membrane separation technique has an advantage of not to change the thermal, chemical or biological properties of the separated material. This membrane technology can also be used for replacing water treatment process i.e. adsorption, ion exchange, and sand filtration.

Membrane consists of a porous and a dense layer that blocks the undesirable particles, and it only allows very small particles or only water molecules to pass through the membrane. Membrane application in different felids are shown in Figure 2.2.

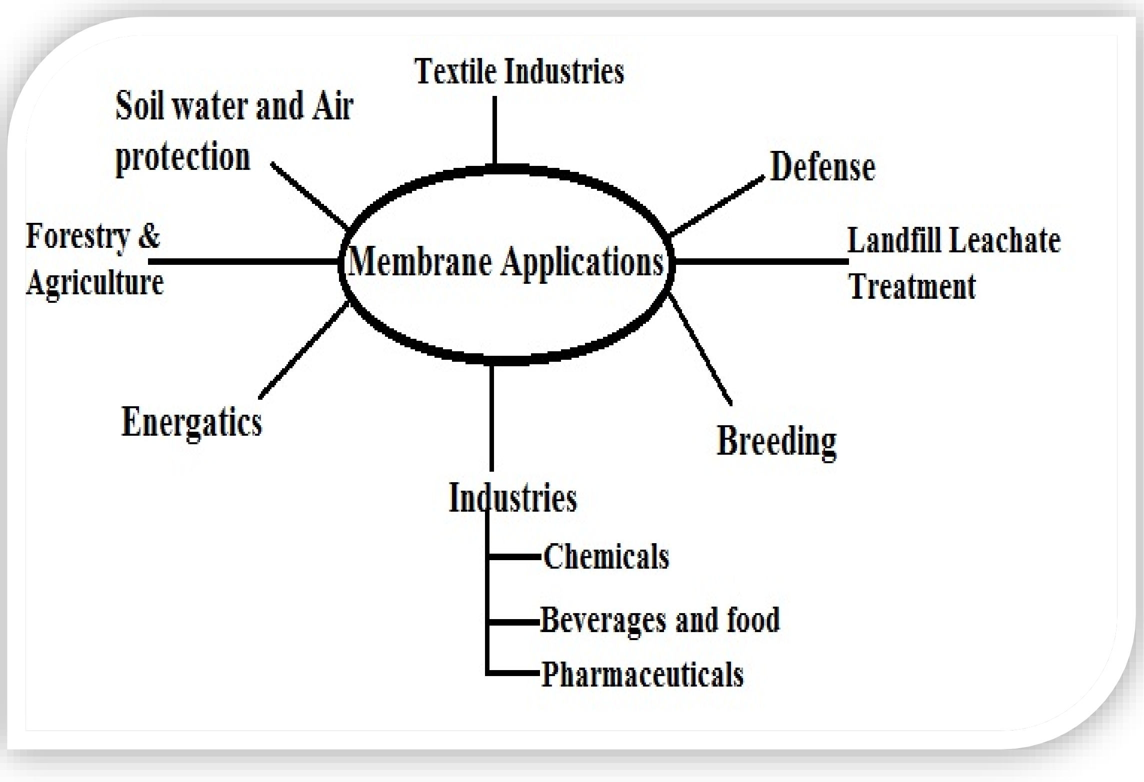


**Figure 2.2.** Membrane applications.

The configuration of membrane filtration can either be dead-end filtration or cross-flow filtration. In dead-end filtration influent moves at an angle of 90 degrees to the membrane surface. In this way, filtered water moves perpendicular to the membrane surface area and the unwanted particles start depositing on the membrane surface. With the passage of time, these depositing particles form a cake over the membrane surface, cause hindrance to the filtration and in this way membrane gets foul more rapidly. Dead-end filtration is subdivided into constant flux dead-end filtration and constant pressure drop dead-end filtration. To achieve constant flux in dead-end filtration enough pressure is applied across the membrane while in constant pressure drop dead-end filtration flux, through membrane starts decreasing with time because of fouling of the membrane. While in the case of cross-flow filtration, influent moves parallel to the membrane surface and part of this stream is passed through the membrane named as permeate fluid containing some soluble or insoluble particles and the influent stream that doesn't pass through the membrane containing unwanted particles that's starts depositing over the membrane surface. In cross-flow filtration membranes doesn't foul quickly as in case of dead-end filtration.

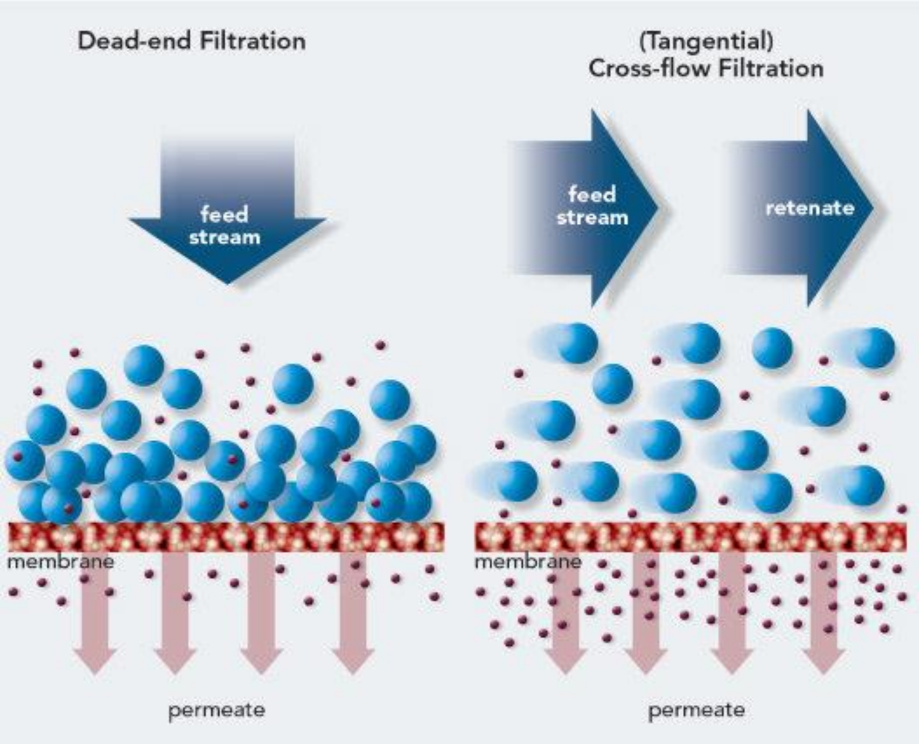


**Figure 2.3.** Mode of filtration a) Dead end or perpendicular b) Cross flow filtration.

### 2.3.2. Membrane Fouling

Membrane fouling is the main problem for all types of membranes. It affects the membrane efficiency and reduces water productivity of the whole system. Thus, there is a need for effective control in the development of fouling layer on the surface of the membrane. UF/MF membrane when used for wastewater treatment then fouling is the main problem. When wastewater is directly applied to the membrane surface, particles start depositing on the surface and create hindrance in the movement of water through the membrane. Foulants like colloidal, biological, and organic substances cause fouling by attaching to the membrane surface, blocking the membrane pores and hence increase the transmembrane pressure.

There are two types of membrane fouling like reversible and irreversible fouling. Reversible type fouling is easily detached by rinsing the membrane with simple tap water, or by physically cleaning the membrane by applying shear force in form of aeration or vibrations. In case of irreversible fouling, membranes can be cleaned by chemicals which includes acidic or basic chemical cleanings.

## 2.4. Forward Osmosis

### 2.4.1. Introduction

Osmosis is a natural process in which water moves from high concentration solution to low concentration solution, forward osmosis follows the same phenomena, and in this process a selectively permeable membrane is used to extract water from high concentration solution to the solution of lower concentration. High osmotic pressure solution (draw solution) is the main driving force to create an osmotic pressure difference between feed (low osmotic pressure) and draw solution to extract water from higher concentration to lower concentration solution. Higher the osmotic difference between two solutions higher the water flux.

### 2.4.2. Principle and Applications

Forward osmosis is an evolving technology that works on osmotically driven membrane process (McGinnis & Elimelech, 2008). Forward osmosis produces a water flow by separating the two solutions (high osmotic pressure draw-solution and low osmotic pressure feed solution) of different osmotic pressure through a semi-permeable membrane. FO operates at low energy, as it doesn't need hydraulic pressure to pass the water through the membrane, and lower membrane fouling (Mi & Elimelech, 2010).

FO operates at lower cost and it also less prone to the fouling (Lay et al. 2010; Mi & Elimelech, 2008). Some studies show that FO can be used to reclaim to treat the wastewater using FO-MBR (Achilli et al. 2009; Cartinella et al. 2006). Many studies show that FO can be used for desalination (McCutcheon et al. 2006), production of drinking water (Wallace et al. 2008), removed the water from high nutrient sludge (Nguyen et al. 2013), removal of water from orange peel process liquor (Castello & McCutcheon, 2011), reclamation of wastewater in space (Cath et al. 2005) and many others.

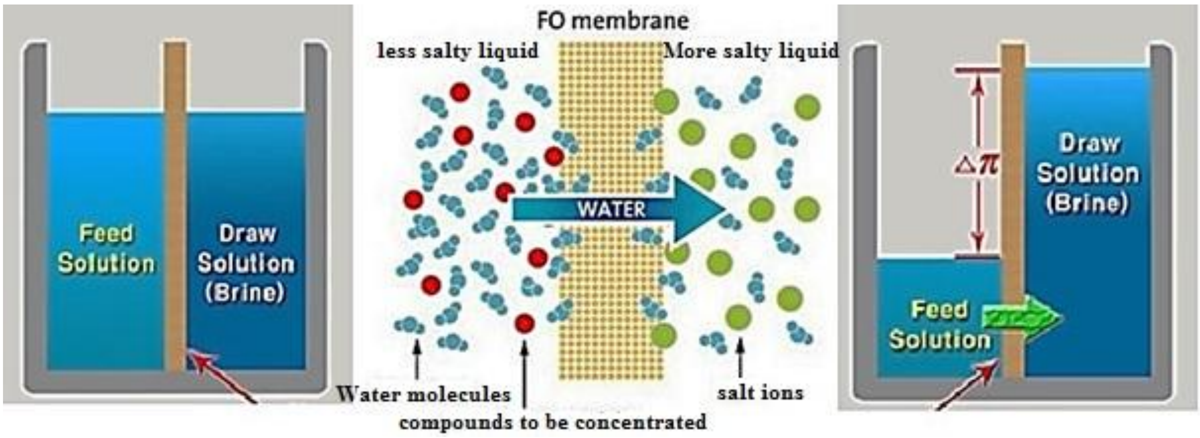


**Figure 2.4**. Process flow diagram of FO.

This Figure 2.4. depicts that wastewater (feed) that has higher water potential and lower total dissolved solids (TDS) starts moving towards draw solution having lower water potential and higher TDS value because of the concentration gradient that developed between these two solutions. FO membrane only allows water molecules to pass through the membrane and retain the contaminants on the feed side.

### 2.4.3. Draw Solutes used in FO-MBR

Draw solutes are used to create an osmotic pressure difference between feed side and draw solution side. This osmotic pressure difference is developed when the concentration of solutes is not same between feed and draw solution. Different draw solutes have different osmotic pressure at constant molar concentration. This osmotic pressure difference between two solutions causes the movement of water from higher osmotic pressure solution to the lower osmotic pressure solution.

Draw solutes vary in their behaviors and characteristics as they have different physical and chemical properties i.e. some of the draw solutions shows higher reverse solute transport, some of them produce higher osmotic pressure at lower so selection of draw solutes is the key consideration in FO process.

Many researchers investigated different draw solution to select the ideal draw solution for different applications of FO. McGinnis & Elimelech, (2007) used $SO_2$ and $KNO_3$ as draw solutes and they can be regenerated by standard means. McCutcheon et al. (2005) used $CO_2$ ($NH_4HCO_3$) and $NH_3$ as draw solutes and they can be regenerated by moderate heating up to 60°C.

Adham et al. (2007) used magnetic nanoparticles, dendrimers, and albumins in FO process as draw solutes where nanoparticles can be regenerated by applying a magnetic field, dendrimers can be regenerated by adjusting PH or by ultrafiltration (UF) membranes and albumins can be regenerated by solidification or by denaturing.

McCormick et al. (2008) used ethanol, salt as draw solute and regenerated through pervaporation. Yen et al. (2010) used 2-Methylimidazole-base solutes as draw solute and regenerated through forward osmosis membrane distillation process. Ling & Chung, (2011) used magnetic nanoparticles as draw solute and regenerate them by applying a magnetic field.

Li et al. (2011) reported the use of stimuli-responsive polymer hydrogel for draw solute and regenerated it by de-swelling the polymer hydrogel. Phuntsho et al. (2011) used different fertilizers as draw solutes. Ling & Chung, (2011) studied the use of hydrophilic nanoparticles as draw solute and regenerated it through ultrafiltration. Iyer et al. (2011) used fatty acid-polyethylene glycol as draw solute and regenerate it by thermal induction. Su et al. (2012) used sucrose as draw solute and regenerated it through nanofiltration. Noh et al. (2012) used solutes that are thermos-sensitive as draw solutes. Yong et al. (2012) used glycol and sueam glucose as draw solute. Carmignani et al. (2012) used copolymers of polyglycol as draw solute and regenerate it through Nano-Filtration(NF). Stone et al. (2013) used organic ionic salts as draw solutes which were regenerated by reverse osmosis (RO). Majeed et al. (2015) used fertilizer based draw solution for irrigating tomato crops. He reported that all nitrogen and potassium based fertilizer draw solution showed higher N- and K-reverse solute flux (RSF). However, MAP exhibited the lowest reverse of P-RSF.

Ansari et al. (2015) used different organic and inorganic salts as draw solutes in the FO-Anaerobic system for the production of methane. Holloway et al. (2015) worked on minimization of reverse transport of solutes in bio-tank and used different mixture of NaCl and $MgCl_2$ in his study.

Nasr & Sewilam, (2016) used ammonium sulfate (SOA) as fertilizer draw solute for direct fertigation and he founded that SOA is an efficient DS for fertilizer draw forward osmosis (FDFO) process because of its high water flux and lower reverse salt flux.

Kim et al. (2016) used different fertilizers as draw solution in anaerobic FO-MBR, results showed that MAP produced very low reverse transport and less effect on microbial community.

### 2.4.4. Application of Forward Osmosis

As it is an energy efficient process to extract water from raw water because water moves from higher concentration to lower concentration solution by natural osmotic force.

FO applications:

- Treatment of Domestic Wastewater
- Treatment of food and beverage industrial wastewater
- Desalination process
- Treatment of high strength wastewater like landfill leachate
- FO for membrane brine concentrator (MBC) process.

### 2.4.5. Forward Osmosis Membranes

Ideal characteristics of FO membranes must provide better chemical stability, high solute rejection, and good chemical strength. FO uses asymmetric, composite membranes that are composed of two layers: a dense support layer and a porous support layer, active layer (AL). The membrane can be placed in two configurations: active layer facing the feed side (AL-FS) and active layer facing the draw solute side (AL-DS). Mostly AL-DS configuration is used for low contaminated water like di-ionize (DI) water or for treated water. AL-FS configuration is used for the treatment of highly contaminated wastewater (Nayak & Rastogi, 2010).

Most commonly used FO membranes are produced by Hydration Technology Innovation (HTI), United State (US). These membranes are hydrophobic in nature with a thickness of not more than 50µm (McCutcheon et al. 2006). These membranes are made up of cellulose acetate (CA) embedded by polyester mesh. Dense selective layer and a porous support layer gave asymmetric structure to these membranes. Selective layer acts as an active layer and a thick layer having pores provides mechanical support.

In comparison with RO, these membrane shows high rejection of contaminants and only allows the movement of water molecules through it. Outperform of HTI membranes are shown below

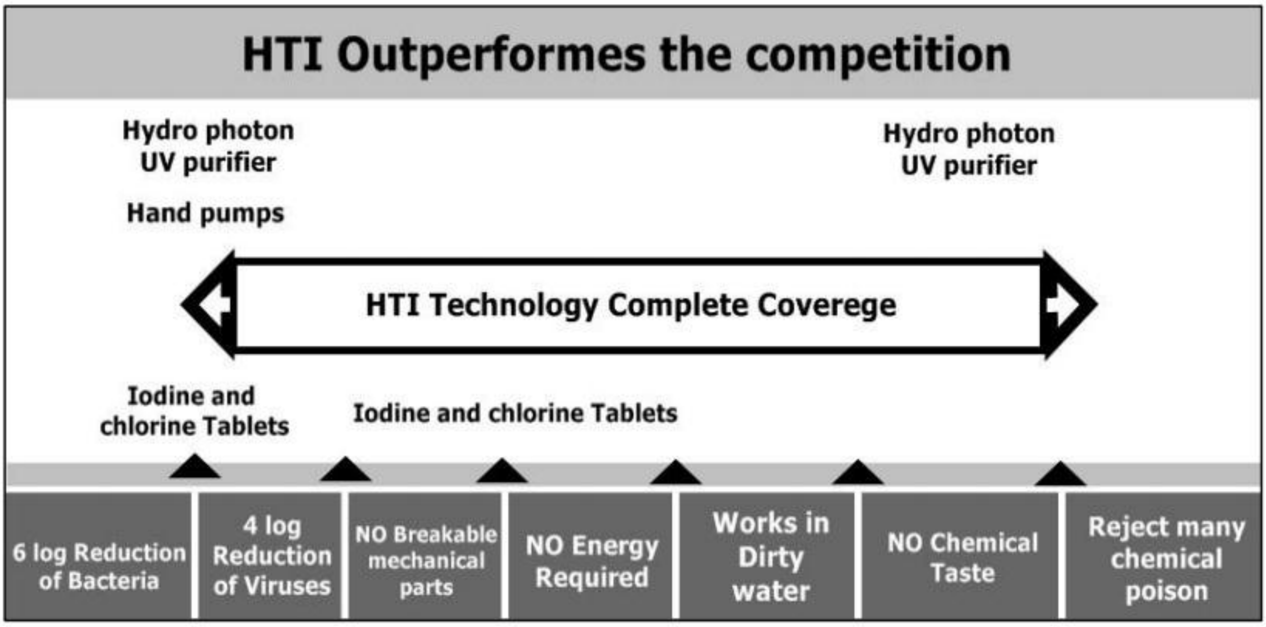


**Figure 2.5.** Hydration technology innovation (HTI) outperforms.

## 2.5. Membrane Bioreactor (MBR)

Membrane bioreactor (MBR) is a combination of a bioreactor and membrane separation technology. Suction pressure is applied to extract the water from stabilized water from bio-tank instead of force of gravity in activated sludge process (ASP) (Judd, 2010). Membranes used for separation are of ultra-filtration or micro-filtration ranges and having a pore size of 0.005 to 0.4 m. A suction pump is required to apply vacuum pressure to the membrane. Trans Membrane Pressure (TMP) is measure through TMP meter.

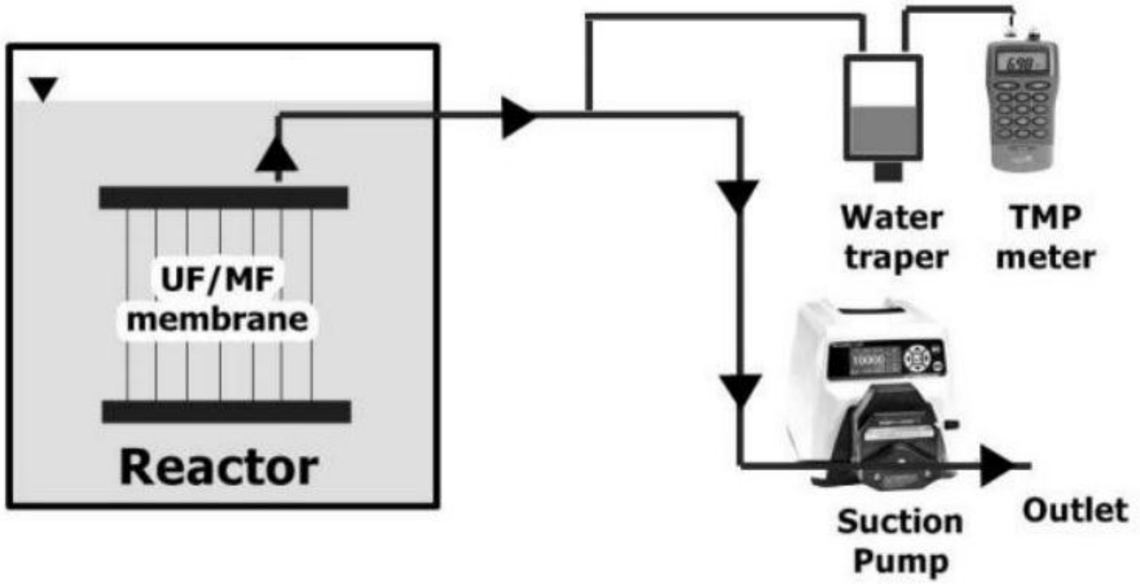


**Figure 2.4.** Process Flow Diagram of membrane bioreactor (MBR).

### 2.5.1. Advantages of MBR

Membrane bioreactor has several advantages over conventional activated sludge wastewater treatment. Because of its compact size, MBR requires smaller footprints. MBR produce high-quality effluent operated at higher MLSS and lower HRT compared with CAS which biologically degrade the wastewater very efficiently. MBR reduces the handling cost of sludge as it produces less amount of sludge than CAS. Through UF or MF membranes MBR produces very high-quality effluent, and it can also operate at constant flux which stabilizes the microbial consortia present in bio tank.

### 2.5.2. Disadvantages of MBR

One of the few disadvantages of MBR is its capital cost. Its capital cost is higher than conventional activated sludge system (CAS). MBR requires high operational cost than CAS in terms of aeration because of high MLSS and membrane scouring; this aeration cost is one-third of the total operational cost of the system. MBR has high operational cost also because suction pumps are also needed to produce vacuum force used to separate liquids from solids through filtration membrane. Membrane fouling is also a problem in MBR because the TMP increases with time and requires chemical cleaning or backwashing to normalize the TMP.

### 2.5.3. Configurations of MBR

Membrane modules in MBR can be attached in two different configurations:

- Submerged MBR
- Side Stream MBR

#### a) Submerged MBR

In this configuration, the membrane module is placed inside the bio-tank and for sludge growth aeration is applied, in this way, membrane fouling can be reduced as well (Van et al., 2002).

#### b) Side Stream MBR

In this configuration membrane module is placed outside the bio-tank, the membrane is more prone to fouling in this configuration and requires high crossflow velocity of water to detach the foulants from the membrane surface, which makes the process less energy efficient than submerged MBR configuration (Clech et al., 2005).

**Table 2.2.** Comparison of different configurations of MBR.

| Elements | Submerged MBR | Side Stream MBR |
|---|---|---|
| Membrane Configuration | Hollow Fiber | Plate and Frame type |
| Mode of Operation | Submerged | Cross-flow |
| Operational Flux | 10-30 LMH | 55-105 LMH |
| Operating Pressure | 5-30(negative) | 200-600 |
| Initial Investment | Low | Reasonably High |
| O&M Cost | Low | High |
| Membrane Cleaning | Hard | Easy |

Source: Clech et al., 2005

## 2.6. Forward Osmosis Membrane Bioreactor (FO-MBR)

### 2.6.1 Introduction

Forward osmosis membrane bioreactor (FO-MBR) is a combination of forward osmosis process and a membrane bioreactor. It is also known as osmotic membrane bioreactor. In this process, the role of the bioreactor is to stabilize the organic matter and forward osmosis membrane then separate the organic matter and extract the clean water by osmotic force. This osmotic force is created by draw solutes which are circulated inside the membrane module.

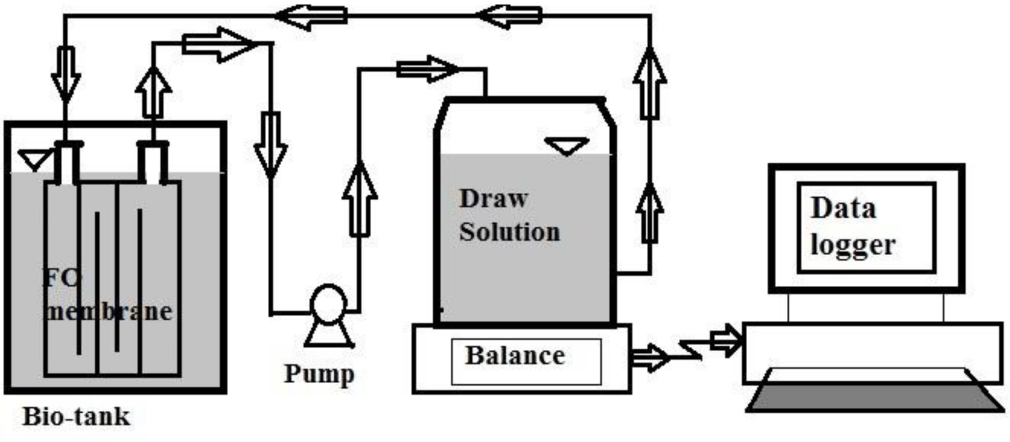


**Figure 2.5.** Flow Diagram of FO-MBR.

In FO-MBR, FO membrane is attached to the module then it is submerged inside the bio-tank, a highly concentrated draw solute is circulated inside the membrane module to produce osmotic pressure difference between draw solute and the wastewater. Due to this osmotic difference water from bio-tank enters inside the membrane module and mix with the draw solute then this diluted draw solute moves back to the draw solution tank. A post-treatment technique is required to re-concentrate the draw solution again where most commonly used regeneration techniques are Membrane Distillation (M.D) and Reverse Osmosis (RO).

**Table 2.3.** General comparison between FO-MBR and MBR.

| **Constituents** | **FO-MBR** | **MBR** |
|---|---|---|
| Membrane Material | CTA | PVDF |
| Operating Configuration | Side stream/submerged | Side stream/submerged |
| Operating Pressure | Osmotic Pressure | Suction Pressure |
| Operating OLR | Can be operated at high OLRs | Best for low OLRs |
| Fouling | Low | High |
| HRT (hr) | 8-12 | <12 |
| Membrane Cleaning | Can be cleaned by simple rinsing | Chemical/Physical |
| Operational Cost | Low | High |

Source: Chang et al., 2001; Cornelsissen et al., 2008

### 2.6.2. Advantages and limitations

It is an energy efficient process as it doesn’t require pumps to extract clean water like MBR, and utilize natural osmosis process, which works on the principle of concentration gradient difference created by using different types of draw solutes.

FO-MBR membranes work on low flux and higher HRT because it is operated under osmotic pressure driven process. Because of higher HRT, the FO-MBR shows better treatment efficiency than conventional MBR and produce better quality effluent.

The main limitation of FO-MBR process is the reverse transport of draw solute into the bio-tank which disturb the microbial community if it increases beyond a certain limit, hence there is a need for suitable draw solutes to minimize this limitation and enhance the efficiency of the system. A post-treatment technique is also required to separate the draw solute from treated water, for this purpose membrane distillation, reverse osmosis and Nano-filtration cell are used depends upon the draw solute type we used in the system.

### 2.6.3. Draw Solutions for FO-MBR

Cornelissen et al. (2008) worked on different draw types of draw solutes in FO-MBR and concluded that divalent salts perform very efficiently and produce higher water flux and lower reverse salts diffusion as compared to monovalent salts. He also studied the effect of activated sludge on membrane flux and membrane fouling by taking first deionized water as feed water and for 8 hours of batch study he observes the fouling of membrane before and after the use of use of activated sludge and concluded that activated sludge doesn’t have any effect on membrane fouling.

Achilli et al. (2009) also, operated FO-MBR using activated sludge and synthetic wastewater as feed water and took meat extract as a source of organics. He concluded that FO-MBR shows higher removal efficiency as compared to conventional MBR and removes about 99% of TOC and about 98% of $NH_4$-N. Salt accumulation in bio-tank results in a decrease in water flux and there was no reversible and irreversible fouling on the membrane.

Phuntsho et al. (2011) used different fertilizers as draw solutes and proposed a new draw solutions types which don’t require separation techniques, to separates the treated water from draw solutes, and make the process more energy efficient, as these diluted fertilizers draw solutions can directly apply on agricultural lands for fertigation.

To reduce the concentration of fertilizers from treated effluent of fertilizer drawn forward osmosis (FDFO), directly mixing of fresh water into the draw solute or blended fertilizers to reduce the individual nutrient concentration are some of the options (Phuntsho et al. 2012).

Alturki et al. (2012) used FO-MBR for the removal of trace organic compounds. Whetton et al. (1993) successfully removed 23 out of 27 TOC. He also concluded that increase in salt concentration in bio-tank has a negative impact on sludge characteristics.

Chen et al. (2014) used FO-MBR with anaerobic sludge for the treatment of low strength wastewater, he concluded that FO-MBR removes 100% of TP, 62% of $NH_4$-N and 96% of TOC, and he eliminates the salinity buildup effect by removing the supernatant after every cycle. He showed that system was producing enough methane gas which was then used for aeration in FO-MBR system.

Wanget al. (2014) studied the effect of two different SRT of 15 and 20 days on the microbial community and fouling of FO membrane and operated the system for 40 days for each SRT. He concluded that lower SRT is very much helpful in the removal of accumulated salts from bio-tank, higher SRT elevate the salt accumulation in the reactor which results in degradation of the microbial diversity.

Wang et al. (2014) found an alternative option for the removal of elevated salinity from the bio-tank, he used a micro-filtration unit inside the bio-tank and maintained the salinity to its lower level and he also reported that Ammonia and TOC removal efficiency increased because of the lower level of salinity.

Holloway et al. (2015) worked on a mixture of draw solutes at two different osmotic pressure and concluded that when a small percent of divalent salts ($MgCl_2$ & $MgSo_4$) are added into monovalent salts (NaCl) then reverse transport of the draw solutes significantly decrease and the increase in flux was also noticed.

Nguyen et al. (2015) prepared an ideal draw solution by mixing Na-EDTA with Triton X-100 and applied to the hybrid MBBR-OMBR system. They concluded that this new draw solution reduces the salinity buildup to a significant level, produced stabilized water flux and efficiently remove nutrients from wastewater.

Ansari et al. (2015) operated the FO system integrated with the anaerobic system and assessed the performance of inorganic and organic draw solutes. He concluded that for anaerobic system organic draw solutes are more suitable as their reverse transport is less and easily degradable and shows no hindrance to the production of gas.

### 2.6.4. Fertilizer Draw Solutions for FO-MBR

Kim et al. (2016) used FDFOMBR system and assessed the performance of six different fertilizers and reported that mono-ammonium phosphate (MAP) was found to be most appropriate for sludge growth and biogas production followed by ammonium sulfate (SOA).

Kim et al. (2017) worked on three different draw solutes MAP, MKP (Potassium di-hydrogen phosphate) and KCl during AnFDFO-ultrafiltration bioreactor and find out that flux decline was severe for each of the fertilizer because of the anaerobic conditions but the flux recovery rate is maximum for KCl. Nutrients accumulation had a detrimental effect on anaerobic microbial community. He also finds out that nutrient accumulation only effected the bacterial community structure.

Chekli et al. (2017) used nine fertilizers draw solutes for FO process and after initial screening in terms of reverse salt flux, initial and final water flux and water flux recovery, he selected MAP, SOA and MKP for long term experiment in An-OMBR in his study.

Wang et al. (2017) used three fertilizer-based draw solutions (SOA, MAP and MKP). He integrated a microfiltration unit inside bio-tank of FO-MBR setup to reduce the salinity buildup and concluded that in (MF-FDFO-MBR) hybrid system, SOA is the most suitable fertilizer because of its high water flux and less salinity buildup.

# Chapter 3

# Materials and Method

## 3.1. Introduction

In this work, lab-scale FO-MBR integrated MD process were operated to find out the most suitable fertilizer for continuous operation of FO-MBR system and investigated their effect on the sludge characteristics.

## 3.2. Experimental setup

For this research, a laboratory scale hybrid FOMBR-MD setup was used as shown in the Figure 3.1. This system included a draw solution tank, feed tank and a bioreactor in which FO membrane module was submerged. For the recovery of draw solution, DCMD unit was also attached. Luo et al. (2014) concluded that, MD membrane appears as a good option for draw solute recovery in comparison with RO, NF and electrolysis because of its precise effluent quality, less salinity effect on flux performance, low capital and operational cost, and low-grade energy(heat) utilization. That’s why, continuous DCMD unit was used in this study for the recovery of draw solution.

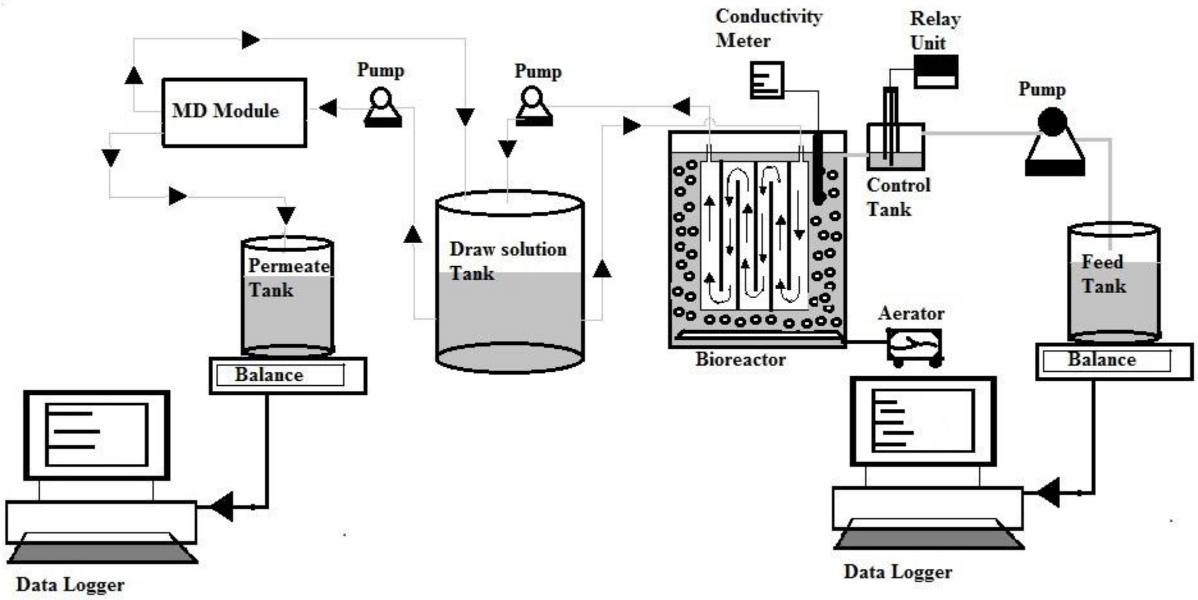


**Figure 3.1.** Process Flow Diagram of a hybrid FOMBR-MD setup.

At FO-MBR side, feed tank was placed on a digital balance (UX6200H, Shimadzu, Japan) attached to a computer to record the flux of FO membrane. To feed the bio-tank, a relay unit (Omron Floatless Level Switch, 61F, Japan) was attached with a peristaltic pump (Cole Parmer, 77200-62, Masterflex, USA). A plate and frame FO module made of PVC was used, with a dimensions length, width, and height of 0.210 m, 0.150 m, and 0.006 m respectively, and submerged in a bioreactor of 1.5 L working volume. The PVC module was provided with 5 baffles each of 6 mm thickness. Flat sheet cellulose triacetate (CTA) FO membrane from Hydration Technology Innovations (HTI) USA was attached to the module with an effective area of 0.042 $m^2$. Active layer facing the feed side (AL-FS) configuration was used in this study because (Aftab et al. 2015) concluded that membrane active layer facing the feed side (AL-FS) configuration was less prone to fouling as compared to active layer facing the draw side(AL-DS). For the growth of microorganisms and for membrane scouring, continuous dissolved oxygen (DO) of 3-4 mg/L was provided by using an air pump. To monitor the increased salinity of bio tank, an in-line conductivity meter (KOMATSU) was used. To recirculate the draw solution through the FO membrane module at 500 ml/min, a peristaltic pump (Cole Parmer, 77200-62, Masterflex, USA) was used in this study. Figure 3.2. demonstrate the FO-MBR setup installed in Water and Wastewater lab, IESE, NUST.

Treated wastewater from FOMBR setup was collected in the draw solution tank. This draw solution tank was also used as a feed tank for MD side. In DCMD unit, there was a flat sheet module made up of acrylic in which a hydrophobic membrane was enclosed having two flow channels. Hydrophobic flat sheet microporous PTFE (Polytetrafluoroethylene) membrane from Porous Membrane Technology, Ningbo, China with an effective area of 0.005 $m^2$ was used for the DCMD set-up.

For the circulation of feed (i.e. DS) and permeate through each channel in a countercurrent manner and to maintain the same circulation velocity on both sides of membrane, two peristaltic pumps (Cole Parmer, 77200-62, Masterflex, USA) were used. To heat the feed water of MD, a heater with a heat conducting glass coil was immersed in a water reservoir.

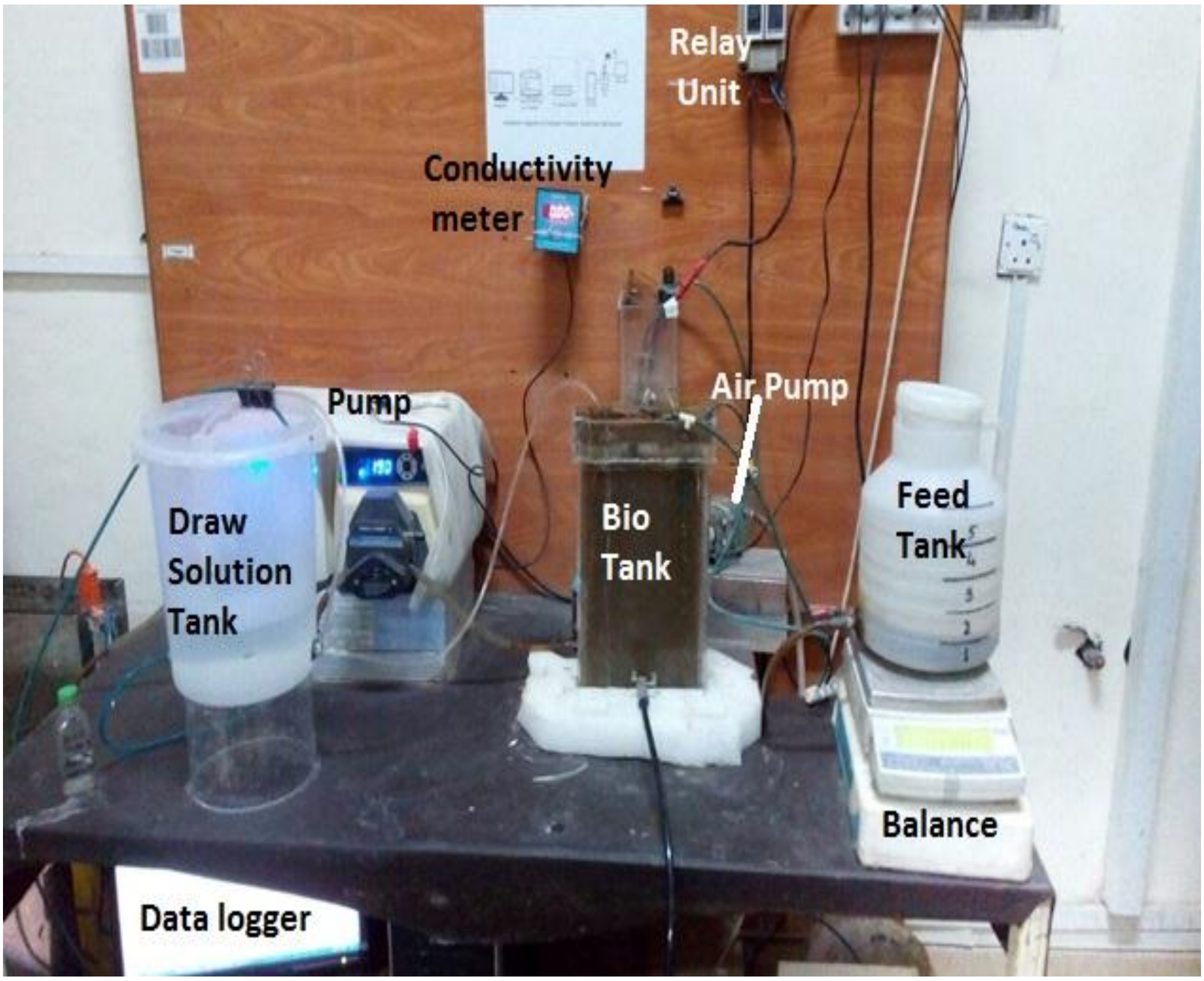


**Figure 3.2.** FO-MBR Setup at IESE, NUST

To measure the incoming and exit temperature of feed (i.e. Hot side), two temperature sensing devices (SANHNG-TPM-900, China) were used. To maintain the temperature gradient between hot and cold side, the permeate was circulated through the chiller. To measure the temperature and TDS of permeate water, an in-line TDS meter with a temperature sensor (KOMATSU) was installed. To record the flux of MD, the permeate tank was placed on the top of loading balance (UX6200H, Shimadzu, Japan) which was connected to the computer.

## 3.3. Feed and Draw Solutions

### 3.3.1. Feed and Draw solutions for FO-MBR

Ammonium sulfate (SOA) and mono-ammonium phosphate (MAP) were selected as DS for continuous operation of FO. Phuntsho et al. (2011) reported that, SOA has a higher water flux as well as lower reverse salt flux (RSF) because of its larger hydrated diameter. Kim et al. (2016) reported that SOA and MAP were appropriate to FO-MBR as they had less salt accumulation and relatively higher water flux. Based on these results, SOA and MAP were selected as DS for FO-MBR system. Properties of the fertilizers DS were determined at 0.25 M concentration and 25 $^0$C by using OLI Stream Analyzer 3.2. and is described in Table 3.1.

Synthetically prepared domestic wastewater was used as feed water and the recipe of the synthetic wastewater is given in Table 3.2.

**Table 3.1.** Properties of the draw solutions used in this study.

| **Draw Solution** | **MW** | **Concentration(M)** | **Osmotic Pressure(bar)** |
|---|---|---|---|
| $NH_4H_2PO_4$ (MAP) | 115.03 | 0.25 | 11.30 |
| $(NH_4)_2SO_4$ (SOA) | 132.1 | 0.25 | 12.30 |
| $KH_2PO_4$ (MKP) | 136.086 | 0.25 | 10.53 |

**OLI Stream Analyzer 3.2.*

**Table 3.2.** Composition of synthetic wastewater.

| **Composition** | **Unit** | **Concentration** |
|---|---|---|
| Glucose ($C_6H_{12}O_6$) | mg/L | 308.40 |
| Ammonium chloride ($NH_4Cl$) | mg/L | 114.60 |
| Magnesium sulfate ($MgSO_4$) | mg/L | 2.92 |
| Potassium Phosphate (MKP) | mg/L | 44.0 |
| Ferric Chloride ($FeCl_3$) | mg/L | 0.88 |
| Calcium Chloride ($CaCl_2$) | mg/L | 2.92 |
| Manganese Chloride ($MnCl_2.4H_2O$) | mg/L | 0.60 |
| Sodium Bicarbonate ($NaHCO_3$) | mg/L | 69.71 |

## 3.4. Operational Protocol

### 3.4.2. Operational Protocol for FO-MBR

FO-MBR was operated using three different draw solutions (SOA, MAP and MKP) having an individual concentration of 0.25M. Bio-tank having submerged FO module was continuously aerated with air diffusers at the rate of 3-4 mg/L. The bioreactor was filled up to its working volume of 1.57 L with activated sludge having MLSS of 8-9 g/L from NUST MBR Plant, Islamabad. Prior to feeding the sludge to FO-MBR-MD system, MBR sludge was acclimatized for 10-15 days with synthetics wastewater used for this study. For each draw solution, new sludge from NUST MBR plant was brought and acclimatized prior to feeding. Initial hydraulic retention time (HRT) of different DS was in the range of 4-5 hour, which was measured by initial water flux of FO membrane. With time, HRT increases as the flux of FO decreases. Constant solids retention time (SRT) of 20 days was maintained throughout the study. This SRT was helpful in reducing the salt accumulation in bio-tank which degrades the microbial community and reduce the system efficiency (Holloway et al. 2015). Draw solution was continuously re-concentrated through MD, running in parallel with FO.

### 3.4.3. Analytical Methods

For each salt, treatment efficiency of FO-MBR system was measured in term of Phosphate Phosphorus ($PO_4^{3-}$-P), Chemical Oxygen Demand (COD) and Ammonium-Nitrogen ($NH_4$-N). Sludge characteristics were measured in terms of capillary suction time (CST), mixed liquor suspended solids (MLSS), mixed liquor volatile suspended solids (MLVSS) and particle size distribution (PSD). All the experiments were performed as per standard method (APHA et al. 2012).

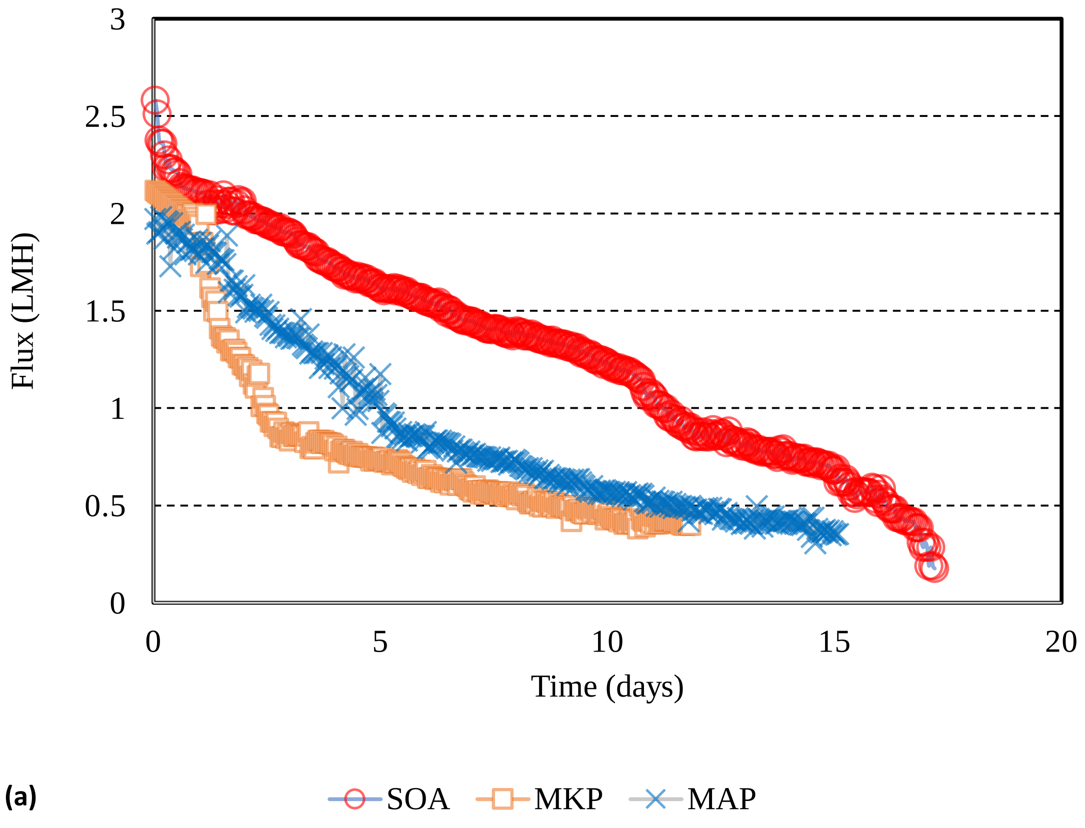
Filterability and conditioning of sludge were measured through CST apparatus (304B-CST, Triton, Canada). Mean particle size of sludge flocs was measured through particle size analyzer (LA-300, HORIBA, Japan).

# Chapter 4

## 4. Results and Discussion

### 4.1. Water flux and reverse salt of fertilizer draw solutes

Performance of the fertilizers was investigated based on their water flux and reverse solute transport. Water reuse and agriculture applications are the main essential criteria for selection of these fertilizers as draw solutes (DS). The water flux of each fertilizer DS as a function of time is presented in the Fig. 4a.



**(a)**

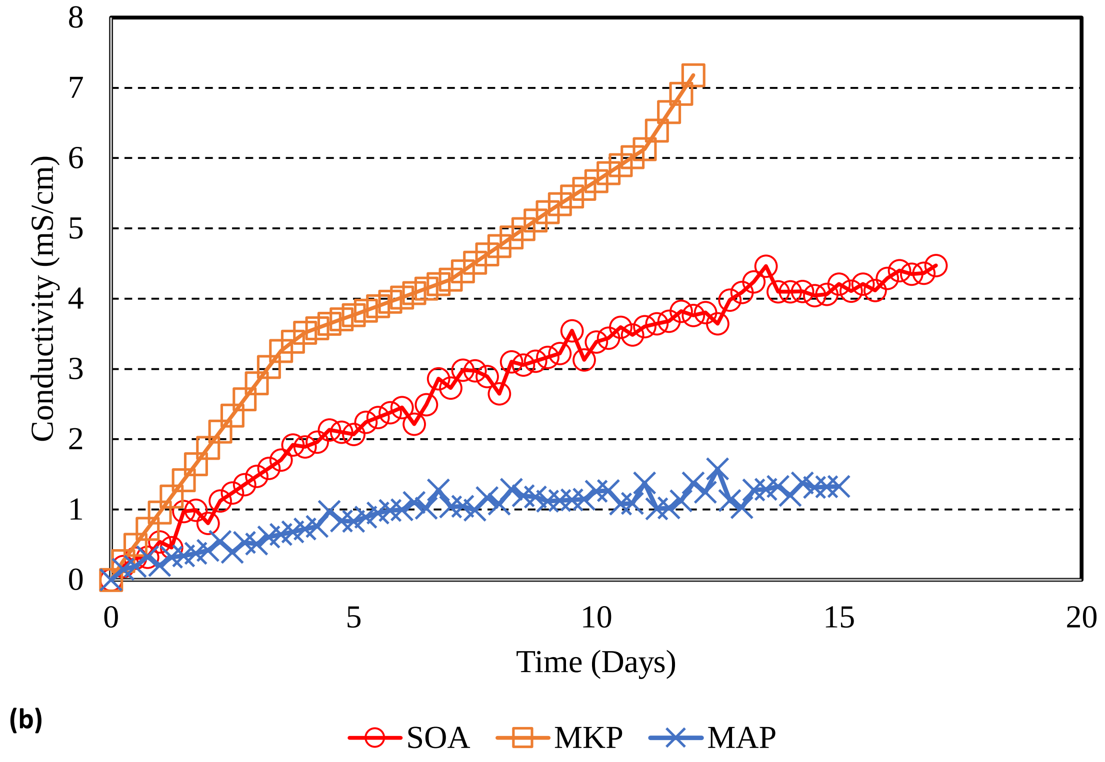


**Figure 4.1.** Variations in (a) water flux and (b) mixed liquor conductivity for different fertilizers at 0.25 M concentration in FO-MBR-MD system.

The draw solution molar concentration was kept constant at 0.25 M and synthetic wastewater was taken as feed solution. Results showed that SOA has the highest initial water flux of 2.58 LMH followed by MKP (2.11 LMH) and MAP (1.97 LMH). However, the osmotic pressure of the fertilizers showed a different trend compared to their water flux as reported in Table 2. Theoretically, SOA showed the highest osmotic pressure of 12.30 bar followed by MAP (11.30 bar) and MKP (10.53 bar). Since the difference in osmotic pressure across membrane is the main driving force of driving in the FO process, the water flux should follow the same trend as the osmotic pressure (Chekli et al. 2017). However, Figure 4a showed that there is no direct relationship between the water flux of DS and their osmotic pressure. It was found that the longest filtration run of 17 days was achieved with SOA followed by MAP and MKP, i.e., 15 and 12 days, respectively. For MKP, the drop in flux was very rapid because of its higher salinity buildup in the bio-tank due to RSF which decreases the concentration gradient between feed solution (FS) and DS. However, SOA and MAP showed relatively stable and prolonged filtration runs as compared to the MKP, because of the less salinity buildup of these DS inside the bioreactor. In case of MAP, the flux drop was due to the membrane fouling as it has a lowest reverse solute transport. At the end of the filtration run, a fouling layer was observed on the membrane which reduces the flux of the FO membrane (Johir et al., 2013).

The reason for this variation in water flux behavior can be  explained by the difference in the extent of internal concentration polarization (ICP) effects, which is induced via mass transfer resistance (K) within the support layer of the membrane facing the DS (McCutcheon et al., 2006; Phuntsho et al., 2011). This mass transfer resistance (K) is basically a function of diffusivity of DS; thus, a DS having higher diffusion coefficient will have a low K value and should exhibit higher water flux. DS with higher diffusivity could have lower flux if it has a lower osmotic pressure (Kim et al. 2016).

Due to the high salt rejection ability of MD membrane, a very less drop in DS concentration occurred. So, the salinity buildup inside the bio-tank (Fig. 4b) was due to RSF, through the rejection of salts by FO membrane and progressive fouling of the membrane. MAP showed lowest salinity buildup of 2 mS/cm and it also exhibited relatively shorter filtration run as compared to SOA with salinity buildup of (9 mS/cm) and longer filtration run. These results are correlated with the previous findings, where (Kim et al. 2016) measured the reverse salt flux (RSF) of these (SOA, MAP and MKP) fertilizers as DS during FO operation, taking DI water as feed water, and concluded that MAP showed the lowest RSF followed by SOA and MKP. The lesser reverse transport of MAP was because of the larger hydrated diameter (Table 3) of PO4- ion which neutrally diffuses the cations of smaller hydrated diameter ($NH_4^+$) back into the DS to maintain the electrical neutrality. While the reverse transport of SOA was more as compared to the MAP because both the ammonium ion and sulfate ions have smaller hydrated diameter as compared to the hydrated diameter of ionic species of other fertilizers used in this study. Due to the higher osmotic stress on the FS, enhanced release of soluble microbial products (SMP) occurs which forms a sticky gel-like layer on the surface of the membrane which led to the rapid drop in water flux (Aftab et al. 2015; Zhang et al. 2014).

**Table 4.1.** Hydrated diameter of ions used in this study

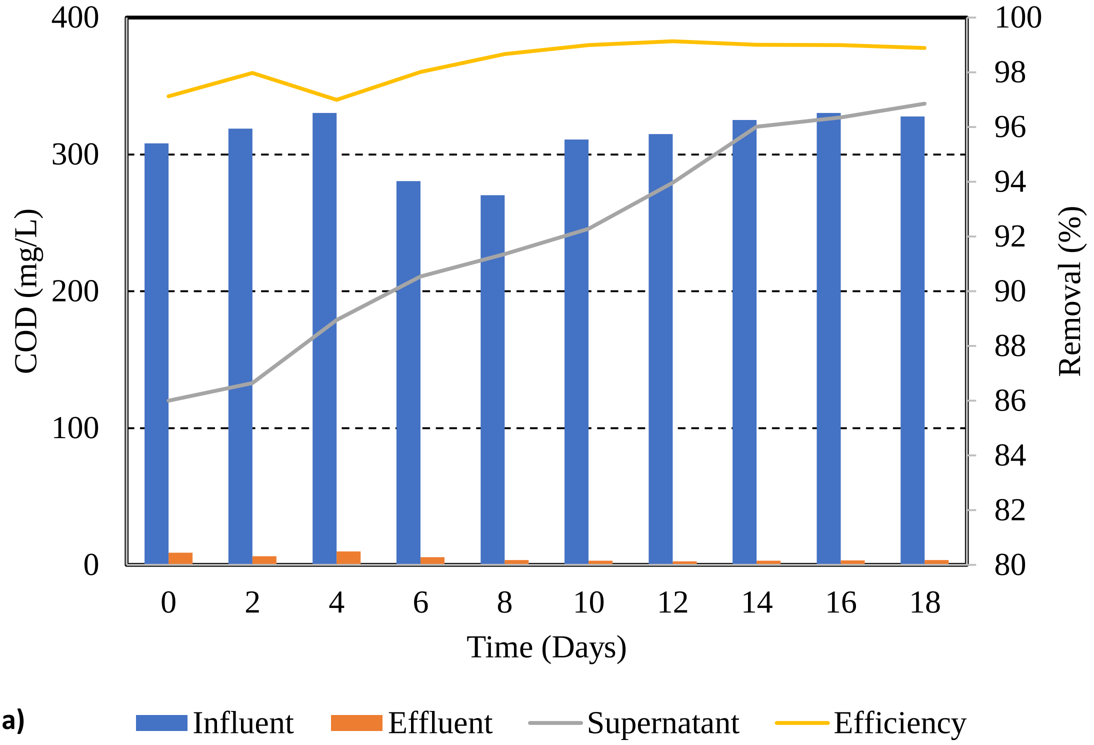
| **Ions** | **Hydrated Diameter ($10^{-12}$ m)** |
|---|---|
| **Anions** | |
| $SO_4^{2-}$ | 393 |
| $PO_4^{3-}$ | 680 |
| **Cations** | |
| $NH_4^+$ | 250 |
| $K^+$ | 300 |

Source: Kiriukhin & Collins, 2002; Ohtaki & Radnai, 1993; Phillip, Yong, & Elimelech, 2010

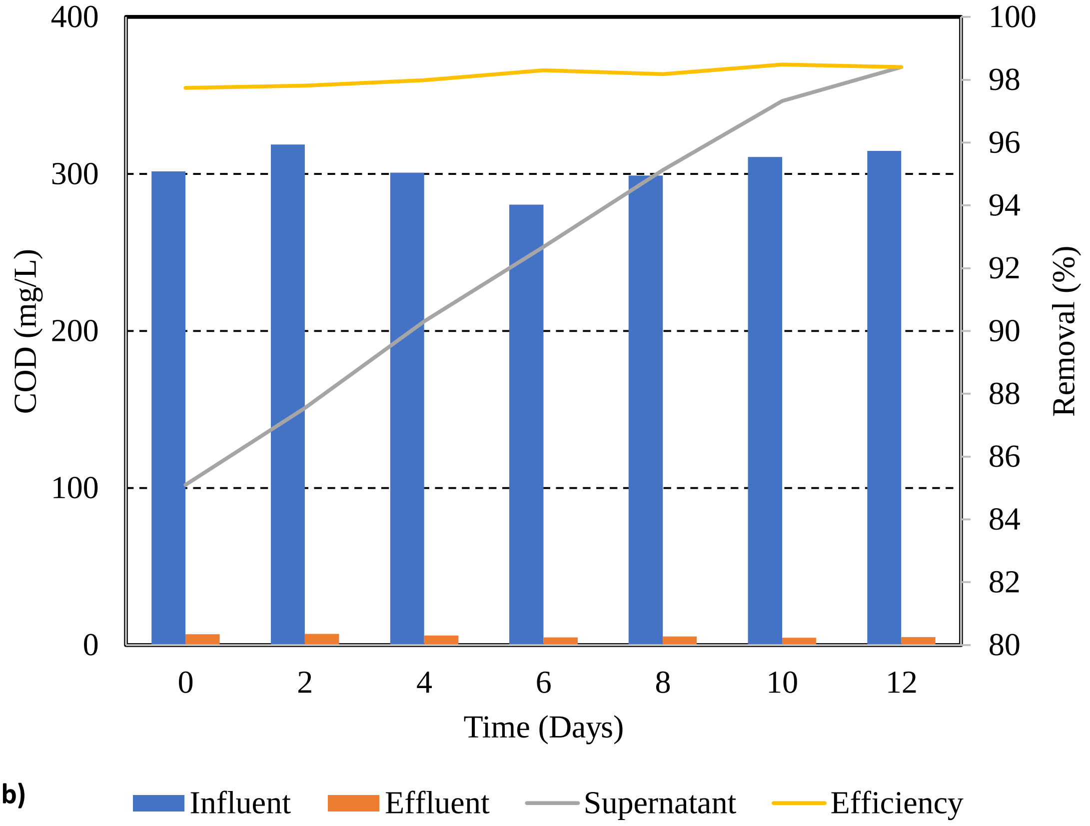
## 4.2. Removal of organic matter and nutrient

### 4.2.1 Removal and buildup of COD

Removal and buildup of organic matter during FO-MBR operation are shown in Figure 4.2. From the start of the operation, the supernatant COD gradually increased for all three fertilizers, due to the high rejection feature of FO membrane which rejects almost all types of organic matters. Figure 3 shows the removal efficiency of COD in the permeate and buildup of COD in the supernatant of bio-tank because of dual barrier membranes (FOMD) and biological treatment for the three fertilizers as DS.


400
300
200
100
0
COD (mg/L)
100
98
96
94
92
90
88
86
84
82
80
Removal (%)
0
2
4
6
8
10
12
14
16
18
Time (Days)
Influent
Effluent
Supernatant
Efficiency

**(a)**


400
300
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COD (mg/L)
100
98
96
94
92
90
88
86
84
82
80
Removal (%)
0
2
4
6
8
10
12
Time (Days)
Influent
Effluent
Supernatant
Efficiency

**(b)**

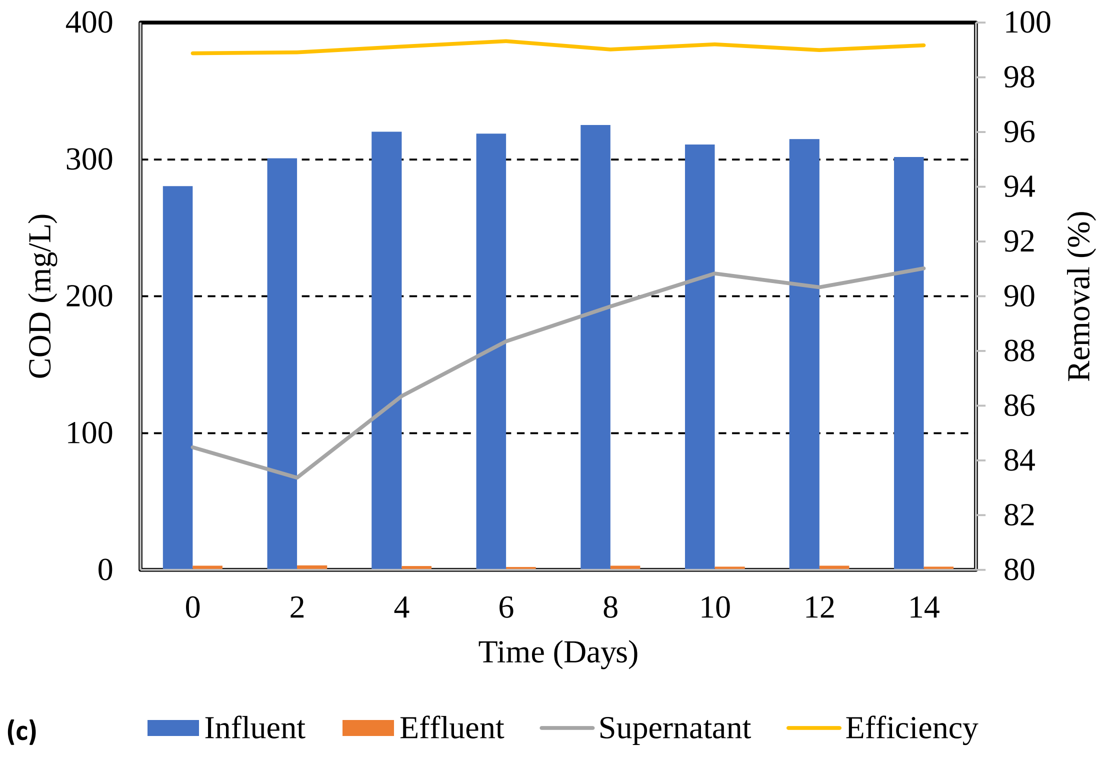


**Figure 4.2.** Variations in COD removal efficiency and buildup inside the bio-tank for each DS a) SOA, b) MKP and c) MAP.

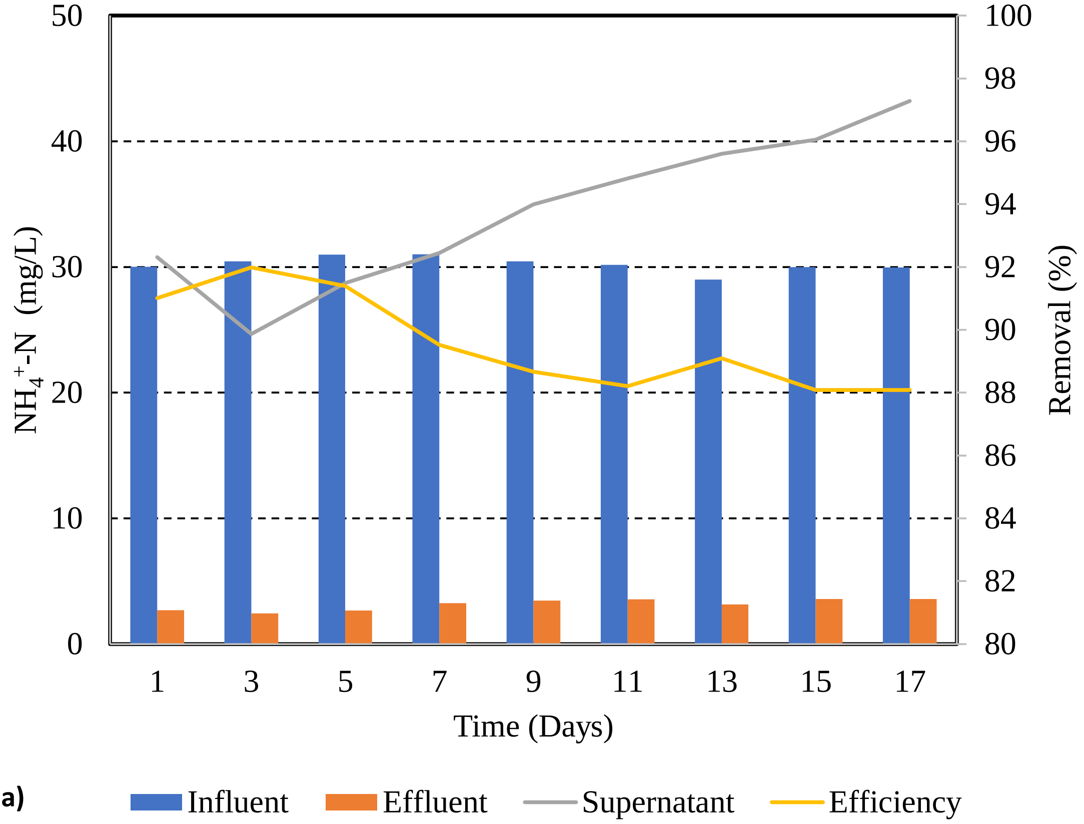
These results are correlated with the previous work Siddique et al., (2017). The accumulation of COD in the supernatant of bio-tank, even at very low reverse transport of DS, was observed which was not only because of the salt accumulation due to reverse permeation through FO membrane but also due to the high retention feature of FO membrane which cause the enrichment of COD in the supernatant of bio-tank. Similar behavior of COD removal and retention (buildup) in the bio-tank was reported earlier studies (Aftab et al. 2015; Qiu & Ting, 2013).

Because of the lowest reverse solute transport of MAP, the salinity buildup inside the bio-tank was lowest as compared to the other fertilizers i.e. SOA and MKP. Less reverse transport of salts also reduces the organic matter accumulation. At lower DS reverse permeation, the enrichment of organic matter can be mainly due to the rejection through FO membrane. Significant accumulation of organic matter was observed in case of SOA and MKP because of their relatively highest reverse salt flux as shown in Figure 3. As the nature of the most of microbial species from activated sludge is non-halophilic so the buildup of salinity causes the degradation of this microbial consortium which results in the enrichment of organic matters in the supernatant of bio-tank.

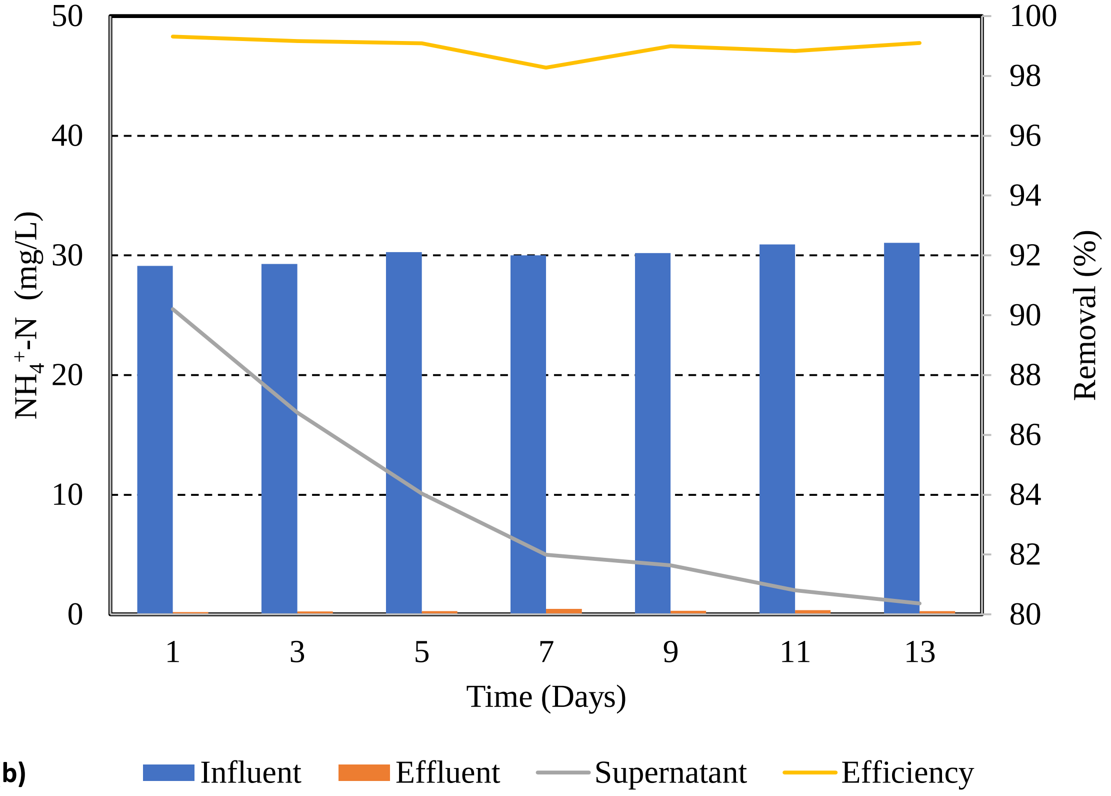
## 4.3. Biological nutrients removal

### 4.3.1. Removal and buildup of nitrogen

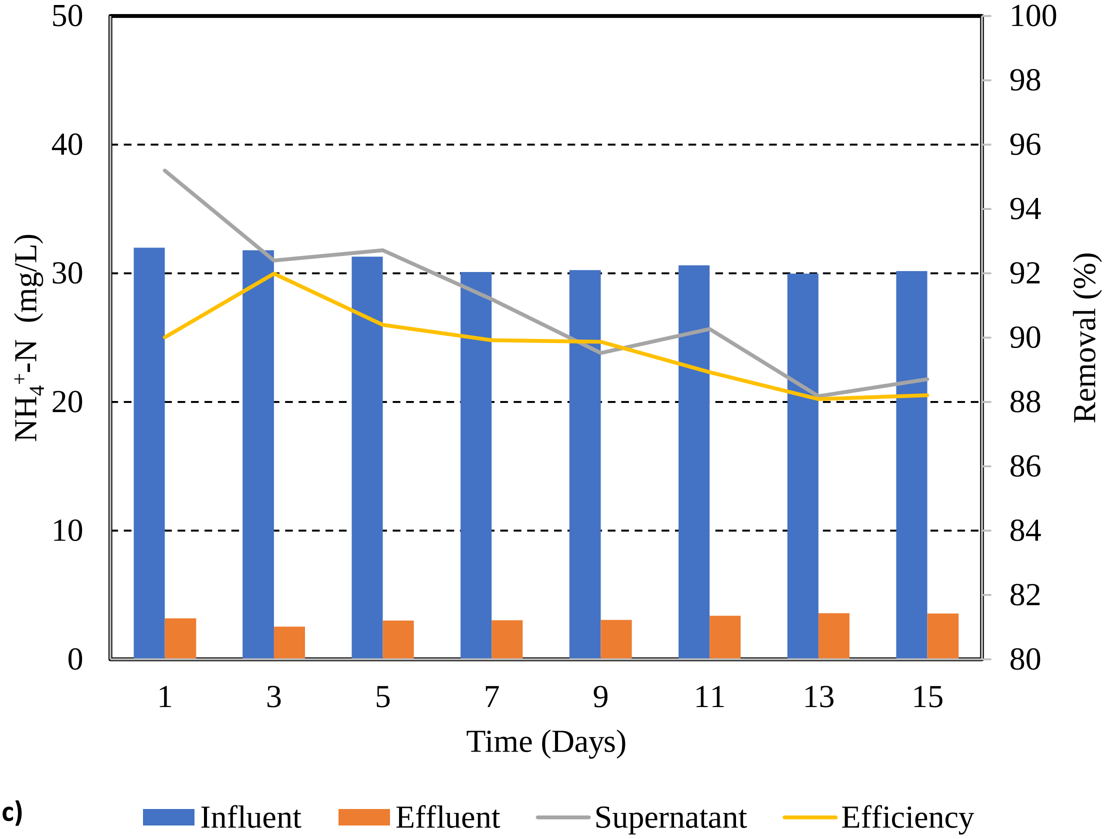
Variations of $NH_4^+$-N in the influent, MD effluent and sludge supernatant is depicted in Figure 4.3. A constant decrease in $NH_4^+$-N concentration was found in the bio-tank supernatant for both MAP and MKP. While SOA exhibits a comparatively different trend in the removal of $NH_4^+$-N from the bio-tank supernatant. First, $NH_4^+$-N decreased concentration then increased in the bio-tank in the case of SOA as DS.



**(a)**


50
40
30
20
10
0
$NH_4^+$-N (mg/L)
100
98
96
94
92
90
88
86
84
82
80
Removal (%)
1
3
5
7
9
11
13
Time (Days)
Influent
Effluent
Supernatant
Efficiency

**(b)**


50
40
30
20
10
0
$NH_4^+$-N (mg/L)
100
98
96
94
92
90
88
86
84
82
80
Removal (%)
1
3
5
7
9
11
13
15
Time (Days)
Influent
Effluent
Supernatant
Efficiency

**(c)**

**Figure 6.3.** $NH_4^+$-N removal efficiency and enrichment in bio-tank supernatant for each DS a) SOA, b) MKP and c) MAP.

.

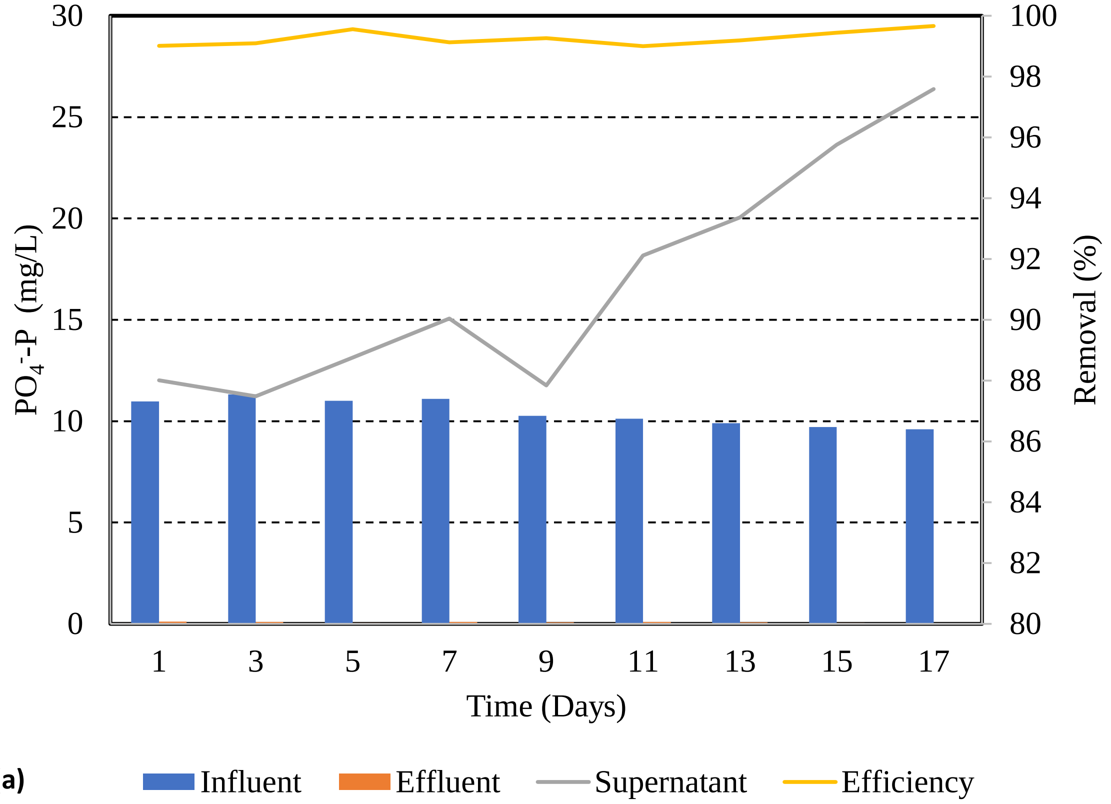
Nitrification is a two-step process which is carried out by two different groups of bacteria; Ammonia Oxidizing Bacteria (AOB) which convert ammonia to nitrite, and Nitrite Oxidizing Bacteria (NOB) which convert nitrite to nitrate (Ginestet et al. 1998; James, 1990). Microbes that are involved in nitrification process are vulnerable to the environmental conditions. Most substantial environmental factors are pH, substrate concentration, DO, salinity and temperature (Chen et al. 2006; Jones & Hood, 1980). Nitrification is very much substrate sensitive as reported by many researchers (Caffrey et al. 2007; Chen et al. 2006).

In FOMBR operation salinity buildup inside the bio-tank was observed with time which affects the efficiency of slow-growing AOBs. SOA showed different trend because of the increased salinity buildup as compared to the other DSs (MAP and MKP) due to continuous reverse transport of ammonium and sulfate ion from DS into the bio-tank. Because of the smaller hydrated diameter of ammonium ion, it passes through FO membrane more easily than the sulfate ion and increases the concentration of ammonia which has a detrimental effect on the ammonia-sensitive bacteria of sludge. Hence the efficiency of AOBs slows down while the accumulation of sulfate ion inside the bio-tank due to its reverse transport from DS into bio-tank causes an inhibitory effect on the NOBs and resulted in the buildup of $NH_4^+$-N inside the bio-tank (Moussa, 2014; Prosser, 2007).

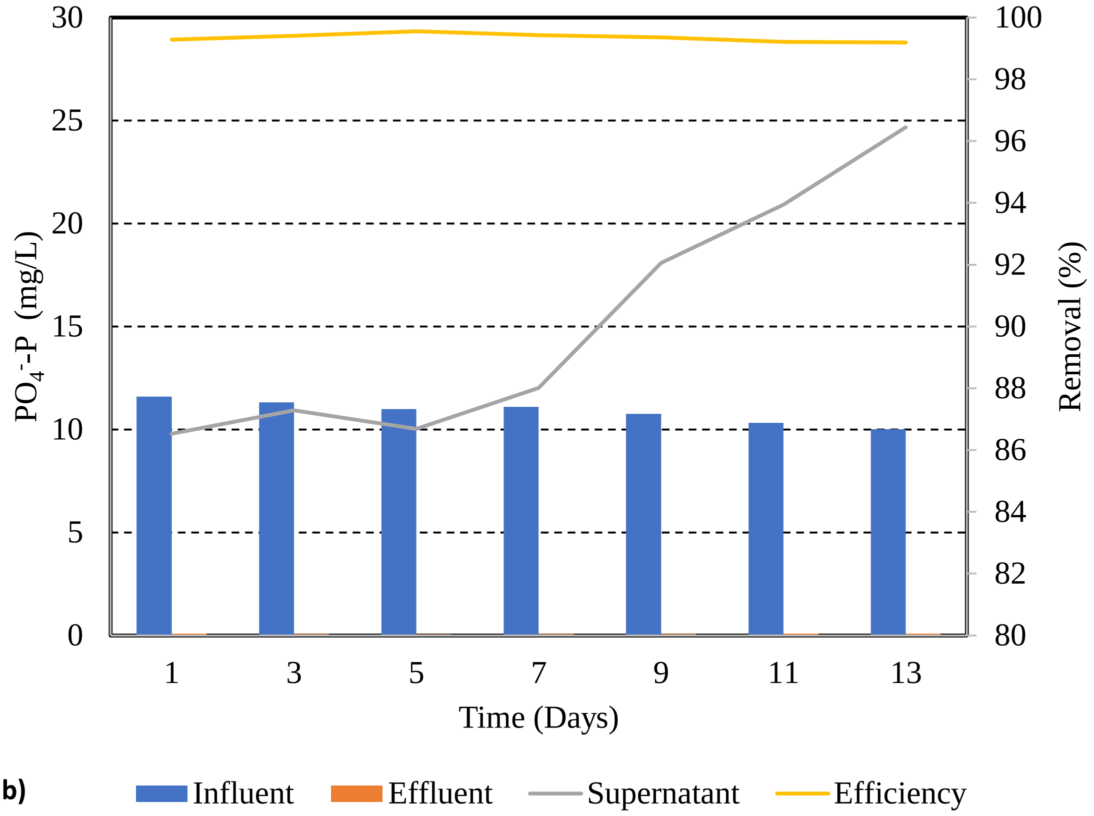
In case of MKP, a continuous drop in the concentration of $NH_4^+$-N was observed which is because of the less inhibitory effect of $K^+$ ion on both the AOBs and NOBs Moussa, (2014). Because of the less reverse transport of MAP, less inhibition of microbes occurs during FO-MBR operation. MAP has an anion ($PO_4^-$) with larger hydrated diameter and it cannot easily pass through FO membrane. Due to less salinity buildup, the biomass activity in case of MAP was higher and led to the more degradation of $NH_4^+$-N in FO-MBR system Luo et al. (2016).

### 4.3.2. Enrichment of $PO_4^-$-P

Removal of phosphorus through activated sludge is basically dependent on the microbial assimilation, particularly by the phosphorus accumulating bacteria (POAs) Zuthi et al. (2013). These microbes are saline sensitive and a small increase in osmotic pressure has a detrimental effect on the phosphorus accumulation capacity of the POAs Lay et al., (2009). The capacity of phosphorus accumulation by POAs is severely dependent on the time of aerobic and anaerobic/anoxic phases, temperature, pH, composition of volatile fatty acids (VFAs), and ion concentrations (Aravind et al. 2015; Chaudhry & Nautiyal, 2011; Yuan et al. 2012).



(a)


30
25
20
15
10
5
0
PO4-P (mg/L)
100
98
96
94
92
90
88
86
84
82
80
Removal (%)
1
3
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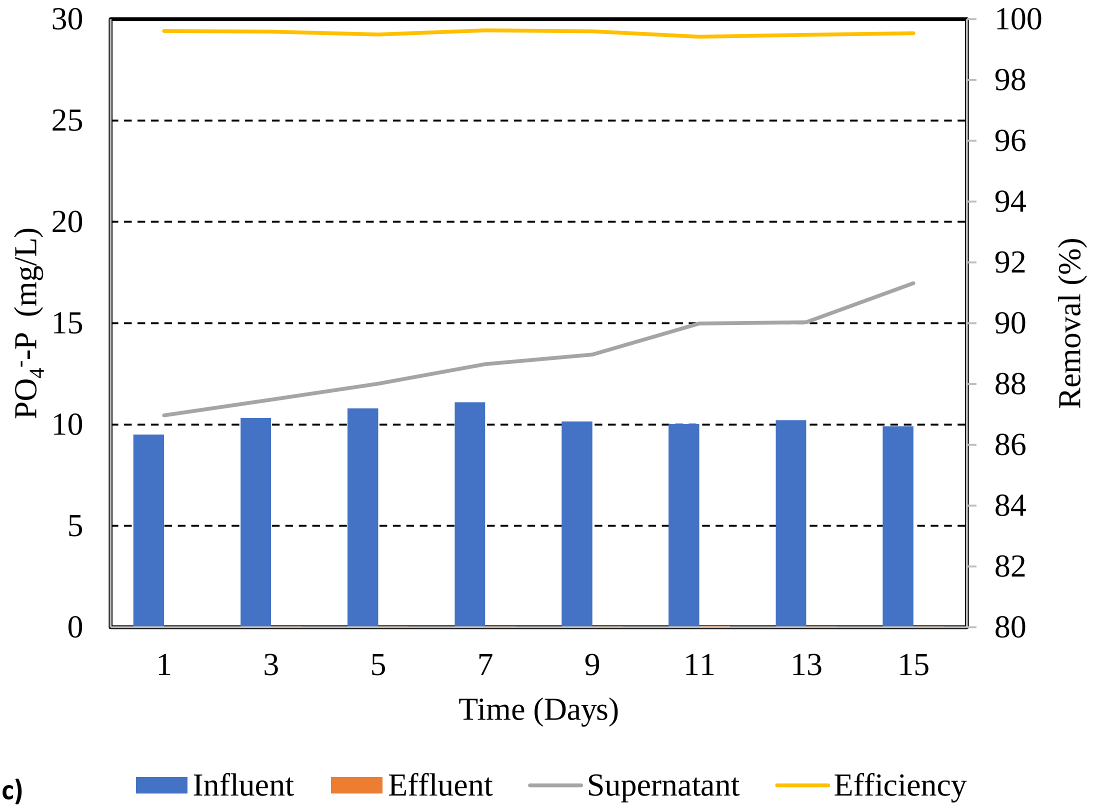
11
13
Time (Days)
Influent
Effluent
Supernatant
Efficiency

**(b)**


30
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PO4-P (mg/L)
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80
Removal (%)
1
3
5
7
9
11
13
15
Time (Days)
Influent
Effluent
Supernatant
Efficiency

**(c)**

**Figure 4.4.** Phosphate-P removal efficiency and accumulation in bio-tank for each DS a) SOA, b) MKP and c) MAP.

Figure 4.4 shows the $PO_4^-$-P concentration in the influent, MD effluent and in the sludge supernatant of each draw solution. Results showed that there is a less increase in the concentration of $PO_4^-$-P in the supernatant of sludge for each of the fertilizer draw solute as compared to the inorganic draw solutes as reported earlier by Siddique et al. (2017). The possible reason for the accumulation of $PO_4^-$-P is because of the high retention feature of FO membrane and because of the electrostatic repulsion of the FO membrane to the negatively charged $PO_4^-$-P (Nguyen et al. 2015; Siddique et al. 2017). Because of the high reverse transport of MKP, the increase in $PO_4^-$-P was also high in comparison with SOA and MAP. Lay et al. (2010) and Luo et al. (2016) reported that an increase in saline stress within the cell deteriorate the sensitivity of PAOs which further resulted in the reduction of the phosphorus accumulating ability of PAOs. The literature showed that high concentration of both $NH_4^+$ and $K^+$ ion causes sludge to deteriorate and lowers the biomass activity which resulted in relatively higher $PO_4^-$-P accumulation in the supernatant (Kara, 2007; Murthy et al. 1998). A higher biomass activity was observed throughout the filtration run with MAP because of its lower salinity buildup. A higher biomass activity resulted in the higher phosphate consumption and a lower phosphate accumulation was noticed throughout the filtration run (Aftab et al. 2015; Siddique et al. 2017).

## 4.4. Biomass characteristics

### 4.4.1. Sludge filterability and floc size

Capillary suction time (CST) was used to determine the filterability and dewaterability of sludge. Higher CST depicts lower sludge filterability. Increase in CST was noticed after employing SOA and MKP as draw solutes.

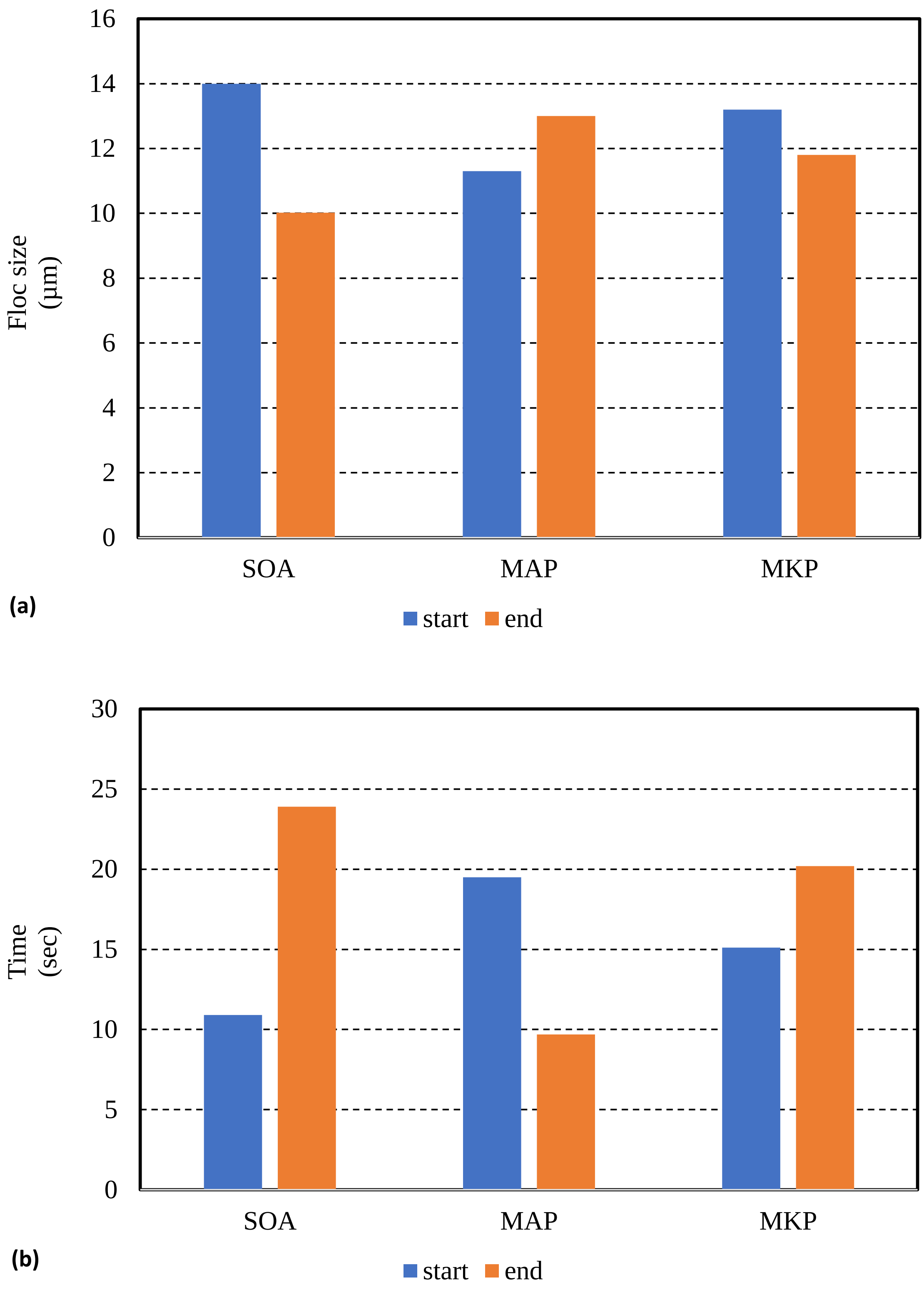


**Figure 4.5.** Effect of fertilizer DSs on (a) floc size (PSA) and (b) sludge filterability (CST).

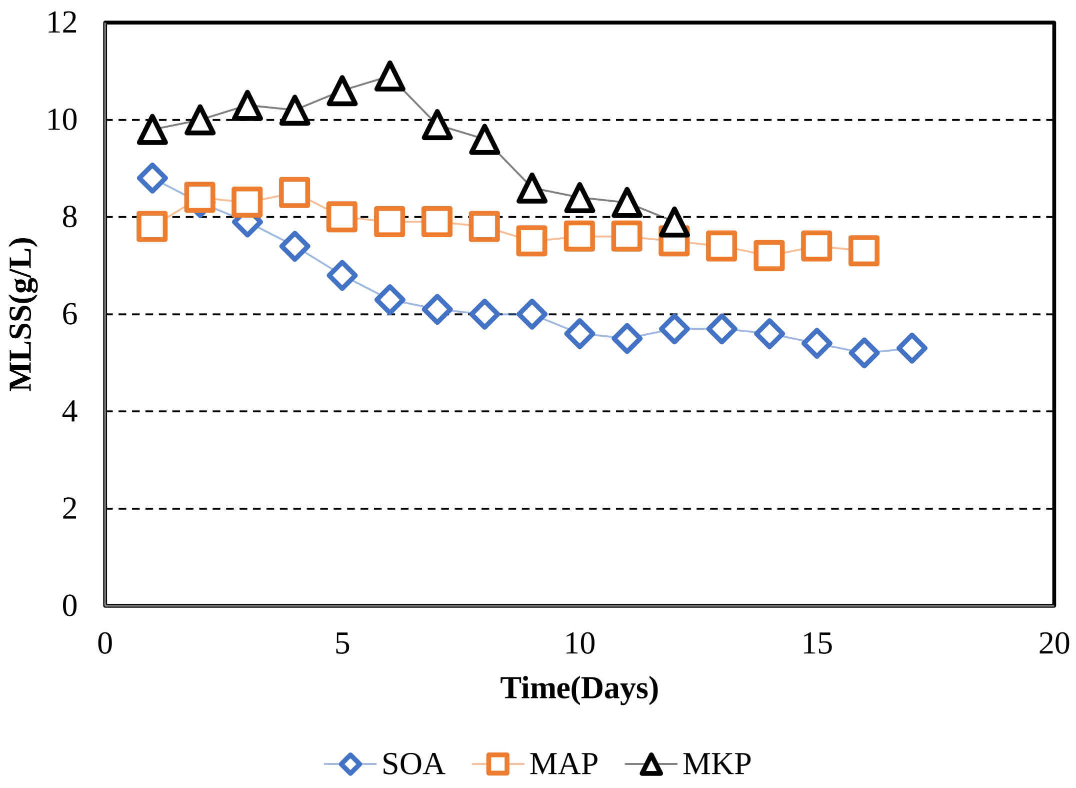
In case of SOA, the reverse of ammonium ion inside the bioreactor lead to the deterioration of the sludge characteristics and also negatively affect the sludge settling and dewatering properties which decrease the sludge filterability and hence increases the CST (Murthy et al. 1998; Novak, 2001). While using MKP as DS, the reverse of $K^+$ ion at low concentration caused the sludge characteristics to improve but after that, at high concentration, it deteriorates the sludge characteristics and decreases the sludge filterability (Kara, 2007; Murthy et al. 1998). In contrast, while using MAP as DS during FO-MBR operation, improved sludge filterability was observed. The possible reason for this is the lower salinity buildup of ammonium ion inside the bio-tank.

The dewaterability of the sludge is mainly dependent on the particle size distribution of sludge since smaller the particle size, poor will be the filterability of sludge (Higgins & Novak, 1997). The decrease in average floc size was observed while using SOA and MKP as draw solutes. In case of SOA, the reverse of ammonia and sulfate ion decreases the sludge settling properties as well as average floc size of the activated sludge (Akhurst et al. 2018; Murthy et al. 1998; Novak, 2001). The reverse of $K^+$ ion in high concentration displace the divalent ions from within the structure of flocs and results in deterioration of flocculability and dissociate the flocs (Kara, 2007). The average floc size reduction was very small because the floc size of the sludge first increases when the addition of $K^+$ ion concentration is in small and when its concentration start increasing, the sludge starts deteriorating (Kara, 2007).

After using MAP as a draw solute, it was observed that the average floc size improved. This is because of the lower transport of ammonium ion into the bio-tank which results in a buildup of lower saline stress condition inside the bio-tank and allow the sludge to grow.

### 4.4.2. Variations in MLSS and MLVSS

Figure 4.6. represents the variations in the concentrations of mixed liquor suspended solids (MLSS) and mixed liquor volatile solids (MLVSS) as a function of time.



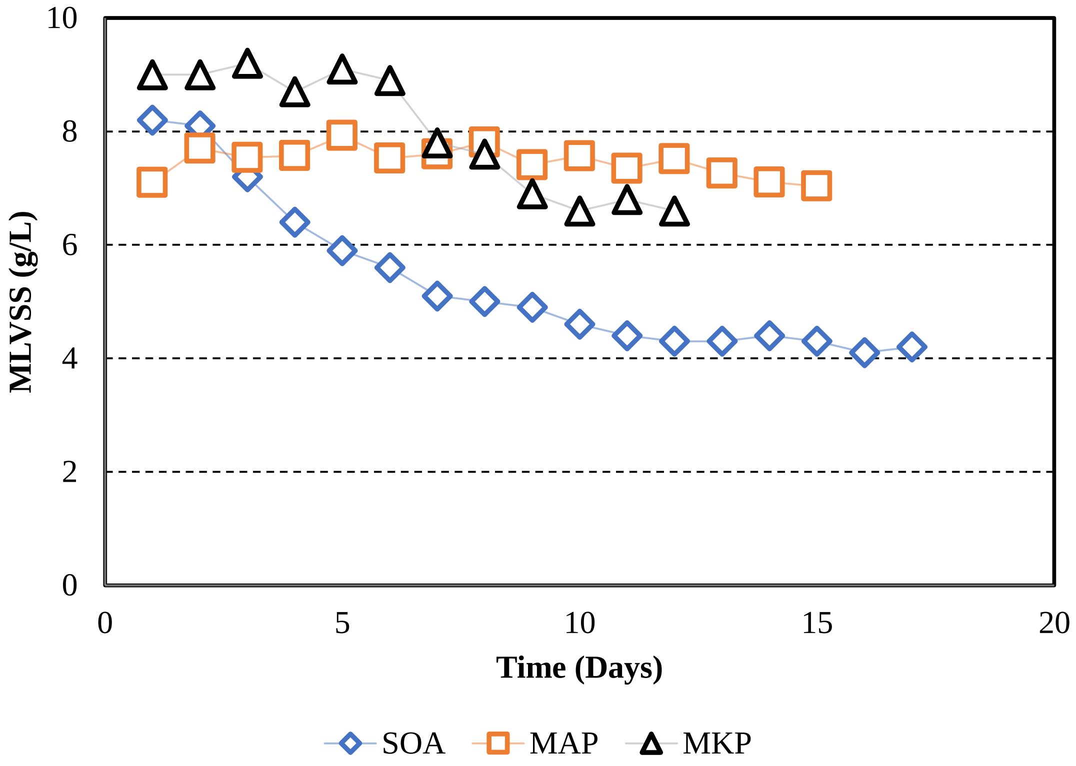


**Figure 4.6.** Effect of fertilizer DSs on mixed liquor suspended solids (MLSS) and mixed liquor volatile solids (MLVSS)

Highly saline stress conditions inside the bio-tank deteriorate the concentration of MLSS and MLVSS by inhibiting the microorganism’s growth (Luo et al. 2016; Tadkaew et al. 2013). Relatively higher salinity buildup was noticed in case of both MKP and SOA resulting in a decrease in MLSS and MLVSS concentrations. But an improvement in the concentration of MLSS and MLVSS was observed in case of MAP because of the less saline stress inside the bio-tank. Drop in the ratio of MLVSS/MLSS from 0.93 to 0.79 and 0.91 to 0.83 was observed throughout the filtration run for SOA and MKP, respectively. This drop in MLVSS/MLSS ratio depicts the decrease of active biomass which not only affects the sludge characteristics but also reduce the biological treatment process (Luo et al. 2015; Siddique et al. 2017). In case of MAP a very less drop in the ratio of MLVSS/MLSS from 0.91 to 0.86 was noticed during the entire filtration run which is accredited to the less salinity buildup inside the bio-tank resulting in the healthy active biomass.

# Chapter 5

## 5. Conclusion and Recommendations

### 5.1. Conclusions

The three fertilizer based draw solutes SOA, MAP, and MKP were selected for FO-MBR operation because of their higher water flux characteristics and lower draw solute accumulation in the bio-tank.

- High reverse transport of draw solute, lower initial water flux and shortest filtration run was observed in case of MKP.
- MAP proved to be the most optimal draw solute in terms of its effect on biomass in comparison with SOA and MKP.
- SOA was also a potential candidate for long-term FO-MBR operation, but the reverse of ammonium ion and sulfate ion reduced the treatment performance and characteristics of sludge.
- High initial water flux and prolonged filtration runs were obtained by using SOA and MAP as draw solutions.
- Slight permeation of ammonia, into the permeate, through MD was observed during regeneration of ammonium based draw solutes.
- Relatively longer filtration run, less salt accumulation, effective growth of biomass and high treated water was achieved with MAP.

## 5.2. Recommendations

- Further investigation of selected fertilizer draw solutes for treatment of textile wastewater may be performed.
- Different blends of these fertilizers may be used in OMBR for treatment of agricultural wastewater.

# References

Achilli, A., Cath, T. Y., Marchand, E. A., & Childress, A. E. (2009). The forward osmosis membrane bioreactor: A low fouling alternative to MBR processes. Desalination, 239(1), 10-21. doi:https://doi.org/10.1016/j.desal.2008.02.022

Adham, S., Oppenheimer, J., Liu, L., & Kumar, M. (2007). Dewatering reverse osmosis concentrate from water reuse applications using forward osmosis. Water Use Foundation Research Report.

Aftab, B., Khan, S. J., Maqbool, T., & Hankins, N. P. (2015). High strength domestic wastewater treatment with submerged forward osmosis membrane bioreactor. Water Science and Technology, 72(1), 141-149.

Akhurst, T., Watson, S., Rose, P. D., Whiteley, C. G., & Pletschke, B. I. (2002). Accelerated sludge solubilisation under sulphate reducing conditions: the effect of hydrolytic enzymes on sludge floc size distribution and EPS composition. In Biennial Conference of the Water Institute of Southern Africa (WISA).

Alturki, A., McDonald, J., Khan, S. J., Hai, F. I., Price, W. E., & Nghiem, L. D. (2012). Performance of a novel osmotic membrane bioreactor (OMBR) system: Flux stability and removal of trace organics. Bioresource Technology, 113(Supplement C), 201-206. doi:https://doi.org/10.1016/j.biortech.2012.01.082

Ansari, A. J., Hai, F. I., Guo, W., Ngo, H. H., Price, W. E., & Nghiem, L. D. (2015). Selection of forward osmosis draw solutes for subsequent integration with anaerobic treatment to facilitate resource recovery from wastewater. Bioresource Technology, 191(Supplement C), 30-36. doi:https://doi.org/10.1016/j.biortech.2015.04.119

Aravind, J., Saranya, T., & Kanmani, P. (2015). Optimizing the production of Polyphosphate from Acinetobacter towneri. Global Journal of Environmental Science and Management, 1(1), 63-70. doi:10.7508/gjesm.2015.01.006

Caffrey, J. M., Bano, N., Kalanetra, K., & Hollibaugh, J. T. (2007). Ammonia oxidation and ammonia-oxidizing bacteria and archaea from estuaries with differing histories of hypoxia. The Isme Journal, 1, 660. doi:10.1038/ismej.2007.79

Carmignani, G., Sitkiewitz, S., & Webley, J. W. (2012). Recovery of retrograde soluble solute for forward osmosis water treatment.

Cartinella, J. L., Cath, T. Y., Flynn, M. T., Miller, G. C., Hunter, K. W., & Childress, A. E. (2006). Removal of Natural Steroid Hormones from Wastewater Using Membrane Contactor Processes. Environmental Science & Technology, 40(23), 7381-7386. doi:10.1021/es060550i

Cath, T. Y., Gormly, S., Beaudry, E. G., Flynn, M. T., Adams, V. D., & Childress, A. E. (2005). Membrane contactor processes for wastewater reclamation in space: Part I. Direct osmotic concentration as pretreatment for reverse osmosis. Journal of Membrane Science, 257(1), 85-98. doi:https://doi.org/10.1016/j.memsci.2004.08.039

Chaudhry, V., & Nautiyal, C. S. (2011). A high throughput method and culture medium for rapid screening of phosphate accumulating microorganisms. Bioresource Technology, 102(17), 8057-8062. doi:https://doi.org/10.1016/j.biortech.2011.05.045

Chang, I. S., Gander, M., Jefferson, B., & Judd, S. J. (2001). Low-cost membranes for use in a submerged MBR. Process Safety and Environmental Protection, 79(3), 183-188.

Chekli, L., Kim, Y., Phuntsho, S., Li, S., Ghaffour, N., Leiknes, T., & Shon, H. K. (2017). Evaluation of fertilizer-drawn forward osmosis for sustainable agriculture and water reuse in arid regions. Journal of Environmental Management, 187, 137-145. doi:https://doi.org/10.1016/j.jenvman.2016.11.021

Chen, L., Gu, Y., Cao, C., Zhang, J., Ng, J.-W., & Tang, C. (2014). Performance of a submerged anaerobic membrane bioreactor with forward osmosis membrane for low-strength wastewater treatment. Water Research, 50(Supplement C), 114-123. doi:https://doi.org/10.1016/j.watres.2013.12.009

Chen, S., Ling, J., & Blancheton, J.-P. (2006). Nitrification kinetics of biofilm as affected by water quality factors. Aquacultural Engineering, 34(3), 179-197. doi:https://doi.org/10.1016/j.aquaeng.2005.09.004

Le-Clech, P., B. Jefferson, and S.J. Judd. 2005. “A Comparison of Submerged and Sidestream Tubular Membrane Bioreactor Configurations.” Desalination 173(2): 113–22.

Cornelissen, E. R., Harmsen, D., de Korte, K. F., Ruiken, C. J., Qin, J.-J., Oo, H., & Wessels, L. P. (2008). Membrane fouling and process performance of forward osmosis membranes on activated sludge. Journal of Membrane Science, 319(1), 158-168. doi:https://doi.org/10.1016/j.memsci.2008.03.048

Elimelech, M., & Phillip, W. A. (2011). The future of seawater desalination: energy, technology, and the environment. science, 333(6043), 712-717.

Frank, B. S. (1972). Desalination of sea water.

Garcia-Castello, E. M., & McCutcheon, J. R. (2011). Dewatering press liquor derived from orange production by forward osmosis. Journal of Membrane Science, 372(1), 97-101. doi:https://doi.org/10.1016/j.memsci.2011.01.048

Ginestet, P., Audic, J.-M., Urbain, V., & Block, J.-C. (1998). Estimation of nitrifying bacterial activities by measuring oxygen uptake in the presence of the metabolic inhibitors allylthiourea and azide. Applied and Environmental Microbiology, 64(6), 2266-2268.

Glew, D. N. (1965). Process for liquid recovery and solution concentration.

Günder, B., & Krauth, K. (1998). Replacement of secondary clarification by membrane separation - results with plate and hollow fibre modules. Water Science and Technology, 38(4-5), 383.

Higgins, M. J., & Novak, J. T. (1997). Characterization of exocellular protein and its role in bioflocculation. Journal of Environmental Engineering, 123(5), 479-485.

Holloway, R. W., Achilli, A., & Cath, T. Y. (2015). The osmotic membrane bioreactor: a critical review. Environmental Science: Water Research & Technology, 1(5), 581-605.

Holloway, R. W., Wait, A. S., Fernandes da Silva, A., Herron, J., Schutter, M. D., Lampi, K., & Cath, T. Y. (2015). Long-term pilot scale investigation of novel hybrid ultrafiltration-osmotic membrane bioreactors. Desalination, 363, 64-74. doi:https://doi.org/10.1016/j.desal.2014.05.040

Hough, W. T. (1970). Process for extracting solvent from a solution.

Iyer, S. (2011). Systems and methods for forward osmosis fluid purification using cloud point extraction.

Johir, M. A. H., Vigneswaran, S., Kandasamy, J., BenAim, R., & Grasmick, A. (2013). Effect of salt concentration on membrane bioreactor (MBR) performances: Detailed organic characterization. Desalination, 322, 13-20. doi:https://doi.org/10.1016/j.desal.2013.04.025

Jones, R. D., & Hood, M. A. (1980). Effects of temperature, pH, salinity, and inorganic nitrogen on the rate of ammonium oxidation by nitrifiers isolated from wetland environments. Microbial ecology, 6(4), 339-347.

Judd, S. (2010). The MBR book: principles and applications of membrane bioreactors for water and wastewater treatment. Elsevier.

Kara, f. (2007). Investigation of sodium and potassium ions in relation to bioflocculation of mixed culture microorganisms. Middle east technical university.

Kessler, J. O., & Moody, C. D. (1976). Drinking water from sea water by forward osmosis. Desalination, 18(3), 297-306. doi:https://doi.org/10.1016/S0011-9164(00)84119-3

Kim, Y., Chekli, L., Shim, W.-G., Phuntsho, S., Li, S., Ghaffour, N. Shon, H. K. (2016). Selection of suitable fertilizer draw solute for a novel fertilizer-drawn forward osmosis–anaerobic membrane bioreactor hybrid system. Bioresource Technology, 210, 26-34. doi:https://doi.org/10.1016/j.biortech.2016.02.019

Kiriukhin, M. Y., & Collins, K. D. (2002). Dynamic hydration numbers for biologically important ions. Biophysical Chemistry, 99(2), 155-168. doi:https://doi.org/10.1016/S0301-4622(02)00153-9

Kravath, R. E., & Davis, J. A. (1975). Desalination of sea water by direct osmosis. Desalination, 16(2), 151-155. doi:https://doi.org/10.1016/S0011-9164(00)82089-5

Lay, W. C., Liu, Y., & Fane, A. G. (2010). Impacts of salinity on the performance of high retention membrane bioreactors for water reclamation: a review. Water research, 44(1), 21-40.

Lay, W. C. L., Liu, Y., & Fane, A. G. (2010). Impacts of salinity on the performance of high retention membrane bioreactors for water reclamation: A review. Water Research, 44(1), 21-40. doi:https://doi.org/10.1016/j.watres.2009.09.026

Lay, W. C. L., Zhang, Q., Zhang, J., McDougald, D., Tang, C., Wang, R. Fane, A. G. (2011). Study of integration of forward osmosis and biological process: Membrane performance under elevated salt environment. Desalination, 283(Supplement C), 123-130. doi:https://doi.org/10.1016/j.desal.2011.01.036

Le-Clech, P., Jefferson, B., & Judd, S. J. (2005). A comparison of submerged and sidestream tubular membrane bioreactor configurations. Desalination, 173(2), 113-122. doi:https://doi.org/10.1016/j.desal.2004.08.029

Li, D., Zhang, X., Yao, J., Zeng, Y., Simon, G. P., & Wang, H. (2011). Composite polymer hydrogels as draw agents in forward osmosis and solar dewatering. Soft Matter, 7(21), 10048-10056. doi:10.1039/C1SM06043K

Ling, M. M., & Chung, T.-S. (2011). Desalination process using super hydrophilic nanoparticles via forward osmosis integrated with ultrafiltration regeneration. Desalination, 278(1), 194-202. doi:https://doi.org/10.1016/j.desal.2011.05.019

Loeb, S., Titelman, L., Korngold, E., & Freiman, J. (1997). Effect of porous support fabric on osmosis through a Loeb-Sourirajan type asymmetric membrane. Journal of Membrane Science, 129(2), 243-249. doi:https://doi.org/10.1016/S0376-7388(96)00354-7

Luo, H., Wang, Q., Zhang, T. C., Tao, T., Zhou, A., Chen, L., & Bie, X. (2014). A review on the recovery methods of draw solutes in forward osmosis. Journal of Water Process Engineering, 4, 212-223.

Luo, W., Hai, F. I., Price, W. E., Elimelech, M., & Nghiem, L. D. (2016). Evaluating ionic organic draw solutes in osmotic membrane bioreactors for water reuse. Journal of Membrane Science, 514, 636-645. doi:https://doi.org/10.1016/j.memsci.2016.05.023

Luo, W., Hai, F. I., Price, W. E., & Nghiem, L. D. (2015). Water extraction from mixed liquor of an aerobic bioreactor by forward osmosis: membrane fouling and biomass characteristics assessment. Separation and Purification Technology, 145, 56-62.

Majeed, T., Sahebi, S., Lotfi, F., Kim, J. E., Phuntsho, S., Tijing, L. D., & Shon, H. K. (2015). Fertilizer-drawn forward osmosis for irrigation of tomatoes. Desalination and Water Treatment, 53(10), 2746-2759.

McCormick, P., Pellegrino, J., Mantovani, F., & Sarti, G. (2008). Water, salt, and ethanol diffusion through membranes for water recovery by forward (direct) osmosis processes. Journal of Membrane Science, 325(1), 467-478. doi:https://doi.org/10.1016/j.memsci.2008.08.011

McCutcheon, J. R., & Elimelech, M. (2006). Influence of concentrative and dilutive internal concentration polarization on flux behavior in forward osmosis. Journal of Membrane Science, 284(1), 237-247. doi:https://doi.org/10.1016/j.memsci.2006.07.049

McCutcheon, J. R., McGinnis, R. L., & Elimelech, M. (2005). A novel ammonia—carbon dioxide forward (direct) osmosis desalination process. Desalination, 174(1), 1-11. doi:https://doi.org/10.1016/j.desal.2004.11.002

McCutcheon, J. R., McGinnis, R. L., & Elimelech, M. (2006). Desalination by ammonia–carbon dioxide forward osmosis: Influence of draw and feed solution concentrations on process performance. Journal of Membrane Science, 278(1), 114-123. doi:https://doi.org/10.1016/j.memsci.2005.10.048

McGinnis, R. L., & Elimelech, M. (2007). Energy requirements of ammonia–carbon dioxide forward osmosis desalination. Desalination, 207(1), 370-382. doi:https://doi.org/10.1016/j.desal.2006.08.012

McGinnis, R. L., & Elimelech, M. (2008). Global Challenges in Energy and Water Supply: The Promise of Engineered Osmosis. Environmental Science & Technology, 42(23), 8625-8629. doi:10.1021/es800812m

Mi, B., & Elimelech, M. (2008). Chemical and physical aspects of organic fouling of forward osmosis membranes. Journal of Membrane Science, 320(1-2), 292-302.

Mi, B., & Elimelech, M. (2010). Gypsum Scaling and Cleaning in Forward Osmosis: Measurements and Mechanisms. Environmental Science & Technology, 44(6), 2022-2028. doi:10.1021/es903623r

Montgomery, M. A., & Elimelech, M. (2007). Water And Sanitation in Developing Countries: Including Health in the Equation. Environmental Science & Technology, 41(1), 17-24. doi:10.1021/es072435t

Moussa, M. S. (2014). Nitrification in saline industrial wastewater: CRC Press.

Murthy, S., T. Novak, J., & Dehaas, R. (1998). Monitoring cations to predict and improve activated sludge settling and dewatering properties of industrial wastewaters (Vol. 38).

Nasr, P., & Sewilam, H. (2016). Investigating the performance of ammonium sulphate draw solution in fertilizer drawn forward osmosis process. Clean Technologies and Environmental Policy, 18(3), 717-727.

Nayak, C. A., & Rastogi, N. K. (2010). Forward osmosis for the concentration of anthocyanin from Garcinia indica Choisy. Separation and Purification Technology, 71(2), 144-151. doi:https://doi.org/10.1016/j.seppur.2009.11.013

Neff, R. A. (1964). Solvent extractor.

Nguyen, N. C., Chen, S.-S., Nguyen, H. T., Ngo, H. H., Guo, W., Hao, C. W., & Lin, P.-H. (2015). Applicability of a novel osmotic membrane bioreactor using a specific draw solution in wastewater treatment. Science of The Total Environment, 518-519(Supplement C), 586-594. doi:https://doi.org/10.1016/j.scitotenv.2015.03.011

Nguyen, N. C., Chen, S.-S., Yang, H.-Y., & Hau, N. T. (2013). Application of forward osmosis on dewatering of high nutrient sludge. Bioresource Technology, 132, 224-229. doi:10.1016/j.biortech.2013.01.028

Noh, M., Mok, Y., Lee, S., Kim, H., Lee, S. H., Jin, G.-w. Lee, Y. (2012). Novel lower critical solution temperature phase transition materials effectively control osmosis by mild temperature changes. Chemical Communications, 48(32), 3845-3847. doi:10.1039/C2CC30890H

Novak, J. T. (2001). The effect of the ammonium ion on activated-sludge settling properties. Water environment research, 73(4), 409-414.

Ohtaki, H., & Radnai, T. (1993). Structure and dynamics of hydrated ions. Chemical Reviews, 93(3), 1157-1204.

Phillip, W. A., Yong, J. S., & Elimelech, M. (2010). Reverse draw solute permeation in forward osmosis: modeling and experiments. Environmental science & technology, 44(13), 5170-5176.

Phuntsho, S., Shon, H. K., Hong, S., Lee, S., & Vigneswaran, S. (2011). A novel low energy fertilizer driven forward osmosis desalination for direct fertigation: Evaluating the performance of fertilizer draw solutions. Journal of Membrane Science, 375(1), 172-181. doi:https://doi.org/10.1016/j.memsci.2011.03.038

Phuntsho, S., Shon, H. K., Majeed, T., El Saliby, I., Vigneswaran, S., Kandasamy, J. Lee, S. (2012). Blended Fertilizers as Draw Solutions for Fertilizer-Drawn Forward Osmosis Desalination. Environmental Science & Technology, 46(8), 4567-4575. doi:10.1021/es300002w

Prosser, J. I. (1990). Autotrophic nitrification in bacteria. In Advances in microbial physiology (Vol. 30, pp. 125-181). Academic Press.

Prosser, J. I. (2007). Chapter 15 - The Ecology of Nitrifying Bacteria A2 - Bothe, Hermann. In S. J. Ferguson & W. E. Newton (Eds.), Biology of the Nitrogen Cycle (pp. 223-243). Amsterdam: Elsevier.

Qiu, G., & Ting, Y.-P. (2013). Osmotic membrane bioreactor for wastewater treatment and the effect of salt accumulation on system performance and microbial community dynamics. Bioresource Technology, 150, 287-297. doi:https://doi.org/10.1016/j.biortech.2013.09.090

Siddique, M. S., Khan, S. J., Shahzad, M. A., Nawaz, M. S., & Hankins, N. P. (2018). Insight into the effect of organic and inorganic draw solutes on the flux stability and sludge characteristics in the osmotic membrane bioreactor. Bioresource technology, 249, 758-766.

Stache, K. (1989). Apparatus for transforming sea water, brackish water, polluted water or the like into a nutrious drink by means of osmosis.

Stone, M. L., Wilson, A. D., Harrup, M. K., & Stewart, F. F. (2013). An initial study of hexavalent phosphazene salts as draw solutes in forward osmosis. Desalination, 312(Supplement C), 130-136. doi:https://doi.org/10.1016/j.desal.2012.09.030

Su, J., Chung, T.-S., Helmer, B. J., & de Wit, J. S. (2012). Enhanced double-skinned FO membranes with inner dense layer for wastewater treatment and macromolecule recycle using Sucrose as draw solute. Journal of Membrane Science, 396(Supplement C), 92-100. doi:https://doi.org/10.1016/j.memsci.2012.01.001

Tadkaew, N., McDonald, J., Khan, S. J., & Nghiem, L. D. (2013). Effects of salinity on the removal of trace organic contaminants by membrane bioreactor treatment for water reuse. Desalination and Water Treatment, 51(25-27), 5164-5171. doi:10.1080/19443994.2013.768415

Van der Roest, H., Lawrence, D. P., & Van Bentem, A. (2002). Membrane bioreactors for municipal wastewater treatment: IWA Publishing.

Wallace, M., Cui, Z., & Hankins, N. P. (2008). A thermodynamic benchmark for assessing an emergency drinking water device based on forward osmosis. Desalination, 227(1), 34-45. doi:https://doi.org/10.1016/j.desal.2007.04.097

Wang, J., Pathak, N., Chekli, L., Phuntsho, S., Kim, Y., Li, D., & Shon, H. K. (2017). Performance of a novel fertilizer-drawn forward osmosis aerobic membrane bioreactor (FDFO-MBR): mitigating salinity build-up by integrating microfiltration. Water, 9(1), 21.

Wang, R., Shi, L., Tang, C. Y., Chou, S., Qiu, C., & Fane, A. G. (2010). Characterization of novel forward osmosis hollow fiber membranes. Journal of Membrane Science, 355(1), 158-167. doi:https://doi.org/10.1016/j.memsci.2010.03.017

Wang, X., Chang, V. W. C., & Tang, C. Y. (2016). Osmotic membrane bioreactor (OMBR) technology for wastewater treatment and reclamation: Advances, challenges, and prospects for the future. Journal of Membrane Science, 504(Supplement C), 113-132. doi:https://doi.org/10.1016/j.memsci.2016.01.010

Wang, X., Chen, Y., Yuan, B., Li, X., & Ren, Y. (2014). Impacts of sludge retention time on sludge characteristics and membrane fouling in a submerged osmotic membrane bioreactor. Bioresource Technology, 161(Supplement C), 340-347. doi:https://doi.org/10.1016/j.biortech.2014.03.058

Wang, X., Yuan, B., Chen, Y., Li, X., & Ren, Y. (2014). Integration of micro-filtration into osmotic membrane bioreactors to prevent salinity build-up. Bioresource Technology, 167(Supplement C), 116-123. doi:https://doi.org/10.1016/j.biortech.2014.05.121

Whetton, P., Fowler, A., Haylock, M., & Pittock, A. (1993). Implications of climate change due to the enhanced greenhouse effect on floods and droughts in Australia. Climatic Change, 25(3-4), 289-317.

Yaeli, J. (1992). Method and apparatus for processing liquid solutions of suspensions particularly useful in the desalination of saline water:

Yen, S. K., Mehnas Haja N, F., Su, M., Wang, K. Y., & Chung, T.-S. (2010). Study of draw solutes using 2-methylimidazole-based compounds in forward osmosis. Journal of Membrane Science, 364(1), 242-252. doi:https://doi.org/10.1016/j.memsci.2010.08.021

Yong, J. S., Phillip, W. A., & Elimelech, M. (2012). Coupled reverse draw solute permeation and water flux in forward osmosis with neutral draw solutes. Journal of Membrane Science, 392-393(Supplement C), 9-17. doi:https://doi.org/10.1016/j.memsci.2011.11.020

Yuan, Z., Pratt, S., & Batstone, D. J. (2012). Phosphorus recovery from wastewater through microbial processes. Current Opinion in Biotechnology, 23(6), 878-883. doi:https://doi.org/10.1016/j.copbio.2012.08.001

Zhang, J., Loong, W. L. C., Chou, S., Tang, C., Wang, R., & Fane, A. G. (2012). Membrane biofouling and scaling in forward osmosis membrane bioreactor. Journal of Membrane Science, 403-404(Supplement C), 8-14. doi:https://doi.org/10.1016/j.memsci.2012.01.032

Zhang, Q., Jie, Y. W., Loong, W. L. C., Zhang, J., Fane, A. G., Kjelleberg, S., . . . McDougald, D. (2014). Characterization of biofouling in a lab-scale forward osmosis membrane bioreactor (FOMBR). Water Research, 58(Supplement C), 141-151. doi:https://doi.org/10.1016/j.watres.2014.03.052

Zuthi, M. F. R., Guo, W. S., Ngo, H. H., Nghiem, L. D., & Hai, F. I. (2013). Enhanced biological phosphorus removal and its modeling for the activated sludge and membrane bioreactor processes. Bioresource Technology, 139, 363-374.